Photoinduced Acid-Catalyzed SiO_2 Formation at the Polymer Surface by Chemical Vapor Deposition

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ABSTRACT: Silicon oxide formation at the near surface of UV-irradiated polymers using a chemical vapor deposition (CVD) method was studied. Copolymers of 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate (NISS) and methyl methacrylate, isopropyl methacrylate, or benzyl methacrylate were synthesized by photoinitiated radical copolymerization. Since the NISS units of the polymers can form *p*-styrenesulfonic acid units on irradiation with UV light, the irradiated polymers sorbed water from the atmosphere. The water sorption was studied using frequency changes of a quartz crystal coated with the polymers. The hydrophobic nature of the methacrylate ester groups reduced the water sorption ability of the polymers. When the irradiated polymer films were exposed to the vapor of tetraalkyl orthosilicates, methyltrimethoxysilane, or methyltriethoxysilane, silicon oxide was formed at the near surface of the irradiated areas of the polymers. No silicon oxide was formed at unirradiated areas. The silicon oxide formation rate was strongly affected by the structure of methacrylate units in the polymers, the rate of hydrolysis of the orthosilicates, and the number of photochemically formed *p*-styrenesulfonic acid units in the polymers.

Introduction

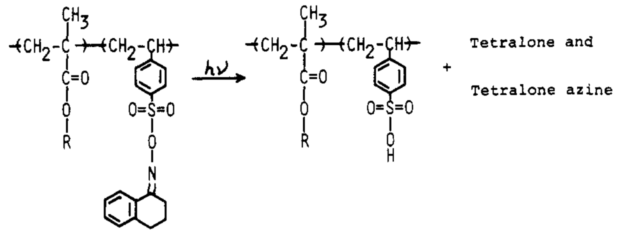
In many applications of polymer materials, the chemical and physical properties of the surfaces are as important as the properties exhibited by the bulk materials. A gas-phase functionalization of exposed or unexposed areas of polymer films by volatile inorganic or organometallic compounds has been studied by Taylor and co-workers.[1,2] The work is important for the photolithography, which needs high resolution. They have studied the systems (i) diborane (B_2H_6) and poly(isoprene) or chlorinated polyacrylates and (ii) $SnCl_4$, $SiCl_4$, or $(CH_3)_2SiCl_2$ and poly(isoprene) derivatives containing bisazide sensitizer. In these systems the gaseous inorganic or organometallic molecules diffused into polymer films can react with either photochemically induced active species at exposed regions or reactive groups at unexposed regions, resulting in a formation of compounds containing the B, Si, or Sn element at the near surface of polymer films. The pattern development for microlithography was achieved using O_2 reactive ion etching (O_2 RIE), which produced a barrier layer of metal oxides at the upper surface of the polymer film. The surface functionalization of polymers bearing photochemically formed phenolic –OH groups using gaseous hexamethyldisilazane was also studied by several workers.[3,4]

Follett and co-workers have reported the development of plasma-developable electron-beam resists.[5] The essential feature involved selective diffusion of dichlorodimethylsilane into the irradiated areas of poly(methyl methacrylate). This step was followed by hydrolysis of the chlorosilane upon exposure to water vapor, resulting in polymerization that formed an interpenetrating matrix of polysiloxane. High resolution of O_2 plasma of the treated areas was achieved. Hydrophobic polymers such as chlorine-containing polystyrenes undergo oxidation to form hydrophilic hydroxyl and carbonyl groups when exposed in air with 248.4- or 193-nm light. The exposed regions sorbed water from the atmosphere. The treatment of the exposed films with gaseous $TiCl_4$ caused the formation of a TiO_2 layer at the film surface.[6–9] The TiO_2 layer acted as a barrier for O_2 RIE.

We have reported that imino sulfonate compounds undergo a photochemical decomposition to form sulfonic acids along with azines and ketones.[10] Polymers bearing 2,3-epoxypropyl or 2,3-epithiopropyl groups and imino sulfonate units in their side chain were photocross-linked with high sensitivity when exposed to UV light.[11] In these systems the photochemically formed sulfonic acid acted as an initiator of the polymerization of epoxy or epithio units. Conversely, copolymers of 2-(dialkylamino)ethyl methacrylates and 9-fluorenylideneamino *p*-styrenesulfonate or terpolymers of methacrylic acid, methyl methacrylate, and 9-fluorenylideneamino *p*-styrenesulfonate became soluble in aqueous alkaline solutions upon irradiation with UV light.[12,13] They were useful as positive photoresists. We have now extended the usefulness of the photoacid generator to the modification of the irradiated polymer surface by a chemical vapor deposition method (CVD). We have synthesized polymethacrylates bearing 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate (NISS) units in their side chains. Upon photolysis the imino sulfonate units were converted to styrenesulfonic acid units. The exposed areas of the polymer films become hydrophilic, and water sorption from the atmosphere occurs at the near surface of the exposed polymer films. It has been reported that some tetraalkyl orthosilicates and their homologues can be rapidly hydrolyzed by water in the presence of acid or base as a catalyst. The hydrated tetrahedral silanol undergoes a polycondensation reaction, resulting in an SiO_2 network.[14,15]

$$n\mathrm{Si(OR)_4} + 2n\mathrm{H_2O} \xrightarrow{\mathrm{H^+}} n\mathrm{SiO_2} + 4n\mathrm{ROH} \qquad (1)$$

The water sorbed at the irradiated polymer surface can react with gaseous tetraalkyl orthosilicates to form an SiO_2 network. The photochemically formed sulfonic acid units are essentially important for the SiO_2 network formation. In a recent communication,[16] we have reported the preliminary results concerning the photoinduced acid-catalyzed SiO_2 network formation at the irradiated polymer surface using chemical vapor deposition method. In this paper we fully report the synthesis and photochemistry of the polymers bearing imino sulfonate units in their side chain, the water sorption to the exposed polymer films, and the formation of SiO_2 networks at the exposed polymer surface by a chemical vapor deposition method.



PMANI : R=CH_3
PPRNI : R=i-C_3H_7
PBZNI : R=$CH_2C_6H_5$

Experimental Section

Materials. 1,2,3,4-Tetrahydro-1-naphthylideneamino *p*-Styrenesulfonate (NISS). To a solution of 1-tetralone oxime (13.7 g, 0.085 mol) in pyridine (32 mL) below 10 °C was slowly added *p*-styrenesulfonyl chloride (19 g, 0.094 mol), which was freshly prepared from potassium *p*-styrenesulfonate and PCl_5 according to the method reported by Iwakura et al.[17] With vigorous stirring the reaction was continued below 20 °C for 3 h. The reaction mixture was poured into 360 mL of ice-cold 5% HCl and extracted with chloroform. After the chloroform layer was washed thoroughly with water, the chloroform layer was dried over K_2CO_3 and evaporated under reduced pressure. The oily residue was continuously extracted with hot *n*-heptane, which yielded white crystals upon cooling. After recrystallization from *n*-heptane, 6.4 g (23%) of pure product was obtained; mp 80–82 °C. IR (KBr): 1370 and 1180 cm^{-1} (O–S–O). ^1H NMR ($CDCl_3$, 270 MHz) δ 1.85 (q, 2 H, CH_2), 2.73 (t, 2 H, CH_2), 2.48 (t, 2 H, CH_2), 5.45–5.90 (dd, 2 H, J = 11, 19 Hz, $CH_2{=}$), 6.77 (dd, 1 H, CH=), 7.17–8.00 (m, 8 H, aryl H). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.06; H, 5.19; N, 4.28. Found: C, 66.27; H, 5.39; N, 3.85.

Polymer Preparation. To prevent the thermal decomposition of NISS, the copolymers were prepared by the photochemically initiated copolymerization of NISS and methacrylates with azobis(isobutyronitrile) (AIBN) as an initiator at 29 °C by irradiation with UV light at wavelengths above 350 nm. A 75-W high-pressure Hg lamp (Toshiba SHL-100 UV) was used. The flux was 4 mW/cm^2. The concentrations of total monomer and AIBN in benzene were 4.5 mol/L and 1.6 × 10^{-2} mol/L, respectively. The sample solution was degassed under vacuum by repeated freeze–thaw cycles before polymerization. The polymers were purified by dissolving in THF or chloroform and precipitating with ethyl ether. The content of NISS units in polymers was determined by measuring the absorbance at 254 nm in CH_2Cl_2. The molar extinction coefficient of the NISS units was estimated to be equal to that of the model compound 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-toluenesulfonate, ϵ being 15 300 L/(mol·cm) at 254 nm in CH_2Cl_2 at room temperature. The temperatures of the onset of decomposition for NISS units determined from differential scanning calorimetry (DSC) using a Rigaku DSC-8230 were 132, 149, and 147 °C for PMANI-(B), PPRNI, and PBZNI, respectively. The characteristics and abbreviations of the polymers prepared are shown in Table I.

Methyl methacrylate (MMA), isopropyl methacrylate (*i*-PrMA), benzyl methacrylate (BzMA), and AIBN were reagent grade and used after purification. Tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), tetra-*n*-propyl orthosilicate (TPOS), methyltrimethoxysilane (MTMOS), and methyltriethoxysilane (MTEOS) were reagent grade and used without 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, ΔF (Hz), is linearly related to the mass sorbed on the quartz plate, according to the equation[18,19]

$$\Delta F = -2.26 \times 10^6 F^2 \Delta m/A$$

where F (MHz) is the initial frequency of the quartz crystal used, Δm (g) is the mass sorbed, and A (cm^2) is the area of the crystal surface occupied by the polymer film. 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 cm^2. 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[20]) was 0.104 mJ/(cm^2·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 cm^2) was placed in a 500-mL four-necked flask. After dry N_2 gas was flowed into the flask for 1 h (80 mL/min), 100 mL of a 2 M KNO_3 aqueous solution was placed at the bottom. The vessel was sealed and equilibrated for 2 h at 25 °C. The frequencies of the quartz crystal under dry N_2 atmosphere and humid atmosphere were recorded, and the water sorption was calculated.

Deposition of SiO_2. 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. 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 95%. During the SiO_2 network formation nitrogen gas (50 mL/min) flowed through a bubbler which contained liquid $Si(OR)_4$ or one of its homologues. The bubbler and reaction vessel were placed in a thermostatic oven at 30 °C. The amounts of SiO_2 formed at the near surface of the polymer were determined from the difference between the weight of the sample plate before and after exposure to the vapor of the silicon compounds.

Quantum Yield. The polymer films (11 × 22 mm) were prepared on glass plates (11 × 50 mm) by casting from dichloromethane solution and drying under vacuum at 60 °C for 20 min. The polymer weight (W) on the glass plate was exactly measured. The absorbances of the films on glass plates were usually below 0.5 at 254 nm. The conversion of photolysis of NISS units is given by $(A_0 - A_t)/(A_0 - A_\infty)$, where A_0, A_t, and A_∞ are the initial absorbance at 254 nm, the absorbance at 254 nm irradiated for t min, and the absorbance at 254 nm photolyzed completely, respectively. A Shimadzu UV-2100 recording spectrophotometer was used. Conversion was always kept below 20%. The quantum yields (Φ) for the photolysis of NISS units in polymer films were determined at room temperature in air as the number of moles of decomposed NISS units per einstein of 254-nm light absorbed by NISS units:

$$\Phi = \left[\frac{fW(A_0 - A_t)}{100M_{av}(A_0 - A_\infty)}\right] / I_0 t S(1 - 10^{-(A_0+A_t)/2})$$

where M_{av}, f, t, and S are the average molecular weight of repeating units of polymers, NISS fraction shown in mole percent, irradiation time, and area of the film. The intensity of the incident light (I_0 = 2.22 × 10^{-10} einstein/(cm^2·s) was determined with a chemical actinometer.[20] The Φ values shown here were the average of three data points.

Results and Discussion

Photoreaction of Imino Sulfonates. 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

Table I
Polymer Properties[a]

polymer	NISS/g	MMA/mL	*i*-PrMA/mL	BzMA/mL	reaction time/h	yield/%	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	NISS fraction/(mol %)	T_g/°C
PMANI (A)	2.0	2.5			20	45	7.0	3.0	25	*c*
PMANI (B)	1.0	3.5			20	33	10.0	2.5	15	*c*
PMANI (C)	0.41	3.0			15	47	11.5	2.0	8	114
PPRNI	0.41		1.8		15	45	13.1	1.9	15	105
PBZNI	0.39			2.5	8	42	15.5	2.3	18	83

[a] [Total monomer] = 4.5 mol/L, [AIBN] = 1.6×10^{-2} mol/L. [b] From GPC versus polystyrene standards. [c] No distinct T_g was observed.

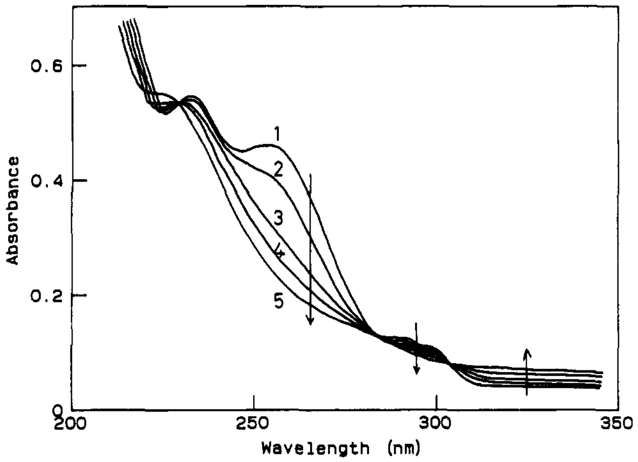
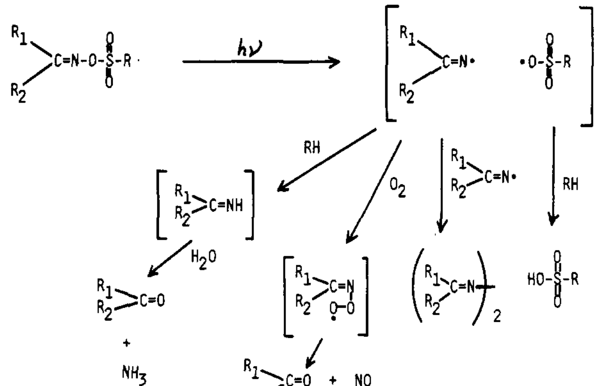


Figure 1. Spectral change of PMANI(C) film upon irradiation with 254-nm light. Irradiation dose: (1) 0, (2) 25, (3) 87, (4) 150, (5) 250 mJ/cm^2. Film thickness: 0.4 μm.

Scheme I



formation of sulfonic acid, azines, and ketones, as shown in Scheme I.[10] For the photolysis of imino sulfonates in polymer films in air, the reaction of imino radicals with oxygen is dominant compared to their dimerization and hydrogen abstraction reactions. For the photolysis in air of 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-toluenesulfonate in poly(methyl methacrylate) film, the *p*-toluenesulfonic acid yield was 76.5%, determined using the merocyanine dye method.[21] Change in the absorption spectrum of polymers bearing NISS units upon irradiation at 254 nm is shown in Figure 1. 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 is due to the formation of tetralone azine. In our system photolytic decomposition of NISS units was complete after 40 min of irradiation (250 mJ/cm^2). The quantum yields (Φ) for the photolysis of NISS units in the polymer films at 254 nm were 0.33, 0.31, 0.36, 0.26, and 0.38 for PMANI(A), PMANI(B), PMANI(C), PPRNI, and PBZNI, respectively. They were not strongly dependent on either the structure of the methacrylate unit or the NISS content of the polymers.

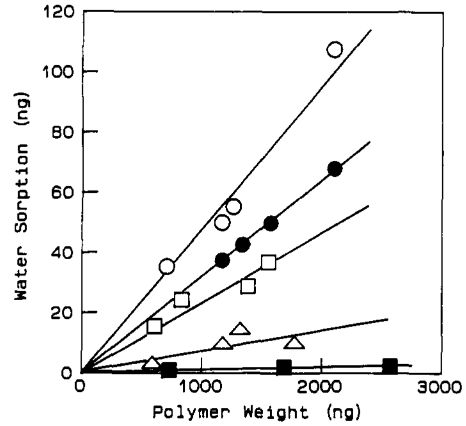


Figure 2. Water sorption of unirradiated polymers at 95% RH and 25 °C. Polymer: (○) PMANI(A), (●) PMANI(B), (□) PMANI(C), (△) PPRNI, and (■) PBZNI.

Water Sorption. Figure 2 shows the water sorption of unirradiated polymer films bearing NISS units at 95% relative humidity. The area of films casted on a quartz crystal was kept constant (0.19 cm^2). The water sorption increased linearly with increasing film thickness for all polymers studied. An introduction of NISS units in polymers enhanced their water sorption ability. The weight fractions of the sorbed water obtained from the slopes of these linear plots were 4.7, 3.1, 2.3, 0.3, and 0.1% for PMANI(A), PMANI(B), PMANI(C), PPRNI, and PBZNI, respectively. The hydrophobic nature of the methacrylate ester groups decreased the water sorption ability. For PMANI series polymers, a plot of the weight fraction of H_2O sorbed vs mole fraction of NISS gave a linear line. The value extrapolated to 0% of the NISS fraction was 1.1%, which was in good agreement with the value (1.05%) measured for poly(methyl methacrylate). The molar ratios of sorbed water to NISS units in polymers were 1.60, 1.50, 1.80, 0.47, and 0.062 for PMANI(A), PMANI(B), PMANI(C), PPRNI, and PBZNI, respectively. The water sorption abilities of NISS units in PPRNI and PBZNI were 31 and 4% that of PMANI(B). As reported for gas sorption in polymer films,[22,23] water sorption seems to occur by two processes: (1) dissolution of water molecules into the polymer matrix according to Henry's law and (2) the Langmuir type adsorption of water molecules at microvoids in the polymer matrix.

Figure 3 shows the relationship between irradiation time and water sorbed into the irradiated PMANI(A) film at various relative humidities. The weights of polymer films cast on the quartz crystal were 1000 ng. If the polymer is assumed to have a density of 1 g/cm^3, the film thickness is 51 nm and the absorbance of the film at 254 nm is <0.1. The relative humidities in the vessel were adjusted to be 95, 58, and 32%. 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 equilibrium amount of water sorbed

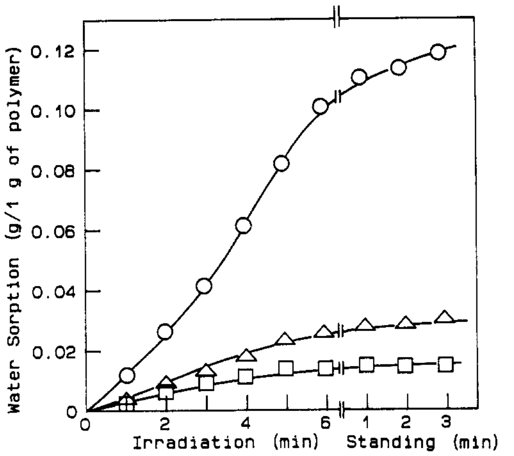


Figure 3. Relationship between irradiation time and water sorption to PMANI(A) at 25 °C. Relative humidity: (○) 95, (△) 58, and (□) 32%. Light intensity: 0.104 mJ/(cm^2·s). Polymer weight: 1000 ng.

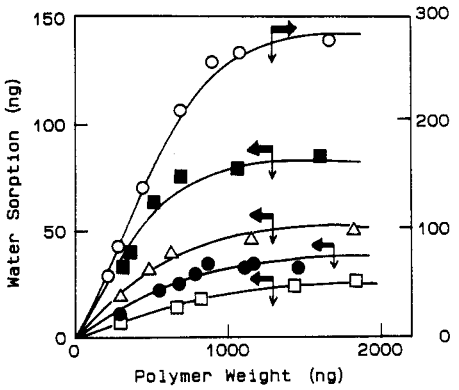


Figure 4. Water sorption at 95% RH into polymers irradiated with 42 mJ/cm^2 of 254-nm light at 25 °C. Polymer: (○) PMANI(A), (■) PMANI(B), (△) PMANI(C), (●) PPRNI, and (□) PBZNI.

increased exponentially with increasing relative humidity. This suggests that the water sorbed initially into the irradiated polymer surface acted as a plasticizer and subsequent sorption occurred in a rubbery state. A similar phenomenon was reported for the sorption of solvent vapor in polyethylene[24] and CO_2 sorption into silicone rubbers[25] and polymethacrylates.[26] Sorbed water was removed, when the sample was placed under a dry nitrogen atmosphere, and sorption and desorption were completely reversible.

Figure 4 shows the relationship between water sorbed and the weight of the irradiated polymer film (area = 0.19 cm^2) on the quartz crystal. The water sorption was measured after a 7-min irradiation and after equilibration for 60 min. The water sorption for all polymers examined increased with increasing polymer weight and reached a constant value at high polymer weight. The maximum amounts of sorbed water were 270, 80, 44, 30, and 20 ng for PMANI(A), PMANI(B), PMANI(C), PPRNI, and PBZNI, respectively. Although the water sorption increased with increasing styrenesulfonic acid units formed photochemically, the hydrophobic nature of the methacrylate ester groups decreased the water sorption. Although a good linear relationship between the water sorption and unirradiated polymer mass was observed (see Figure 2), a saturation phenomenon for the water sorption was observed above ca. 1000 ng (thickness = 51 nm) for the irradiated polymers. 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.

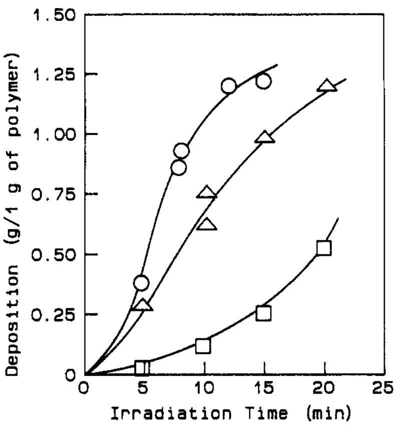


Figure 5. Effect of irradiation time on the SiO_2 deposition using TMOS. Polymer: (○) PMANI(A), (△) PMANI(B), and (□) PMANI(C). CVD treatment time: 4 min at 30 °C. Relative humidity: 95%. Polymer weight: 2 × 10^{-4} g. Surface area: 1.9 cm^2.

Upon photolysis of the NISS units, 1-tetralone and 1-tetralone azine, which have poor affinity for water, could be formed in addition to sulfonic acid. The sorption of water at the surface of the irradiated polymer films may induce the aggregation of 1-tetralone and/or 1-tetralone azine in the layer, which may act as a "hydrophobic barrier" to prevent further diffusion of water molecules. To test this hypothesis, irradiated PMANI(B) was exposed to the vapor of a mixed solvent of water and methanol (60/20, v/v), the latter having good affinity for 1-tetralone and its azine. The relationship between the gas sorption and the thickness of the polymer films was measured, and the vapor sorption was observed to increase linearly with increasing polymer weight. No saturation phenomenon was observed.

Silicon Oxide Deposition. In the presence of water and strong acids, the hydrolysis and subsequent polycondensation reactions of $Si(OR)_4$ and its homologues lead to the formation of silicon oxide networks, which is well-known as the sol–gel process for silica glass formation.[14,15] When the irradiated polymers bearing NISS units were exposed to the vapor of $Si(OR)_4$ or $CH_3Si(OR)_3$ at room temperature, SiO_2 was formed in the near surface region of the films. SiO_2 formation was confirmed by IR analysis. Irradiated PMANI(A) film exposed to TMOS vapor showed new peaks at 1080 (Si–O–Si), 940 (Si–OH), and 3300 cm^{-1} (Si–OH). The presence of Si–OH peaks suggests that the polycondensation reaction of $Si(OH)_4$ does not occur completely and silanol groups still remain in the film. It has been reported that silicon glasses obtained from the sol–gel processes at relatively low temperatures contain silanol groups.[14,15] No SiO_2 formation was observed in the unirradiated areas of the polymer films, since the styrenesulfonic acid units formed photochemically are essentially for catalyzing the hydrolysis of the silicon compounds.

Figure 5 shows the relationship between irradiation time and SiO_2 formation in PMANI polymers. SiO_2 formation increased with increasing irradiation time and decreased in the order PMANI(A) > PMANI(B) > PMANI(C). This means that the SiO_2 formation rate is proportional to the number of sulfonic acids formed photochemically in the polymer matrix. It has been reported that the rate of hydrolysis of tetraalkyl orthosilicates in solution is first order in acid concentration under conditions of excess water.[27,28] The amount of water initially sorbed into the irradiated polymers was not enough for the formation of SiO_2 at the polymer surfaces (see Figures 2 and 4). Thus water must be supplied from the atmosphere during SiO_2

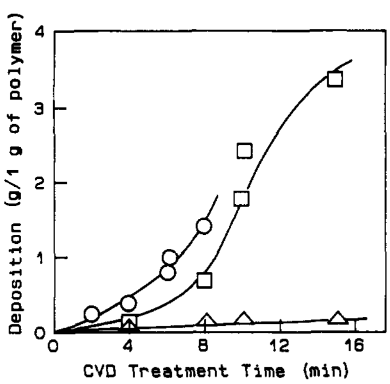


Figure 6. Relationship between CVD treatment time and SiO$_2$ deposition at surface of irradiated PMANI(B) film using TMOS at 30 °C. Relative humidity: (○) 95, (□) 58, and (△) 32%. Exposure dose: 62 mJ/cm^2. Polymer weight: 2×10^{-4} g. Surface area: 1.9 cm^2.

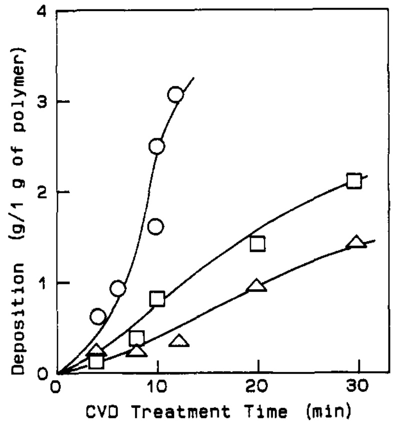


Figure 7. Effect of the polymer structure on the SiO$_2$ deposition using TMOS at 30 °C. Polymer: (○) PMANI(B), (□) PPRNI, and (△) PBZNI. Exposure dose: 62 mJ/cm^2. Relative humidity: 95%. Polymer weight: 2×10^{-4} g. Surface area: 1.9 cm^2.

network formation.

Figure 6 shows the effect of relative humidity on SiO$_2$ formation in exposed PMANI(B) at 30 °C. The relative humidity was adjusted to 95, 58, and 32% by placing aqueous solutions of 2 M KNO$_3$, saturated NaBr, and saturated CaCl$_2$ at the bottom of the vessel, respectively. SiO$_2$ formation decreased with decreasing relative humidity and was negligible at a relative humidity of 32%.

Figure 7 shows the influence of the methacrylate structure on SiO$_2$ formation at the irradiated polymer surface. The NISS content of the three polymers was almost the same. SiO$_2$ formation decreased in the order PMANI(B) > PPRNI > PBZNI, the same trend observed in water sorption experiments.

Figure 8 shows the effects of the thickness of the irradiated PMANI(A) and PMANI(C) films on SiO$_2$ formation. The treatment times for the irradiated polymer films to TMOS gas were 4 and 15 min, respectively, at 30 °C. SiO$_2$ formation increased with increasing polymer thickness and showed a saturation at thicknesses above ca. 400 and 800 nm for PMANI(A) and PMANI(C), respectively. This roughly corresponds to the penetration depth of UV light, which induces the photolysis of NISS units, since the absorbances of PMANI(A) (400-nm-thickness) and PMANI(C) (800-nm-thickness) films were 1.2 and 1.1 at 254 nm, respectively.

The dependence of SiO$_2$ formation on the thickness of polymer films means that TMOS diffuses into the polymer film and the hydrolysis and subsequent polycondensation reactions occur beneath the film surface and at the film–air interface. The maximum depth for the SiO$_2$ network formation can be determined by the light penetrating depth. The saturation phenomenon was not due to the diffusion depth of the alkoxysilane vapor during the CVD treatment time. Because the saturated point did not depend on the CVD treatment time under the present experimental conditions. The depth of the SiO$_2$ network layer was beyond the depth of the water sorption layer of the irradiated polymers (see Figure 4). The methanol liberated during the hydrolysis of TMOS in the film may help the diffusion of water in the film by destroying the "hydrophobic barrier" of the photochemically formed 1-tetralone and/or 1-tetralone azine as discussed above for the sorption of the vapor of a mixture of water and methanol by the irradiated polymers.

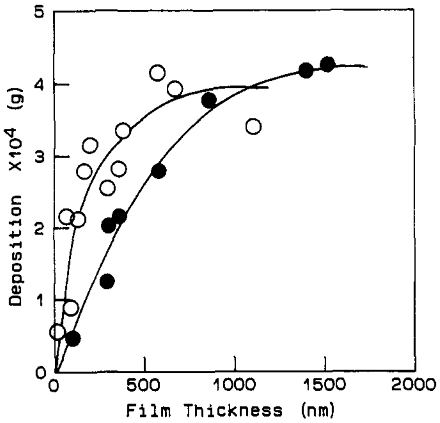


Figure 8. Effect of film thickness on the SiO$_2$ deposition using TMOS at 30 °C. Polymer: (○) PMANI(A) and (●) PMANI(C). CVD treatment time: 4 min for PMANI(A) and 15 min for PMANI(C). Relative humidity: 95%. Exposure dose: 62 mJ/cm^2. Surface area: 1.9 cm^2.

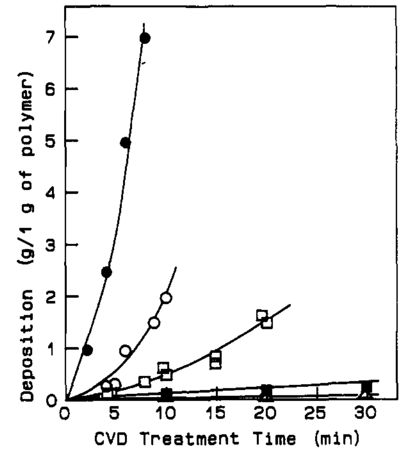


Figure 9. Effect of silicon compound structure on SiO$_2$ deposition in irradiated PMANI(B) at 30 °C. Silicon compounds: (●) MTMOS, (○) TMOS, (□) MTEOS, (■) TEOS, and (△) TPOS. Exposure dose: 62 mJ/cm^2. Polymer weight: 2×10^{-4} g. Surface area: 1.9 cm^2. Relative humidity: 95%.

Figure 9 shows SiO$_2$ formation in irradiated PMANI(B) film using tetraalkyl orthosilicates and their homologues. The SiO$_2$ formation rate decreased in the order MTMOS > TMOS > MTEOS > TEOS > TPOS. SiO$_2$ formation using TPOS was negligibly small. Table II shows the pseudo-first-order rate constants (k_{obs}) for the hydrolysis of the silicon compounds in acetone at 25 °C using *p*-toluenesulfonic acid as a catalyst and the concentration (V_c) of the silicon compounds in the vapor phase. The k_{obs} values were obtained from the change in the concentration of silicon compounds in actone solution using gas chromatography (GC) with a glass column packed with

Table II
Pseudo-First-Order Rate Constants (k_{obs}) for the Hydrolysis and Concentrations (V_c) of the Silicon Compounds in a Nitrogen Atmosphere

silicon compound	$k_{obs}{}^a/s^{-1}$	$V_c{}^b$/(mol/L)	bp^c/°C
TMOS	2.80×10^{-4}	1.46×10^{-4}	121
TEOS	2.52×10^{-5}	2.64×10^{-5}	168
TPOS	2.34×10^{-5}	3.32×10^{-7}	94/(5 mmHg)
MTMOS	5.28×10^{-4}	3.84×10^{-4}	102
MTEOS	6.55×10^{-4}	3.44×10^{-5}	141

[a] In acetone at 25 °C: [silicon compound] = 0.10 mol/L, [H_2O] = 1.10 mol/L, [*p*-toluenesulfonic acid] = 4.10×10^{-5} mol/L. [b] At 30 °C in a nitrogen atmosphere. [c] Boiling point cited from the *Handbook of Fine Chemicals*; Aldrich Chemical Co.: Milwaukee, WI, 1990.

poly(ethylene glycol). To obtain the V_c values, the flowing N_2 gas containing silicon compounds was trapped with liquid nitrogen and the silicon compounds trapped during certain periods were subjected to GC analysis. The k_{obs} values decreased in the order MTEOS ≈ MTMOS > TMOS > TEOS ≈ TPOS. The V_c values decreased in the order MTMOS > TMOS > MTEOS > TEOS > TPOS, which is consistent with their boiling points. Although the k_{obs} values for TEOS and TPOS were almost the same, the SiO_2 formation at the irradiated polymer surface using TPOS was much lower than that using TEOS. Although V_c values for TEOS and MTEOS were almost the same, SiO_2 formation from MTEOS was much higher than that from TEOS. Thus the SiO_2 formation rates in the irradiated polymers was determined by both k_{obs} and V_c values. The irradiated polymer surfaces exposed to MTMOS and MTEOS were clear, but the surfaces exposed to TMOS or TEOS were opaque. The methyl group on the Si atom affects the growing process of SiO_2 networks.

Since SiO_2 network has been known to function as an etch barrier for O_2 RIE, this system seems to be useful for the negative tone oxygen-plasma-developable resist systems.

Conclusions

The photosensitive polymers containing 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate (NISS), which forms *p*-styrenesulfonic acid upon UV irradiation, were synthesized by the photoinitiated radical copolymerization of NISS and either methyl methacrylate, isopropyl methacrylate, or benzyl methacrylate. Water sorption of these polymers was enhanced upon UV irradiation. The hydrophobic nature of the methacrylate units inhibited water sorption in both irradiated and unirradiated polymers. When the UV-irradiated polymers were exposed to the vapor of tetraalkyl orthosilicates and their homologues under humid conditions at 30 °C, SiO_2 network formation was observed. The SiO_2 formation rate was strongly dependent on the water sorption ability of the polymers, the number of the photochemically formed *p*-styrenesulfonic acid units, the hydrolytic reactivity of the silicon compounds and the concentrations of the silicon compounds in the vapor phase.

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