Catalytic Cross-Dehydrocoupling Polymerization of Phenylsilane with Water. A New Approach to Poly(phenylsilsesquioxane)

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ABSTRACT: Catalytic cross-dehydrocoupling polymerization of phenylsilane (**1**) with water was investigated. Among transition metal derivatives investigated, $Pd_2(dba)_3$ is the most active catalyst for the polymerization, which affords a high molecular weight polymer (**P1**) soluble in common organic solvents ($M_w/M_n = 62200/25400$). The polymer can be cast into a film. The polymerization was monitored by SEC and ^{29}Si NMR. It was shown that hydrolysis of SiH and cross-dehydrocoupling reaction between SiH and SiOH are faster compared to dehydration of SiOH in this polymerization, and plausible reaction mechanism was suggested. Chemical structure and thermal property of **P1** was characterized by NMR, IR, and TGA.
    KEY WORDS   Phenylsilane / Water / Pd Catalyst / Dehydrocoupling / Poly(phenylsilsesquioxane) / Thermal Property /

Poly(silsesquioxane), having the empirical formula $RSiO_{1.5}$ (R = Ph, Me, and H etc.), is a kind of interesting silicone polymer. It shows excellent properties, such as high thermal stability, low dielectric constant, oxidative resistance, and has been used widely as silicone resin, electrical insulating, and protective coating materials.[1] Generally, poly(silsesquioxane) is prepared by hydrolysis and condensation of trichlorosilane or trialkoxysilane in the presence of an acid or base as catalyst.[2,3] The reaction usually gives high molecular weight product, but control of chemical structure of the formed polymer is not easy because of the occurrence of Si–O bond cleavage and recombination processes. Thus, establishment of reliable synthetic method is still required.

Meanwhile, we reported a clean method to obtain siloxane–arylene polymer by catalytic cross-dehydrocoupling polymerization of bis(silane) with water under neutral condition.[4] Here, we present our results on the application of the catalytic cross-dehydrocoupoling reaction of phenylsilane with water in the direction of the synthesis of poly(silsesquioxane) (Scheme 1).

EXPERIMENTAL SECTION

General

NMR (^1H, 500 MHz; ^{13}C, 125.5 MHz; ^{29}Si, 99.5 MHz) spectra were obtained in $CDCl_3$ on a Varian UNITY INOVA. Chemical shifts are reported in ppm relative to internal $CHCl_3$ (7.26) for ^1H, $CDCl_3$ (77.00) for ^{13}C, and external tetramethylsilane (0.00)
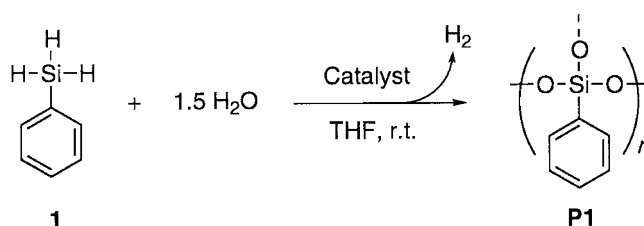
Scheme 1.   Poly(phenylsilsesquioxane) from phenylsilane and water.

for ^{29}Si. Size exclusion chromatography (SEC) analyses were performed on a JASCO HPLC with combinations of Shodex KF-801 and KF-802 (exclusion limit $M_n = 5.0 \times 10^3$), and KF-803L and KF-804 (exclusion limit $M_n = 4.0 \times 10^5$) using tetrahydrofuran as an eluent. IR spectra were obtained on a JASCO VALOR-III spectrophotometer. Mass spectra (MS) were taken on Shimadzu QP-5000 mass spectrometer. The thermogravimetric analysis (TGA) was performed on a Seiko SSC/5200H instrument at a heating rate of $5 \,°C \, min^{-1}$ under air.

Polymerization

A typical polymerization procedure is shown (run 2 in Table I). In a 25 mL Schlenk flask were placed tris(dibenzylideneacetone)dipalladium(0)-chloroform ($Pd_2(dba)_3$) (0.052 g, 5.0×10^{-2} mmol), phenysilane (**1**) (1.082 g, 10 mmol), and H_2O (0.270 g, 15 mmol) at room temperature. As THF (2 mL) was added, a violent evolution of hydrogen gas occurred. After 42 h, the reaction was stopped by filtering the catalyst through a short celite column (Et_2O eluent). Reprecipitation of the concentrated polymer solution into the mixture of ethanol/hexane (4/6) gave a white solid

Table I. Cross-dehydrocoupling polymerization of **1** with water[a]

run	catalyst	yield(%)	M_n[b]	M_w[b]	PD[b]
1[c]	$Pd_2(dba)_3$	~100	750	3330	4.44
2		~100 (36)	1750 (25400)	21400 (62200)	12.2 (2.45)
3[d]		67	860	5510	6.41
4	$PdCl_2$	68	1050	2950	2.81
5	10%Pd/C	60	1880	4300	2.29
6	$H_2PtCl_6 \cdot 6H_2O$	99	2300	23100	10.0
7	$Pt(PPh_3)_4$	~100	1180	2810	2.38
8	$RhCl(PPh_3)_3$	~100	940	2430	2.59
9	$[RhCl(cod)]_2$	98	1600	14400	9.00

[a]Reaction conditions: 0.010 mol of phenylsilane (**1**) and 0.015 mol of water in 2 mL THF for 42 h; 0.005 mol of metal mol^{-1} of silane. [b]Estimated by SEC with polystyrene standards before (after) reprecipitation. [c]For 2 h. [d]Bulk.

P1 (0.460 g, yield 36%). SEC (exclusion limit $M_n = 4.0 \times 10^5$): $M_w/M_n = 62200/25400$. ^{1}H NMR: δ 2.70–3.60 (br, SiO*H*), 6.40–7.80 (br, C$_6$*H*$_5$). ^{13}C NMR: δ 127.66, 130.32, 134.07 (C$_6$H$_5$). ^{29}Si NMR: δ −79.09 (Ph*Si*(O–)$_3$), −70.45 (Ph*Si*(O–)$_2$OH), −67.97(Ph*Si*(O–)(OH)$_2$). IR (KBr, cm^{-1}): 3622, 3369 (υ_{OH}), 3074, 3052, 2245, 1964, 1892, 1826, 1777, 1594, 1491, 1431, 1135–997 (υ_{SiOSi}), 883, 739, 697, 484.

In studying the progress of the polymerization, an aliquot of the sample was pulled out with a syringe for SEC analysis, or the reaction was stopped by filtering off the catalyst after diluting the system with chloroform for ^{29}Si NMR analysis, at 30 sec, 15 min, 3 h, 8 h, 18 h, and 42 h. The initial reaction products at 30 sec were separated by preparative SEC (exclusion limit $M_n = 5.0 \times 10^3$) from the reaction mixture after terminating the reaction with trimethylcholorosilane in pyridine.

RESULTS AND DISCUSSION

Some transition metal derivatives were investigated as catalyst, and the results are summarized in Table I. $Pd_2(dba)_3$, reported[4a] as an efficient catalyst for the cross-dehydrocoupling polymerization, gave only low molecular weight oligomers in 2 h {$M_w/M_n = 3330/750$ (run 1)}. After 42 h, the molecular weight of the product increased, but apparent molecular weight distribution became very broad with roughly bimodal distribution {Figure 1f, $M_w/M_n = 21400/1750$ (run 2)}. The lower molecular weight fraction could be removed by reprecipitation into ethanol/hexane. The insoluble fraction was proved to be a high molecular weight polymer (Figure 1 g, $M_w/M_n = 62200/25400$). When the polymerization was carried out in bulk, a small portion of the product became insoluble, but soluble fraction was still oligomeric products {$M_w/M_n = 5510/860$ (run 3)}. $PdCl_2$ or palladium on charcoal (10% Pd/C) catalyzed polymerization also yielded low
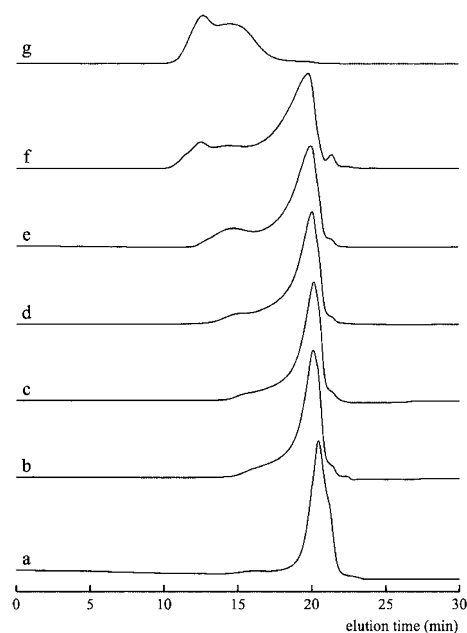

Figure 1. SEC of the polymerization products (run 2): (a) 30 sec, (b) 15 min, (c) 3 h, (d) 8 h, (e) 18 h, (f) 42 h, and (g) after reprecipitation into EtOH/Hexane.

molecular weight products {$M_w/M_n = 2950/1050$ (run 4), $M_w/M_n = 4300/1880$ (run 5)}. $H_2PtCl_6 \cdot 6 H_2O$ was an efficient catalyst to give a high molecular weight product, but the catalyst might be acting as an acid {$M_w/M_n = 23100/2300$ (run 6)}. $Pt(PPh_3)_4$ yielded only low molecular weight oligomer {$M_w/M_n = 2810/1180$ (run7)}. $RhCl(PPh_3)_3$ was not a suitable catalyst for the polymerization {$M_w/M_n = 2430/940$ (run 8)}. $[RhCl(cod)]_2$ was a relatively efficient catalyst, but gave a polymer with wide molecular weight distribution {$M_w/M_n = 14400/1600$ (run 9)}. Thus, among the transition metal derivatives investigated, $Pd_2(dba)_3$ is the most active catalyst for the dehydrocoupling polymerization of **1** with water.

^{1}H NMR spectrum of polymer **P1** showed two broad signals at around 2.70–3.60, and 6.40–7.80 ppm, which are ascribed to hydroxyl and phenyl proton. In the polymer obtained from **1** with deuterium oxide (D_2O),
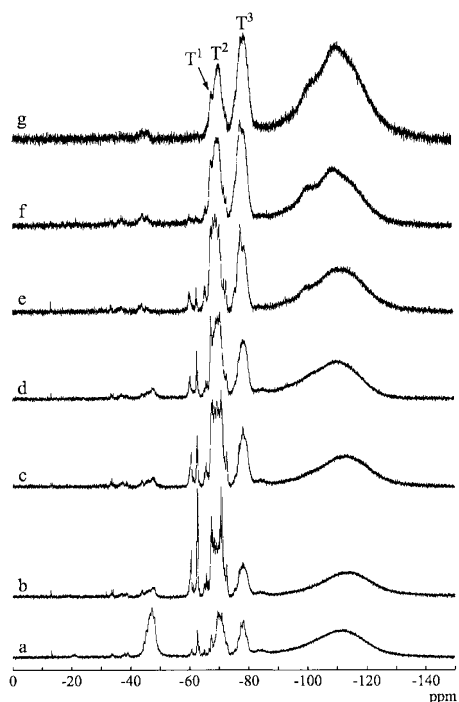
Figure 2. ^{29}Si NMR of the polymerization products: (a) 30 sec, (b) 15 min, (c) 3 h, (d) 8 h, (e) 18 h, (f) 42 h, and (g) after reprecipitation into EtOH/Hexane.

Figure 3. SEC of the trimethylsilylated products of the reaction at 30 sec.

Table II. The compounds of fractions[6]

A	not determined
B	$\{(Me_3SiO)_2PhSi\}_2O$, $\{(Me_3SiO)PhSiO\}_3$
C	$(Me_3SiO)_2PhSiOSiPhH(OSiMe_3)$
D	$PhSi(Me_3SiO)_3$
E	$PhSiH(Me_3SiO)_2$
F	stabilizer of THF
G	$(PhCH_2CH_2)_2C=O$
H	not determined

the signal at around 2.70–3.60 ppm disappeared. ^{13}C NMR spectrum showed three signals of phenyl carbons at 127.66, 130.32, and 134.07 ppm. ^{29}Si NMR spectrum exhibited main signals at −79.09, −70.45, and −67.97 ppm, which are assigned to PhSi(O–)$_3$ (T^3), PhSi(O–)$_2$OH (T^2) and PhSi(O–)(OH)$_2$ (T^1) structure,[5] respectively (Figure 2g). The area ratio is roughly 60 : 31 : 9. The fact that the polymer is soluble in common organic solvent strongly suggests that the polymer has only small amounts of cross-linking even with about 60% of T^3 structure.

The progress of the polymerization (run 2) was monitored by SEC (exclusion limit $M_n = 4.0 \times 10^5$) (Figure 1a–f) by pulling out an aliquot of sample from the reaction mixture at 30 sec, 15 min, 3 h, 8 h, 18 h, and 42 h. After 30 sec, the molecular weight of the product is low with narrow molecular weight distribution. After 15 min, a shoulder peak appeared in higher molecular weight region, and whose molecular weight increased with reaction time. Molecular weight of lower molecular weight fraction did not change so much with reaction time. A small peak at 21.38 min was separated and determined as 1,5-diphenyl-3-pentanone by NMR and MS,[6] which was produced by the reduction of dibenzylideneacetone (dba) ligand of Pd$_2$(dba)$_3$ by liberated hydrogen on Pd.

To obtain the insights of the polymerization at initial stage, the polymerization was stopped after 30 sec by capping the products with Me$_3$SiCl. The SEC (ex-
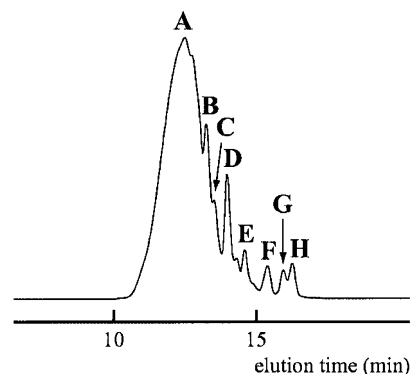
clusion limit $M_n = 5.0 \times 10^3$) of the product mixture exhibited several peaks (Figure 3). Some of these peaks were separated and characterized, using model compound as reference, if necessary, and the results are summarized in Table II. The fractions **D** and **E** are assigned as PhSi(Me$_3$SiO)$_3$ and PhSiH(Me$_3$SiO)$_2$ by ^{1}H, ^{13}C, ^{29}Si NMR, and MS.[6] The fraction **C** is $(Me_3SiO)_2PhSiOSiPhH(OSiMe_3)$. Fraction **B** is a mixture of two compounds, which were separated by recycling SEC. One is $\{(Me_3SiO)_2PhSi\}_2O$, and the other is a cyclotrisiloxane $\{(Me_3SiO)PhSiO\}_3$.

Compounds **D** and **E** should be formed from phenylsilanetriol $\{PhSi(OH)_3\}$ (**4**) and phenylsilanediol $\{PhSiH(OH)_2\}$ (**3**). The amount of **D** detected is more than that of **E**, namely **4** was present more than **3** in the reaction system. It should be stressed that no phenylsilane (PhSiH$_3$) (**1**), nor phenylsilanol (PhSiH$_2$OH) (**2**) was detected in the reaction system. This fact suggests that hydrolysis of SiH function with water by Pd catalyst is fast in the very early stage of the reaction, and that not only the first but also the second silane functions are more reactive than the third silane function toward hydrolysis. This also indicates that **1**, **2**, and **3** have been consumed faster than **4** in the successive reactions in the polymerization. Cross-dehydrocoupling reaction between SiH of **1**–**3** and SiOH functions of **2**–**4** seems responsible for the faster consumption of SiH functions. Dehydration reaction of **4** is a relatively slower process compared with the reactions which consume SiH function as re-
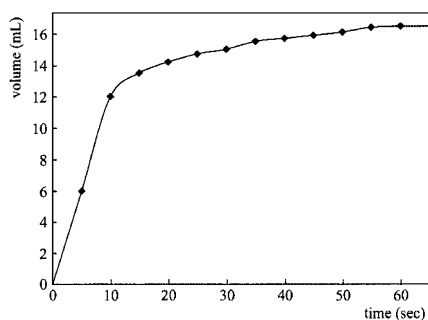
Figure 4. Evolution of hydrogen gas in polymerization.

ported in synthesis of siloxane–arylene polymer from bis(silane) with water.[4a] This inference is in accordance with hydrogen evolution from the system as shown in Figure 4 under the similar condition with the polymer synthesis in small scale,[7] where a violent evolution of hydrogen corresponding to about 70% of calculated amounts occurred in the initial 10 sec, and almost quantitative amount of hydrogen was generated {16.5 mL (the calculated amount, 16.8 mL)} after 60 sec. Thus, cross-dehydrocoupling of two molecules of **3**, or between **2** and **4** is considered to be the major path to give compound **C** as the trimethylsilylated product. Compound {$(Me_3SiO)_2PhSi$}$_2$O in **B** seems to be formed *via* cross-dehydrocoupling of **3** with **4**. Cyclotrisiloxanes {$(Me_3SiO)PhSiO$}$_3$ should be produced as the trimethylsilylated cyclized products *via* intramolecular dehydrocoupling reaction from the linear trimers, such as PhH(OH)SiOSi(Ph)(OH)OSiPh(OH)$_2$, which, in turn, formed by successive dehydrocoupling between SiH and SiOH functions of **1–4**, typically from the condensation of tree molecules of **3**. The major fraction **A** was a mixture of several compounds. Cyclotrisiloxanes and cyclotetorasiloxanes seem to be contained, although their NMR spectra are too complicated to allow a determination of their chemical structure. The fraction **G** was 1,5-diphenyl-3-pentanone as mentioned above.
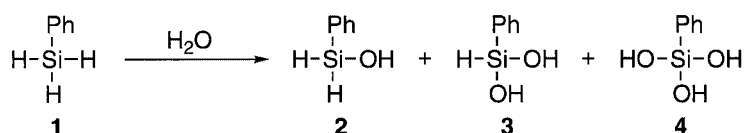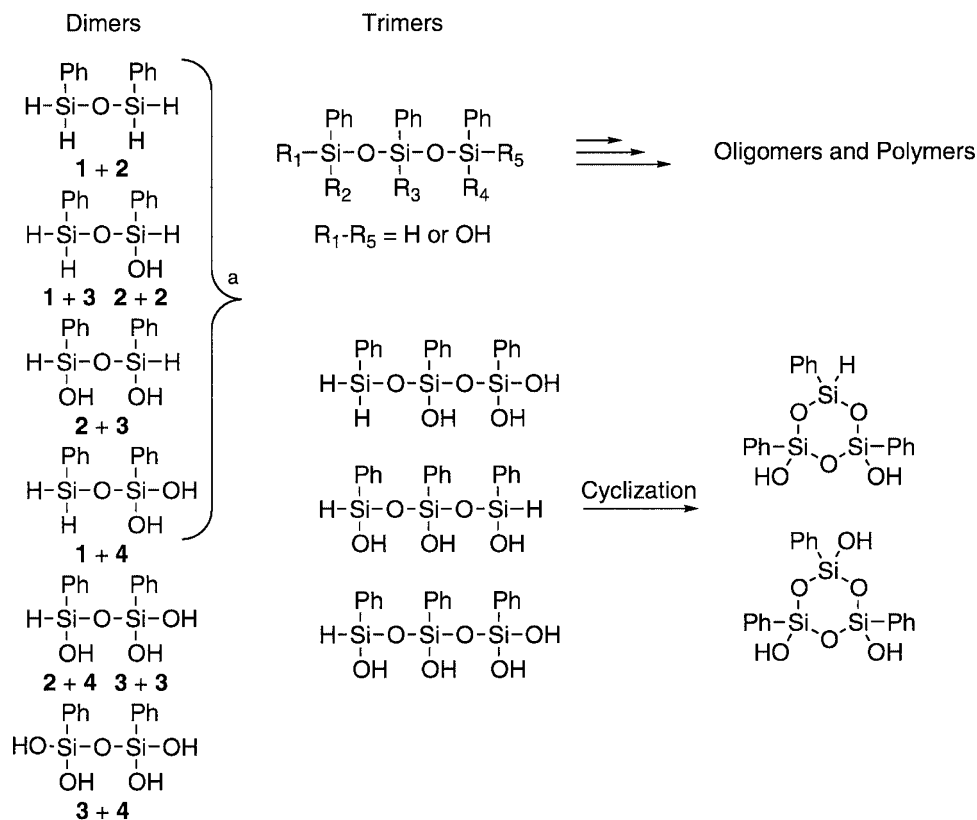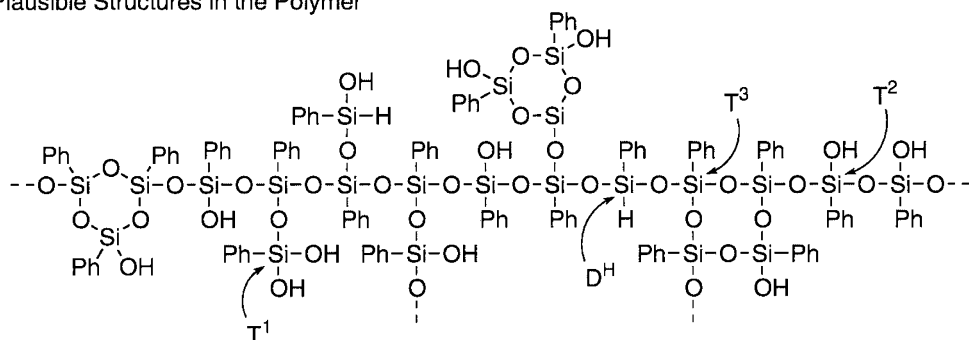
^{29}Si NMR analysis was carried out to detect the progress of the polymerization (Figure 2a–f). In ^{29}Si NMR after 15 min, basically five kinds of signals were observed at around −78.4, −70.5, −67.4; −65.9, −62.8; −60.7, and −47.5 ppm. The signal at −78.4 ppm is assigned to T^3, and that at −70.5 to T^2. The signals at −67.4; −65.9 ppm are assigned mainly as T^1 (may include the signal of *Si*OEt, since it was later found that the stabilizer ethanol in chloroform is reacting with the SiH function when the reaction system was diluted), respectively. Sharp signals at −62.8; −60.7 ppm are reasonably considered to originate from T^2 of low molecular weight products, for example, cyclic structure like cyclotrisiloxane. The multiplicity of the signals is considered to reflect stereochemical structures of the cyclic

compounds. The signal at −47.5 ppm might be assigned to PhSi(O–)$_2$H (D^H), by referring the chemical shift of $(Me_3SiO)_2PhSiH$ (−49.38 ppm) as in the case of the signal at 30 sec. The peak in this area did not change with reaction time, especially after 3 h. Accordingly, the peak at around −47.5 ppm after 3 h should not be assigned to D^H. The origin of the peak is unclear at present. The broad signal at 90–130 ppm arose from NMR glass tube.

In the signal after 30 sec, the major peaks are observed at −78.5, −70.2, and −47.4 ppm. It should be stressed that in the very early stage of the polymerization, the species present in the system are, T^3, T^2, and D^H and only small amounts of T^1 present. After 15 min, the signal of D^H almost disappeared, and instead, the signals of T^2 and T^1 (−70.5, −62.8; −60.7 and −67.4; −65.9 ppm) and T^3 (−78.4 ppm) became stronger. The signals at −62.8; −60.7 and −67.4; −65.9 ppm assignable to T^2 and T^1 decreased gradually with reaction time after taking maximum, and became weak after 42 h. Especially the change of T^2 assignable to low molecular weight products is notable. The signal of T^2 at −70.5 ppm became stronger and broader with reaction time, and that of T^3 also became stronger. After 42 h, the peak of T^3 became the strongest. The major structure of polymer is consisted of T^2 and T^3 structure.

The results of SEC and ^{29}Si NMR indicated that the basic reactions occurring in this polymerization are (1) fast hydrolysis of SiH functions of **1** with water, and (2) cross-dehydrocoupling reaction between SiH and SiOH, followed by (3) slow condensation of SiOH functions. Intramolecular cyclization between SiH and SiOH functions are also occurring in the early stage of the polymerization. The reactions to give oligomers might be depicted as Scheme 2.

The solubility in organic solvent and the ratio of T^1, T^2, and T^3 strongly suggest non cross-linked structure of the polymer having cyclic moiety as shown in Scheme 2. Judging from the structures of initial oligomers, it will be reasonable to assume that the principal chemical structure of the polymer is poly{oxy(phenylhydroxysilylene)} with branched SiH(OH), Si(O–)OH or Si(OH)$_2$ functions. In the early stage of the polymerization, when higher concentration of SiH functions present compared to later stage of the polymerization, branching and cyclization should occur more frequently. Cyclization of D^H functions in the branches, or reaction of {Ph(OH)SiO}$_2$(PhHSiO) with T^1 or T^2 functions of the main chain or branches is quite plausible to reduce the amounts of D^H, T^1 or T^2 relatively to T^{3}structure, and result in 2 : 3 T^2 and T^3 ratio in the polymer. Cross-linking through the condensation

Hydrolysis of **1**

$$\underset{\textbf{1}}{\overset{\text{Ph}}{\underset{\text{H}}{\text{H}-\overset{|}{\underset{|}{\text{Si}}}-\text{H}}}} \quad \xrightarrow{\text{H}_2\text{O}} \quad \underset{\textbf{2}}{\overset{\text{Ph}}{\underset{\text{H}}{\text{H}-\overset{|}{\underset{|}{\text{Si}}}-\text{OH}}}} \quad + \quad \underset{\textbf{3}}{\overset{\text{Ph}}{\underset{\text{OH}}{\text{H}-\overset{|}{\underset{|}{\text{Si}}}-\text{OH}}}} \quad + \quad \underset{\textbf{4}}{\overset{\text{Ph}}{\underset{\text{OH}}{\text{HO}-\overset{|}{\underset{|}{\text{Si}}}-\text{OH}}}}$$

Cross-dehydrocoupling of **1**, **2**, **3**, and **4**

Dimers

Trimers

H-Si-O-Si-H (H, H) **1 + 2**

H-Si-O-Si-H (H, OH) **1 + 3   2 + 2**

H-Si-O-Si-H (OH, OH) **2 + 3**

H-Si-O-Si-OH (H, OH) **1 + 4**

H-Si-O-Si-OH (OH, OH) **2 + 4   3 + 3**

HO-Si-O-Si-OH (OH, OH) **3 + 4**

$$\text{R}_1-\underset{\text{R}_2}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{R}_3}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{R}_4}{\overset{\text{Ph}}{\text{Si}}}-\text{R}_5 \quad \Longrightarrow \quad \text{Oligomers and Polymers}$$

R₁-R₅ = H or OH

H-Si-O-Si-O-Si-OH (H, OH, OH)

H-Si-O-Si-O-Si-H (OH, OH, OH)

H-Si-O-Si-O-Si-OH (OH, OH, OH)

Cyclization →

Ph, H / Ph-Si, Si-Ph / HO, OH (cyclic)

Ph, OH / Ph-Si, Si-Ph / HO, OH (cyclic)

Plausible Structures in the Polymer[b]

Scheme 2. Plausible polymerization mechanism. [a]Not isolated. [b]Concentration of SiH is very low.

of SiOH groups of T² units seems quite slow.

Polymer can be cast into a transparent rather fragile film. When cast on polyethylene, the film can be removed. Contrary, the film cast on glass sticks the substrate very strongly, and could not be removed. This polymer may find an application as a coating material.

Thermal stability of polymer **P1** was studied by thermo-gravimetric analysis (TGA) in air, and the result is shown in Figure 5. The mass was lost gradu- ally (8.5%) from room temperature through at around 500 °C, presumably because of elimination of water by condensation of SiOH of T² structure. In IR spectrum of the residue at 500 °C, the absorption of OH (3369 cm^{-1}) was disappeared. The weight loss was observed at around 510 °C, which was caused by the removal of phenyl group. The residual weight of 46.7% is close to the expected value, 46.5%, calculated based on the assumption that all the Si is oxidized to SiO₂.
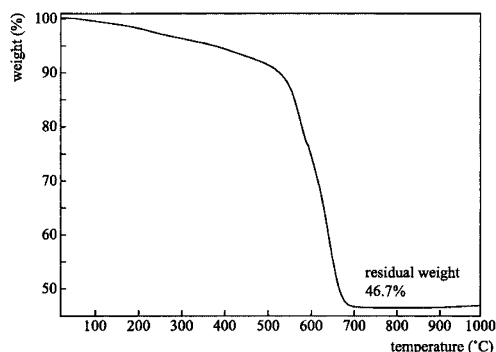
Figure 5. TGA of polymer **P1**.

CONCLUSION

The cross-dehydrocoupling polymerization of **1** with water in the presence of Pd, Pt, and Rh derivatives was investigated. It was found that $Pd_2(dba)_3$ is an efficient catalyst for this polymerization, which affords a high molecular weight poly(phenylsilsesquioxane) (M_w/M_n = 62200/25400 by SEC). Hydrolysis of SiH and cross-dehydrocoupling reaction between SiH and SiOH are very fast and principal reactions to give polymers. In early stage of the polymerization, not only linear but also cyclic oligomers are formed. Polymer seems to have branched structure, especially in the early stage of the polymerization. Condensation of SiOH is quite slow and soluble polymer in common organic solvents are produced. When heated, dehydration of SiOH groups occurs to give cross-linked insoluble polymer.

This study affords a novel route to access poly(silsesquioxane)s, and appropriate selection of reaction condition will give a better controlled structure of the polymer.

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6. Selected spectroscopic data: $PhSiH(Me_3SiO)_2$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.14 (s, 18 H, SiCH_3), 4.97 (s, 1 H, SiH), 7.34–7.46 (m, 3 H, Ph), 7.53–7.60 (m, 2 H, Ph). ^{13}C NMR (125.5 MHz, CDCl$_3$): δ 1.72, 127.76, 130.00, 133.10, 137.02. ^{29}Si NMR (95.5 MHz, CDCl$_3$): δ −49.38, 10.77. MS (EI, *m/z*): 283 ([M−H]$^+$), 269 ([M−Me]$^+$). $PhSi(Me_3SiO)_3$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.11 (s, 27 H, SiCH_3), 7.29–7.41 (m, 3 H, Ph), 7.52–7.58 (m, 2 H, Ph). ^{13}C NMR (125.5 MHz, CDCl$_3$): δ 1.60, 127.60, 129.58, 133.93, 135.64. ^{29}Si NMR (95.5 MHz, CDCl$_3$): δ −77.81, 8.83. MS (EI, *m/z*): 357 ([M−Me]$^+$). $(Me_3SiO)_2PhSiOSiPhH(OSiMe_3)$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.072, 0.079, 0.087 (3 s, 27 H, SiCH_3), 5.05 (s, 1 H, SiH), 7.28–7.45 (m, 6 H, Ph), 7.54–7.60 (m, 4 H, Ph). ^{13}C NMR (125.5 MHz, CDCl$_3$): δ 1.66, 127.54, 127.69, 129.68, 130.07, 133.27, 133.89, 134.60, 136.40. ^{29}Si NMR (95.5 MHz, CDCl$_3$): δ −78.42, −49.87, 9.52, 11.11. MS (EI, *m/z*): 494 ([M]$^+$). $\{(Me_3SiO)_2PhSi\}_2O$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.07 (s, 36 H, SiCH_3), 7.28–7.45 (m, 6 H, Ph), 7.53–7.59 (m, 4 H, Ph). ^{13}C NMR (125.5 MHz, CDCl$_3$): δ 1.67, 127.40, 129.51, 133.98, 134.90. ^{29}Si NMR (95.5 MHz, CDCl$_3$): δ −79.79, 9.08. MS (EI, *m/z*): 567 ([M−Me]$^+$). $\{(Me_3SiO)PhSiO\}_3$: ^{1}H NMR (300 MHz, CDCl$_3$): δ −0.034, 0.084, 0.203 (3 s, 27 H, SiCH_3), 7.18–7.50 (m, 9 H, Ph), 7.58–7.64 (m, 4 H, Ph), 7.74–7.79 (m, 2 H, Ph). ^{13}C NMR (125.5 MHz, CDCl$_3$): δ 1.38, 1.55, 1.73, 127.58, 127.62, 127.66, 130.12, 130.21, 130.32, 132.44, 132.58, 132.75, 133.92, 134.03, 134.09. ^{29}Si NMR (95.5 MHz, CDCl$_3$): δ −70.85, −70.56, −70.45, 11.26, 11.33, 11.46. MS (EI, *m/z*): 615 ([M−Me]$^+$). $(PhCH_2CH_2)_2C=O$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.71 (t, 4 H, PhCH$_2$CH_2, *J* = 7.8 Hz), 2.89 (t, 4 H, PhCH_2, *J* = 8.1 Hz), 7.14–7.22 (m, 6 H, Ph), 7.24–7.31 (m, 4 H, Ph). ^{13}C NMR (125.5 MHz, CDCl$_3$): δ 29.71, 44.50, 126.10, 128.29, 128.48, 140.99, 209.11. MS (EI, *m/z*): 238 ([M]$^+$).
7. Reaction condition: 0.250 mmol of **1**, 0.375 mmol of water, and 0.001 mmol of $Pd_2(dba)_3$ in 0.05 mL THF.