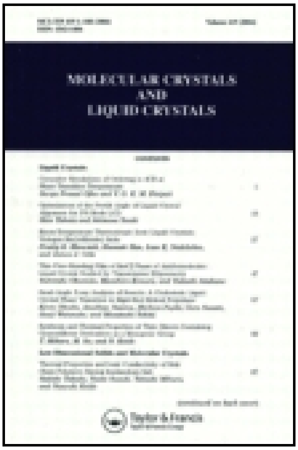

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High Performance Siloxane-Containing Polymers

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HIGH PERFORMANCE SILOXANE-CONTAINING POLYMERS

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Catalytic cross-dehydrocoupling polymerization of silane and water, and deaminative polymerisation between silanol and aminosilane are used to synthesize a variety of silicon-containing polymers with controlled structure. n-Hexylamine-2-ethylhexoate was used to catalyze silanol condensation. Among transition metal derivatives investigated, $Pd_2(dba)_3$ is the most active catalyst for the dehydrocoupling polymerisation, and deaminative polymerisation proceeded smoothly by heating. Optically active siloxane materials of branched structure were obtained from (S,S)-1,3-dimethyl-1,3-diphenyldisiloxanediol and (S,S)-1,5-di(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane (>99% ee) as optically active building blocks.

INTRODUCTION

Modern advanced technologies have continuous demands on the development of high temperature heat resistant or flame retardant materials. As elastomers for electronic application, thermal stability up to several hundred degree is required simultaneously maintaining flexibility to temperatures much lower than ambience. In conventional technologies, halogen, nitrogen, or phosphorous containing polymers are widely used as heat resistant or fire retardant polymer, such as fluorocarbon polymers [1], polyimide [2], polyphosphazenes [3]. The drawback of these materials in application is possible emission of toxic and corrosive gasses during combustion.

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Polysiloxane is a kind of another good candidate for such functional materials because of flexible and heat resistant Si-O-Si backbone, which is also the origin of good dielectric and surface properties [4,5], and silarylene-siloxane polymers, derivatives of polysiloxanes by partially replacing -O- by arylene groups, show better mechanical property than polysiloxane [6,7]. Corriu [8] elucidated that the main course of degradation of these polymers is the intermolecular followed by intramolecular exchanges of Si–O bonds leading to depolymerization.

Silphenylene-siloxane polymers can be synthesized from 1,4-bis(hydroxydimethylsilyl)benzene (**BHSB**) and difunctional silane or siloxane. Variety of functional substituents, such as vinyl, phenyl, hydrido, and flouroalkyl, can be introduced into the polymer structure. Among them, vinyl group was found superior to others for enhancing the thermal stability [9,10].

Merker reported polycondensation of **BHSB** to give poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] [11], commonly called as poly(tetramethyl-*p*-silphenylenesiloxane) (**PTMPS**). This **PTMPS** contains the maximum number of rigid phenylene groups, and should be more reluctant to siloxane rearrangement and highly thermally stable. Meanwhile, we reported a clean method to obtain **PTMPS** by catalytic cross-dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with water under neutral condition [12]. However, **PTMPS** is not good as high temperature elastomer because it is crystalline, and proper chemical modification of the structure should be made to gain low temperature elasticity. We recently reported a kind of poly(silphenylenesiloxane)s containing silicon hydride and vinyl side groups, which have been proved to be promising candidates for high temperature elastomers [13]. Vinyl side functions, besides high temperature vulcanizable nature, can also be chemically cured or modified by various reactions such as hydrosilylation to give the polymer new functionality or a 3-D network structure. The cross-linking density may also be controlled over a broad range depending on the ratio of the cross-linker to vinyl groups.

Poly(silsesquioxane), having the empirical formula $RSiO_{1.5}$ (R = Ph, Me, H etc.), is another kind of interesting silicone polymer. It also shows excellent properties, such as high thermal stability, low dielectric constant, oxidative resistance [14], and establishment of reliable synthetic method is still required. Considerable attention is also given to highly branched three dimensional macromolecules such as dendrimers and hyperbranched polymers due to the wide applicability to novel macromolecular architecture and functional polymers [15].

Meanwhile, much attention has been also paid in recent years to the fabrication of chiral polymeric materials. However, many materials with chirality induced by asymmetric silicon atoms in the main chain have not been reported yet, although chirality is introduced to the side chain or the main chain [16]. We have prepared several stereoregular and optically active polymers having asymmetric silicon atoms in the main chain [17–20]. There have not been many efforts made to create an optically active hyperbranched system [21,22] in contrast to the precisely constructed optically active dendrimers. Optically active hyperbranched polymers prepared by an one-pot polymerization of optically active monomer allow the introduction of optical active units and functional groups to the interior and terminal of the molecules which may lead to efficient asymmetric catalysts or chiral recognition materials.

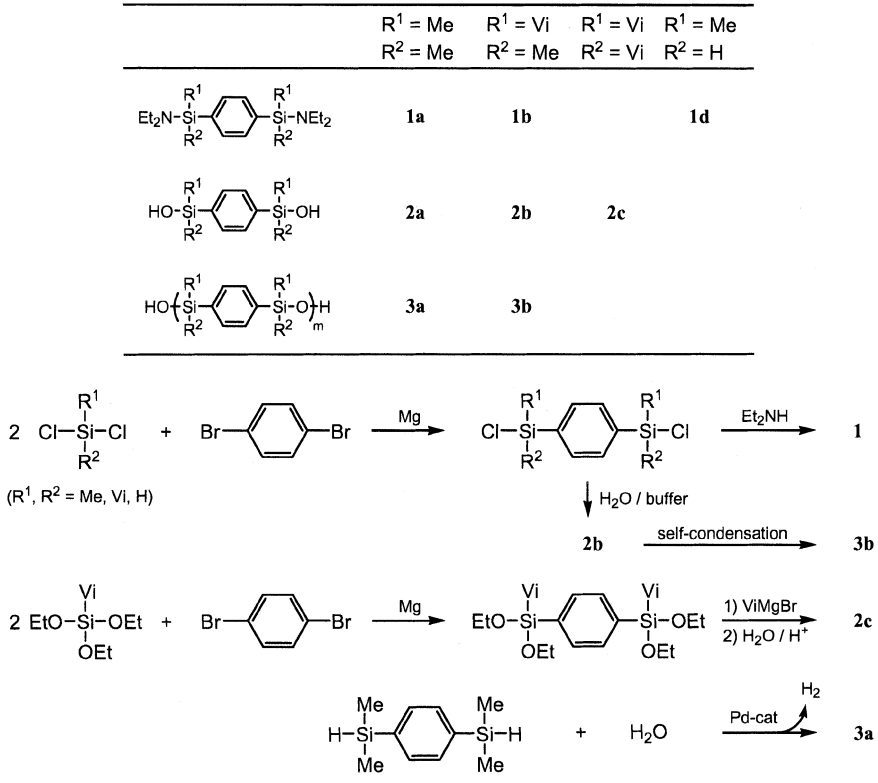
RESULTS AND DISCUSSION

Poly(silphenylene-siloxane)

Silphenylene-siloxane polymers have been generally synthesized by homocondensation reaction of phenylene disilanol or heterocondensation of disilanol with suitable difunctional silane or siloxane. When considering the preparation of monomer and removal of byproducts with ease, the silanol-aminosilane condensation polymerization is the best choice for its high efficiency. The synthesis of monomers and polymers are shown in Schemes 1 and 2. When preparing 1,4-bis(methylchlorosilyl)benzene, the reaction was controlled to proceed at around room temperature within a relatively short reaction time in order to minimize the unexpected disproportionation reaction of the silane derivatives. By using slightly excessive amount of water in the palladium-catalyzed dehydrocoupling polymerization of **BSB** with water, the prepolymer **3a** with hydroxy terminal and narrow polydispersity ($M_n = 2840$, $PD = 1.03$) was obtained.

The exactly alternating structure of –$(CH_3)_2$Si-Ph-Si$(CH_3)_2$-O– (**TMPS**) and functional group substituted –(R)(CH_3)Si-Ph-Si(R)(CH_3)-O– (**RMPS**, R = H or Vi) units in polymer structure was confirmed by NMR. ^{29}Si NMR of **PH25**-*alt* shows only two sharp singlets at −13.73 ppm and 0.86 ppm due to the two kinds of backbone silicon atoms, methylhydridosilylene and dimethylsilylene, and **PV25**-*alt* presents two sharp singlets at −12.76 ppm and −0.40 ppm corresponding to methylvinylsilylene and dimethylsilylene respectively. **PV25**-*ran* shows two sets of signals at –0.38, –1.25, and –12.01, –12.76 ppm (Fig. 1). The signals at –0.38 and –12.76 ppm are reasonably assigned to the dimethylsilylene and methylvinylsilylene in the disiloxane linkages of the alternating cross diad units in **PV25**-*ran*. The signals at –1.25 and –12.01 ppm are obviously generated by the dimethylsilylene and methylvinylsilylene in their homo diad units in the random building blocks.

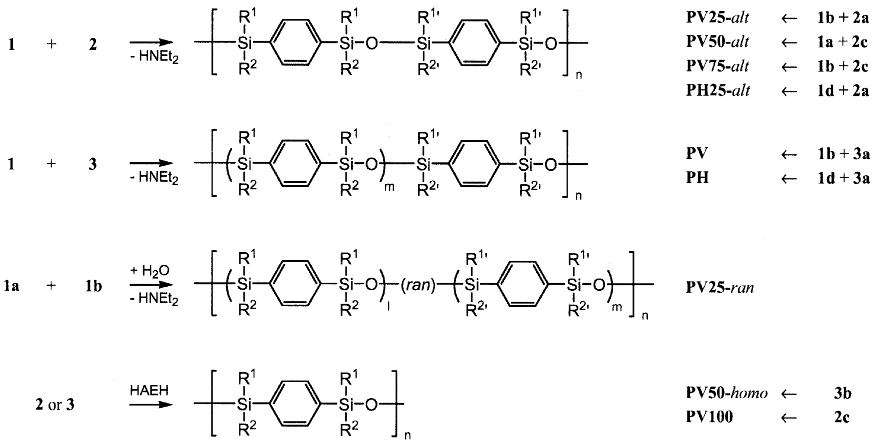
Polymerization of prepolymer **3a** with diethylamino-functionalized monomers led smoothly to give polymers with hydrido or vinyl function,



SCHEME 1 Syntheses of bis(silyl)benzenes (**1**, **2**) and prepolymers (**3**).

which have another alternating structure of chain segment–[$(CH_3)_2$Si-Ph-Si$(CH_3)_2$-O]$_n$– and **RMPS** unit. The functional units, **RMPS**, are very well dispersed in the polymer chain. ^{29}Si NMR of both polymers show one major peak of -Me$_2$*Si*- (at –1.26 ppm for **PH** and –1.17 ppm for **PV** and two minor peaks corresponding to -MeR*Si*- (at –13.82 ppm for **PH** and –12.71 ppm for **PV**) and -Me$_2$*Si*- (at 0.86 ppm for **PH** and –0.33 ppm for **PV**) which is adjacent to -MeR*Si*-.

Deaminative polycondensation of **2c** with bis(aminosilane)s **1a** or **1b** also proceeded smoothly to give polymers **PV50**-*alt* and **PV75**-*alt*, in which vinyl contents are 50% and 75% respectively. Similar to **PV25**-*alt*, these polymers have very defined exactly alternating structures from the disilanol and bis(aminosilane) components. The disilanol **2b** derived from 1,4-bis(methylvinylchlorosilyl)benzene did self-condensation quickly to form a mixture of silanol-terminated oligomer **3b**. Employing this oligo-disilanol **3b** to the further dehydrative polycondensation catalyzed by



SCHEME 2 Polymerization of **1**-**3**.

n-hexylamine-2-ethylhexonate, polymer **PV50**-*homo* containing 50% vinyl substituent was obtained in good yield. Similarly, *n*-hexylamine-2-ethylhexonate catalyzed dehydration of disilanol **2c** was also successful to give fully-vinyl substituted **PV100**.

All polymers have glass transition temperatures (T_g) ranging from –22°C to –52°C, which are relatively lower than ambient temperature. Compared with **PTMPS**, introducing hydride and vinyl functions to the polymer side chain has not only diminished the crystallinity, but also decreased the glass transition temperature. DSC measurement of polymers **PH** and **PV** revealed that the T_gs of them are about 10°C higher than **PH25**-*alt* and **PV25**-*alt* and partial crystallization occurred at 11°C for **PH** and 23°C for **PV**. The T_gs and T_cs are very similar to that of **PTMPS** ($T_g = -22°C$, $T_c = 15°C$). The lowest T_g was given by **PV50**-*homo*, in which every silicon atom in the backbone is an asymmetric center. The existence of asymmetric center and vinyl side group should be the reason of disappearance of crystallinity and the decrease of T_g.

TGA curves of polymers under nitrogen atmosphere are shown in Figure 2. It can be seen that a single-step process occurred for degradation in nitrogen, while a multi-step process involved in air. Each polymer has an onset degradation temperature above 400°C, and an end temperature of major degradation higher than 600°C, except for **PH25**-*alt*. Compared to **PTMPS**, there is a dramatic increase of the residue yield for both SiH-substituted **PH25**-*alt* and vinyl-substituted **PV25**-*alt* and **PV25**-*ran*, even for **PV** just containing a very low percentage of vinyl content. **PV25**-*ran* shows the almost same degradation behavior with **PV25**-*alt*, but its weight loss at the end is 6% more than **PV25**-*alt*. This slight decrease of thermal

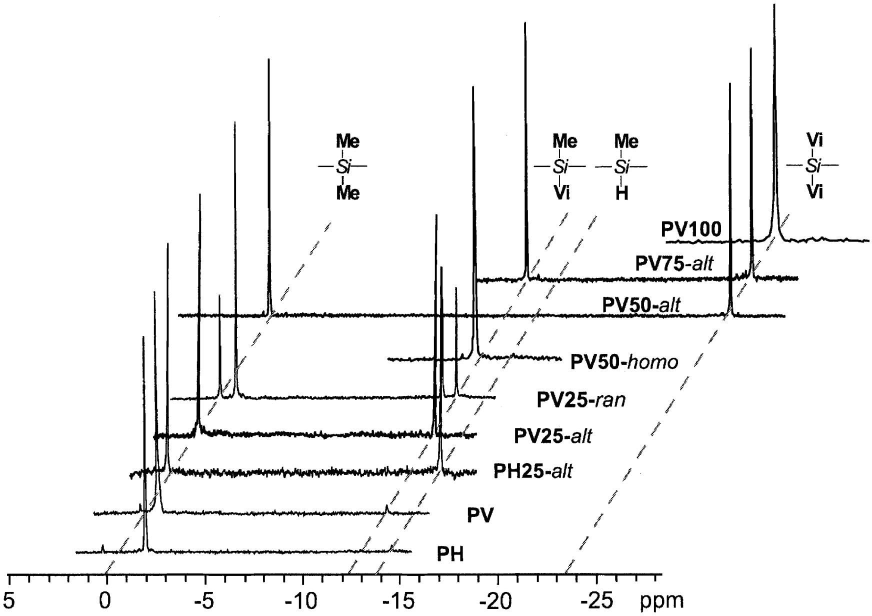


FIGURE 1 ^{29}Si NMR spectra of vinyl containing polymers.

stability of **PV25**-*ran* may be caused by its random structure and relative low molecular weight. It can be seen that introducing SiH functions made the polymer **PH25**-*alt* produce the highest residue yield, although it showed a lower initial temperature of degradation. Compared with **PTMPS**, the onset degradation of all polymers containing high contents of vinyl substituents was shifted to higher temperature, and the residual yields were significantly increased. The data of all dynamic and isothermal TGA were summarized in Table 1. It can be seen that the T_d at 5% weight loss and residual yield in nitrogen seemed to increase as a function of the increase of vinyl content. Introducing 25% vinyl groups has elevated the T_d in nitrogen to 498°C from 431°C of **PTMPS**, and the residue yield increased to 67% compared with 36% of **PTMPS**. **PV50**-*homo* and **PV50**-*alt* showed their degradation curve quite similarly and ended at a same 83% residue yield. Fully vinyl-substituted **PV100** lost 5% weight at 611°C and only 10% when heated to 1000°C, which was undoubtedly the most thermally stable.

In air (Fig. 3), it is clear that the major weight loss step of the functionalized polymers moved to higher temperatures compared to **PTMPS**. All polymers containing functional side groups show the temperature of 50% weight loss well above 600°C, and final residues higher than that of

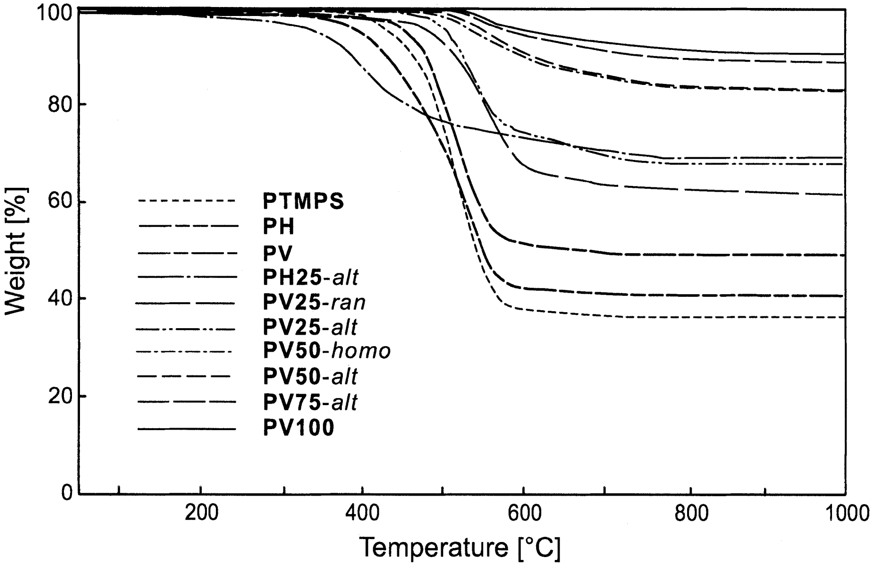
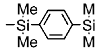
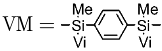
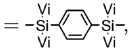
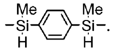


FIGURE 2 TGA curves of all phenylene-disiloxane polymers measured under nitrogen.

TABLE 1 Characteristics of all Phenylene-Disiloxane Polymers.

Polymers	Repeating units[a]	Vinyl content [%]	M_w[b]	M_w/M_n[b]	T_g[c] [°C]	$T_{d,onset}$[d] [°C]		Residue at 1000°C [%]	
						in N_2	in air	in N_2	in air
PTMPS	—MM—	0	20,100	1.52	−22	431	387	36	31
PV25-*alt*	—MM—VM—	25	31,300	2.92	−33	498	521	67	54
PV25-*ran*	—MM—(*ran*)—VM	~25	4,700	1.30	−40	475	481	61	44
PV50-*alt*	—MM—VV—	50	88,700	4.73	−32	541	515	83	56
PV-50-*homo*	—VM—	50	72,700	4.85	−52	553	548	83	58
PV75-*alt*	—VM—VV—	75	37,100	3.60	−47	583	524	88	60
PV-100	—VV—	100	57,400	3.58	−45	611	582	90	79
PV	—$(MM)_m$—VM—	<5	39,800	1.83	−24	460	499	48	47
PH25-*alt*	—MM—HM—		69,300	2.97	−38	345	362	68	57
PH	—$(MM)_m$—HM—		39,500	2.21	−23	407	388	40	38

[a] MM = , VM = , VV = , HM = .

[b] Estimated by GPC with polystyrene standard.

[c] Determined by DSC analysis.

[d] Temperature of 5% weight loss.

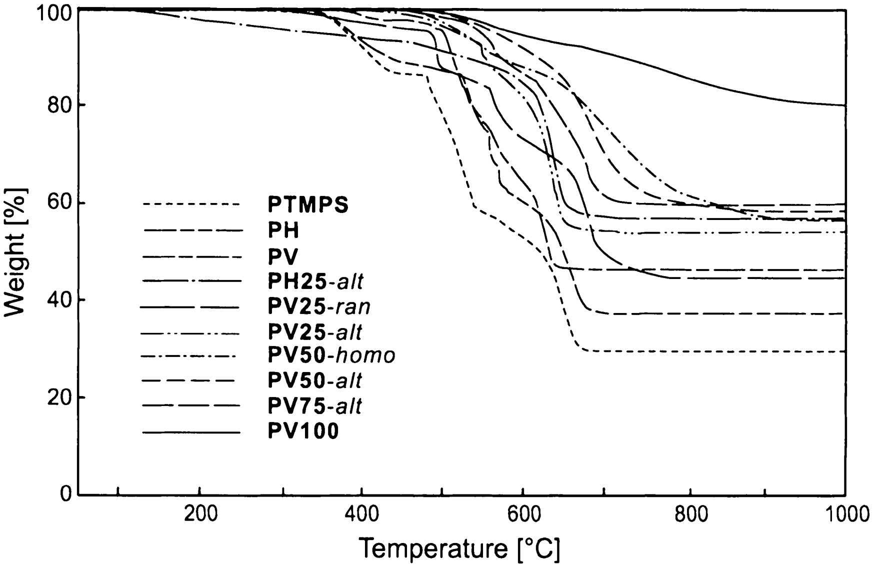


FIGURE 3 TGA curves of all phenylene-disiloxane polymers measured in air.

PTMPS. Consistent with the result in nitrogen, polymers of alternating structure (**PH25**-*alt* and **PV25**-*alt*) have higher stability than that of **PH**, **PV**, or **PV25**-*ran*. After undergoing a complicate multi-step degradation process, the residue of every polymer is white hard solid, which looks quite different from the black residue of degradation in nitrogen. The white residue is considered to be silica formed from the thermo-oxidative degradation in air, but the black one in nitrogen is still unsure in detail.

The TGA carried out in air indicated that the thermo-oxidative stability was also greatly improved by introducing thermally vulcanizable vinyl side functions. The most stable **PV100** with 100% vinyl content had its T_d elevated to 582°C and gave 79% residue at 1000°C. These dynamic TGA results proved the poly(silphenylenesiloxane)s with high vinyl-content have maintained interesting thermal stability to about 500°C and surprisingly high residue yields even to 1000°C.

Polysilsesquioxanes

$Pd_2(dba)_3$, reported as an efficient catalyst for the cross-dehydrocoupling polymerization, gave only low molecular weight oligomers in 2 h ($M_w/M_n = 3{,}330/750$). After 42 h, the molecular weight of the product increased, but apparent molecular weight distribution became very broad with roughly bimodal distribution ($M_w/M_n = 21{,}400/1{,}750$). 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 ($M_w/M_n = 62{,}200/25{,}400$).

^{1}H NMR spectrum of polymer showed two broad signals at around 2.70–3.60, and 6.40–7.80 ppm, which are ascribed to hydroxyl and phenyl proton. ^{29}Si NMR spectrum, in Figure 4, exhibited main signals at –79.1 –70.45, and –67.97 ppm, which are assigned to Ph*Si*(O-)$_3$ (T^3), Ph*Si*(O-)$_2$ OH (T^2) and Ph*Si*(O-)(OH)$_2$ (T^1) structure, [23] respectively. 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 was monitored by SEC (exclusion limit $M_n = 4.0 \times 10^5$). After 30 seconds, the molecular weight of the product is low with narrow molecular weight distribution. $PhSi(Me_3SiO)_3$, $PhSiH(Me_3SiO)_2$,$(Me_3SiO)_2PhSiOSiPhH(OSiMe_3$, $\{(Me_3SiO)_2PhSi\}_2O$, and $\{(Me_3SiO)PhSiO\}_3$ were isolated among the products in the initial stage, after capping the products with Me_3SiCl. These compounds should be formed from phenylsilanediol (**6**) and phenylsilanetriol (**7**). It should be stressed that no phenylsilane (**4**), nor phenylsilanol (**5**) 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 the first and second silane functions are more reactive than the third silane function toward hydrolysis. Cross-dehydrocoupling reaction between SiH

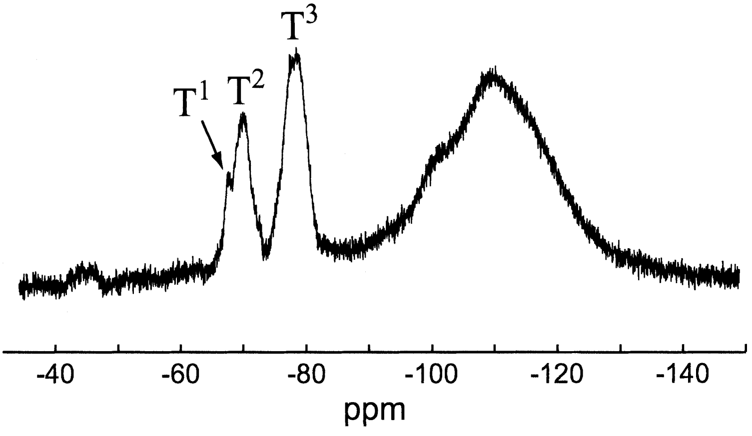


FIGURE 4 ^{29}Si NMR spectrum of polysilsesquioxane obtained by dehydrogentaive polycondensation of phenylsilane and water.

and SiOH functions of these compounds seems responsible for the faster consumption of SiH functions. Dehydration reaction is a relatively slower process compared with the reactions which consume SiH function as reported in synthesis of siloxane-arylene polymer from bis(silane) with water.

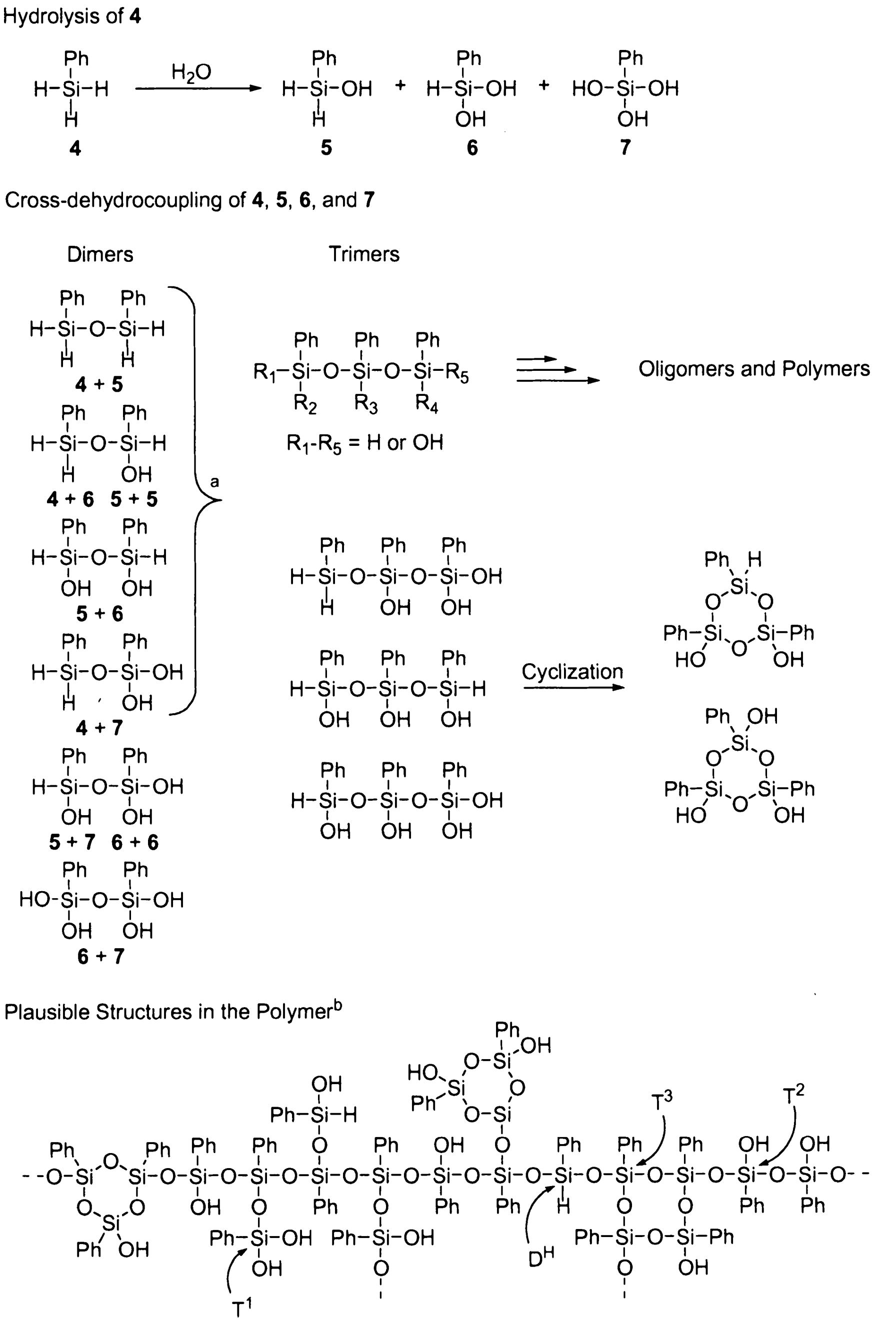
In ^{29}Si NMR after 15 minutes, basically five kinds of signals were observed at around –78.4, –70.5, –67.4; –65.9, –62.8; –60.7, and –47.5 ppm. The signal at –78.4 ppm is assigned to T^3, and that at –70.5 to T^2. The signals at –67.4; –65.9 ppm are assigned mainly as T^1, respectively. Sharp signals 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 signal at –47.5 ppm might be assigned to $\mathrm{Ph}\mathit{Si}(\mathrm{O}\text{-})_2\mathrm{H}(\mathrm{D}^{\mathrm{H}})$. In the signal after 30 seconds, 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^1decreased 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 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 3. Polymer can be cast into a transparent rather fragile film. This polymer may find an application as a coating material.

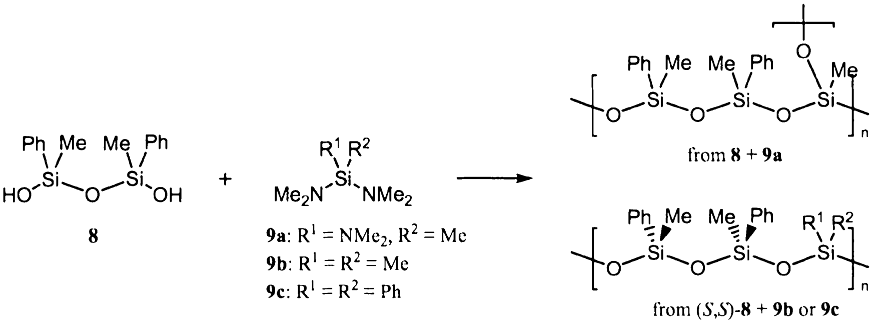
The mass was lost gradually (8.5%) in thermo-gravimetric analysis (TGA) in air from room temperature through at around 500°C, presumably because of elimination of water by condensation of SiOH of T^2 structure. In IR spectrum of the residue at 500°C, the absorption of OH (3369 cm^{-1}) was disappeared. 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 SiO_2 [24].

Siloxane Gel

Siloxane gels were prepared by deamination reaction as shown in Scheme 4. In the early stage, the polymer has low molecular weight but with narrow molecular weight distribution (10, 20 min). After 30 min, a



SCHEME 3 Plausible mechanism of polymerization. [a]Not isolated. [b]Concentration of SiH is very low.



SCHEME 4 Synthesis of siloxane gel and polysiloxanes.

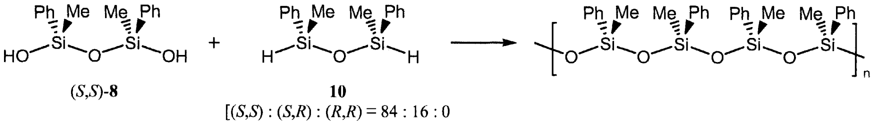
shoulder peak of cyclic compounds appeared, and after 1 hr, the molecular weight of the products increased (M_w as high as 350,000 (polystyrene standard)) and polydispersity became wide. After about 3 hr, the reaction mixture became insoluble.

After 10 min in ^{29}Si NMR, the signal of monomer (should be observed at –22.77 ppm) already disappeared completely, and the signals of cyclic compounds were observed at around –31 ppm (five peaks –31.12, –30.92, –30.85, –30.76 ppm) and at –20.91 ppm (apparent singlet), respectively. The peak at –21.09 ppm next to the signal of cyclic compound is considered to originate from MePh*Si*(O-)OH of chain end. The peak at –26.09 ppm might be ascribed to intermediately formed Me*Si*(O-)$(NMe_2)_2$, in which one amino group of **9a** condenses with silanol. The signal seen at around –31.5 ppm is considered assignable to cyclic structure in the polymer, which was formed by condensation of amino group in polymer chain with silanol function of chain end. The major signal at –33.72 ppm is assigned to MePh*Si*$(O\text{-})_2$ of disiloxane unit in the polymer, and the signal at –66.95 ppm, which appeared after 30 min and became strong with reaction time ([Me*Si*$(O\text{-})_3$]/[MePh*Si*$(O\text{-})_2$] = 1/6.9 (1 hr), 1/5.4 (2 hr)), is assigned to Me*Si*$(O\text{-})_3$ of cross-linking unit. The signal at around –57 ppm is considered as Me*Si*$(O\text{-})_2NMe_2$ or Me*Si*$(O\text{-})_2OH$ in which two amino groups of **9a** condense with silanol, or amino group of Me*Si*$(O\text{-})_2NMe_2$ was hydrolyzed with H_2O formed by self-condensation of **8**. The GPC trace and ^{29}Si NMR analysis indicated that, in the early stage of the polymerization, cyclization by self-condensation of **8** and oligomerization occurred. The first and second amino group of **9a** seems to have higher reactivity than that of the third amino group. In the later part of the polymerization, branching occurred by the reaction of the remaining third amino group with silanol function to form hyperbranched structure, followed by the gradual cross-linking to give insoluble siloxane gel [25].

Stereoregular Polysiloxane

Stereoregular polysiloxane was synthesized according to Scheme 5.

ipso-Carbon peaks ($I = 137.1$, $H = 136.9$, $S = 136.7$ppm) showed definite splitting based on the triad tacticity. The triad tacticity of poly (methylphenylsiloxane) prepared from (*S,S*)-**8** and **10** [(*S,S*):(*S,R*): (*R,R*) = 84:16:0] in the presence of Et_3N was estimated as S:H:I = 60:32:8 from the *ipso*-carbon peaks [26].



SCHEME 5 Synthesis of syndiotactic poly(methylphenylsiloxane) (**PMPS**).

Optically Active Siloxane Gel

Polycondensation of (*S,S*)-**8** with bis(dimethylamino)dimethylsilane **9b** or bis(dimethylamino)diphenylsilane **9c** was carried out (Scheme 4), and the results are summarized in Table 2.

The information about the regularity in the connection of the two successive disiloxane units (stereoregularity) was obtained by the analysis of ^1H signals of $SiMe_2$ sandwiched between (*S* or *R*)-PhMeSi*O and (*S* or *R*)-OSi*MePh [(*S* or *R*)-Si and (*S* or *R*)-Si] in successive units. As a first approximation, the two methyl groups should appear as a singlet when sandwiched between two silicon atoms of the same absolute configuration, and two singlets when sandwiched by two silicon atoms of opposite configuration. There is only one possible combination of the configuration of (*S*)-Si-SiMe_2-(*S*)-Si for **P1** from (*S,S*)-**8**, thus the methyl groups of the **P1** from (*S,S*)-**8** gave basically a singlet. This polymer is considered to be rich in (*S,S*)-diisotacticity together with the analysis of the stereochemistry of the disiloxane unit.

The diisotactic **P1** showed the positive optical rotation ($[\alpha]_D^{24} = +2.3$, entry 1), whereas that of diisotactic **P2** showed negative optical rotation ($[\alpha]_D^{24} = -2.0$, entry 4) [27].

This reaction was applied for the synthesis of optically active siloxane gels. The polycondensation reaction of phenylsilane and (*S,S*)-1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol gave the poly(silsesqioxane) with molecular weight (M_n) 15,000 (purified by repeated reprecipitation into MeOH) by GPC (exclusion limit $M_n = 4.0 \times 10^5$), when the reaction was stopped after 2 hr. This polymer showed optical activity ($[\alpha]_D^{27} = -1.77$ ($c = 1.25$, $CHCl_3$)), which is considered to be induced by the asymmetric silicon atoms of (*R,R*)-**8** unit in the polymer structure. The polymer is

TABLE 2 Synthesis of Optically Active Polysiloxanes *via* Polycondensation of **8** with **9**

Entry	**8**	**9**	Polymer	Yield [%][d]	M_n[e]	M_w/M_n[e]	$[\alpha]_D^{24}$	T_g[°C][h]
1	(*S*,*S*)[a]	**a**	(*S*,*S*)-diisotactic **P1**	48	51,200	1.85	+2.3[f]	−56
2	*meso*[b]	**a**	*meso*-atactic **P1**	49	50,300	2.10		−53
3	*diastereomer*[c]	**a**	atactic **P1**	65	74,300	1.51		−54
4	(*S*,*S*)[a]	**b**	(*R*,*R*)-diisotactic **P2**	53	18,400	2.86	−2.0[g]	−2
5	*meso*[b]	**b**	*meso*-atactic **P2**	38	43,800	2.18		−10
6	*diastereomer*[c]	**b**	atactic **P2**	51	49,100	1.70		−11

[a] (*S*,*S*) : (*S*,*R*) : (*R*,*R*) = 86 : 14 : 0.
[b] Pure isomer.
[c] (*S*,*S*) : (*S*,*R*) : (*R*,*R*) = 25 : 50 : 25.
[d] Isolated yields after reprecipication into methanol.
[e] Estimated by GPC (THF as an eluent) with polystyrene standard.
[f] $c = 0.870$, $CHCl_3$.
[g] $c = 0.820$, $CHCl_3$.
[h] Determined by DSC with heating rate of a 5°C min^{-1} on second scan.

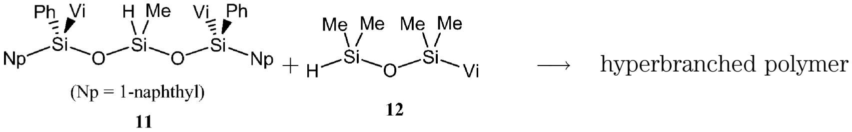
considered to have potential applications as enantiorecognitive separating membrane or chiral column packing materials.

Optically Active Hyperbranched Polymer

Hydrosilylation polymerization reactions with various feed ratio of (*S*,*S*)-**11** (AB_2 monomer) and **12** (A'B' monomer) were carried out in bulk at 60–80°C for 12 h in the presence of 0.1 mol% of $Pt(0)(DVTMDS)_2$ to give optically active hyperbranched polymers with chain end Vi functional groups (Table 3). The existence of Si-H groups in **P3** was confirmed by means of ^1H NMR ($4.51 \sim 4.83$ ppm, [Si-H] : [Vi] = 1 : 9) and IR ($2154\,cm^{-1}$). Apparent degree of polymerization (DP) for **P3** is calculated as about 8 (clacd.M_n = 4,700), which agrees with the M_n (= 4,320) determined by VPO.

The information about the branching structures for **P3** was obtained by ^{29}Si NMR analysis of $–CH_2CH_2\boldsymbol{Si}Me(O–)_2$ signals at –20.1, −18.6, and −17.9 ppm which reflect the branching structures such as dendritic (*D*), terminal (*T*), and linear (*L*) [28] units as shown in Figure 5. Assignment was done using model compounds. The relative percentages of each branching silicon atom can be determined from these signals of the *T* (−17.9 ppm), *D*(–20.1 ppm), and *L*(−18.6 ppm) units in **P3**, respectively. The relative percentage of *T* : *L* : *D* in **P3** is found to be 20 : 57 : 23. The degree of branching (*DB*) of hyperbranched polymers is defined as follows;

TABLE 3 Polymerization Reactions with Various Feed Ratio of (*S*,*S*-**11** and **12**



Entry	Feed ratio (*S*,*S*)-**11**:**12**	Polymer	Yield [%]^d	$M_n{}^e$	$M_w/M_n{}^e$	Polym. comp. (*S*,*S*)-**11**:**12**	$DB_{obsd.}$	$DB_{calcd.}$	$[\alpha]_D{}^{24}$	T_g [°C]
1	100:0	*meso*/DL-**P3**	90	3,970	1.8	100:0	0.45	0.50		26
2	100:0	**P3**	87	4,320	2.1	100:0	0.43	0.50	+13.1	34
3	66:34	**P4**	89	4,530	2.4	63:37	0.38	0.48	+9.8	22
4	50:50	**P5**	86	6,240	2.5	49:51	0.35	0.44	+8.3	10
5	34:66	**P6**	82	6,850	3.2	33:67	0.31	0.38	+5.9	−12
6	25:75	**P7**	72	9,370	3.6	26:74	0.27	0.32	+4.5	−29
7	0:100	**P8**	71	4,700	1.8	0:100				−49

[a] Isolated yields after reprecipication into methanol.

[b] Estimated by GPC (THF as an eluent) with polystyrene standard.

$$DB_{AB2} = \frac{T + D}{T + L + D}$$

P4 ~ **P7** showed the optical rotation [α] with the same positive sign as the (*S*,*S*)-**11** used for polymerization. This is in accordance with the expectation that in hydrosilylation polymerization proceeded with 100% retention of configuration, in which chiral silicon center remains unaffected. The absolute value of [α] (13.1°) observed for **P3** having 14 ~ 16 chiral silicon atoms is higher than that of monomer (6.9°) [28].

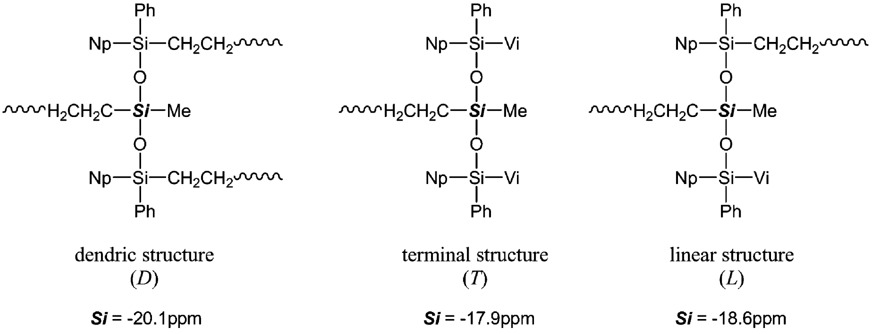


FIGURE 5 Possible branching structures of **P3** and their ^{29}Si NMR chemical shifts of ***Si***.

EXPERIMENTAL

General

NMR (^{1}H, 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 ^{1}H, $CDCl_3$ (77.00) for ^{13}C, and external tetramethylsilane (0.00) for ^{29}Si. Solid state NMR (^{13}C, 100.4 MHz; ^{29}Si, 79.6 MHz) spectra were obtained on a 400 MHz UNITY INOVA. Chemical shifts are reported in ppm relative to external hexamethylbenzene (δ 17.30) for ^{13}C CP MAS, and tetramethylsilane (δ 0.00) for ^{29}Si MAS. IR spectra were obtained on a JASCO VALOR-III spectrophotometer. GC and DI EI-Mass analyses (MS) were carried out on a Shimadzu QP-5000 mass spectrometer. High-resolution electrospray ionization mass (HRESIMS) analyses were carried out on a Bruker DALTONICS Bio-Apex 70 E mass spectrometer. Specific optical rotations were measured with a JASCO DIP-370S digital polarimeter. Size exclusion chromatography (SEC) and HPLC analyses were performed on a JASCO HPLC model Gulliver 900 with combinations of Shodex KF-801 and KF-802 (exclusion limit $M_n = 5.0 \times 10^3$), KF-803L and KF-804 (exclusion limit $M_n = 4.0 \times 10^5$), and KF-805L and KF-806L (exclusion limit $M_n = 2.0 \times 10^7$) using tetrahydrofuran as an eluent (flow rate, 1 ml/min), and on a Daicel Chem. Ind., CHIRALCEL® OD [cellulose tris(3,5-dimethylphenylcarbamate)] optically active stationary phase using n-hexane as an eluent (1 ml/min). Vapor pressure osmometry (VPO) analysis was performed on a CORONA ELECTORIC CO., Ltd. Model 114 using benzene as solvent. Differential scanning calorimetric (DSC) analysis was performed on a Seiko DSC6200 instrument at a heating rate of 5.0°C/min under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a Seiko Instruments TGA/DTA 220 with a heating rate of 5.0°C/min under nitrogen flow or in air.

Materials

Details of the information on the reagents and procedures used in this report can be obtained from references published.

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