Tris(pentafluorophenyl)borane as a Superior Catalyst in the Synthesis of Optically Active SiO-Containing Polymers

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ABSTRACT: Tris(pentafluorophenyl)borane was found to be an effective catalyst in the synthesis of optically pure and completely diisotactic phenyl- and naphthyl-substituted poly(siloxane)s by the reaction between (*R,R*)-1,3-dimethyl-1,3-diphenyl {or di(1-naphthyl)}-1,3-disiloxanediol and 1,1,3,3-tetramethyl-1,3-disiloxane, 1,1,6,6-tetramethyl-1,6-disilahexane, or 1,4-bis(dimethylsilyl)benzene under mild reaction conditions. The optically active disloxane units in the produced polymers had better controlled chemical and stereoregular structures than those obtained from the bis(silanol)s and bis(dimethylamino)-dimethylsilane. Homopolymerization of the starting bis(silanol) could be almost completely suppressed. Effects of the structure of the starting bis(silane)s on the yield, molecular weight, optical activity, and thermal properties of the resulting SiOSi-containing polymers were studied.

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] Syntheses 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, a class of unique organic−inorganic hybrid polymers, have been extensively used 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.

Polycondensation is considered suitable for preparation of well-defined polymers. Cross-coupling reactions of organosilanols with hydrosilanes or aminosilanes are particularly convenient to synthesize polysiloxanes. Hydrogen or low molecular weight amine as a byproduct can be used for foaming and easily removed from the reaction mixture.

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 a 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-enantiorecognitive 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 β-cyclodextrin.[11] In this article, we described the synthesis and stereochemical characterization of the formed polymers by the analyses of NMR and optical rotation.

Experimental Section

General. NMR spectra (^{1}H: 499.4 MHz; ^{13}C: 125.6 MHz; ^{29}Si: 99.2 MHz) were obtained in $CDCl_3$ on a Varian 500 MHz spectrometer, model Unity INOVA. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26 for ^{1}H), $CDCl_3$ (δ 77.0 for ^{13}C), and tetramethylsilane (δ 0.0 for ^{29}Si). IR spectra were obtained on a JASCO VALOR-III spectrophotometer. GC and DI EI mass analyses were carried out on a Shimazu 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. Combination of Shodex KF-803L (30 cm, exclusion limit: $M_n = 7.0 \times 10^4$, polystyrene) and KF-804 (30 cm, exclusion limit: $M_n = 4.0 \times 10^5$, polystyrene) columns (linear calibration down to $M_n = 100$) were used for molecular weight analysis with tetrahydrofuran (THF, 1.0 mL/min) as an eluent. CHIRALCEL OD (0.46 diameter × 25 cm, cellulose carbamate derivative) or CHIRALPAK AD (0.46 diameter × 25 cm, amylose carbamate derivative) optically active stationary phase was used for optical purity analysis with hexane and 2-propanol as mobile phase at 35 °C (0.4 mL/min, 9−10 kg/cm^2) detected by UV (254 nm) and circular dichroism (CD, 254 nm). For preparative separation, columns of the size 2.0 diameter × 25 cm with 4.0 mL/min solvents were used. 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.

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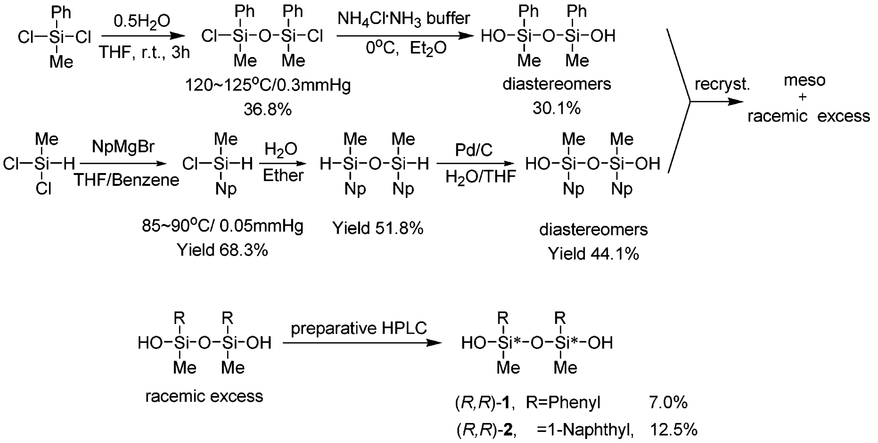
Scheme 1. Synthesis and Separation of Optically Active (*R,R*)-1 and (*R,R*)-2



Materials. Bis(dimethylamino)dimethylsilane and 1,3-dihydro-1,1,3,3-tetramethyldisiloxane (TMDS) were obtained from Shin-Etsu Chemical. 1,4-Bis(dimethylsilyl)benzene (BSB) was prepared according to the literature.[12] Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was a gift from Tosoh Finechem Corp. Chloro(1,5-cyclooctadiene)rhodium(I) dimer [$RhCl(cod)]_2$, tris(triphenylphosphine)chlororhodium(I) [$RhCl(PPh_3)_3$], and tris(dibenylideneacetone)dipalladium(0)−chloroform adduct [$Pd_2(dba)_3{\cdot}CHCl_3$] were purchased from Sigma-Aldrich. THF, hexane, benzene, and toluene were distilled from sodium prior to use.

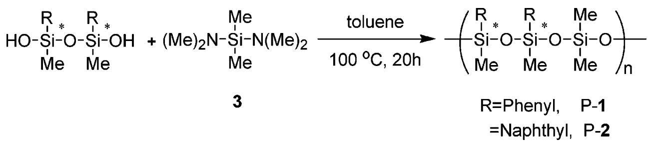
1,4-Bis(dimethylsilyl)butane (BDMSB) was synthesized as follows: To a 300 mL flask were added Mg tunings (3.6 g, 0.15 mol), dimethylchlorosilane (9.45 g, 0.1 mol), and THF (10 mL). A THF (50 mL) solution of 1,4-dibromobutane (10.8 g, 0.05 mol) was added slowly to the flask for 2 h. After the reaction system was stirred for 30 h, the product mixture was diluted with hexane, filtered to remove the salts, and washed with water. The organic layer was separated and dried on $MgSO_4$. Evaporation of the solvent and distillation gave a colorless liquid (4.28 g, 49.2%); bp 66−68 °C/20 mmHg.

NMR (δ) ^{1}H: 0.05−0.06 (d, $J_1 = 3.57$ Hz, 12H), 0.56−0.62 (m, 4H), 1.35−1.40 (m, 4H), 3.80−3.86 (m, $J_1 = 3.57$ Hz, $J_2 = 3.30$ Hz, 2H). ^{13}C: −4.41, 14.03, 28.01. ^{29}Si: −14.3. IR (neat, cm^{-1}): 2957, 2917, 2113, 1250, 886, 836. Calculated molecular weight: 174.43. MS (*m/e*) 173 ($[M-H]^+$), 159 ($[M-CH_3]^+$), 144 ($[M-2CH_3]^+$).

(*R,R*)-1,3-Dimethyl-1,3-diphenyl- or di(1-naphthyl)-1,3-disiloxanediol [(*R,R*)-**1** or -**2**] was synthesized according to Scheme 1. (*R,R*)-**1**: H_2O (0.90 g, 0.05 mol) in THF (30 mL) was added dropwise to methylphenyldichlorosilane (19.1 g, 0.1 mol) in THF (150 mL) at 0 °C. The reaction mixture was stirred for 4 h at room temperature. Removal of the solvent and distillation afforded 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane (120−125 °C/0.3 mmHg, 6.02 g, yield 36.8%). The product was hydrolyzed by adding to a two-layer system consisting of $NH_4Cl{\cdot}NH_3$ aqueous buffer (150 mL) and Et_2O (150 mL) at 0 °C. The reaction mixture was stirred for 1 h at the temperature. Organic phase was separated and dried over anhydrous Na_2SO_4. Removal of the solvent afforded a crude product **1**. Recrystallization from hexane gave **1** as a colorless solid. Further recrystallization from hexane:2-propanol = 10:1 at 0 °C gave *meso*-**1** (1.87 g, 12.9% yield) as a colorless crystal. Evaporation of the solvent of the filtrate gave **1** rich in racemic isomers (2.43 g). Optically pure (*R,R*)-**1** was isolated by preparative HPLC on CHIRALPAK AD (hexane:2-propanol = 10:1, detection at 254 nm, flow rate 4.0 mL/min) using 0.04 g of **1** rich in racemic isomers as the sample. The first eluted (*R,R*)-isomer was collected (1.02 g, mp 96.0 ∼ 97.4 °C; $[\alpha]^{23}_{D} = -6.8$, $c = 1.00$, $CHCl_3$).

NMR (δ) ^{1}H: 0.40 (s, 6H), 2.86 (br s, 2H), 7.35−7.42 (m, 6H), 7.64 and 7.65 (2d, $J = 6.50$ Hz, 4H). ^{13}C: −1.08, 127.9, 130.1, 133.4, 136.40. ^{29}Si: −22.8. IR (KBr, cm^{-1}) 3211, 3072, 3052, 2960, 1592, 1489, 1430, 1262, 1126, 1044, 1029, 997. EI-MS (*m/e*) 290 (M^+), 197 ($[M-Me-Ph]^+$). Calculated for $C_{14}H_{18}O_3Si_2$ (290.46): C, 57.89; H, 6.25. Found: C, 57.63; H, 7.47.

Scheme 2



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(*R,R*)-**2**: 1,3-Dihydro-1,3-dimethyl-1,3-di(1-naphthyl)disiloxane was obtained by the hydrolysis of methyl(1-naphthyl)cholorosilane and purified by flash column chromatography (silica gel 60; eluent, hexane) (4.64 g, 51.8%) as a colorless liquid. (*R,R*)-**2** was synthesized by the hydrolysis of 1,3-dihydro-1,3-dimethyl-1,3-di(1-naphthyl)disiloxane with excess water in the presence of 10% palladium on carbon (0.06 g) in THF (100 mL). After removal of the catalyst by passing through a short Celite column, a white solid (4.3 g, 44.1%) was obtained when the reaction mixture was precipitated into pentane:CH_2Cl_2 = 10:1. Further recrystallization from hexane: 2-propanol = 10:1 at 0 °C gave a crystal rich in *meso*-**2**. Isolation of optically pure (*R,R*)-**2** was performed by preparative HPLC on CHIRALAK AD (hexane:2-propanol = 6:1) using 0.03 g of **2** rich in racemic isomers. The first eluted (*R,R*)-isomer was collected (1.22 g, mp 147.3−151.6 °C, $[\alpha]^{23}_{D} = -1.0$, $c = 1.01$, $CHCl_3$).

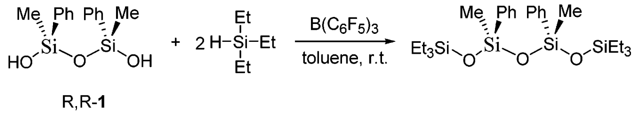
NMR (δ) ^{1}H: 0.52 (s, 6H), 3.26 (br s, 2H), 7.41−7.49 (m, 6H), 7.86 (d, $J = 8.00$ Hz, 2H), 7.90 (d, $J = 7.00$ Hz, 2H), 8.31 (d, $J = 8.00$ Hz, 2H). ^{13}C: 0.48, 125.02, 125.59, 126.21, 128.25, 128.90, 130.82, 133.37, 134.04, 134.48, 136.40. ^{29}Si: −21.8. IR (KBr, cm^{-1}): 3198, 3063, 2962, 1590, 1568, 1505, 1428, 1322, 1260, 1220, 1148, 1047, 1024, 988. EI-MS (*m/e*) 390 (M^+). Calculated for $C_{22}H_{22}O_3Si_2$ (390.58): C, 67.65; H, 5.68. Found: C, 67.59; H, 7.00.

Deaminative Polycondensation. As a typical example, polymerization of (*R,R*)-**1** with bis(dimethylamino)dimethylsilane (**3**) was described (Scheme 2). In a 30 mL two-necked flask, **3** (0.146 g, 1.0 mmol) was added to (*R,R*)-**1** (0.290 g, 1.0 mmol) in toluene (1 mL), and the reaction system was stirred at 100 °C for 20 h with N_2 bubbling. After pouring into methanol, the precipitate was collected and dried in vacuo to give the polymer **1** (0.215 g, 63.5% yield, $M_n = 43\,300$, $M_w/M_n = 2.36$, $[\alpha]^{23}_{D} = -1.26$, $c = 1.00$, $CHCl_3$).

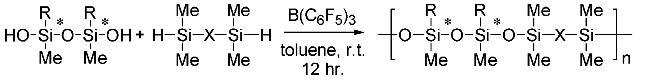
NMR (δ) ^{1}H: −0.04 (s, 6H), 0.24 (s, 6H), 7.20 (br, 4H), 7.30 (br, 2H), 7.46 (br, 4H). ^{13}C: −0.23, 1.04, 127.5, 129.5, 133.3, 137.3. ^{29}Si: −34.5, −20.3. IR (neat, cm^{-1}): 3072, 3026, 2963, 2765, 1593, 1429, 1125, 1097, 1021, 906, 849, 798, 731, 700.

Cross-Dehydrocoupling Polymerization. Model Reaction. To a solution of (*R,R*)-**1** (0.029 g, 0.1 mmol) and tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (0.0002 g, 0.4 mol %) in toluene (0.4 mL) was slowly added triethylsilane (0.0232 g, 0.20 mmol) at room temperature. After the reaction mixture was stirred for 2 h, removal of the solvent afforded a crude product. The product was purified by flash column chroma-

Scheme 3



Scheme 4



1 R=Phenyl
2 =1-Naphthyl

4 X=O
5 =$(CH_2)_4$
6 =$(p\text{-}C_6H_4)$

polymer	R	X
P-**3**	Phenyl	-O-
P-**4**		$-(CH_2)_4-$
P-**5**		$-(p\text{-}C_6H_4)-$
P-**6**	1-Naphthyl	-O-
P-**7**		$-(CH_2)_4-$
P-**8**		$-(p\text{-}C_6H_4)-$

tography (Florisil with hexane as an eluent) to give the product 1,1,1,4,4,4-hexaethyl-2,3-dimethyl-2,3-diphenyltetrasiloxane as a colorless liquid (0.0474 g, 91.4% yield, $[\alpha]^{23}_D = -3.55$, $c = 1.00$, $CHCl_3$).NMR (δ) ^1H: 0.32 (s, 6H), 0.52 (q, $J = 8.00$ Hz 12H), 0.88 (t, $J = 8.00$ Hz, 18H), 7.29−7.38 (m, 6H), 7.53 (2d, J1 = 7.69 Hz, J2 = 1.65 Hz, 4H). ^{13}C: −0.21, 6.23, 6.67, 127.48, 129.39, 133.30, 138.14. ^{29}Si: −35.3, 11.4. IR (neat, cm^{-1}): 2955, 2911, 2876, 1520, 1485, 1429, 1259, 1238, 1123, 1052, 1005, 972. EI-MS (*m/e*) 490 ($[M-Et]^+$).

A similar procedure in the presence of rhodium complex $[RhCl(cod)]_2$ gave the product only in 34% yield at 50 °C, and side reaction occurred.

Polymerization. As a typical example, the synthetic procedure to obtain P-**3a** from (*R,R*)-**1** and 1,3-dihydro-1,1,3,3-tetramethyldisiloxane (**4**) was described (Scheme 4). To a solution of (*R,R*)-**1** (0.290 g, 1.0 mmol) and $B(C_6F_5)_3$ (0.002 g, 0.4 mmol%) in toluene (1 mL) was slowly added the silane **4** (0.134 g, 1.0 mmol) at room temperature. The reaction mixture was stirred for 12 h. After pouring into methanol, the precipitate was collected and dried in vacuo to get the polymer P-**3a** (0.105 g, 25.1% yield; SEC: $M_n = 56\,600$, $M_w/M_n = 1.75$; $[\alpha]^{23}_D = -0.90$, $c = 1.00$, $CHCl_3$).NMR (δ) ^1H: −0.02−0.01 (d, $J = 10.50$ Hz, 12H), 0.31 (s, 6H), 7.26−7.29 (m, 4H), 7.32−7.34 (m, 2H), 7.53−7.55 (m, 4H). ^{13}C: −0.17, 0.98, 1.01, 127.53, 129.503, 133.33, 137.53. ^{29}Si: −34.6, −21.0. IR (neat, cm^{-1}): 3071, 3052, 3015, 2962, 2902, 1654, 1593, 1559, 1429, 1411, 1261, 1098, 1020, 851, 789, 699.

P-**4a** to P-**8a** were prepared similarly with P-**3a**.

P-**4a**: Colorless liquid (0.180 g, 38.9% yield). SEC: $M_n = 12\,500$, $M_w/M_n = 2.59$; $[\alpha]^{23}_D = -1.12$, $c = 1.00$, $CHCl_3$. NMR (δ) ^1H: 0.06−0.07 (d, $J = 2.80$ Hz, 12H), 0.35 (s, 6H), 0.50 (br, 4H), 1.26 (br, 4H), 7.32−7.39 (m, 6H), 7.57−7.59 (m, 4H). ^{13}C: −0.03, 0.21, 18.00, 26.94, 127.54, 129.45, 133.32, 138.04. ^{29}Si: −34.6, 9.1. IR (neat, cm^{-1}): 3070, 3051, 3005, 2957, 2918, 1429, 1410, 1258, 1192, 1124, 1045, 987, 840, 788, 731, 699.

P-**5a**: Colorless liquid (0.268 g, 55.7% yield): SEC: $M_n = 13\,500$, $M_w/M_n = 2.19$; $[\alpha]^{23}_D = +10.4$, $c = 1.00$, $CHCl_3$. NMR (δ) ^1H: 0.33−0.34 (d, $J = 4.00$ Hz, 12H), 0.36 (s, 6H), 7.28−7.31 (m, 4H), 7.35−7.38 (m, 2H), 7.50 (s, br, 4H); 7.55−7.57 (d, 4H). ^{13}C: −0.10, 0.67, 0.69, 127.60, 129.566, 132.26, 133.35, 137.53, 140.43. ^{29}Si: −33.5, −1.1. IR (neat, cm^{-1}): 3071, 3051, 3003, 2958, 2925, 2850, 1592, 1429, 1381, 1259, 1139, 1124, 1081, 1043, 1020, 822, 784, 732, 699.

P-**6a**: Colorless liquid (0.201 g, 38.5% yield): SEC: $M_n = 13\,000$, $M_w/M_n = 2.55$; $[\alpha]^{23}_D = -1.30$, $c = 1.00$, $CHCl_3$. NMR (δ) ^1H: −0.22 to −0.19 (d, $J = 4.00$ Hz, 12H), 0.40 (s, 6H), 7.17−7.25 (m, 4H), 7.32−7.35 (m, 2H), 7.68−7.70 (br d, 2H), 7.74−7.76 (m, 4H), 8.16−8.17 (br d, 2H). ^{13}C: 0.74, 0.85, 1.16, 124.71, 125.20, 125.52, 128.47, 128.71, 130.21, 133.23, 133.62, 135.32, 136.36. ^{29}Si: −34.0, −21.1. IR (neat, cm^{-1}): 3071, 3039, 2964, 1506, 1261, 1219, 1148, 1094, 1021, 828, 796, 778, 749.

P-**7a**: Colorless liquid (0.401 g, 71.4% yield): SEC: $M_n = 91\,000$, $M_w/M_n = 2.49$; $[\alpha]^{23}_D = +2.36$, $c = 1.00$, $CHCl_3$. NMR (δ) ^1H: −0.05 to −0.04 (d, $J = 3.4$ Hz, 12H), 0.29 (br, 4H), 0.50 (s, 6H), 1.03 (br, 4H), 7.29−7.40 (m, 6H), 7.76−7.85 (m, 6H), 8.25−8.27 (br d, 2H). ^{13}C: 0.01, 0.03, 1.35, 17.78, 26.78, 124.76, 125.23, 125.43, 128.53, 128.89, 130.17, 133.28, 133.53, 135.90, 136.44. ^{29}Si: −34.01, 9.24. IR (neat, cm^{-1}): 3051, 3040, 2956, 2918, 1506, 1457, 1407, 1258, 1218, 1148, 1051, 987, 836, 795, 779, 746.

P-**8a**: Colorless liquid (0.419 g, 72.1% yield): SEC: $M_n = 12\,200$, $M_w/M_n = 2.88$; $[\alpha]^{23}_D = +11.7$, $c = 1.00$, $CHCl_3$. NMR (δ) ^1H: 0.14−0.15 (d, $J = 5.5$ Hz, 12H), 0.42 (s, 6H), 7.11−7.15 (m, 2H), 7.22−7.40 (m, 8H), 7.68−7.75 (m, 6H), 8.16−8.18 (d, 2H). ^{13}C: 0.40, 0.44, 1.30, 124.76, 125.27, 125.542, 128.51, 128.81, 130.28, 132.13, 133.24, 133.68, 135.40, 136.34, 140.10. ^{29}Si: −33.0, −1.1. IR (neat, cm^{-1}): 3053, 3005, 2957, 2901, 1589, 1506, 1320, 1259, 1218, 1139, 1046, 987, 825, 779, 748.

Results and Discussion

The absolute configurations of **1** and **2** were assumed by referencing the reported (*S,S*)-**1** (ee = 72%, $[\alpha]^{25}_D = +3.3$).[13] The isolated optically pure **1** in this study had $[\alpha]^{23}_D = -6.8$, 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 $[\alpha]^{23}_D = -1.0$ and was considered as (*R,R*)-**2.** Deaminative polycondensation of optically pure (*R,R*)-**1** with **3** was carried out to obtain diisotactic and optically active poly(siloxane)s (P-**1**) (Scheme 2). For comparison, polycondensation reactions of *diastereomer*-**1** and *meso*-**1** were also carried out to obtain *atactic* and *meso atactic* polysiloxanes, respectively (Table 1). The resulting polymers were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. ^{29}Si NMR was not sensitive enough to analyze the stereoregularity of polymers. The ^1H signals of methyl groups of P-**1** reflected the stereoregularity of the polymer (Figure 1). The P-**1** prepared from (*R,R*)-**1** showed a strong peak at 0.23 ppm, which was considered to arise from SiPh*Me* of *racemic* disiloxane units. Only one peak at 0.20 ppm was observed for **P-1** prepared from *meso*-**1** assignable to the two equivalent methyl groups in the *meso* disiloxane units. Moreover, two sharp peaks at 0.23 and 0.20 ppm were observed in P-**1** prepared from *diastereomer*-**1**, reflecting the methyl groups from the *meso* and *racemic* disiloxane units. Further evidence for the tacticity of P-**1** was given by the signal of *meta-Ph*SiMe splitting in ^{13}C NMR (Figure 1). The peaks at 127.56 and 127.52 ppm could be assigned to *meso* and *racemic* disiloxane repeating unit, respectively. However, there were some unidentified broad peaks near the main peaks, which might indicate the presence of a homocondensation product of

Table 1. Deaminative Polycondensation of 1 or 2 with 3[a]

run	**1** or **2**	polymers	yield (%)[b]	M_n[c]	M_w/M_n	$[\alpha]^{23}_D$ (deg)
1	**1** diastereomer	atactic	67.2	64 300	2.64	
2	*meso*	*meso*-atactic	62.1	52 900	1.87	
3	*R,R*	(*R,R*)-diisotactic	63.5	43 300	2.36	−1.26
4	**2** diastereomer	atactic	47.6	4 600	1.50	
5	*R,R*	(*R,R*)-diisotactic	39.0	4 800	2.36	−2.46

[a] Aminosilane: 1 mmol, toluene(1 mL), 100 °C. [b] Isolated yields after reprecipitation into MeOH. [c] Polystyrene standards.

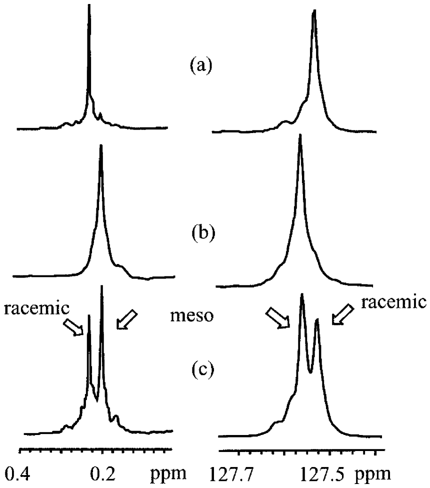


Figure 1. ^{1}H NMR spectra of SiPh*Me* and ^{13}C NMR of *meta-Ph*SiMe of **P-1**: (a) (*R,R*)-diisotactic; (b) *meso*-atactic; (c) atactic.

the bis(silanol). It is well-known that silanol groups could undergo self-condensation in high temperature or under basic conditions. Such reaction will lead to disruption of the desirable perfectly alternating architecture. From ^{1}H and ^{13}C NMR spectra and the negative optical rotation ($[\alpha]^{23}_D = -1.26$), P-**1** prepared from (*R,R*)-**1** with **3** was concluded as a polymer rich in (*R,R*)-diisotacticity.

Only low molecular weight polymer ($M_n = 4800$, $M_w/M_n = 2.36$) was obtained from the naphthyl derivative, (*R,R*)-**2**, probably due to steric hindrance by the naphthyl group attached to the silicon atom.

The dealkylative or dehydrogenative coupling of organohydrosiloxanes with organomethoxysilanes or organosilanols by tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] reported by Rubinsztajn seems particularly convenient to synthesize desired polysiloxane due to its high activity.[14] Side reactions, like homocondensation of silanol groups and disproportionation process, may not be significant in this system. If the stereochemistry of the cross-coupling reactions was controlled, this reaction might be more suitable for the preparation of well-controlled structure of poly(siloxane)s.

Cross-dehydrocoupling reaction of (*R,R*)-**1** with triethylsilane, as a model reaction, was carried out in toluene at room temperature using $B(C_6F_5)_3$ (Scheme 3), and the results are summarized in Table 2 together with the data with metallic catalysts.

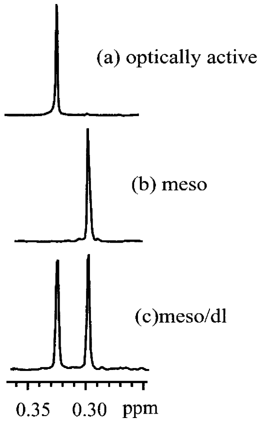


Figure 2. ^{1}H NMR spectra of SiPh*Me* in model compound: (a) optically active; (b) *meso*; (c) diastereomer.

Transition metal catalysts $[RhCl(cod)]_2$, $RhCl(PPh_3)_3$, and $[Pd_2(dba)_3{\cdot}CHCl_3]$ showed high activity in the cross-dehydrocoupling reaction,[7b,15] whereas, in this model reaction, almost no reaction was observed with $[Pd_2(dba)_3{\cdot}CHCl_3]$ and $RhCl(PPh_3)_3$ (entries 8–11). $[RhCl(cod)]_2$ showed only low activity, and side reaction occurred (yield 35%, conversion 100%, LiH as additive, entry 14). Because the reaction temperature was too high (entry 12), or too basic (entries 13 and 14), a lot of cyclic oligomers were formed. Thus, rhodium catalysts, used in the synthesis of poly(methylphenylsiloxane) rich in syndiotacticity (95% retention of configuration), were not effective. The substituents on silicon exerted a significant steric effect on the reactivity of cross-dehydrocoupling reaction.

The condensation reaction took place at room temperature in the presence of very low levels of $B(C_6F_5)_3$. The reaction was completed in 2–3 h. The reaction had very high selectivity and activity when used in nonpolar solvents, and no byproduct was observed (entries 1–4). However, when polar solvent was used, no expected product was obtained (entries 5–7). The ^{1}H NMR of SiPh*Me* obviously reflected the reaction was very stereospecific (99% ee retention) (Figure 2). The model product prepared from optically pure (*R,R*)-**1** or *meso*-**1** showed only one singlet peak at 0.33 or 0.29 ppm, respectively. The configuration of silicon atoms of (*R,R*)-**1** was not affected during the cross-dehydrocoupling with the hydrosilane. Compared with metallic catalysts, $B(C_6F_5)_3$ showed higher reactivity and stereoselectivity in the cross-dehydrocoupling reaction.

Table 2. Cross-Dehydrocoupling Reaction of 1 with Triethylsilane[a]

entry	1	catalyst	solvent	time, h	yield (conv),%[b]	stereochemistry[c]
1	diastereomer	$B(C_6F_5)_3$	toluene	3	92.1 (100)	
2	*meso*	$B(C_6F_5)_3$	toluene	3	91.4 (100)	99% retention
3	(*R,R*)	$B(C_6F_5)_3$	toluene	3	93.1 (100)	98% retention
4	*meso*	$B(C_6F_5)_3$	pentane	3	92.3 (100)	99% retention
5	*meso*	$B(C_6F_5)_3$	CH_2Cl_2	10	– (100)	
6	*meso*	$B(C_6F_5)_3$	THF	10	– (100)	
7	*meso*	$B(C_6F_5)_3$	ether	6	– (100)	
8	*meso*	$Pd_2(dba)_3$	toluene	12	no reaction	
9	*meso*	$Pd_2(dba)_3$	toluene	4	no reaction	
10	*meso*	$Pd_2(dba)_3$	THF	4	no reaction	
11	*meso*	$RhCl(PPh_3)_3$	toluene	5	no reaction	
12	*meso*	$[RhCl(cod)]_2$	toluene	5	33.7 (100)	
13[d]	*meso*	$[RhCl(cod)]_2$	toluene	18	14.0 (72.6)	
14[e]	*meso*	$[RhCl(cod)]_2$	toluene	18	35.3 (100)	

[a] 1 (0.1 mmol) with triethylsilane (0.2 mmol) at 20 °C (except for **9–12**: 50 °C) in the presence of 0.4 mmol% catalyst. [b] Isolated yield; conversions are in parentheses. Yields of **12–14** were determined by NMR. [c] Determined by NMR. [d] Additive: 1.0 equiv of Et_3N. [e] Additive: 1.0 equiv of LiH.

Table 3. Synthesis of Polymer P-3 to Polymer P-8 by Cross-Dehydrocoupling Reaction[a]

polymer	**1** or **2**	X	yield (%)[b]	M_n[c]	M_w/M_n	T_g (°C)[d]	$[\alpha]^{23}_D$ (deg)
P-**3a** **1**	(*R*,*R*)	–O–	25.1	56 600	1.75	−69.4	−0.90
P-**3b**	*meso*		28.9	45 000	3.07	−69.8	
P-**3c**	diastereomer		27.2	17 900	2.18	−70.0	
P-**4a**	(*R*,*R*)	$-(CH_2)_4-$	38.9	12 500	2.59	−63.9	−1.12
P-**4b**	*meso*		46.2	19 100	4.26	−63.0	
P-**4c**	diastereomer		48.2	14 900	2.66	−63.6	
P-**5a**	(*R*,*R*)	$-(p\text{-}C_6H_4)-$	55.7	13 500	2.19	−34.1	+10.4
P-**5b**	*meso*		66.5	13 200	2.92	−33.1	
P-**5c**	diastereomer		72.7	7 600	2.18	−34.1	
P-**6a** **2**	(*R*,*R*)	–O–	38.5	13 000	2.55	−16.3	−1.30
P-**6b**	diastereomer		35.0	8 760	2.01	−29.0	
P-**7a**	(*R*,*R*)	$-(CH_2)_4-$	71.4	9 100	2.49	−17.6	+2.36
P-**7b**	diastereomer		70.2	8 100	3.62	−19.5	
P-**8a**	(*R*,*R*)	$-(p\text{-}C_6H_4)-$	72.1	12 200	2.88	15.6	+11.7
P-**8b**	diastereomer		81.1	6 500	2.64	8.34	

[a] [Catalyst]/[silane] = 0.2%, silane: 1 mmol, catalyst: $B(C_6F_5)_3$, toluene (1 mL), 20 °C. [b] Isolated yields after reprecipitation into MeOH. [c] Polystyrene standards. [d] Determined by DSC with heating rate of 10 °C min^{-1} on the second scan.

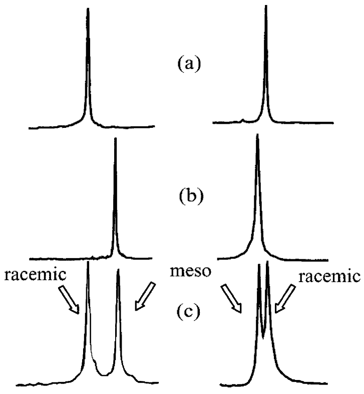


Figure 3. ^{1}H NMR spectra of SiPh*Me* and ^{13}C NMR of *meta-Ph*SiMe of **P-3**: (a) (*R,R*)-diisotactic; (b) *meso*-atactic; (c) atactic.

Cross-dehydrocoupling polymerizations of optically pure (*R*,*R*)-**1** or (*R*,*R*)-**2** with the bis(hydrosilane)s were also carried out (P-**3** to P-**8**) (Scheme 4). The results are summarized in Table 3.

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

Purified P-**3a**, prepared from (*R*,*R*)-**1** with **4**, showed a strong peak at 0.31 ppm, which is considered to arise from SiPh*Me* of *racemic* disiloxane units. Only one sharp peak at 0.27 ppm was observed in P-**3b** prepared from *meso*-**1** due to the two equivalent methyl groups in the *meso* disiloxane units. Moreover, two sharp peaks at 0.31 and 0.27 ppm were observed for P-**3c** prepared from *diastereomer*-**1**, reflecting the methyl groups in the *racemic* and *meso* disiloxane units. Tacticity of P-**3** was also elucidated by the signal of *meta* Si*Ph*Me carbon splitting in ^{13}C NMR (Figure 3). Only one sharp singlet at 127.5 or 127.6 ppm was observed for the polysiloxane prepared from (*R*,*R*)-**1** or *meso*-**1** due to the two equivalent methyl groups in the *racemic* or *meso* repeating disiloxane unit, respectively. On the other hand, two peaks at 127.6 and 127.5 ppm in almost equal intensity were observed for the polymer prepared from *diastereomer*-**1**, reflecting the methyl groups from the *meso* and *racemic* disiloxane units in equal quantity. These peaks were very sharp and not contaminated with broad unidentified peaks.

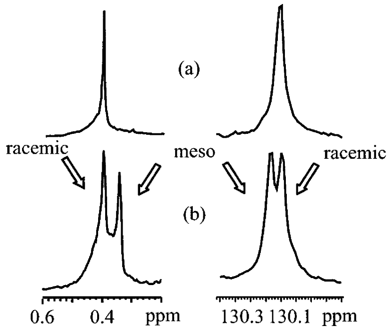


Figure 4. ^{1}H NMR spectra of SiNp*Me* and ^{13}C NMR of Si*Np*Me of **P-6**: (a) (*R,R*)-diisotactic; (b) atactic.

For the naphthyl-substituted poly(siloxane)s, ^{1}H and ^{13}C NMR showed the similar results with phenyl-substituted polymers (Figure 4). The ^{1}H signals of SiNp*Me* of P-**6a** prepared from (*R,R*)-**2** showed a strong peak at 0.40 ppm. Moreover, two peaks at 0.40 and 0.34 ppm were observed in P-**6b** prepared from *diastereomer*-**2**, reflecting the methyl groups from the *racemic* and *meso* disiloxane units. The tacticity of P-**6** was also elucidated by the Si*Np*Me signal in ^{13}C NMR (Figure 4). The peaks at 130.3 and 130.2 ppm were assigned to *meso* and *racemic* disiloxane repeating unit, respectively.

From ^{1}H and ^{13}C NMR spectra, P-**3a** and P-**6a** formed from (*R,R*)-**1** or (*R,R*)-**2**, respectively, with **4** were concluded as predominantly diisotactic polymers. Though it was not possible to distinguish whether the polymer was either (*R*,*R*)- or (*S*,*S*)-diisotactic only by the result of ^{1}H and ^{13}C NMR, P-**3a** and P-**6a** showed negative optical rotations ($[\alpha]^{23}_D = -0.90$ and $[\alpha]^{23}_D = -1.30$, respectively); it might be reasonable to consider that the polymers **3a** and **6a** are (*R,R*)-diisotactic as discussed above.

Thermal properties of the polymer were evaluated using DSC and TGA. All the poly(siloxane)s exhibited only one glass transition temperature without any other transitions. T_g of (*R,R*)-diisotactic P-**3a** was −70 °C, which was a little different from that of *meso*-atactic P-**3b** (−69.8 °C) and atatic P-**3c** (−69.4 °C). TGA also showed similar behavior (Figure 5). (*R,R*)-Diisotactic P-**3a** showed an onset decomposition temperature at 487 °C, and for *meso*-atactic and atactic P-**3**, no obvious changes were observed in their onset decomposition

Table 4. DSC and TGA Data of Optically Active Polymer P-3a to Polymer P-8a[a]

	P-**3a**	P-**4a**	P-**5a**	P-**6a**	P-**7a**	P-**8a**
T_g (°C)	−69.4	−63.9	−34.1	−16.3	−17.6	15.6
T_d(onset) (°C)	487	468	500	500	512	534
char yield (750 °C) (%)	24	2.5	45	18	3.6	30

[a] DSC: second heating (10 °C/min) in air; TGA: 10 °C/min under nitrogen flow (200 mL/min).

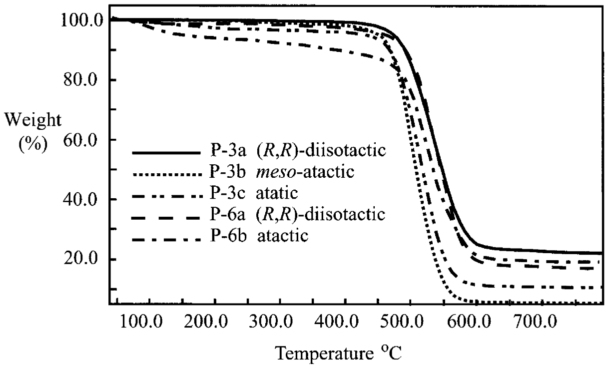


Figure 5. TGA thermograms of polymers **3** and **6**.

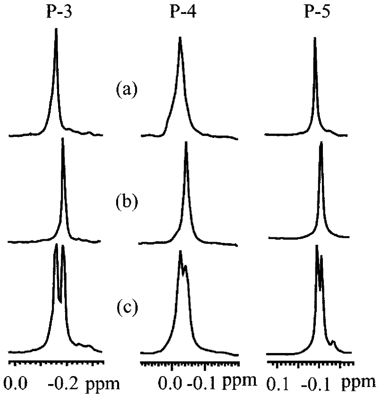


Figure 6. ^{13}C NMR spectra of SiPh*Me* in polymers **3**−**5**: (a) (*R,R*)-diisotactic; (b) *meso*-atactic; (c) atactic.

temperatures (T_d = 478 and 471 °C, respectively). For the naphthyl-substituted poly(siloxane)s P-**6**, T_g of (*R,R*)-diisotactic P-**6a** was −16.3 °C, which is a little different from that of atatic P-**6a** (−29.0 °C), and onset decomposition temperature at 500 and 497 °C, respectively. Stereoregularity of the polymers **3** and **6** had only a small influence on its thermal properties.

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 3).

From ^{13}C NMR spectra of SiPh*Me* and the optical rotation, the polymers prepared from (*R,R*)-monomers with the bis(hydrosilane)s by $B(C_6F_5)_3$ were concluded to have completely controlled sequence and diisotacticity (Figures 6 and 7). Introduction of the flexible structure makes it easy to form the cyclic oligomers as byproducts. However, introduction of the long spacer group and rigid structure increased the yields of polymers (Table 3). The order of molecular weight of the polymers was P-**3** > P-**4** > P-**5** and P-**6** > P-**7** > P-**8**. The reactivity of hydrosilane groups decreased with the introduction of the long spacer group [$-(CH_2)_4-$], rigid structure [$-(p\text{-}C_6H_4)-$], and bulkier group (naphthyl).

As the X group was changed from −O− to $-(CH_2)_4-$ or $-(p\text{-}C_6H_4)-$, the optical rotation increased remarkably from −0.90 (P-**3a**) to +1.12 (P-**4a**) and +10.4 (P-**5a**), but introduction of bulky naphthyl group in the side chain increased the optical rotation only a little.

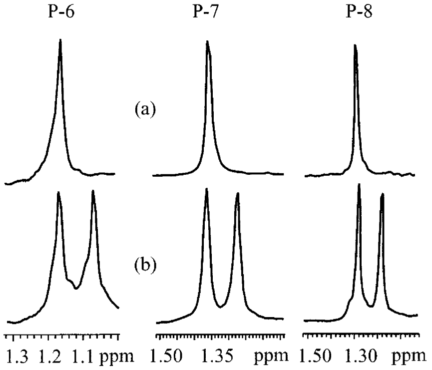


Figure 7. ^{13}C NMR spectra of SiNp*Me* of polymers **6**−**8**: (a) (*R,R*)-diisotactic; (b) atactic.

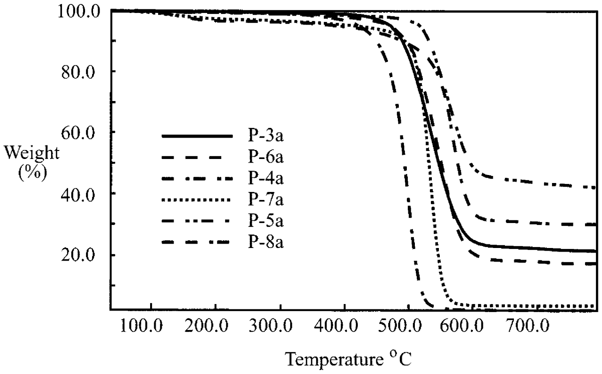


Figure 8. TGA thermograms of polymers **3a**−**8a**.

The thermal properties of polymers are represented in Figure 8 and Table 4. P-**3a**, a well-known thermally stable polymer, showed the glass transition temperature (T_g) at −69.4 °C and the onset decomposition temperature (T_d) at 487 °C, and the residual weight was 24% when heated at 750 °C under nitrogen. As the X group was changed to $-(CH_2)_4-$ (P-**4a**), 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 $-(p\text{-}C_6H_4)-$ in the main chain and bulkier naphthyl group in the side chains greatly increased the thermal stability: P-**5a** (T_g = −34.1 °C, T_d = 500 °C, residual yield 45%), P-**6a** (T_g = −16.3 °C, T_d = 500 °C, residual yield 18%), and P-**8a** (T_g = 15.6 °C, T_d = 534 °C, residual yield 30%).

Conclusions

Optically pure organosilicon compounds, (*R,R*)-1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol and (*R,R*)-1,3-dimethyl-1,3-di(1-naphthyl)-1,3-disiloxanediol, were separated by HPLC. Contrary to that, optically active and diisotactic poly(siloxane)s, but not completely pure, were prepared by deaminative polycondensation with bis(dimethylamino)dimethylsilane; cross-dehydrocoupling reaction in the presence of $B(C_6F_5)_3$ under mild reaction conditions gave polymers with the chiral silicon units being completely optically pure and diisotactic. Stereoregular, *meso*-atactic, and atactic polymers showed similar thermal properties. Introduction of the rigid $-(p\text{-}C_6H_4)-$ to the main chain increased the optical activity and improved the thermal properties of polymers. Bulky naphthyl groups in the side chain had significant effects on the thermal properties, but not on optical property.

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