

SHORT COMMUNICATIONS

Formation of Poly(silsesquioxane) Gel Containing Optically Active 1,3-Dimethyl-1,3-diphenyldisiloxane as a Connecting Unit

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Much attention has been paid in recent years to the fabrication of chiral separation materials based on silicon-containing polymers by incorporating chiral groups to either the side chain or the main chain.¹ However, chiral separation materials with chirality induced by asymmetric silicon atoms in the main chain have not been reported yet. We have prepared several optically active polymers having asymmetric silicon atoms in the main chain,^{2–5} and are moving toward finding possible application of these polymers as a new class of chiral separation materials based on the property derived from the asymmetry of the silicon atom itself in the polymer backbone.

Meanwhile, poly(silsesquioxane) is a kind of interesting silicon-containing polymers. It has been widely used as matrix for guest molecules⁶ due to the unique properties such as high thermo-stability and chemisorption behavior. If optical activity is induced, the resulting poly(silsesquioxane) is expected to find new potential applications as enantiorecognitive separating membrane or chiral column packing materials.

Recently, we reported the synthesis of optically active and stereoregular poly(siloxane) *via* polycondensation of optically active 1,3-dimethyl-1,3-diphenyldisiloxanediol with bis(dimethylamino)dimethylsilane.⁷ This approach is expected to be applicable to the synthesis of optically active poly(silsesquioxane). Here, we report our preliminary observation on the first synthesis of optically active poly(silsesquioxane) gel having asymmetric silicon atom in the polymer network.

EXPERIMENTAL

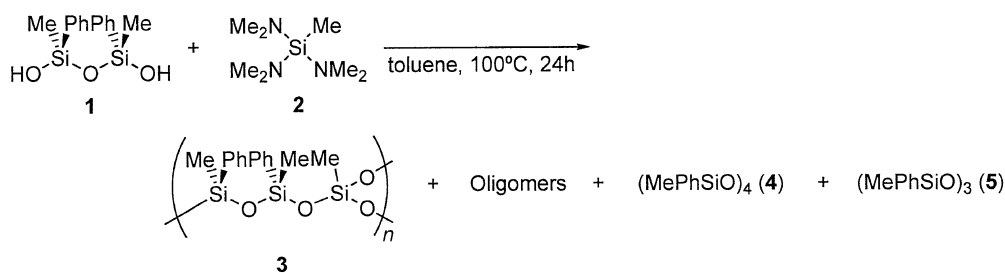
General

NMR (¹H, 500 MHz; ¹³C, 125.5 MHz; ²⁹Si, 99.5 MHz) spectra were obtained in CDCl₃ on a Varian 500 MHz UNITY INOVA. Chemical shifts are reported in ppm relative to internal CHCl₃ (δ 7.26) for ¹H, CDCl₃ (δ 77.00) for ¹³C, and external tetramethylsilane (δ 0.00) for ²⁹Si. Solid state NMR (¹³C, 100.4 MHz; ²⁹Si, 79.6 MHz) spectra were obtained on a Varian 400 MHz UNITY INOVA. Chemical shifts are reported in ppm relative to external hexamethylbenzene (δ 17.30) for ¹³C CP MAS, and external tetramethylsilane (δ 0.00) for ²⁹Si MAS. Size exclusion chromatography (SEC) analysis was performed on a JASCO HPLC 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. Specific optical rotations were measured with a JASCO DIP-370S digital polarimeter.

Materials

Optically active (*R,R*)-1,3-dimethyl-1,3-diphenyldisiloxanediol (**1**), *racemic-1*, and *meso-1* were prepared according to our previous report.^{8,9} Optical rotation of (*R,R*)-**1** was $[\alpha]_D^{27} = -3.80$ ($c = 1$, CHCl₃), determined to be 100% ee by polarimeter and HPLC. Methyltris(dimethylamino)silane (**2**) was offered by Shin-Etsu Chemical Co., Ltd.

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Scheme 1. Synthesis of **3** via polycondensation of **1** with **2**.

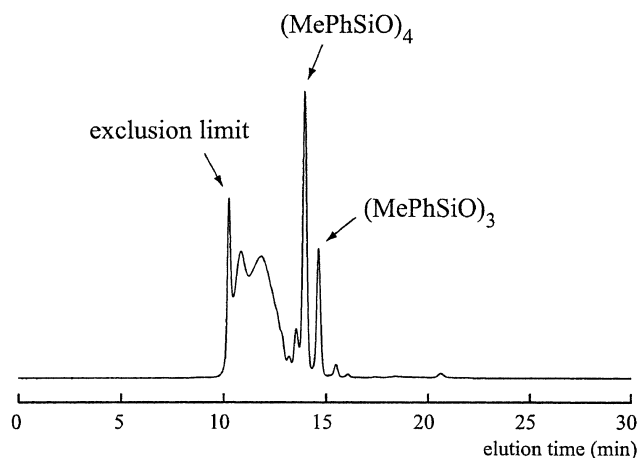


Figure 1. GPC of the Soxhlet extracted fraction from **3**.

Synthesis of Poly(silsesquioxane) Gel (**3**)

Scheme 1 shows the reaction path to obtain **3**. To a 15 mL Schlenk flask were added *racemic-1* (1.308 g, 4.5 mmol), **2** (0.525 g, 3 mmol) and toluene (1.5 mL) under nitrogen. The reaction mixture was stirred at 100°C for 24 h with nitrogen bubbling. The *racemic-3* was washed by Soxhlet extraction with CHCl₃, and dried in vacuum (0.856 g, 60% yield). ¹³C CP MAS: δ 0.15 (CH₃PhSi(O–)₂), 127.93, 133.63 (MeC₆H₅Si(O–)₂). ²⁹Si MAS: δ –66.52 (MeSi(O–)₃), –33.68 (MePhSi(O–)₂). IR (KBr, cm^{–1}): 3072, 3051, 3005, 2965, 2907, 2364, 1593, 1429, 1263, 1128, 1089, 1027 (ν_{SiOSi}), 788, 728, 697. Optically active poly(silsesquioxane) gel ((*R,R*)-**3**) were prepared similarly from (*R,R*)-**1** (0.131 g, 0.45 mmol) with **2** (0.053 g, 0.3 mmol) in toluene (0.15 mL) (0.086 g, 60% yield).

RESULTS AND DISCUSSION

The conceptual reaction path of 1,3-dimethyl-1,3-diphenyldisiloxanediol (**1**) with methyltris(dimethylamino)silane (**2**) is shown in Scheme 1. We firstly studied the gelation condition using *racemic-1*. It was found that the concentration over 3 mol L^{–1} of **1** is nec-

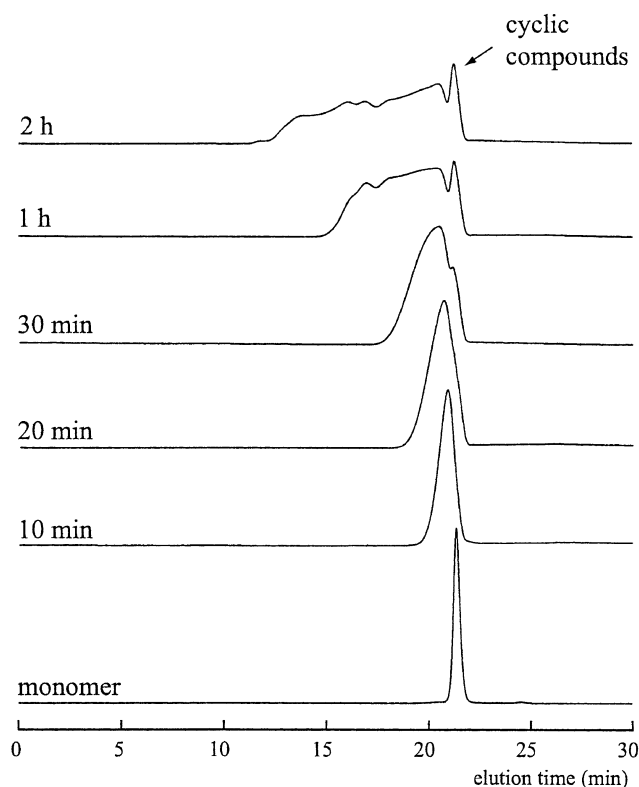
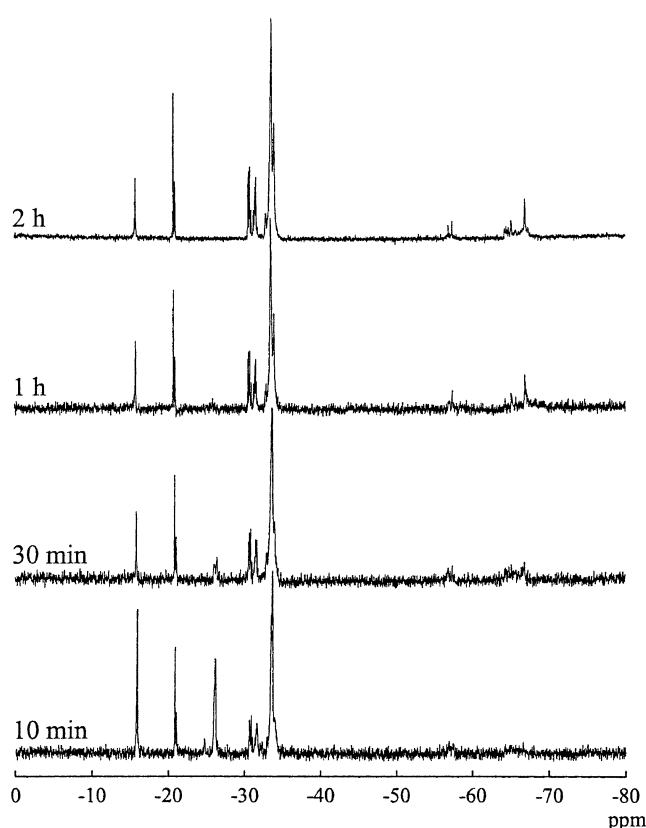


Figure 2. GPC traces of the product mixture of polycondensation of **1** with **2**.

essary for obtaining insoluble product (**3**). The GPC chromatogram (exclusion limit $M_n = 5.0 \times 10^3$) of the Soxhlet-extracted fraction with CHCl₃ is shown in Figure 1. In the extracted solution, several oligomers were contained. An apparent peak observed at 10.28 min was attributed to the exclusion limit of the column. Two sharp peaks at 13.98 and 14.66 min were separated and determined as cyclotetrasiloxane (MePhSiO)₄ (**4**) and cyclotrisiloxane (MePhSiO)₃ (**5**) by ¹H, ²⁹Si NMR, and Mass spectra.^{10–12} Thus self-condensation of **1** seems occurring to give oligo(methylphenylsiloxane) chain during the reaction process, and the cyclic compounds seem to be formed by the following back-biting reaction. To examine gelation process in detail, the progress

Table I. ^{29}Si NMR chemical shifts of some silicon compounds

Compounds	Chemical shifts of signals/ppm
HOMePhSi(OSi)MePhOH(1)	-22.77
MeSi(NMe ₂) ₃ (2)	-16.04
(MePhSiO) ₄ (4) ¹¹	-30.42, -30.33, -30.29, -30.25, -30.11
(MePhSiO) ₃ (5) ¹²	-20.90, -20.89, -20.87
MePhSi(O-) ₂ (6) ¹³	-34.90
MeSi(O-) ₃ (7) ¹⁴	-68.00
(Me ₃ SiO) ₂ MeSiN(Et) ₂ (8)	-48.19
(Me ₃ SiO) ₂ MeSiOH(9)	-54.59

**Figure 3.** ^{29}Si NMR traces of the product mixture of polycondensation of **1** with **2**.

of the reaction was monitored by GPC using column with higher exclusion limit ($M_n = 2.0 \times 10^7$). The result is shown in Figure 2. In the early stage, the polymer has low molecular weight but with narrow molecular weight distribution (10, 20 min). After 30 min, a shoulder peak of cyclic compounds appeared, and after 1 h, the molecular weight of the products increased (M_w as high as 350000 (polystyrene standard)) and polydispersity became wide. After 2 h, the polydispersity of polymer became wider (M_w as high as 4900000), and after about 3 h, the reaction mixture became insoluble. The ^{29}Si NMR analysis was also carried out to detect the progress of the reaction (Figure 3). The ref-

erence data of ^{29}Si NMR was shown in Table I. After 10 min, the signal of monomer **1** (should be observed at -22.77 ppm) already disappeared completely, and the signals of cyclic compounds **4** and **5** were observed at around -31 ppm (five peaks -31.12, -30.92, -30.85, -30.76, -30.68 ppm) and at -20.91 ppm (apparent singlet), respectively.^{11, 12} The peak at -15.89 ppm could be ascribed to monomer **2**. The peak at -21.09 ppm next to the signal of cyclic compound **5** is considered to originate from MePhSi(O-)OH of chain end. The peak at -26.09 ppm might be ascribed to intermediately formed MeSi(O-)(NMe₂)₂, in which one amino group of **2** condenses with silanol. The chemical shift seems reasonable since the ^{29}Si NMR chemical shift of **2** moved to higher magnetic field by 10 ppm on substitution of one nitrogen atom with one oxygen atom. After 2 h, this peak disappeared completely. 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 MePhSi(O-)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 ($[\text{MeSi(O-)}_3]/[\text{MePhSi(O-)}_2] = 1/6.9$ (1 h), 1/5.4 (2 h)), is assigned to MeSi(O-)₃ of cross-linking unit by referring the chemical shift of model compounds **6**¹³ and **7**.¹⁴ The signal at around -57 ppm is considered as MeSi(O-)₂NMe₂ or MeSi(O-)₂OH in which two amino groups of **2** condense with silanol, or amino group of MeSi(O-)₂NMe₂ was hydrolyzed with H₂O formed by self-condensation of **1**. The chemical shifts of model compounds **8** and **9** were -48.19 and -54.59 ppm, and close to -57 ppm comparatively.

The GPC trace and ^{29}Si NMR analysis indicated that, in the early stage of the polymerization, cyclization by self-condensation of **1** and oligomerization occurred.

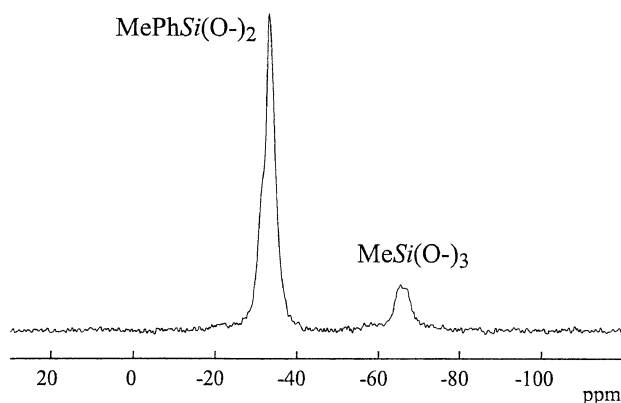


Figure 4. Solid state ^{29}Si MAS NMR spectrum of **3**.

The first and second amino group of **2** 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 **3**.

The chemical structure of insoluble **3** was characterized by solid state NMR. In ^{13}C CP MAS NMR, two signals of aromatic carbons of $\text{MeC}_6\text{H}_5\text{Si}(\text{O}-)_2$ were observed at 127.93 and 133.63 ppm, and a signal of methyl carbon of $\text{CH}_3\text{PhSi}(\text{O}-)_2$ was observed at 0.15 ppm. In the ^{29}Si MAS NMR (Figure 4), two signals at -33.68 and -66.52 ppm were observed, which could be ascribed to $\text{MePhSi}(\text{O}-)_2$ and $\text{MeSi}(\text{O}-)_3$, respectively. Apparent shoulder assignable to cyclic structure was also observed at -31.5 ppm. Integral ratio of $\text{MePhSi}(\text{O}-)_2$ and $\text{MeSi}(\text{O}-)_3$ is 5.4/1, which is larger than the feed molar ratio of 3/1. This result indicates that the formed **3** contains oligo $\text{MePhSi}(\text{O}-)_2$ chain (linear or cyclic structure) longer than the ideal disiloxane unit shown in Scheme 1, together with of $\text{MeSi}(\text{O}-)_3$ as cross-linking unit.

To obtain optically active **3**, the polycondensation of optically active (*R,R*)-**1** with **2** was carried out under similar reaction condition with *racemic*-**1**. Optical activity was evaluated for the polycondensation products before the gelation occurred. The polycondensation reaction gave the poly(silsesquioxane) with molecular weight (M_n) 15000 (purified by repeated reprecipitation into MeOH) by GPC (exclusion limit $M_n = 4.0 \times 10^5$), when the reaction was stopped after 2 h. 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*)-**1** unit in the polymer structure. The poly(silsesquioxane)s prepared from

racemic-**1** and *meso*-**1** for comparison, did not show any optical activity. These results strongly support that **3** prepared from (*R,R*)-**1** has asymmetric silicon atoms in siloxane network, and is optically active. The NMR spectra of the poly(silsesquioxane)s did not show any different splitting patterns reflecting optical activity of polymer. The **3** prepared from (*R,R*)-**1** is considered to have potential applications as enantioselective separating membrane or chiral column packing materials.

In conclusion, we have demonstrated the formation of poly(silsesquioxane) gel (**3**) via polycondensation of 1,3-dimethyl-1,3-diphenyldisiloxanediol (**1**) with methyltris(dimethylamino)silane (**2**). The GPC and ^{29}Si NMR analysis revealed that **3** is constituted of oligo $\text{MePhSi}(\text{O}-)_2$ and $\text{MeSi}(\text{O}-)_3$ units. The soluble poly(silsesquioxane) prepared from (*R,R*)-**1** showed optical activity.

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