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Mechanism for the Formation of Poly(phenylsilsesquioxane)

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ABSTRACT: Poly(phenylsilsesquioxane) with molecular weight of 1400 was synthesized by hydrolysis of phenyltrichlorosilane, followed by condensation of the resulting hydrolyzates in the presence of a catalytic amount of hydrochloric acid in methyl isobutyl ketone. The progress of dehydration of the hydrolyzates leading to poly(phenylsilsesquioxane) was monitored by ^{29}Si NMR spectroscopy. Dehydration of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane as a model compound was also investigated by the ^{29}Si NMR technique. The mechanism for the formation of poly(phenylsilsesquioxane) is discussed.

Introduction

Recently, considerable interest has been focused on the synthesis of polymers that can be used as microelectronics at the temperature above 400 °C. It is well-known that thermal stability of polymers depends on the bond energy of the atoms used for constraction of the polymer backbone. Polymers composed of an Si−O bond are very attractive for the heat-resistant substances since the bond energy of the Si−O bond is much higher than that of the C−C and C−O bonds.

When linear organopolysiloxanes are heated at the temperature above 300 °C, the Si−O bonds in the polymer chain are cleaved to form cyclosiloxanes.[1,2] On the other hand, poly(organosilsesquioxane)s that have a ladder structure are thermally stable. They do not decompose to give the cyclic or cage products even at above 300 °C.[3]

The poly(organosilsesquioxane)s are the polymers that have a cis-syndiotactic double-chain structure and are soluble in common organic solvents, such as tetrahydrofuran and methyl isobutyl ketone. When a solution of the polymers is coated on a substrate such as a silicone wafer by a spinner, a thin film can be obtained.

The first synthesis of poly(organosilsesquioxane) was reported by Brown et al. in 1960.[4] They used a two-step method, involving hydrolysis of phenyltrichlorosilane and dehydration of the resulting hydrolyzates in the presence of a potassium hydroxide catalyst in toluene, for the synthesis of the polymer. Since that time, many papers concerning the synthesis of the poly(organosilsesquioxane)s have been published.[5,6] The polymers have frequently been synthesized by hydrolysis of organotrichlorosilane such as phenyltrichlorosilane, followed by condensation of the resulting hydrolyzates. It has been reported that the rate of hydrolysis of the organotrichlorosilanes in these reactions is very fast and difficult to control.[4] Furthermore, it seems to be difficult to prepare the polymers with molecular weight higher than 10 000 by the use of this method. To our knowledge, the mechanism for the hydrolysis of organotrichlorosilane and condensation of its hydrolyzates has not yet been well-defined, although mechanistic studies on the hydrolysis of organoltrialkoxysilanes and organotrichlorosilanes have been reported so far.[7−9]

In this paper, we report the results of the ^{29}Si NMR spectrometric analysis for the condensation reaction of the hydrolyzates produced by the hydrolysis of phenyltrichlorosilane. We also report the mechanism for the formation of poly(phenylsilsesquioxane) on the basis of the results obtained by the ^{29}Si NMR spectrometric analysis.

Experimental Section

Synthesis of Poly(phenylsilsesquioxane). To a solution of 106 g (0.50 mol) of phenyltrichlorosilane in 300 mL of methyl isobutyl ketone was added dropwise 136 g (8.5 mol) of water at 0 °C for 45 min. The mixture was stirred at room temperature for 2 h. The organic layer was separated and washed with water. The solvent was evaporated in vacuo to give 52 g (80% yield) of poly(phenylsilsesquioxane) whose molecular weight was determined to be $M_w = 1400$.[10,11] In this hydrolysis, small aliquots of the solution were extracted at suitable intervals for ^{29}Si NMR spectrometric analysis and soaked immediately in liquid nitrogen.[12] To this was added a small amount of $Cr(acac)_3$ in acetone-d_6 to suppress the long spin−lattice relaxation time of ^{29}Si. The ^{29}Si NMR spectrum was determined by 59.62 MHz at −57 °C, using tetramethylsilane as an internal standard. The negative nuclear Overhauser effect (NOE) was suppressed by gate decoupling. Data for poly(phenylsilsesquioxane): ^{1}H NMR (δ in $CDCl_3$) 6.52−8.10 (br). ^{13}C NMR (δ in $CDCl_3$) 128.51 (s, 2C), 131.05 (s, 1C), 134.52 (s, 2C). ^{29}Si NMR (δ in $CDCl_3$) −78.1 (br), −69.9 (br), −60.0 (br). FT-IR (cm^{-1}) 3600−3000, 3000−2800, 2000−1700, 1275, 1130−1040, 850.[10,11]

Synthesis of *cis*-(1,3,5,7-Tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane. *cis*-(1,3,5,7-Tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane was obtained by the method reported by Hayashi et al.[13] At first, a cold mixture of 196 g (0.93 mol) of phenyltrichlorosilane and 360 mL of acetone at 0 °C was added slowly to 7100 g (394.11 mol) of an ice−water slurry with vigorous stirring. After stirring for 24 h, the resulting white precipitates were filtered. The precipitates were suspended in carbon disulfide to dissolve oily materials and then filtered. Once again the filtrate was washed with

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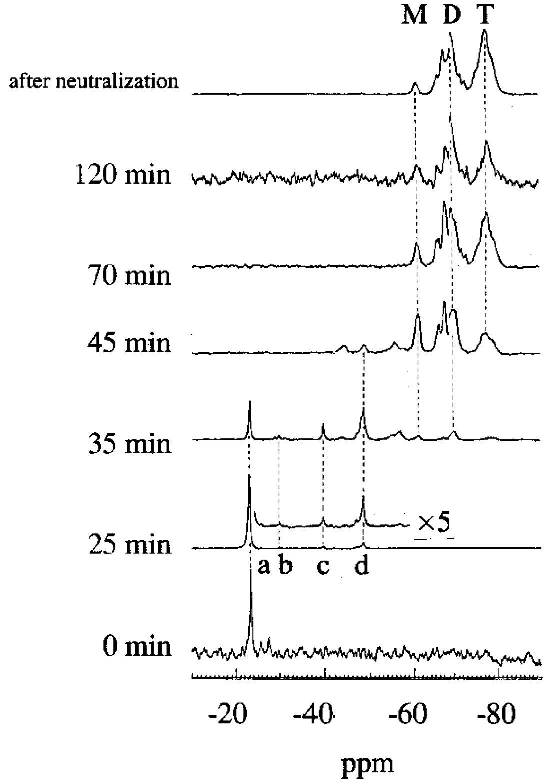


Figure 1. ^{29}Si NMR spectra of the hydrolysis reaction of phenyltrichlorosilane.

cold carbon disulfide to give 105 g of white solids. Data for white solids: ^{1}H NMR (δ in $CDCl_3$) 7.51 (d, 8H), 7.32 (t, 4H), 7.22 (dd, 8H), 3.90 (br, 4H). ^{29}Si NMR (δ in $CDCl_3$) −69.8.[14] GPC $M_w = 553$ (ps).[13]

Dehydration of *cis*-(1,3,5,7-Tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane. A solution of 10 g (0.02 mol) of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane in 50 mL of methyl isobutyl ketone was stirred in the presence of 2.0 mL of 0.01 N hydrochloric acid at 0 °C for 24 h. During the reaction, small aliquits were extracted from the reaction mixture at suitable intervals and analyzed by ^{29}Si NMR spectrometry. After separation of the aqueous layer, the organic layer was washed with water. Evaporation of the solvent gave the condensation product in 95% yield. Data for condensation product: ^{1}H NMR (δ in $CDCl_3$) 5.82−8.19 (br). ^{13}C NMR (δ in $CDCl_3$) 128.51 (s, 2C), 131.05 (s, 1C), 134.52 (s, 2C). ^{29}Si NMR (δ in $CDCl_3$) −78.1 (br), −70.0 (br). FT-IR (cm^{-1}) 3600−3000, 3000−2800, 2000−1700, 1275, 1130, 1040, 850.

Results and Discussion

To learn more about the reaction mechanism for the formation of poly(phenylsilsesqioxane)s, we followed the progress of the dehydration reaction of the hydrolyzates obtained from hydrolysis of phenyltrichlorosilane by the ^{29}Si NMR technique. As can be seen in Figure 1, four signals at δ −23, −30, −40, and −50 ppm were observed in the starting hydrolyzates. The signal at δ −23 ppm was identical with that of the starting phenyltrichlorosilane.[15] As expected, this signal decreased with the progress of the reaction and disappeared after 45 min reaction. Intensities of other three signals increased in the early stages of the reaction and passed through a maximum after about 35 min and then decreased gradually. The signal at δ −30 ppm was identical with that of dichlorohydroxyphenylsilane, while the signals at −40 and −50 ppm were identifiled as those of chlorodihydroxyphenylsilane and trihydroxyphenylsilane, respectively. In fact, ^{29}Si chemical shifts for mono-, di-, and trihydroxysilyl compounds have been reported to be observed at δ −30, −40, and −50 ppm, respectively.[15,16] At this point, new signals at δ −60, −70, and −78 ppm were obviously observed, and their signal intensities increased with the elapse of time. For new signals which appeared at δ −60, −70, and −78 ppm, we tentatively assigned as those of the silicon atoms in dihydroxyphenylsiloxy, hydroxyphenylsiloxy, and phenylsiloxy units, respectively.[15,16]

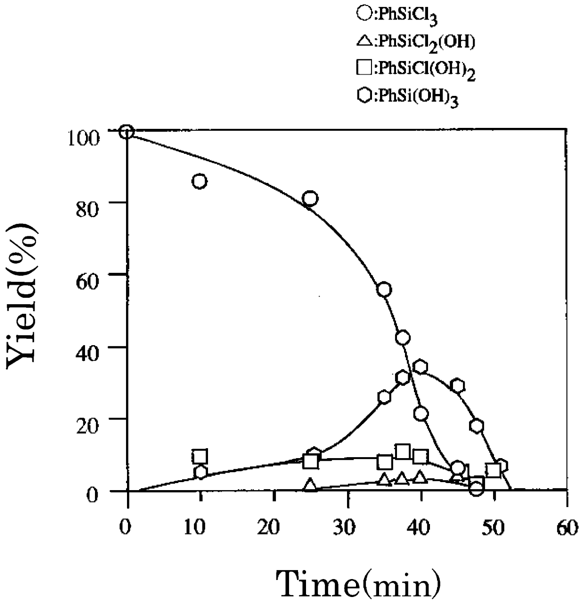


Figure 2. Conversion of phenyltrichlorosilane in silanol species as a function of time.

Figure 2 illustrates relative yields of the products for conversion of phenyltrichlorosilane into silanol species. The yields of chlorodihydroxyphenylsilane and trihydroxyphenylsilane increased with decrease of the starting phenyltrichlorosilane. No signal attributed to dichlorohydroxysilane was observed in early stages of the hydrolysis. However, a small amount of this compound was detected in the reaction mixture after 25 min reaction. At this stage, trihydroxyphenylsilane was observed to be the most abundant species, while dichlorohydroxyphenylsilane was the least one. The yields of these compounds decreased gradually, after all phenyltrichlorosilane was completely consumed. Klingebiel has reported that hydrolysis of dialkyldichlorosilane affords dialkyldihydroxysilane by way of chlorohydroxydialkylsilane.[17] Similar results have been obtained in methanolysis of ethylchlorosilanes.[18] Therefore, it seems likely that phenyltrichlorosilane would be converted to dichlorohydroxyphenylsilane, and this compound may be transformed into dihydroxychlorophenylsilane. Finally, dihydroxychlorophenylsilane undergoes further hydrolysis to give trihydroxyphenylsilane.

For the broad signals at δ −45 and −56 ppm, we assigned to those of the silicon atoms in dichlorophenylsiloxy and chlorohydroxyphenylsiloxy units, respectively, in the linear polysiloxane (see Figure 1). In fact, when a chlorine atom on the dimethylchlorosiloxy unit was replaced by a hydroxy group, the signal of this silicon atom shifted by 12 ppm to the higher field compared with that of the dimethylchlorosiloxy unit. As the hydroxy atom of dimethylhydroxysiloxy unit was replaced by a siloxy unit, the signal of this silicon atom shifted by 9 ppm to the higher field compared with that of the dimethylhydroxysiloxy unit.[16] These signals with

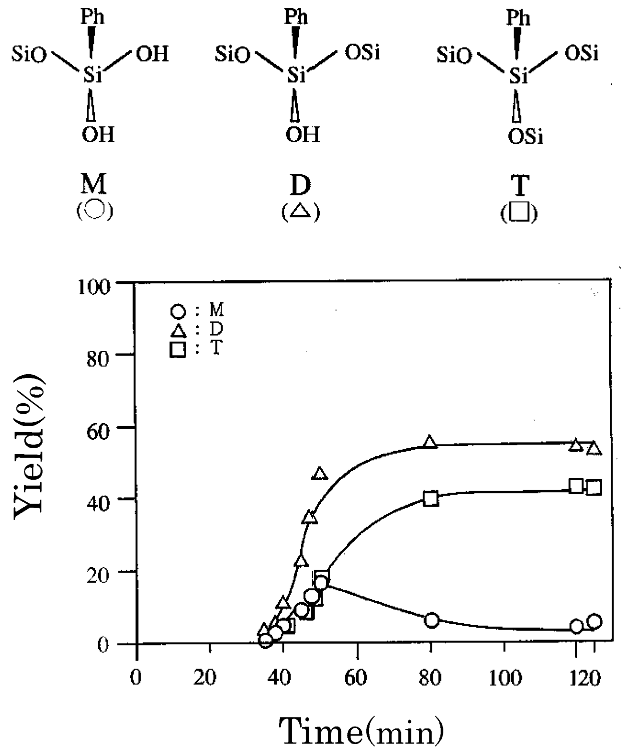


Figure 3. Conversion of condenced species to monohydroxyphenylsiloxane and phenylsiloxane as a function of time (○, silicon atom of the dihydroxyphenylsiloxy unit; △, silicon atom of the monohydroxyphenylsiloxy unit; □, silicon atom of the phenylsiloxy unit).

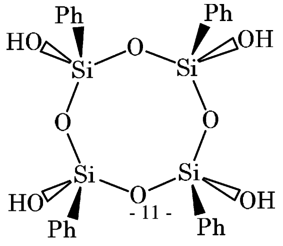


Figure 4. Structure of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane.

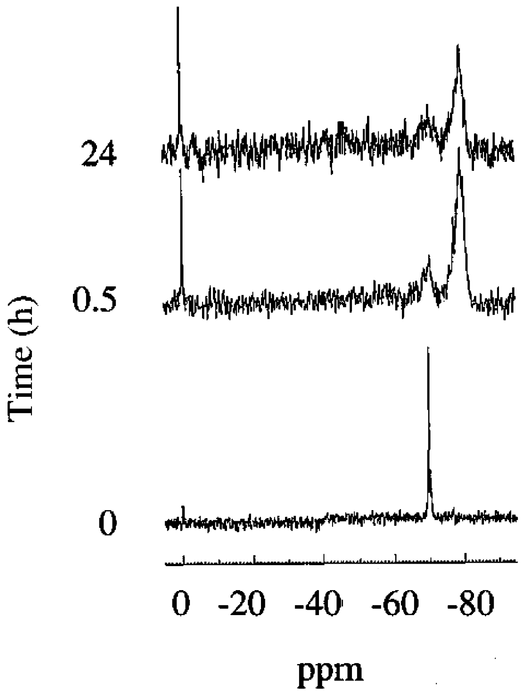


Figure 5. ^{29}Si NMR spectra of the condensation reaction of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane.

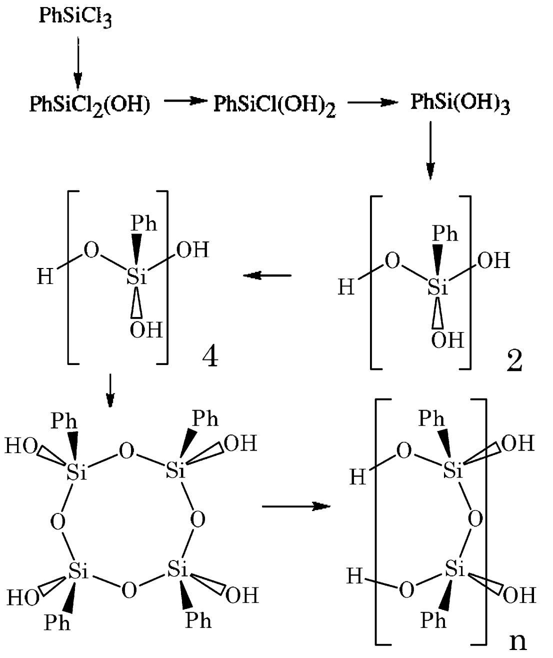
low intensities disappeared completely during further reaction.

Figure 3 shows profiles for the conversion of phenyltrichlorosilane into condenced species. Signal intensities for the silicon atoms in dihydroxyphenylsiloxane, hydroxyphenylsiloxane, and phenylsiloxane increased with the decrease of the starting compound and hydrolysis products, dichlorohydroxyphenylsilane, chlorodihydroxyphenylsilane, trihydroxyphenylsilane (see Figure 1). The intensities of the silicon atoms due to the dihydroxyphenylsiloxy, hydroxyphenylsiloxy, and phenylsiloxy units increased continuously up to 50 min reaction. After 50 min reaction, the signal intensity due to the dihydroxyphenylsiloxy unit decreased; however, those of the hydroxyphenylsiloxy and phenylsiloxy units still increased. No other signals were observed in the reaction mixture during the reaction. Therefore, it seems likely that the dihydroxyphenylsiloxy unit is transformed into the hydroxyphenylsiloxy unit whose chemical shift is identical with that of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane (see Figure 4). The hydroxyphenylsiloxy unit thus formed undergo further condensation to give phenylsiloxy unit, poly(phenylsilsesquioxane). From these results, we considered that the ladderlike siloxane, poly(phenylsilsesquioxane), should be produced by condensation of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane.

To clarify this hypothesis, we carried out the condensation reaction of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane prepared by the reaction of phenyltrichlorosilane and followed the progress of the reaction by ^{29}Si NMR spectrometry. As can be seen in Figure 5, two broad signals at δ −70 and −78 ppm were observed during the condensation of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane after 30 min reaction. These signals can be assigned to the silicon atom due to the hydroxyphenylsiloxy and phenylsiloxy units, respectively. The chemical shifts of these signals were identical with those of the condensation product obtained from the hydrolysis of phenyltrichlorosilane.[10,11] These signals were still observed after 24 h reaction, and their intensity did not change in the period of 30 min−24 h. The broad signal at δ −78 ppm may be assigned to the silicon atom of the terminal hydroxyphenylsiloxy unit, while the signal at δ −70 ppm can be assigned to the phenylsiloxy unit in the ladder structure.[15,16] As a result, the ladderlike siloxane is presumably produced by the condensation reaction of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane.

A possible mechanism for the hydrolysis of phenyltrichlorosilane and the condensation reaction of the resulting hydrolyzates may be illustrated as shown in Scheme 1. In the first step, a chlorine atom in the starting phenyltrichlorosilane would be replaced by a hydroxy group to give dichlorohydroxyphenylsilane. Similar replacement of the chlorine atom in the dichloro derivative by the hydroxy group produces chlorodihydroxyphenylsilane, and finally trihydroxyphenylsilane would be formed. The trihydroxyphenylsilane thus formed undergoes further reaction to give oligomers that have the hydroxyphenylsiloxy unit and phenylsiloxy

Scheme 1



unit. Miyamoto et al. have reported that hydrolysis of trimethoxymethylsilane affords a linear tetramer, and then this compound undergoes cyclization to give *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane.[19] In the present case, dehydration of trihydroxyphenylsilane would also produce the linear tetramer which undergoes cyclization to afford *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane. It seems reasonable to assume that the condensation of this cyclooctasiloxane produces a final product, polysilsesquioxane that has the ladder structure.

In conclusion, hydrolysis of trichlorophenylsilane affords trihydroxyphenylsilane via dichlorohydroxyphenylsilane and chlorodihydroxyphenylsilane, and condensation of trihydroxyphenylsilane gives a linear tetramer. The tetramer thus formed gives cis cyclotetramer which undergoes further condensation to give poly(phenylsilsesquioxane).

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