

Study on Organosilicon Positive Resist. I. Syntheses and Characterization of Silsesquioxane, Siloxane, and Silmethylene Polymers with Phenolic Hydroxy Groups

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SYNOPSIS

Silsesquioxane, siloxane, and silmethylenes polymers with phenolic hydroxy groups were prepared in order to obtain alkali-soluble organosilicon polymers. These polymers have structures in which the phenol moieties are separated by one carbon from the silicon. The hydroxy groups were protected as methoxy groups in polymerization processes, then were changed into hydroxy groups by a reaction with trimethylsilyl iodide followed by alcoholysis. In the course of discussion on the characteristics of these polymers, silsesquioxane with phenolic hydroxy groups is found to possess excellent properties for matrix resins of alkali-developable organosilicon resists, such as O₂RIE resistance and heat resistance.

INTRODUCTION

Alkali-soluble polymers, such as novolac resin and polyvinylphenol, have been widely used as matrix resins of alkali-developable radiation sensitive resists for semiconductor lithography.¹ These resists are composed of an alkali-soluble matrix resin and a radiation sensitive compound (a dissolution inhibitor). For instance, composites prepared with quinone diazide, bisazide, and poly(olefin sulfone) are used for positive photoresist, negative photoresist, and positive EB resist, respectively. These resists have been preferably adopted in present semiconductor manufacturing because they have good resolution and high resistance to halogen reactive ion etching (RIE). Further, organic solvents are not used in the development processes.

On the other hand, as VLSI circuit density increases, multilayer resist systems have been extensively studied to achieve higher resolution below submicron levels on nonplanar device surfaces.² In these systems the device surface is planarized with an organic layer, which is patterned by Oxygen RIE (O₂RIE) through an etching mask. Multilayer resist

systems are classified into a bilayer resist system and a trilayer resist system, depending on whether the etching mask is made from inorganic materials, which served also as an imaging material, or were patterned by a conventional lithographic procedure. The bilayer resist system is superior to the trilayer resist system because of its simplicity. However, the resist for the bilayer resist system is required to have O₂RIE resistance, which conventional resists do not have. Thus, many kinds of organosilicon resists have been investigated since they are changed into silicon oxide by O₂ plasma and become the etching mask.^{3,4} Especially, alkali-developable organosilicon resists have been sought for their compatibility with the conventional lithographic procedure. Consequently, the alkali-soluble organosilicon polymers have come to be important in the development of the alkali-developable organosilicon resist for the bilayer resist system.

Two types of organosilicon polymers have been reported and used for the matrix resins: those in which silicon atoms are introduced into the polymer side chain of alkali-soluble organic polymers,⁵⁻⁹ and those in which silicon atoms are present in the polymer main chain.¹⁰⁻¹³ Recent studies on O₂RIE resistance of organosilicon polymers have revealed that the latter type has, generally, higher O₂RIE resistance than the former type. Also O₂RIE resistance

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increases when the silicon content in the polymer is increased. Thus, we synthesized novel alkali-soluble organosilicon polymers, which belong to the latter type, with phenolic hydroxy groups in the polymer side chain. The phenolic hydroxy group has been known to give adequate alkali-solubility to polymers. In this study, we present the syntheses and characterization of the novel, alkali-soluble organosilicon polymers and we exhibit their usefulness as the matrix resin of alkali-developable organosilicon resists.

EXPERIMENTAL

Measurement

$^1\text{H-NMR}$, IR, and UV spectra were recorded on a Hitachi R24A 60 MHz NMR spectrometer, a Hitachi 345 IR spectrometer, and a Hitachi 200-10 UV spectrometer, respectively. Melting point was determined by a Yanaco Micro Melting Point Apparatus. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on an ULVAC thermal analyzer system DSC-1500 and HP-5000, respectively. Molecular weight distributions were measured on a Hitachi 635 High Pressure Liquid Chromatograph fitted with a Hitachi 635M Multiwavelength UV Monitor (connected Shodex PAK A-804 and A-803 columns, THF flow rate 1 mL/min). The instrument was calibrated with polystyrene standard. Oxygen reactive ion etching was carried out by using a parallel plate dry etching reactor (13.56 MHz, RF 200W, O_2 pressure 20 mtorr, bias voltage -130 – -140V).

Materials

p-Methoxybenzyltrichlorosilane

In a 2-L, three-necked flask, equipped with a stirrer, condenser, dropping funnel, and thermometer, were placed 30.0 g (1.23 gatom) of magnesium powder, 170 g (1.00 mol) of silicon tetrachloride, and 500 mL of dry diethyl ether. To the flask, cooled below 10°C , 100 g (0.639 mol) of *p*-methoxybenzyl chloride in 200 mL of dry diethyl ether was added dropwise over a period of 4 h. After stirring at room temperature for 1 h, excess magnesium and magnesium chloride were removed by filtration under reduced pressure. The filtrate was distilled to give 44.0 g (0.172 mol) (26.9% yield) of the desired product: bp $101.5^\circ\text{C}/3$ mmHg; $^1\text{H-NMR}$ δ (ppm in CCl_4 , CH_2Cl_2 , δ 5.33): 2.91 (2H, s), 3.90 (3H, s), 6.91 (2H, d, $J = 8$ Hz), 7.20 (2H, d, $J = 8$ Hz).

In a 5-L, three-necked flask, equipped with a stirrer, condenser, and dropping funnel, were placed 79 g (0.80 mol) of cuprous chloride and 1261 g (8.800 mol) of tri-*n*-propylamine. A mixture of 1256 g (8.020 mol) of *p*-methoxybenzyl chloride and 1184 g (8.740 mol) of trichlorosilane was added dropwise over a period of 5 h under nitrogen atmosphere. After stirring for 5 h, 1 L of *n*-hexane was added to the flask, and the precipitated salt was removed by filtration under reduced pressure. The filtrate was distilled to give 1182 g (4.620 mol) (57.70% yield) of the desired product.

Poly(p-methoxybenzylsilsesquioxane)

In a 5-L, three necked flask, equipped with a stirrer, condenser, dropping funnel, and HCl trap, was placed 2 L of water. To this, 1182 g (4.620 mol) of *p*-methoxybenzyltrichlorosilane in 1 L of toluene was added dropwise over a period of 1.5 h. After stirring for 1.5 h at room temperature, the organic layer was separated and toluene was distilled away. The hydrolyzate was heated at 200°C for 1 h under reduced pressure to remove trace amounts of toluene and water. After cooling to room temperature, 12 g of 10 wt % potassium hydroxide in methanol was added to the hydrolyzate. The mixture was heated to 200°C for 2 h without stirring, and the heating was continued for more than 1 h under reduced pressure to remove trace amounts of water. Obtained was 797 g (99.4% yield) of the desired polymer: Mw 3000; $^1\text{H-NMR}$ δ (ppm in CDCl_3 , CH_2Cl_2 , δ 5.33): 1.95 (2 H, br.s), 3.83 (3 H, br.s), 6.80 (4 H, br.s); IR: 2940, 2850, 1620, 1520, 1470, 1305, 1260, 1190, 1130, 1040, 845 cm^{-1} .

Poly(p-hydroxybenzylsilsesquioxane)

A 500-mL, three-necked flask, equipped with a stirrer, condenser, dropping funnel, and thermometer, was filled with dry nitrogen. In the flask were placed 56.0 g (0.323 mol, $\text{MeOC}_6\text{H}_4\text{SiO}_{3/2}$ unit) of poly(*p*-methoxybenzylsilsesquioxane), 150 mL of dry chloroform, and trimethylsilyl iodide prepared with 40.0 g (0.273 mol) of hexamethyldisilane and 65.6 g (0.259 mol) of iodide. After the mixture was stirred for 30 h at 50 – 60°C , 200 mL of methanol was added dropwise at 50 – 60°C . Low boiling fractions were distilled away under reduced pressure and the residue was extracted with a mixed solvent of diethyl ether and tetrahydrofuran. The extract was washed with an aqueous sodium hydrogen sulfite, aqueous sodium hydrogen carbonate, and brine. After the solvent was distilled away under reduced pressure,

the crude polymer was reprecipitated from tetrahydrofuran/water and acetone/hexane, and was dried at 120°C under reduced pressure. Obtained was 44.0 g (94.0% yield) of the desired polymer.

A 5-L, three-necked flask, equipped with a stirrer, condenser, dropping funnel, and HCl trap, was filled with dry nitrogen. In the flask were placed 797 g (4.60 mol, MeOC₆H₄SiO_{3/2} unit) of poly(*p*-methoxybenzylsilsequioxane) in 600 mL of dry acetonitrile and 1378 g (9.200 mol) of sodium iodide. To the flask was added dropwise 999 g (9.20 mol) of trimethylsilyl chloride over a period of 4 h under refluxing. After the mixture was stirred for 18 h, 200 mL of water was added dropwise, and water and acetonitrile were further added until the mixture was separated into a hexamethyldisiloxane layer, an acetonitrile layer, and a water layer. The mixture was then heated under refluxing for 6 h. The acetonitrile layer was separated and washed with an aqueous sodium hydrogen sulfite and brine. After the acetonitrile layer was added to a large amount of water, the crude polymer was reprecipitated from acetonitrile/water and dried at 120°C under reduced pressure. Obtained was 368 g (50.2% yield) of the desired polymer: Mw 3500; ¹H-NMR δ (ppm in DMSO-d₆, CH₂Cl₂ δ 5.68): 1.75 (2 H, br.s), 6.61 (4 H, br.s), 8.93 (1 H, br.s); IR: 3350, 1620, 1520, 1430, 1250, 1190, 1130, 1050, 845, 805, 760 cm⁻¹.

Methyldichloro-*p*-methoxybenzylsilane

In a 1-L, three-necked flask, equipped with a stirrer, condenser, dropping funnel, and thermometer, were placed 82.6 g (0.640 mol) of methyltrichlorosilane, and 200 mL of dry diethyl ether. To the flask cooled below 10°C, 50.0 g (0.319 mol) of *p*-methoxybenzyl chloride in 300 mL of dry diethyl ether was added dropwise over a period of 4 h. After stirring at room temperature for 1 h, excess magnesium and magnesium chloride were removed by filtration under reduced pressure. The filtrate was distilled to give 48.8 g (0.208 mol) (65.2% yield) of the desired product: bp 86–88°C/2 mmHg; ¹H-NMR δ (ppm in CCl₄, CH₂Cl₂, δ 5.33): 0.79 (3 H, s), 2.68 (2 H, s), 3.84 (3 H, s), 6.80 (2 H, d, J = 9 Hz), 7.18 (2 H, d, J = 9 Hz); IR: 1620, 1520, 1480, 1310, 1260, 1190, 1100, 1050, 850, 810, 755 cm⁻¹.

Methyl-*p*-methoxybenzylsiloxane trimer

In a 1-L, three-necked flask, equipped with a stirrer, condenser, and dropping funnel, was placed 200 mL of water. Added dropwise was 85.6 g (0.364 mol) of methyldichloro-*p*-methoxybenzylsilane in 200 mL of diethyl ether over a period of 4 h at room tem-

perature. After stirring for 1 h, the ether layer was separated and was washed with water until the water was neutralized. The ether solution was dried over sodium sulfate and diethyl ether was distilled away. The distillation was then continued over calcium hydride to give 20.3 g (37.5 mmol) (30.9% yield) of the desired product: bp 241°C/0.08 mmHg–253°C/0.13 mmHg; ¹H-NMR δ (ppm in CCl₄, CH₂Cl₂, δ 5.33) –0.02, 0.03, 0.16 (9 H, 3 s), 1.96, 2.07 (6 H, 2 s), 3.79 (9 H, s), 6.74 (6 H, d, J = 9 Hz), 6.98 (6 H, d, J = 9 Hz); IR: 1620, 1520, 1470, 1305, 1260, 1220, 1185, 1090, 1030, 840, 815, 770 cm⁻¹.

Poly(methyl-*p*-methoxybenzylsiloxane)

In a 100-mL flask, containing a magnet rod, were placed 9.0 g (17 mmol) of methyl-*p*-methoxybenzylsiloxane trimer and 45 mg of 0.5 wt % tetramethylammonium hydroxide in methanol. The stoppered flask was dipped in an oil bath at 80°C, and was stirred for 1 h to give the desired polymer: Mw 19,000; ¹H-NMR δ (ppm in CCl₄, CH₂Cl₂, δ 5.33) 0.00 (3 H, br.s), 1.94 (2 H, br.s), 3.71, 3.80 (3 H, 2s), 6.82 (4 H, br.s); IR: 2975, 2850, 1620, 1520, 1475, 1305, 1260, 1225, 1190, 1090, 1040, 845, 810, 775, 755 cm⁻¹.

Poly(methyl-*p*-hydroxybenzylsiloxane)

In a 100-mL, three-necked flask, equipped with a stirrer, condenser, and dropping funnel, were placed 5.01 g of poly(methyl-*p*-methoxybenzylsiloxane) (Mw = 23,000, 27.8 mmol, MeOC₆H₄CH₂SiMeO unit) in 15 mL of dry chloroform and 8.57 g (42.8 mmol) of trimethylsilyl iodide, and the mixture was stirred for 4 h at room temperature. After 30 mL of methanol was added dropwise, the stirring was continued for 3 h, and then the low-boiling fractions were distilled away under reduced pressure at room temperature. The residue was extracted with tetrahydrofuran and diethyl ether. The extract was washed with an aqueous sodium hydrogen sulfite, an aqueous sodium hydrogen carbonate, and brine. The solvent was distilled away under reduced pressure. The crude polymer was reprecipitated from tetrahydrofuran/water and acetone/hexane and was dried at 120°C under reduced pressure to give 3.41 g (73.9% yield) of the desired polymer: Mw 10,000; OH-conversion 80%; mp 53–68°C; Td 140°C; ¹H-NMR δ (ppm in DMSO-d₆, CH₂Cl₂ δ 5.68): –0.07 (–CH₃, br.s), 1.85 (–CH₂–, br.s), 4.00 (–OCH₃, br.s), 6.61 (ring protons, br.s), 8.81 (–OH, br.s); IR: 3320, 1620, 1510, 1450, 1270, 1240, 1180, 1070, 840, 800 cm⁻¹.

Chlorodimethyl-*p*-methoxybenzylsilane

In a 2-L, three-necked flask, equipped with a stirrer, condenser, dropping funnel, and thermometer, were placed 31.0 g (1.28 mol) of magnesium powder, 129 g (1.00 mol) of dimethyldichlorosilane, and 500 mL of dry diethyl ether. To the flask cooled below 10°C, 100 g (0.639 mol) of *p*-methoxybenzyl chloride in 250 mL of dry diethyl ether was added dropwise over a period of 4 h. After stirring at room temperature for 1 h, excess magnesium and magnesium chloride were removed by filtration under reduced pressure. The filtrate was distilled to give 87.8 g (0.409 mol) (64.0% yield) of the desired product: bp 80°C/1 mmHg; ¹H-NMR δ (ppm in CCl₄, CH₂Cl₂, δ 5.33): 0.46 (6 H, s), 2.40 (2 H, s), 3.83 (3 H, s), 6.82 (2 H, d, J = 9 Hz), 7.08 (2 H, d, J = 9 Hz); IR: 2970, 1620, 1520, 1475, 1310, 1260, 1195, 1090, 1056, 855, 825, 780 cm⁻¹.

Bromo-*p*-methoxyphenylchlorodimethylsilylmethane (dl)

In a 500-mL, three-necked flask, equipped with a stirrer and condenser, were placed 43.2 g (0.200 mol) of chlorodimethyl-*p*-methoxybenzylsilane and 200 mL of carbon tetrachloride. Added slowly was 35.6 g (0.200 mol) of *N*-bromosuccinimide, and this mixture was stirred for 1 h. Succinimide was removed by filtration under reduced pressure. The filtrate was distilled to give 31.7 g (0.108 mol) (54.0% yield) of the desired product: bp 113–117°C/2.5 mmHg; mp lower than 30°C; ¹H-NMR δ (ppm in CCl₄, TMS): 0.50 (3 H, s), 0.60 (3 H, s), 3.73 (3 H, s), 4.32 (1 H, s), 6.73 (2 H, d, J = 9 Hz), 7.19 (2 H, d, J = 9 Hz); IR: 1610, 1510, 1465, 1305, 1260, 1185, 1040, 865, 845, 820, 800 cm⁻¹.

Poly(1,1-dimethyl-2-*p*-methoxyphenylsilmethylene)

In a 500-mL, three-necked flask, equipped with a Herschberg stirrer, condenser, and dropping funnel, with the atmosphere therein replaced by nitrogen, were placed 7.6 g (0.33 gatom) of dispersed sodium and 120 mL of toluene. To this, 44.1 g (150 mmol) of bromo-*p*-methoxyphenylchlorodimethylsilylmethane in 30 mL of toluene was added dropwise over a period of 1 h with refluxing. After stirring for 1 h, the reaction mixture was poured into methanol to remove excess sodium and to precipitate the polymer. After filtration, the polymer dissolved in tetrahydrofuran was poured into water to remove the sodium salt. The crude polymer was washed with methanol, and was dried at 120°C under reduced pressure. Obtained was 10.0 g (54.1 mmol) (37.4%

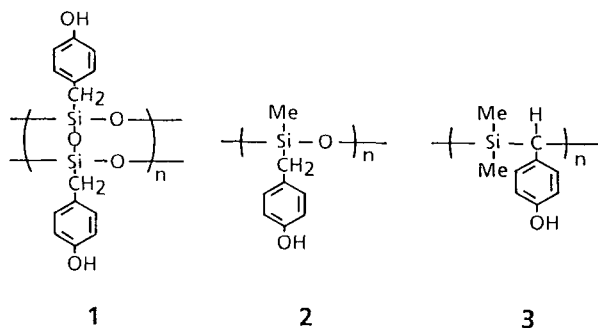
yield) of the desired polymer: Mw 3400; Softening point 121–125°C; ¹H-NMR δ (ppm in C₆D₆, CH₂Cl₂ δ 5.33): 1.27 (6 H, br.s), 4.43 (3 H, br.s), 7.4–8.7 (4 H, br.s), benzyl proton undetectable; IR: 2960, 2850, 1610, 1510, 1470, 1385, 1300, 1260, 1100, 1045, 860, 790 cm⁻¹.

Poly(1,1-dimethyl-2-*p*-hydroxyphenylsilmethylene)

In a 200-mL, three-necked flask, equipped with a stirrer, condenser, and dropping funnel, were placed 6.11 g of poly(1,1-dimethyl-2-*p*-methoxyphenylsilmethylene) (Mw 3000, 34.3 mmol, MeOC₆H₄CHSiMe₂ unit) in 40 mL of dry chloroform and 11.0 g (54.8 mmol) of trimethylsilyl iodide. After the mixture was stirred for 140 h at 50°C, 80 mL of methanol was added, and the stirring was continued for 3 h. Low-boiling fractions were distilled away at room temperature under reduced pressure. The residue was extracted with tetrahydrofuran and diethyl ether. The extract was washed with an aqueous sodium hydrogen sulfite, an aqueous sodium hydrogen carbonate and brine. The solvent was distilled away under reduced pressure. The crude polymer was reprecipitated with tetrahydrofuran/water and dried at 120°C under reduced pressure to give 5.10 g (20.9% yield) of the desired polymer: Mw 2300; OH-conversion 86%; Softening point 107–113°C; Td 155°C; ¹H-NMR δ (ppm in DMSO-d₆, CH₂Cl₂ δ 5.68): -0.09 (-CH₃, br.s), 3.68 (-OCH₃, br.s), 6.56 (ring protons br.s), benzyl and hydroxy protons undetectable; IR: 3380, 2980, 1510, 1270, 1100, 1040, 860, 810 cm⁻¹.

RESULTS AND DISCUSSION**Molecular Design**

We selected well-known organosilicon polymers, polysilsesquioxane, polysiloxane, and polysilmethylene for the polymer main chain. These skeletons could be converted efficiently to silicon oxide by oxygen plasma. To add alkali-solubility to the polymers, it is necessary to introduce phenolic hydroxy groups in the polymer side chain. However, combining silicon and phenol directly should be avoided because the protodesilylation reaction or rearrangement reaction might occur, resulting in cleavage of a silicon-phenol bond.^{14,15} Therefore, we would insert one carbon between them and adopt smaller organic substituents as the polymer side chain in order to increase the silicon contents in polymers. Scheme 1 shows the designed molecular structures of the alkali-soluble organosilicon polymers.



Scheme 1 Molecular structures of alkali-soluble organosilicon polymers.

Syntheses and Structures

The most important feature of these syntheses is the protection of the reactive phenolic hydroxy group. The protecting group must stand against the severe acidic and basic reaction conditions. Thus, we adopted the methoxy group as the protection group of the hydroxy group and finally changed it into a hydroxy group by a reaction with trimethylsilyl iodide in chloroform followed by methanolysis.¹⁶ This conversion could also be carried out by a reaction with trimethylsilylchloride/sodium iodide in acetonitrile followed by hydrolysis.¹⁷ Each preparative method is as follows.

Poly(p-hydroxybenzylsilsequioxane) (1)

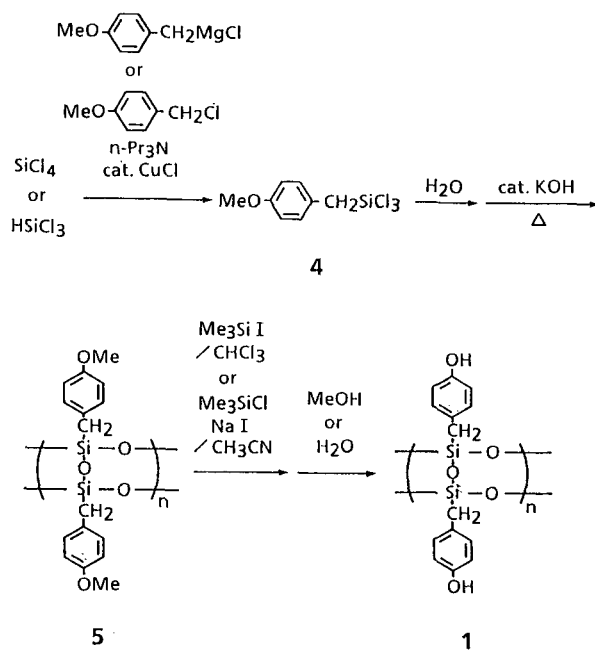
See Scheme 2: *p*-Methoxybenzyltrichlorosilane (**4**) was obtained by a reaction of tetrachlorosilane with *p*-methoxybenzyl magnesium chloride or a reaction of trichlorosilane with *p*-methoxybenzyl chloride in the presence of catalytic cuprous chloride.¹⁸ **4** was hydrolyzed in water and then was condensed in the presence of catalytic potassium hydroxide^{19,20} to yield poly(*p*-methoxybenzylsilsequioxane) (**5**). **5** was converted into **1** by the above-mentioned deprotection reactions.

Poly(methyl-p-hydroxybenzylsiloxane) (2)

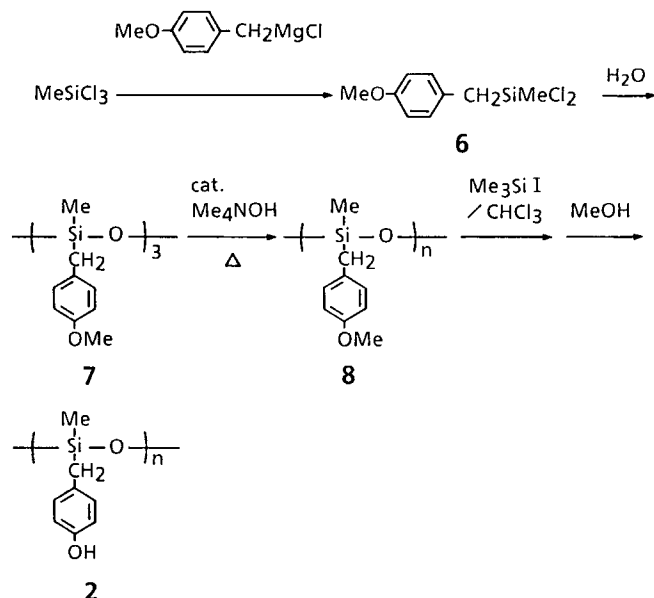
See Scheme 3: *p*-Methoxybenzylmethyldichlorosilane (**6**) was obtained by a reaction of methyltrichlorosilane with *p*-methoxybenzyl magnesium chloride. **6** was hydrolyzed in water to give a siloxane trimer (**7**), which underwent a ring opening polymerization reaction in the presence of catalytic tetramethylammonium hydroxide²¹ to yield poly(methyl-*p*-methoxybenzylsiloxane) (**8**). **8** was finally changed into **2** by a reaction with trimethylsilyl iodide followed by methanolysis.

Poly(1,1-dimethyl-2-p-hydroxyphenylsilmethylene) (3)

See Scheme 4: *p*-Methoxybenzylchlorodimethylsilane (**9**) was obtained by a reaction of dimethyldi-



Scheme 2 Synthesis of poly(*p*-hydroxybenzylsilsequioxane) (**1**).

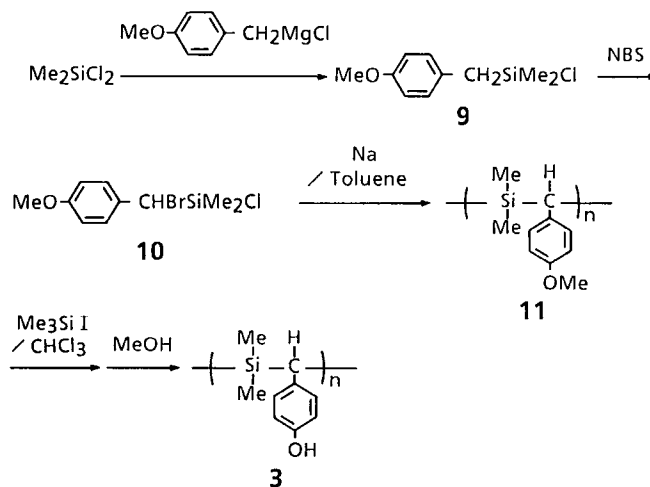


Scheme 3 Synthesis of poly(methyl-*p*-hydroxybenzylsiloxane) (2).

chlorosilane with *p*-methoxybenzyl magnesium chloride and its benzyl position was brominated by *N*-bromosuccinimide to yield brom-*p*-methoxyphenylchlorodimethylsilylmethane (10). 10 was polycondensated by sodium in toluene to give poly(1,1-dimethyl-2-*p*-methoxyphenylsilmethylene) (11), which was converted into 3 by a reaction with trimethylsilyl iodide followed by methanolysis.

NMR spectra, IR spectra, and molecular distributions of the hydrolyzate of 4, 5, and 1, formed during the synthesis process of 1, are shown in Figures 1–3, respectively. The hydrolyzate of 4 has an average molecular weight of about 2000 and shows

a broad and intensive absorption of ν Si–OH at 3400 cm⁻¹ in the IR spectrum. This might indicate that the hydrolyzate has a structure in which about eleven *p*-methoxybenzyltrihydroxysilane, on average, are condensed at random with dehydration. Polymerization of the hydrolyzate in the presence of base catalyst gives a polymer that has an average molecular weight of about 4000 and displays a few peaks in the GPC chart. No absorption of ν Si–OH is present in the IR spectrum. Therefore, it might be considered that the hydrolyzate was condensed with dehydration in an intramolecular manner that resulted in the complete disappearance of Si–OH.



Scheme 4 Synthesis of poly(1,1-dimethyl-2-*p*-hydroxyphenylsilmethylene) (3).

It then underwent an intermolecular ring opening polymerization among a few molecules. The ladder structure of **5** is judged from the appearance of split peaks at 1100 cm^{-1} in the IR spectrum, which is assigned to the stretching bands of two kinds of SiOSi.²⁰ The average molecular weight scarcely changed from 3000 to 4500 on the bases of many polymerization experiments and the molecular distribution never changed in the process of the conversion from methoxy to hydroxy. The methoxy group could be converted clearly into the hydroxy group by a reaction with trimethylsilyl iodide followed by alcoholysis, which was proved by the appearance of an OH signal at 8.93 ppm, with a disappearance of the OMe signal at 3.83 ppm in the NMR spectrum, and the appearance of a νOH signal at 3350 cm^{-1} in the IR spectrum. The conversion rate was about 85–95% on average. Here it should be noted that treatment with sodium hydrogen sulfite, which quenches iodide, plays an important role in working up. This treatment bleaches iodide color and prevents the polymer from crosslinking. If the reaction mixture was heated without this treatment, the polymer would be insoluble, probably because of crosslinking by the radical reaction at the benzyl position.

Molecular distributions of **7**, **8**, and **2** are shown in Figure 4. A low molecular weight fraction of about

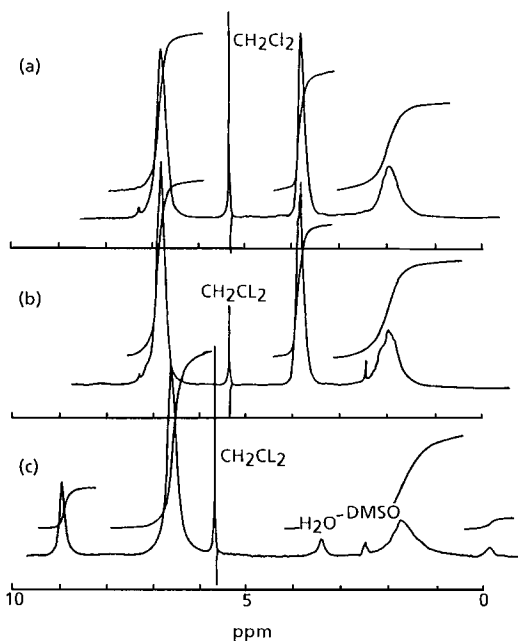


Figure 1 ^1H -NMR spectra of (a) hydrolyzate of *p*-methoxybenzyltrichlorosilane (**4**) in CDCl_3 , (b) poly(*p*-methoxybenzylsilsesquioxane) (**5**) in CDCl_3 , and (c) poly(*p*-hydroxybenzylsilsesquioxane) (**1**) in DMSO-d_6 .

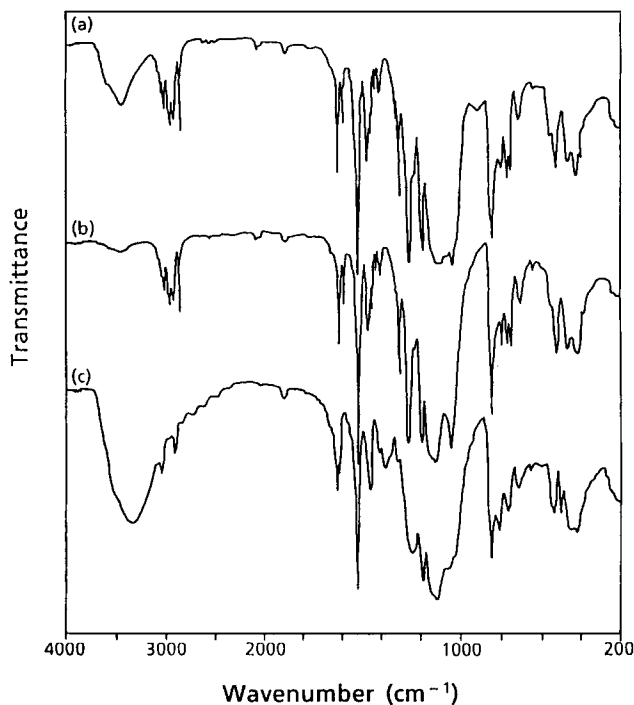


Figure 2 IR spectra of (a) hydrolyzate of *p*-methoxybenzyltrichlorosilane (**4**), (b) poly(*p*-methoxybenzylsilsesquioxane) (**5**), and (c) poly(*p*-hydroxybenzylsilsesquioxane) (**1**).

1000 and a high molecular weight fraction of about 20,000–30,000 were obtained after the ring opening polymerization of **7**. The low molecular weight frac-

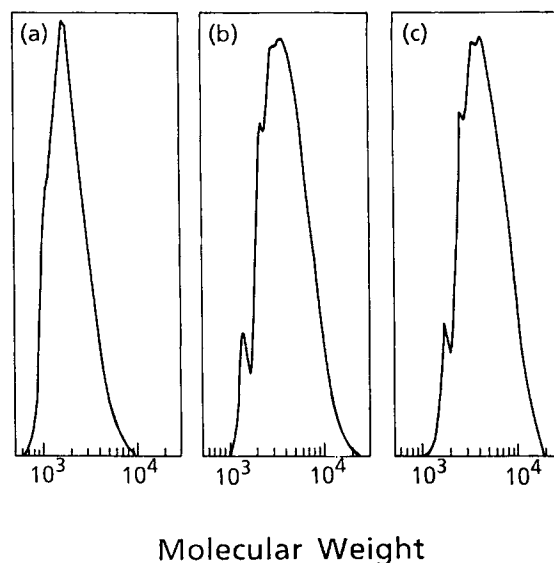


Figure 3 Molecular distributions of (a) hydrolyzate of *p*-methoxybenzyltrichlorosilane (**4**), (b) poly(*p*-methoxybenzylsilsesquioxane) (**5**), and (c) poly(*p*-hydroxybenzylsilsesquioxane) (**1**).

tion is considered to be formed by a degradation of polysiloxane during the polymerization. The molecular weight of the higher molecular weight fraction decreased during the conversion process from the methoxy group to the hydroxy group because of the degradation by generated acid. Furthermore, it was difficult to extract the higher molecular weight fraction. Hence, the molecular weight of the higher molecular weight fraction of the obtained polymer **2** became about 10,000.

Molecular distributions of **11** and **3** are shown in Figure 5. There are two different reaction sites in compound **10**. Therefore, polymer **11** is considered to contain Si-Si bonds and Si-C bonds. However, the Si-Si bond in **11** undergoes a disproportionate reaction with trimethylsilyl iodide, which results in the elimination of the polymer composed of the Si-Si bond. Actually, the average molecular weight of **3** decreased a little compared to that of **11**.

Characterization

The above mentioned polymers are soluble in alkaline water as well as in polar solvents such as methanol, tetrahydrofuran, *N,N*-dimethylacetamide, cyclohexanone, *iso*-amylacetate, 2-ethoxyethanol, and dimethylsulfoxide. They are, however, insoluble in nonpolar solvents such as toluene, *n*-hexane, and carbon tetrachloride.

The thermal properties are summarized in Table I. **1** is a glassy powder and its softening point is

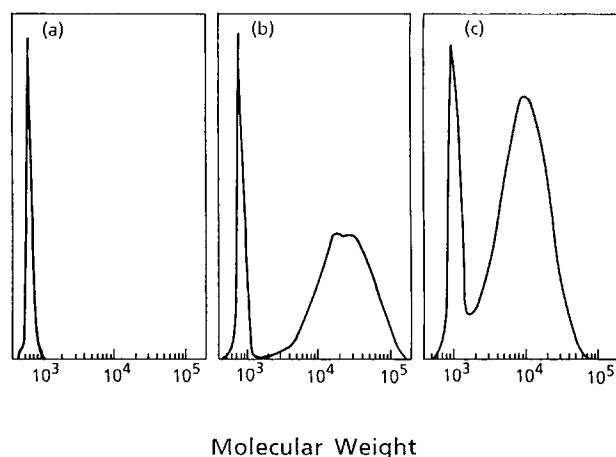


Figure 4 Molecular distributions of (a) methyl-*p*-methoxybenzylsiloxane trimer (**7**), (b) poly(methyl-*p*-methoxybenzylsiloxane) (**8**), and (c) poly(methyl-*p*-hydroxybenzylsiloxane) (**2**).

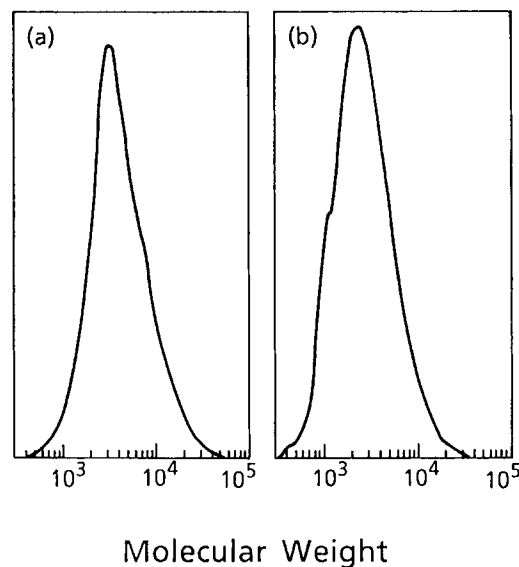


Figure 5 Molecular distributions of (a) poly(1,1-dimethyl-2-*p*-methoxyphenylsilmethylene) (**11**) and (b) poly(1,1-dimethyl-2-*p*-hydroxyphenylsilmethylene) (**3**).

between 125–135°C. The differential thermal analysis shows 107°C as T_g . **2** is a soft glass and melts at 53–68°C. **3** is a powder and its softening point is 107–113°C. The thermal gravimetric analyses of these polymers are shown in Figure 6. The degradation temperature (10°C/min in air) of **1**, **2**, and **3** are 373, 140, and 155°C, respectively. The thermal property of resist materials is an important factor in withstanding the high temperature semiconductor processes. In this respect, **1** has an adequately high heat resistance among the three polymers.

O₂RIE rates of the three polymers and PIQ (polyimide resin, Hitachi Chemical Co.) are shown in Figure 7. The O₂RIE rates are 2.3 nm/min for **1**, 29 nm/min for **2**, and 8.6 nm/min for **3**, while the rate of PIQ is 122 nm/min for the same conditions.

Table I Properties of Alkali-Soluble Organosilicon Polymers

| Polymer | 1 | 2 | 3 |
|--|----------|----------|----------|
| Si Content (wt %) | 18 | 15 | 17 |
| Softening Point (°C) | 125–135 | — | 107–113 |
| Heat Resistance (°C) ^a | 373 | 140 | 155 |
| O ₂ RIE Resistance ^b | 53 | 4 | 14 |

^a Degradation temperature (10°C/min in air).

^b O₂RIE rate ratio (PIQ/polymer).

The etching rate ratios of PIQ to the polymers are given in Table I. The Si contents in the polymers are also given in Table I. Polymer **1** exhibited the highest O₂RIE resistance among the three polymers; it was 53 times higher than that of PIQ. The fact that the O₂RIE resistance of **1** is much higher than that of **3**, in spite of almost the same Si content and adequate heat resistances, might indicate the importance of the polymer structure. That is, **1** has the structure most similar to silicon oxide. Thus, **1** could be easily changed into silicon oxide. This idea might bring about the expectation that the O₂RIE resistance of **2** would be second. However, **2** exhibited the lowest O₂RIE resistance among the three polymers. This is most likely because of the poor thermal property of **2**; **2** melts during the O₂RIE process, therefore, it is hard to form a silicon oxide resistance layer on the polymer surface.

We finally selected **1** as the best organosilicon polymer for the matrix resin of alkali-developable organosilicon resist, taking into consideration alkali-solubility, O₂RIE resistance, and thermal properties. In following articles, we will describe alkali-developable organosilicon positive resists prepared with **1**.

CONCLUSIONS

Poly(*p*-hydroxybenzylsilsesquioxane) (**1**), poly(methyl-*p*-hydroxybenzylsiloxane) (**2**), and

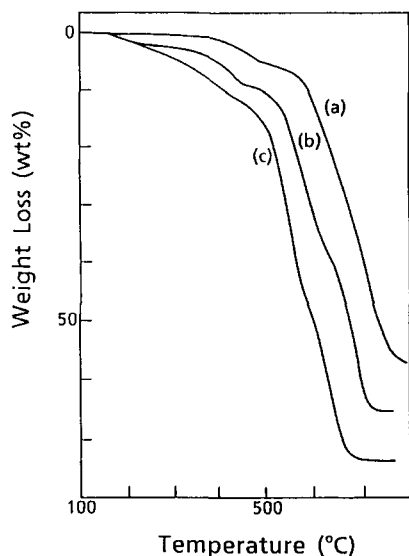


Figure 6 Thermal gravimetric analyses of (a) poly(*p*-hydroxybenzylsilsesquioxane) (**1**), (b) poly(methyl-*p*-hydroxybenzylsiloxane) (**2**), and (c) poly(1,1-dimethyl-2-*p*-hydroxyphenylsilmethylene) (**3**) (10°C/min in air).

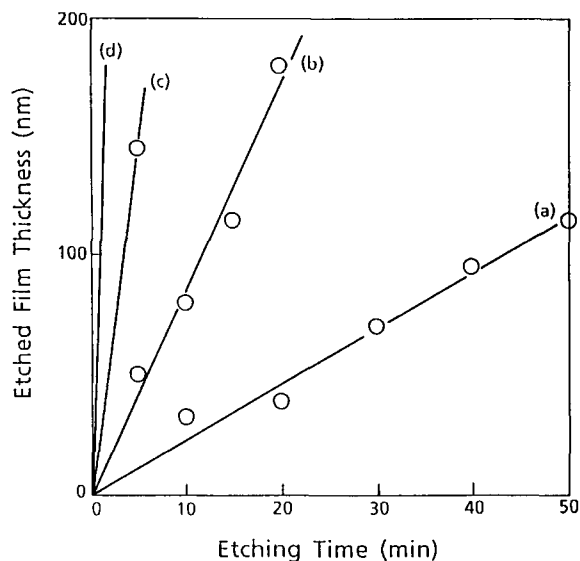


Figure 7 O₂RIE characteristics of (a) poly(*p*-hydroxybenzylsilsesquioxane) (**1**), (b) poly(methyl-*p*-hydroxybenzylsiloxane) (**2**), (c) poly(1,1-dimethyl-2-*p*-hydroxyphenylsilmethylene) (**3**), and (d) PIQ (13.56 MHz, RF 200 W, O₂ pressure 20 mtorr, bias voltage -130/-140V).

poly(1,1-dimethyl-2-*p*-hydroxyphenylsilmethylene) (**3**) were prepared in order to obtain alkali-soluble organosilicon polymers that are used for the matrix resin of alkali-developable organosilicon resists. Among the three polymers, **1** possesses the best properties for a matrix resin, such as O₂RIE resistance (53 times higher than that of PIQ) and thermal properties ($T_g = 107^\circ\text{C}$, $T_d = 373^\circ\text{C}$).

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