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Syntheses of Polysilanes with Functional Groups. 2. Polysilanes with Carboxylic Acids

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ABSTRACT: Polysilanes with carboxylic acids were synthesized by the reaction of phenol-linked polysilanes with carboxylic acid anhydrides. Saturated carboxylic acid and the unconjugated double bond were easy to introduce, but the introduction of allyl and conjugated double bonds was not achieved satisfactorily. The introduction of carboxylic acid drastically increased the solubility of the polysilanes to an aqueous basic solution. The unsaturated double bond in the carboxylic moiety reacted when polysilanes were photodecomposed. In this case, molecular scission surpassed the cross-linking which was brought by the reaction of the unsaturated bond. However, the double bond reacted thermally at 170 °C to cause cross-linking. An exothermic reaction occurred drastically at 250 °C. The base solubility depended on the content of carboxylic acid moieties and the molecular weight. The base solubility of the polysilanes increased rapidly under $M_w = 5 \times 10^{-4}$. Lines (0.3 μm) and spaces were fabricated.

Introduction

Various polysilanes which are soluble in organic solvents have been synthesized.[1-10] Most of them have hydrophobic moieties like alkyl or aromatic groups. The authors have been interested in polysilanes with hydrophilic moieties, especially phenol moieties, because (1) there have been no reports on the polymer syntheses and the polymer properties and (2) various functional groups may be substituted by reacting the phenol moieties with other functional molecules. For example, the reaction of the phenol moieties with acid anhydrides, acid chlorides, isocyanates, and alkyl halides produces carboxylic acids, esters, urethanes, and ethers, rather mildly. It was considered an important point whether polysilanes with phenol moieties could be prepared or not, because, usually, polysilanes are synthesized under a vigorous reaction condition, such as in Na dispersion at around 110 °C, and it was thought that the organic functional group may be damaged and/or may inhibit the Wurtz reaction between SiCl and SiCl. Syntheses of chlorosilanes with phenol moieties (monomer) were another important area. Simple silanes substituted with phenol moieties, such as *p*-(triphenylsilyl)phenol and *p*-(trimethylsilyl)phenol, were synthesized from bromophenol, lithium, and triphenylchlorosilane[11] or from [(trimethylsilyl)oxy]chlorobenzene and trimethylsilyl chloride in dispersed Na.[12]

The latter method is probably suitable for the preparation of polysilanes, since the hydrolysis of (trimethylsilyl)oxy groups is rather easy. However, the reaction of phenyltrichlorosilane with [(trimethylsilyl)oxy]phenyl chloride in dispersed Na did not produce [[(trimethylsilyl)oxy]phenyl]phenyldichlorosilane, because the Wultz reaction between phenyltrichlorosilane and another phenyltrichlorosilane is much faster than the reaction between phenyltrichlorosilane and [(trimethylsilyl)oxy]phenyl chloride. The authors found a new route for synthesizing silane monomers substituted with both chloro- and [(trimethylsilyl)oxy]phenyl moieties.[13] The reaction used was the hydrosilylation of methyldichlorosilane and isopropenylphenols, by which the desired silane monomer could be synthesized easily. Polysilanes substituted with phenol moieties could be obtained by using the Wurtz reaction, followed by hydrolysis of the trimethylsilyl group. The (trimethylsilyl)oxy group was a suitable protector for the phenolic moiety. These results have been reported previously.[13]

Our next goal was to synthesize polysilanes containing carboxylic acid groups. Silane monomers substituted with both chloride and $COOSiMe_3$ were difficult or impossible to synthesize by this route, because the hydrosilylation of unsaturated double bonds containing $COOSiMe_3$ with methyldichlorosilane was unsuccessful. The reason was that the Pt catalyst could not effectively coordinate with the unsaturated double bond, presumably due to complexation of the carbonyl group. Furthermore, it seemed likely that even if the monomer could have been synthesized, the polysilane would not have been obtained, because the COO group was labile under polymerization conditions. Therefore, the introduction of carboxylic acid was carried out by the polymer reaction of the phenolic-substituted polysilanes with acid anhydrides.

This paper describes (i) the yield of polysilanes substituted with carboxylic acids, (ii) the dependence of the former on the acid anhydride structure, (iii) the relative photodecomposition rates, and (iv) the dependence of solubility in organic alkaline solutions on molecular weight.

Experimental Section

All experiments were carried out in an argon atmosphere. The solvents were purified and dried by CaH_2 before use.

Synthesis of Methyl[2-[3-[(trimethylsilyl)oxy]phenyl]propyl]dichlorosilane (M-1). Methyldichlorosilane (200 g) was mixed with trimethylsilylated *m*-isopropenylphenol (200 g), which was prepared by the reaction of *m*-isopropenylphenol with hexamethyldisilazane at room temperature followed by distillation. *m*-Isopropenylphenol was purchased from Mitsui Petroleum Chemical Co. Then 1 g of a Pt complex catalyst, purchased from Toshiba Silicone Co. (not commercially available), was added slowly. A conventional catalyst, H_2PtCl_6, can also be used in this reaction. However, because of the strong acidity of the catalyst,

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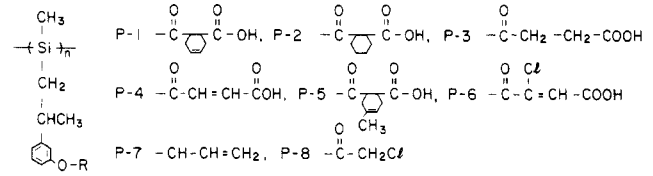
Table I
Syntheses of Functional Polysilanes[a]

polymer	yield, %	moiety content	moiety
P-1	90	0.30	COOH, =
P-2	94	0.44	COOH
P-3	93	0.50	COOH
P-4[b]	5	0.30	COOH, =
P-5	90	0.16	COOH, =
P-6[b]	gel		COOH, =, Cl
P-7[b]	gel		=
P-8[c]	95	0.30	Cl

[a] Reaction temp 40 °C. [b] 50 °C. [c] 20 °C.



the oligomerization of the isopropenyl phenol increased, and the conversion of the desired product decreased. The reaction mixture turned red immediately, which was accompanied by a slight temperature rise. After it was stirred for 3 h, the reaction mixture was distilled under reduced pressure. Yield 49%, bp 130–135 °C (14 mmHg); NMR ($CDCl_3$) δ 0.23 (s, $Si(CH_3)_3$), 0.55 (s, $SiCH_3$), 1.34 (d, J = 3.5 Hz, CH_3), 1.52 (d, J = 7.4 H_3, CH_2), 3.06 (m, CH), 6.67–7.15 (m, Ar H).

Synthesis of Poly[methyl[2-(3-hydroxyphenyl)propyl]-silane] (PHS-I). The polymerization was carried out in the same way as that reported previously.[1,2] The typical procedure is as follows. One mole of sodium was dispersed in 150 mL of toluene at 120–130 °C. Dichlorosilane, 0.33 mol, was added dropwise to the dispersed sodium. Then the mixture was stirred at 110 °C for 3 h. The reaction mixture was filtered and the toluene-soluble fraction was collected. After the toluene was removed, methanol was added to the residue and stirred until the residue was dissolved, during which the trimethylsilyl moiety was removed by methanolysis. After the removal of methanol under reduced pressure, the residue was dissolved in distilled water; the solution was basic due to the sodium methoxide from methanolysis, and the insoluble matter was filtered. The aqueous solution was slightly acidified with HCl, precipitating the polymer. The polymer was extracted with diethyl ether and the ether layer was dried by adding $MgSO_4$; then ether was removed. The polymer was dissolved in a small amount of methanol and precipitated in toluene in order to obtain a high molecular weight polymer. Before the hydrolysis of the trimethylsilyl moiety, the polymer was soluble in nonpolar solvents, like xylene and toluene. However, after hydrolysis, the polymer became soluble in more polar solvents like alcohol.

Syntheses of Polysilanes with Carboxylic Acid Anhydride. Tetrahydrophthalic acid anhydride (R-1), hexahydrophthalic acid anhydride (R-2), succinic acid anhydride (R-3), maleic acid anhydride (R-4), methyltetrahydrophthalic acid anhydride (R-5) (commercially available from Hitachi Kasei, HN2200), and 2-chloromaleic acid anhydride (R-6) were utilized in the syntheses. Allyl bromide (R-7) and chloroacetyl chloride (R-8) were also used to synthesize polysilanes with unsaturated bonds or halogen.

Table I summarizes the reaction temperature, catalyst, moiety content, and structure of the moieties. Typical reaction conditions were as follows.

Reaction of PHS-I and R-3 (Polymer P-3). PHS-I, 1.78 g (0.01 mol), and 1.00 g (0.01 mol) of R-3 were dissolved in 10 mL of tetrahydrofuran. Triethylamine, 1.01 g (0.01 mol), was added dropwise into the mixture at room temperature and the solution was stirred mechanically. The temperature was gradually increased to 40 °C and stirred for 2 h. The reaction mixture was then poured into H_2O. After the water layer was slightly acidified with dilute HCl (1 N), the polymer was extracted with ether. The ether layer was washed with a dilute HCl aqueous solution and water three times and then dried by adding $MgSO_4$. The ether was removed and the polymer was dried at 40 °C under reduced pressure (0.5 mmHg). The polymer yield was 93%, and the

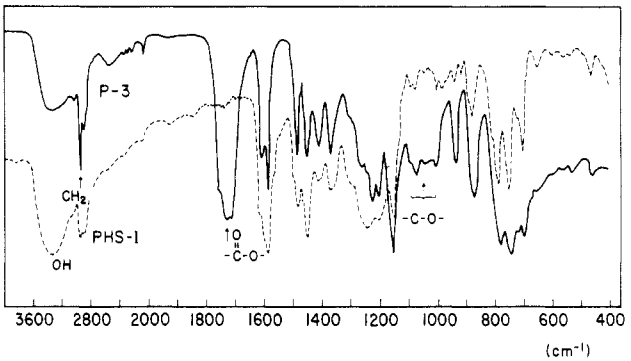


Figure 1. IR spectra of PHS-I and P-3 KBr disks. The absorptions assigned to CH_2, esters and carboxylic acid increase.

content of carboxylic acid versus phenol moiety was 0.50. This was determined by ^1H NMR spectroscopy: IR (KBr disk), Figure 1; ^1H NMR δ (acetone-d_6) 0.34 (MeSi), 1.21 ($SiCH_2$, Me), 2.93 (CH_2CH^*), 3.31 ($COCH_2CH_2CO$), 6.52–7.01 (Ar H); UV (film, thickness 0.32 μm) λ_{max} 280 nm (absorbance, 1.17/0.32 μm). The UV absorption of the film was measured as follows. P-3 in THF was spin coated on a quartz plate. The residual THF was evaporated at 90 °C for 5 min and the UV spectra of the P-3 were measured. λ_{max} of P-3 was shorter, compared to that of poly(methyl-β-phenethylsilane) (λ_{max}, 303 nm).[14]

There are three possible reasons for this phenomenon: (i) Low molecular weights. This possibility is denied strongly by the fact that the molecular weight of the polysilane is more than 10^5. (ii) Conjugation interruption in the backbone caused by the presence of heteroatoms. This possibility is also denied by the fact that the ^{13}C NMR spectra of the polysilane is simple and there is no peak assigned to the isomerization structure. The presence of a Si–O–C linkage is also denied because the molecular weight does not decrease by methanolysis. (iii) Strongly conformationally distorted polymer backbones. This is most probable.

The authors explain this phenomenon as a strong conformational distortion of the polymer backbones which is presumably caused by the hydrogen bond of phenol or carboxylic acid.

Reaction of PHS-I with R-4 Using *p*-Toluenesulfonic Acid as Catalyst (Polymer P-4). PHS-I, 1.78 g (0.01 mol), and 0.98 g (0.01 mol) of R-4 were dissolved in 10 mL of tetrahydrofuran. A small amount of *p*-toluenesulfonic acid was added into the reaction mixture, which was stirred mechanically for 2 h at 50 °C. The mixture was then poured into water three times in order to eliminate the catalyst. The precipitated polymer was dissolved in ether and dried over $MgSO_4$. The ether was removed under reduced pressure. The resulting yield was 5%: IR (cm^{-1}) 3330, 3020, 2940, 2840, 1710, 1570, 1480, 1450, 1255, 1060, 935, 870, 777, 700, 560; ^1H NMR δ (acetone-d_6) 0.32 (SiMe), 1.25 (CH_2*CH-(CH_3*)), 3.15 (CH), 6.54–7.16 (Ar H and CH=CH).

Reaction of PHS-I with R-4 Using a Base Catalyst. PHS-I, 1.78 g (0.01 mol), and 0.98 g (0.01 mol) of R-4 were dissolved in 10 mL of tetrahydrofuran. Triethylamine, 1.01 g (0.01 mol), was added into the reaction mixture. The reaction and polymer purification were carried out in the same way as for P-3. The yield was 5%. When 0.14 g (0.001 mol) of benzyldimethylamine was used as a catalyst, almost no COO absorption was detected in the IR spectra during the reaction.

Reaction of PHS-I with R-2 (Polymer P-2). The reaction and purification were carried out in the same way as for the reaction of P-3. Polymer yield, 94%; moiety content, 0.44; IR (cm^{-1}, KBr) 3350, 2950, 1710, 1590, 1485, 1450, 1410, 1370, 1240, 1150, 1072, 1000, 936, 868, 780, 745, 700, 533; ^1H NMR δ (acetone-d_6) 0.47 (SiMe), 1.34 (CH_2*CH(CH_3*)), 1.52 (cyclohexane ring CH_2, 3- and 4-position), 1.92 (cyclohexane ring CH_2, 2- and 5-position), 3.04 ($CH_2CH^*(CH_3)$), 3.74 (cyclohexane ring CH), 6.70–7.24 (Ar H).

Reaction of PHS-I with R-5 (Polymer P-5). The reaction was carried out in the same way as for P-3. The yield was 90%, and the moiety content was 0.16. The low moiety content is due to the reactivity decrease of the acid anhydride ring against nucleophilic reaction, which is caused by the introduction of the methyl group into the cyclohexane ring. This tendency was also experienced in case of the copolymerization of acid anhydrides

and epoxides. IR (cm^{-1}, KBr) 3350, 3025, 2950, 2900, 1720, 1590, 1485, 1450, 1410, 1371, 1245, 1200, 1150, 1075, 1002, 940, 870, 780, 743, 700; ^1H NMR δ (acetone-d_6), 0.34 (SiMe), 1.21–1.43 (CH_2*$CH(CH_3$*), cyclohexenyl–Me), 2.90 (CH_2CH*(CH_3)), 3.28 (cyclohexenyl CH), 5.58 (cyclohexenyl CH), 6.57–6.97 (Ar H), 8.04 (OH).

Reaction of PHS-I with R-1 (Polymer P-1). The reaction was carried out in the same way as for P-3. Yield, 90%; moiety content, 0.30; IR (cm^{-1}, KBr) 3300, 2920, 1705, 1580, 1475, 1445, 1400, 1360, 1250, 1145, 995, 930, 860, 775, 740, 695; ^1H NMR δ (acetone-d_6) 0.38 (SiMe), 1.27–1.50 (CH_2*$CH(CH_3$*)), 2.52 (cyclohexenyl CH_2), 2.97–3.19 (CH_2CH*(CH_3) and cyclohexenyl CH), 5.65 (cyclohexenyl CH), 6.59–7.21 (Ar H), 8.06 (OH).

H_2SO_4 Catalyst. PHS-I, 1.78 g (0.01 mol), and 1.52 g (0.01 mol) of R-1 were dissolved in 10 mL of tetrahydrofuran. Two drops of concentrated H_2SO_4 was added. Then the mixture was stirred mechanically at 60 °C for 1 h. The polymer was purified three times to eliminate the catalyst by precipitation into water, followed by drying under reduced pressure at 50 °C. The yield was 62% and the moiety content was 0.34. While there was no molecular weight decrease during the polymer reactions in the case of the triethylamine catalyst, the H_2SO_4 catalyst decreased the molecular weight from 2.3×10^5 to 5×10^4.

Reaction of PHS-I with R-8 (Polymer P-8). The reaction was carried out in the same way as for P-3. The yield was 65% and the moiety content was 0.30. IR (cm^{-1}) 3450, 3040, 2925, 2875, 1770, 1605, 1580, 1480, 1440, 1405, 1370, 1305, 1220, 1140, 1000, 1940, 875, 780, 737, 690; ^1H NMR δ (acetone-d_6) 0.37 (SiMe), 1.29 (CH_2*$CH(CH_3$*)), 2.80 (CH_2CH*(CH_3)), 4.41 (CH_2Cl), 6.71–7.01 (Ar H), 8.22 (OH).

Reaction of PHS-I with R-7 and PHS-I with R-6 (Polymers P-7 and P-6). The reactions were carried out in the same way as for P-3. However, the reaction mixtures became insoluble in any solvent.

Photolyses. Polymer solutions in tetrahydrofuran were spin coated on quartz plates, followed by baking at 90 °C for 5 min. The quartz plate was exposed by using a high-pressure mercury lamp (400 W, no filter) or a low-pressure mercury lamp (254 nm, no filter). UV spectra were measured through the quartz plate. The molecular weight decreased after the photolysis was measured by GPC. The molecular weights were determined by using standard polystyrenes.

Solubility of Polymer in a Base Solution. The polymer dissolved in tetrahydrofuran was coated on a Si wafer by a spin coater, followed by baking at 90 °C for 5 min. The polymer film on the Si wafer was immersed into an aqueous tetramethylammonium hydroxide (TMAH) solution at 25 °C. The thickness of the polymer film was measured by TALY STEP-ST200 (Taylor-Hobson).

Patterning of Polysilanes. Polysilanes in acetoxyethyl ethyl ether were spin coated on Si wafers (thickness, 0.70 μm), followed by baking at 90 °C for 5 min. The polymer on the Si wafer was exposed by a Kr/F excimer laser reduction step and repeat system (reduction ratio 10:1, NA = 0.37). After exposure, the Si wafer was dipped into a tetramethylammonium hydroxide (TMAH) aqueous solution. The cross section of the pattern was measured by scanning electron microscopy (SEM), SIGMA–II (AKASHI).

The molecular weight distribution of the polymers was determined with a Toyo Soda Model 801 gel permeation chromatograph at 40 °C. Four columns were connected in series, each packed with G-2000H ×3 and G-4000H_8 (Toyo Soda polystyrene gel), in that order. Tetrahydrofuran was used as a solvent, and the instrument was calibrated to a first approximation with a polystyrene standard of known molecular weight.

^1H NMR spectra were measured by a JEOL FX 90Q spectrometer.

Results and Discussion

Syntheses of Polysilanes with Carboxylic Acid. Phenol is known to react with carboxylic acid anhydrides, and the reaction is catalyzed by an acid or base. The question was whether or not, during the reaction, the Si linkages were damaged to decrease the molecular weight. Before the reaction between the polymer and carboxylic acid anhydride, the molecular weight change of polysilane was examined in the presence of H_2SO_4 or triethylamine. Triethylamine, 1.01 g (0.01 mol), or two drops of H_2SO_4 were added into 1.78 g (0.01 mol) of PHS-I in 10 mL of THF and then the mixture was stirred at 50 °C. After 1 h, the molecular weight decreased from 2.3×10^5 to 5×10^4. However, there was no change after that for either catalyst.

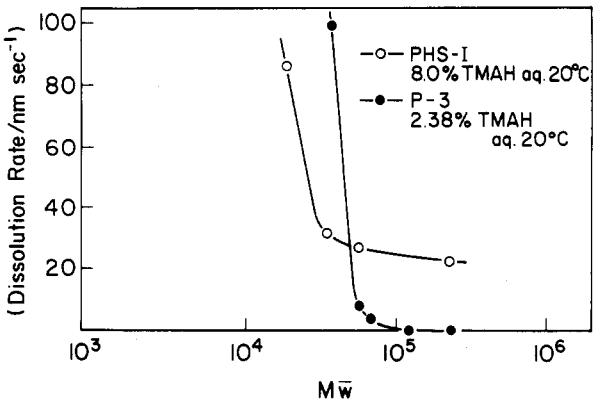


Figure 2. Relation between dissolution rate in tetramethylammonium hydroxide aqueous solution and molecular weight. Exposure, high-pressure mercury lamp, 0.70-μm-thick polymer film on Si wafer; development, 25 °C; molecular weight, GPC, calibrated by standard polystyrenes in all experiments.

A decrease in the molecular weight of PHS-I when the polymer reacted with R-1 using a triethylamine catalyst was not seen. On the contrary, the molecular weight decreased from 2.3×10^5 to 5×10^4 when H_2SO_4 was used. Triethylamine would be neutralized by carboxylic acid formed as the reaction proceeds, as opposed to an acid catalyst which remains in the reaction mixture. Since functional group incorporation was almost the same for both catalysts, a basic catalyst seems to be preferable to an acid catalyst.

Table I shows the polymer yields and moiety contents. Polysilanes were obtained at high yields in the case of P-1, P-2, P-3, and P-5, which have saturated or unconjugated double bonds.

The polymer yields of P-4, which has a conjugated double bond, were low. Considering that a large amount of insoluble matter was formed, the conjugated double bond seems to promote cross-linking. 2-Chloromaleic acid anhydride (R-6) and allyl bromide (R-7) are the extreme cases, and insoluble gel products were obtained.

The reason double bonds were introduced was to examine whether or not unsaturation in the side chain causes cross-linking by reactive silyl radicals or silylenes which are generated by photolysis of polysilanes. Halogen was introduced in the side chain to examine the effect of the halogen moiety on photolyses.[7]

Solubility of Carboxylic Acid in a Tetramethylammonium Hydroxide Aqueous Solution (TMAH). Figure 2 shows the relation between the solubility rate in a TMAH aqueous solution and the polymer molecular weight. The samples were obtained by the photolysis of the original polysilanes. The solubility increased rapidly when the molecular weight reached 3×10^4 in the case of PHS-I and 5×10^4 for P-3; thus development by using TMAH is possible. The introduction of carboxylic acid groups increased the solubility of the polysilanes in a base. In this regard, the solubility increased from 0 to 109 nm/s when the moiety content increased from 0 to 0.5, as shown in Table II.

Photolyses of Polysilanes. West reported that silyl radicals released in polysilane photolysis can initiate vinyl polymerization.[15] The question is whether or not unsat-

Table II
Dissolution Rates of Polysilanes with Carboxylic Acid

run	moiety content y, %	solubility (2.38%),[a] nm/s
PHS-I	0	0
P-3-1	10	0
P-3-2	20	0
P-3-3	50	109

[a] Tetramethylammonium hydroxide aqueous solution (26 °C).

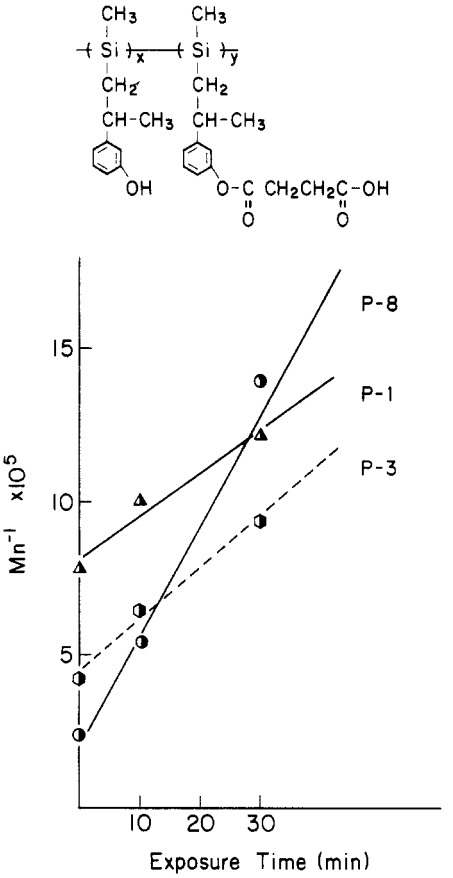


Figure 3. Photodegradation of polysilanes (relation between $1/M_n$ and dose). Exposure, high-pressure mercury lamp, polymer film on Si wafer; molecular weight, GPC; see Experimental Section.

urated moieties cause cross-linking by the photolysis intermediates. Another question is whether halogens in the side chain accelerate polysilane photolysis or cause cross-linking, because it has been reported that halogen compounds accelerate polysilane photolysis[7] and that halogen in the side chain causes cross-linking.[16,17] Therefore, the effects of halogen and the double bond substituted in the side chain on photolysis of polysilanes were examined.

Figure 3 shows the decrease in the number-average molecular weights of some polysilanes during photolyses. There was no difference in the slopes for P-3 and P-1. It is known that when $1/M_n$ or $1/M_w$ increases linearly with an increase in dose, photoscission takes place at random, and the quantum yields for scission and cross-linking are simultaneously determined from the plots of $1/M_n$ and $1/M_w$ versus the dose.[18-20] In the authors' experiments, the ratio (photodecomposition (ϕ_s)/photocross-linking (ϕ_x)) of PHS-I was almost the same as that of the copolymers of PHS-I with dimethylsilyl, methyl-*n*-hexylsilyl, and methylcyclohexylsilyl groups, namely, 4.0–5.0. However, ϕ_s/ϕ_x of the copolymer of PHS-I with the methylphenyl silyl group was rather low, namely, 1.2. It follows that a phenyl group adjacent to Si causes increased cross-linking.

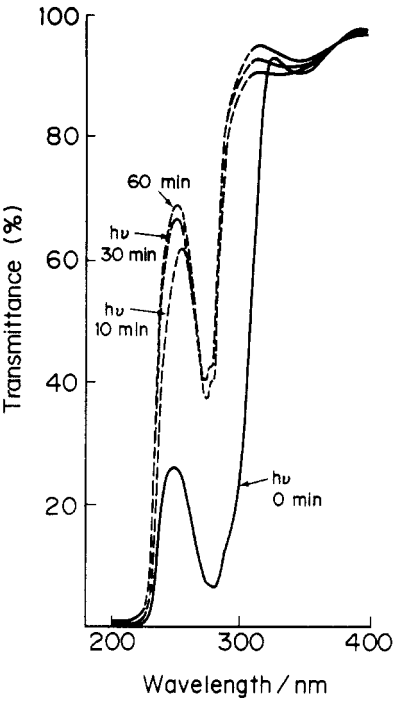


Figure 4. Bleaching of UV absorption for P-3 during photolysis. Exposure, high-pressure mercury lamp, 0.34-μm-thick polymer film on quartz or wafer.

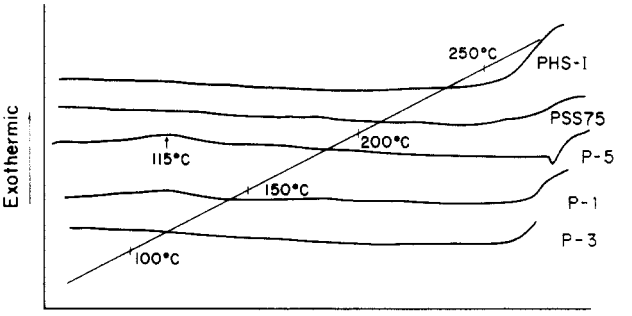


Figure 5. DSC curves for some polysilanes.

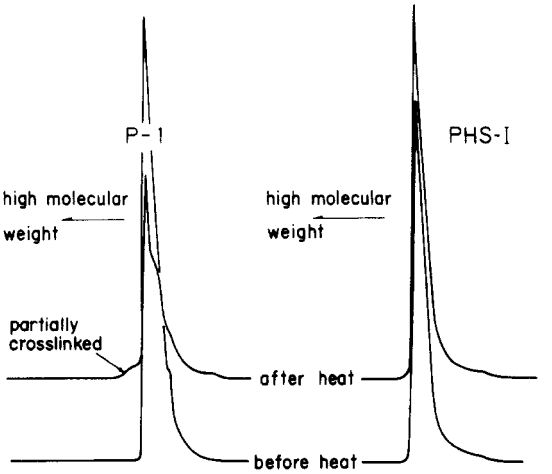


Figure 6. GPC curves of polysilanes (P-1 and PHS-I) before and after heat treatment. Heat treatment, 2 °C/min from 15 to 170 °C in DSC apparatus. THF-soluble matter was measured. There was insoluble matter in P-1. The higher molecular weight part after heat treatment showed a molecular weight increase by partial cross-linking.

West also reported the same phenomena.[20] In the photolyses of phenyl-substituted disilane, the silyl moiety was reported to be rearranged to the ortho position of the benzene ring.[21] Our results can be explained by taking this reaction as a significant cross-linking mechanism.

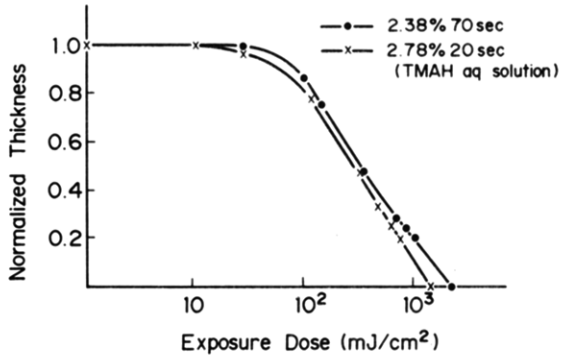


Figure 7. Sensitivity curve of P-3-2. Exposure, Kr/F excimer laser reduction step and repeat system; development, tetramethylammonium hydroxide aqueous solution, 25 °C.

Figure 4 shows the bleaching of UV absorption observed upon the formation of shorter wavelength fragments. The UV absorption decreased when UV light was radiated, but the UV absorption assigned to the phenyl moiety still remained.

Contrary to the results obtained when the phenyl group was adjacent to Si, the unconjugated double bonds substituted in the side chain did not cross-link during photolysis.

When P-1 was photodecomposed by using a high-pressure mercury lamp for 30 min until there was no decrease in the UV absorption at 275 nm (λ_{max}) upon further irradiation, the double bond of P-1 decreased from 15 mol % to 10 mol %, which was measured by ^{1}H NMR spectroscopy. This result shows that, by 30-min air UV irradiation, double-bond reactions, as well as the photodegradation of the polysilane backbone, occur. However, photodegradation was predominant in this case. Recently, West and co-workers reported that the [[2-(3-cyclohexenyl)ethyl]-methyl]silylene copolymer primarily cross-links when irradiated with UV.[7] The difference between our results and West's may lie in the amount of the double bond in each polymer. The double-bond content in P-1, which was used in this photolysis, was 15 mol %, while that of [[2-(3-cyclohexenyl)ethyl]methyl]silylene was reported to be around 50%. Another difference is that P-1 has a phenol moiety. Considering that the double bond reacts with radicals, the phenol moiety may inhibit this reaction.

Polysilane with a halogen moiety, P-8, photodecomposed rapidly, compared with P-1 or P-3. Halogen substitution in the polymer side chain does not seem to cross-link the polymer. The introduction of a chloride moiety is effective for the sensitization of photodegradation.

Thermal Stability. The thermal stabilities of polysilanes containing carboxylic acid moieties were measured and compared with that of poly(phenylmethylsilane). Poly(phenylmethylsilane-*co*-dimethylsilane) (polysilastyrene, PSS75), which is commercially available from SHIN-NISSO KAKOU, (phenylmethylsilyl/dimethylsilyl) = 75/25 mol, began to decompose thermally at 250 °C, which was detected by DSC. The introduction of the phenol moiety did not decrease thermal stability and the phenol-containing polysilanes began to decompose at around 250 °C. The behavior of P-1 and P-5, which have unsaturated bonds, was somewhat different. Both polymers had exothermic reactions at 110–120 °C, as well as around 250 °C. The exothermic reactions at 110–120 °C were not detected in the case of PHS-I (Figure 5).

In order to examine what reaction occurs, P-1 was heated in an Al pan in a DSC apparatus at 2 °C/min from 15 to 170 °C, and the molecular weight distribution was measured by GPC. The higher molecular weight part appeared by heat treatment, but PHS-I did not (Figure 6). The original polymer contained 15 mol % of tetrahydrophthalic carboxylic acid moieties. When the polymer was treated thermally, the content of the double bond decreased to 6.0%, accompanied by a production of 3.5 mol % of tetrahydrophthalic acid anhydride, which was identified with ^{1}H NMR (6.01 ppm, cyclohexenyl CH; 4.6 ppm, cyclohexenyl CH and cyclohexenyl CH_2). The remaining double bonds (5.5%) apparently polymerized with cross-linking. That is why the higher molecular weight part appeared by heat treatment in the case of P-1; i.e., the higher molecular weight part was partially cross-linked polymers. The as-

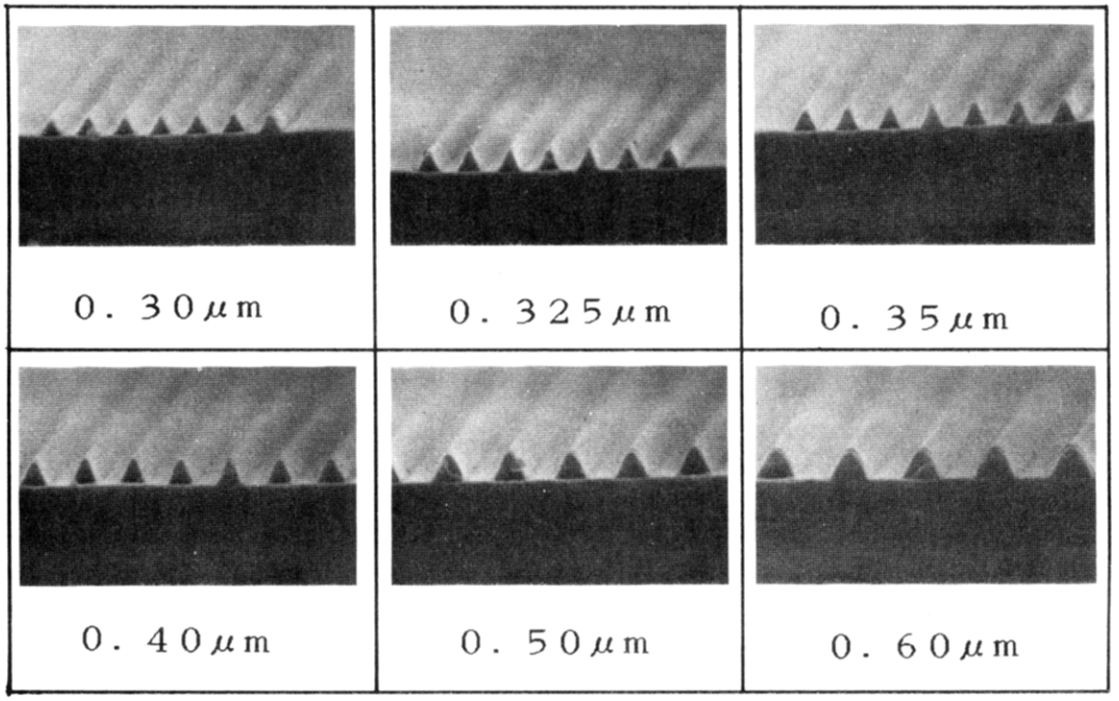


Figure 8. Cross section of the 0.300–0.425-μm line and space patterns using polymer P-3-2. Exposed by Kr/F excimer laser stepper, reduction ratio 10:1; NA, 0.37. Initial resist thickness 0.70 μm, exposure dose 1.2 J/cm² developed with 2.38% tetramethylammonium hydroxide aqueous solution, 25 °C, 50 s.

sumption was supported by the fact that THF-insoluble matter was present in the thermal treatment of the polymer. Similar results have been reported in the case of [2-(3-cyclohexenyl)ethyl]methylsilylene copolymers.[7] P-3, which does not have an unsaturated bond, also formed an acid anhydride at around 200 °C, but there was no insoluble matter in THF. The reaction was not detected by DSC, but P-3 was more unstable thermally than PHS-I, considering the reaction of the side chain. However, the Si–Si linkage stability was the same as that of PHS-I. The presence of a double bond substituted in PHS-I plays a significant role in thermal behavior compared to photodecomposition.

Lithography. A basic water-soluble polysilane would make the application range wider. Resists will be the most appropriate one.

What polysilanes are applicable to deep-UV photoresists has been reported previously.[22-25] The large difference between the previous report and this report is that the development is carried out by using an organic solvent like methylcyclohexane–isopropyl alcohol in the case of the conventional polysilanes, but basic water can be used in the case of these new polysilanes. P-3-2 acetoxyethyl ethyl ether solution, 20 wt %, was spin coated to 0.70-μm thickness on a Si wafer and baked at 90 °C for 5 min. Then the wafer was exposed through a mask to a Kr/F excimer laser reduction step and repeat system (reduction ratio, 10:1; NA, 0.37). Figure 7 shows the relation between the film thickness and exposure when developed with a TMAH aqueous solution. When the resist thickness was normalized, the sensitivity was 1.5–2.5 J/cm^2. The photograph shows the cross-section pattern of the resist developed with a 2.38% TMAH aqueous solution.

The mask used had an equal line-space pattern. All the resist patterns shown in the photograph in Figure 8 were obtained by 1.2 J/cm^2 exposure and 50 s, 25 °C development. Therefore, the resist patterns, from the 0.600-μm line and space to the 0.325-μm line and space, were the same as those of the mask patterns. However, the 0.30-μm line and space pattern was underdeveloped or underexposured. The 0.275-μm line and space pattern was not fabricated.

The resist pattern was triangular, which was probably due to a strong UV absorption assigned to the phenyl moiety. The authors are presently investigating the syntheses of polysilanes containing alkyl alcohols, in which carboxylic acid is introduced in the same way. The syntheses and lithographic results will be reported elsewhere.

Conclusion

Polysilanes containing carboxylic acid groups were synthesized. These polysilanes were more soluble in basic water than simple phenol-substituted polysilanes. These hydrophilic polysilanes will make it possible to study the characteristics of polysilanes under aqueous conditions. This investigation also showed that polysilanes with various functional groups can be synthesized.

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Registry No. M-1, 111351-19-0; methyldichlorosilane, 75-54-7; trimethylsilylated *m*-isopropenylphenol, 119480-63-6.

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