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# Synthesis of Optically Active Siloxane-containing Polymers and Siloxane Gels

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## Introduction

Nature uses chirality as one of the key structural factors to perform a series of complicated functionalities, such as molecular recognition and catalytic activities.[1] Synthesis of optically active and/or stereoregular polymers have been a challenging theme in the field of polymer synthesis in recent years. Optically active polymers can be obtained by polymerization of optically active monomers or by stereoselective polymerization of racemic or prochiral monomers using optically active catalysts. Configurationally optically active polymers are interesting as well as conformationally optically active polymers.[2] Meanwhile, poly(siloxane)s,[3] consisting of [SiRR'O] repeating units, one class of unique organic-inorganic hybrid polymers, have been extensively studied as one of the most important thermally stable rubbery and insulating materials. Especially, poly(dimethylsiloxane)s have been widely used as silicone oil, silicone rubber, main chain for liquid crystalline polymers[4], and polymer support for metallocene catalysts by taking advantage of their highly flexible structure and high thermal stability.

Configurationally optical active poly(siloxane)s are expected to exhibit novel unique properties different from those of ordinary poly(siloxane)s without controlled stereochemistry. It will be very interesting to correlate the stereoregularity of polysiloxane with their physical properties, but there are only few reports on the control of the stereochemistry of silicon atoms in the polymer main chains. Recently, we reported the synthesis of stereoregular and/or optically active polycarbosilane,[5] poly(carbosiloxane)s,[6] polysiloxanes,[7] and polysilsesquioxane gel[8] having asymmetric silicon atom centers in the repeating units using optically pure silicon-containing monomers.

Stereoregular and/or optically active polysiloxanes may widen the possible applications of silica, as the support for optically active compounds, as self-enantio-recognitive separating membranes, chiral column packing materials,[9] and polymeric supports for asymmetric catalysts.[10] Furthermore, bulky and hydrophobic naphthyl groups are expected to stabilize the conformation of the polymer by supramolecular interaction with  $\beta$ -cyclodextrin.[11] In this article, we described the efficient routes to obtain the optically active polymers containing asymmetric silicon atoms in main chain. Stereochemical characterization of the formed polymers was used by the analyses of NMR and optical rotation. The thermal stability also was evaluated.

## Experimental

NMR spectra ( $^1\text{H}$ : 499.4 MHz,  $^{13}\text{C}$ : 125.6 MHz,  $^{29}\text{Si}$ : 99.2 MHz) were obtained in  $\text{CDCl}_3$  on a Varian 500 MHz spectrometer, model Unity INOVA. IR spectra were obtained on a JASCO VALOR-III spectrophotometer. GC and DI EI mass analyses were carried out on a Shimadzu QP-5000 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. CHIRALCEL OD (cellulose carbamate derivative) or CHIRALPAK AD (amylose carbamate derivative) optically active stationary phase was used for optical purity analysis and preparative separation with hexane and 2-propanol as mobile phase at 35°C detected by UV and circular dichroism. Elemental analysis (EA) was performed on a Vario EL III elemental analyzer. Differential scanning calorimetric (DSC) analysis was performed on a Seiko DSC6200 instrument at a heating rate of 10.0 °C/min. The thermogravimetric analysis (TGA) was performed on a Seiko Instruments TGA/DTA 220 with a heating rate of 10.0 °C/min under nitrogen flow.

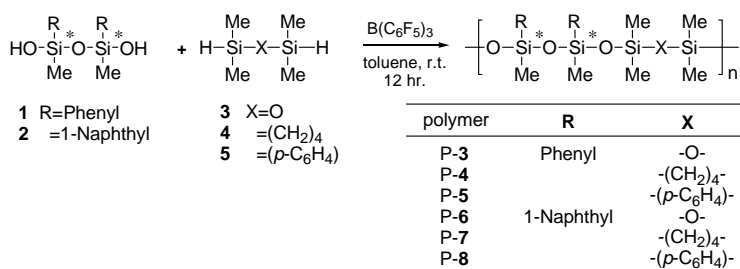
## Results and discussion

The absolute configuration of **1** and **2** were assumed by referencing the reported (*S,S*)-**1** (ee = 72%,  $[\alpha]_{\text{D}}^{25} = +3.3$ ).[12] The isolated optically pure **1** in this study had  $[\alpha]_{\text{D}}^{23} = -6.8$ , and considered to be (*R,R*)-**1**, although the

optical rotation was a little too large. Isolated optically pure **2** also had minus optical rotation of  $[\alpha]_D^{23} = -1.0$ , and was considered as *(R,R)*-**2**.

Cross-dehydrocoupling polymerizations of optically pure *(R,R)*-**1** or *(R,R)*-**2** with the bis(hydrosilane)s were also carried out (P-**1** to P-**6**) (Scheme 1).

The results were summarized in Table 1.



Scheme 1

Table 1. Synthesis of Polymers P-1 to P-6 by Cross-dehydrocoupling Reaction<sup>a</sup>.

polymer	1 or 2	X	yield (%) <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub>	T <sub>g</sub> (°C) <sup>d</sup>	$[\alpha]_D^{23}$ (deg)
P-1a	<b>1</b> ( <i>R,R</i> )	-O-	25.1	56600	1.75	-69.4	-0.90
	<b>b</b> <i>meso</i>		28.9	45000	3.07	-69.8	
	<b>c</b> diastereomers		27.2	17900	2.18	-70.0	
P-2a	<b>1</b> ( <i>R,R</i> )	-(CH <sub>2</sub> ) <sub>4</sub> -	38.9	12500	2.59	-63.9	-1.12
	<b>b</b> <i>meso</i>		46.2	19100	4.26	-63.0	
	<b>c</b> diastereomers		48.2	14900	2.66	-63.6	
P-3a	<b>1</b> ( <i>R,R</i> )	-(p-C <sub>6</sub> H <sub>4</sub> )-	55.7	13500	2.19	-34.1	+10.4
	<b>b</b> <i>meso</i>		66.5	13200	2.92	-33.1	
	<b>c</b> diastereomers		72.7	7600	2.18	-34.1	
P-4a	<b>2</b> ( <i>R,R</i> )	-O-	38.5	13000	2.55	-16.3	-1.30
	<b>b</b> diastereomers		35.0	8760	2.01	-29.0	
P-5a	<b>2</b> ( <i>R,R</i> )	-(CH <sub>2</sub> ) <sub>4</sub> -	71.4	9100	2.49	-17.6	+2.36
	<b>b</b> diastereomers		70.2	8100	3.62	-19.5	
P-6a	<b>2</b> ( <i>R,R</i> )	-(p-C <sub>6</sub> H <sub>4</sub> )-	72.1	12200	2.88	15.6	+11.7
	<b>b</b> diastereomers		81.1	6500	2.64	8.34	

<sup>a</sup>[catalyst] / [silane]= 0.2 %, silane: 1 mmol, catalyst: B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, toluene(1mL), 20 °C. <sup>b</sup>Isolated yields after reprecipitation into MeOH. <sup>c</sup>Polystyrene standards. <sup>d</sup>Determined by DSC with heating rate of 10 °C min<sup>-1</sup> on the second scan.

Although the yield of polymer was not high due to the unavoidable formation of cyclotetrasiloxane as by-product through intramolecular cyclization between terminal silanol and hydrosilyl groups, homo-condensation of the bis(silanol) was completely suppressed. Polymers could be purified by reprecipitation.

From <sup>1</sup>H and <sup>13</sup>C NMR spectra, P-**1a** and P-**4a** formed from *(R,R)*-**1** or *(R,R)*-**2** respectively with **2** were concluded as predominantly diisotactic polymers. Though it was not possible to distinguish if the polymer was either *(R,R)*- or *(S,S)*-diisotactic only by the result of <sup>1</sup>H, <sup>13</sup>C NMR, P-**1a** and P-**4a** showed negative optical rotations ( $[\alpha]_D^{23} = -0.90$ , and  $[\alpha]_D^{23} = -1.30$ , respectively), it might be reasonable to consider that the polymer **1a** and polymer **4a** are *(R,R)*-diisotactic as discussed above.

Flexible structure (**TMDS**), long spacer group (**BDMSB**), and rigid structure (**BSB**) were introduced to the polymers to study the effects of these groups on their optical and thermal properties (Table 1).

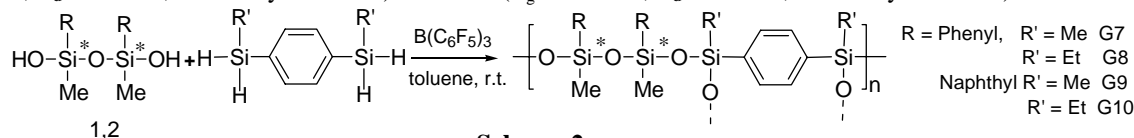
From <sup>13</sup>C NMR spectra of SiPhMe and the optical rotation, the polymers prepared from *(R,R)* monomers with the bis(hydrosilane)s by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> were concluded to have completely controlled sequence and diisotacticity.

Introduction of the flexible structure makes it easy to form the cyclic oligomers as by-products. However, introduction of the long spacer group and rigid structure increased the yields of polymers (Table 1). The order of molecular weight of the polymers was P-**1**>P-**2**>P-**3** and P-**4**>P-**5**>P-**6**. The reactivity of hydrosilane groups decreased with the introduction of the long spacer group [-(CH<sub>2</sub>)<sub>4</sub>-], rigid structure [-(p-C<sub>6</sub>H<sub>4</sub>)-] and bulkier group (naphthyl).

As the X group was changed from -O- to -(CH<sub>2</sub>)<sub>4</sub>-, or -(p-C<sub>6</sub>H<sub>4</sub>)-, the optical rotation increased remarkably from -0.90 (P-**1a**) to +1.12 (P-**2a**) and +10.4 (P-**3a**), but introduction of bulky naphthyl group in the side chain increased the optical rotation only a little.

The thermal properties of polymers were characterized TGA and DSC. P-**1a**, a well-known thermally stable polymer, showed the glass transition temperature (T<sub>g</sub>) at -69.4 °C and the on-set decomposition temperature (T<sub>d</sub>) at 487 °C, and residual weight was 24 % when heated at 750 °C under nitrogen. As the X group was changed to -(CH<sub>2</sub>)<sub>4</sub>-

(P-2a), no obvious change was observed in its  $T_g$  ( $-63.9$  °C) and  $T_d$  ( $468$  °C), while the residual yield after heating was remarkably decreased (2.5 %). On the other hand, rigid  $-(p-C_6H_4)-$  in the main chain and bulkier naphthyl group in the side chains greatly increased the thermal stability: P-3a ( $T_g = -34.1$  °C,  $T_d = 500$  °C, residual yield 45 %), P-4a ( $T_g = -16.3$  °C,  $T_d = 500$  °C, residual yield 18 %) and P-6a ( $T_g = 15.6$  °C,  $T_d = 534$  °C, residual yield 30 %).



Poly(silsesquioxane) gels were also obtained by direct polycondensation of the optically active disiloxanediols with 1,4-bis(alkylsilyl)benzenes in the presence of tris(pentafluorophenyl)borane. The cross-dehydrocoupling reaction was very fast and gave high yield. The yield of G7, G9, G8 and G10 were 86.5, 83.5, 73.8 and 75.7%, respectively. The chemical structure of insoluble fraction (G series) was analyzed by solid state NMR. The thermal properties of gels were characterized by TGA.

The slightly cross-linked systems, prepared under dilute condition, or in early stage of the condensation, show optical activity, which strongly suggests that the cross-linked insoluble gel systems are also optically active. The cross-dehydrocoupling reaction of (R,R)-1 or (R,R)-2 with HMSB and HESB were carried out at lower concentration under similar reaction condition.

The Optically active gels prepared from (R,R)-1 or (R,R)-2 were considered to have potential applications as enantioselective separating membrane or chiral column packing materials.

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