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Notes

Synthesis of Optically Active and Highly Stereoregular Poly[oxy{(*S*)-(1-naphthyl)phenylsilylene}ethylene(dimethylsilylene)ethylene{(*S*)-(1-naphthyl)phenylsilylene}oxydimethylsilylene] by Polycondensation Reaction

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Introduction

A practical method to prepare configurationally optically active polymers is to synthesize polymers consisting of an optically active stereorepeating unit of the type −A−X*−B− (X*, chiral center; A ≠ B) from optically active monomers via stereospecific polymerization. The polymer becomes optically active when the chiral centers are excess in one enantiomeric structure. We reported isotactic and optically active poly(carbosiloxane)s, to which much attention has been given,[1,2] starting from optically active (1*S*)-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane as monomer via direct polyaddition reaction, or by ring-opening polymerization of the cyclized compound, (*S*)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane, and indicated the possibility of using dimethylsilyl group as a “stereochemical probe” to detect the stereoregularity of the polymer.[3,4] An isotactic and optically active poly(carbosilane) was also reported.[5]

In this paper, we will describe our further development of this idea to synthesize poly[oxy{(*S*)-(1-naphthyl)phenylsilylene}ethylene(dimethylsilylene)ethylene{(*S*)-(1-naphthyl)phenylsilylene}oxydimethylsilylene] of reasonably high molecular weight starting from optically pure (>99%) (1*S*),(7*S*)-1,7-di(1-naphthyl)-1,7-diphenyl-4,4-dimethyl-1,4,7-trisilaheptane-1,7-diol with bis(dimethylamino)dimethylsilane by a polycondensation reaction. The two asymmetric silicon centers are separated by long spacer group with an intention to avoid a cyclization reaction. The stereoregularity of the formed polymer was evaluated.

Experimental Section

Analytical Methods. The 500 MHz ^{1}H, 125.7 MHz ^{13}C, and 99.3 MHz ^{29}Si NMR spectra were obtained in $CDCl_3$ on Varian 500 MHz Unity INOVA spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26 for ^{1}H), $CDCl_3$ (δ 77.00 for ^{13}C), and tetramethylsilane (δ 0.00 for ^{29}Si). IR spectra were obtained on a JASCO VALOR-III spectrophotometer. Specific optical rotations were measured with a JASCO DIP-370S digital polarimeter. Size exclusion chromatography (SEC) and high performance liquid chromatography (HPLC) on an optically active stationary phase were performed on a JASCO HPLC on the combination of Shodex KF-803L (exclusion limit: $M_n = 7 \times 10^4$, polystyrene) and KF-804 (exclusion limit: $M_n = 4 \times 10^5$, polystyrene) columns (linear calibration down to $M_n = 100$, polystyrene) using tetrahydrofuran (THF) as an eluent, and on a Daicel CHIRALCEL OD column (cellulose carbamate derivative), respectively. CD spectrum was measured with a JASCO J-720 spectrometer. Glass transition temperatures (T_g) of the polymers were determined using a Seiko Instruments Inc. DSC120 differential scanning calorimeter (DSC) at a heating rate of 5 °C/min and a heating range of −50 to +250 °C. Thermogravimetric analyses (TGA) were performed on a Seiko Instruments Inc. TGA/DTA220 with heating rates of 10 °C/min and a heating range of 25−620 °C in a N_2 flow.

Materials. The platinum−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt−DVTMDS) benzene solution (0.01 M) was prepared from hexachloroplatinic acid (0.10 g, 1.93×10^{-4} mol) and 1,3-divinyltetramethyldisiloxane (DVTMDS) (0.20 g, 1.07×10^{-3} mol) following the literature.[6]

(1*S*),(7*S*)-1,7-Di(1-naphthyl)-1,7-diphenyl-4,4-dimethyl-1,4,7-trisilaheptane-1,7-diol [(*S*),(*S*)-4]. The synthetic route to monomer [(*S*),(*S*)-**4**] is shown in Scheme 1. The starting optically pure (*S*)-(1-naphthyl)phenylvinyl-(−)-menthoxysilane[(*S*)-**1**] (>99% de, 5.06 g, 12.2 mmol), prepared similarly to the literature,[7] was reacted with dimethylchlorosilane (2.31 g, 24.4 mmol) at 55 °C in the presence of Pt−DVTMDS (0.12 mL as 0.01 M benzene solution) for 5 h. After excessive dimethylchlorosilane was removed under reduced pressure, ether (10 mL) was added to the residue, and the chlorosilyl function of the crude product was selectively reduced by lithium aluminum hydride (0.19 g, 5.0 mmol) to give (*S*)-[(2-dimethylhydrosilyl)ethyl]-(1-naphthyl)phenyl-(−)-menthoxysilane, (*S*)-**2**, as a yellowish liquid (5.28 g, 91.1% yield from (*S*)-**1**) after column chromatographic separation on silica gel with *n*-hexane/toluene (85/15 v/v). (*S*)-**2** was further reacted with (*S*)-**1** (4.70 g, 11.3 mmol) in the presence of Pt−DVTMDS (0.11 mL as 0.01 M benzene solution) at 80 °C overnight to give (1*S*),(7*S*)-1,7-di{(−)-menthoxy}-1,7-di(1-naphthyl)-1,7-diphenyl-4,4-dimethyl-1,4,7-trisilaheptane, (*S*),(*S*)-**3** (6.28 g, 63.5% yield from (*S*)-**2**). (*S*),(*S*)-**3** (6.28 g, 7.1 mmol) was converted to (*S*),-(*S*)-**4** via hydrolysis to bis(potassium silanolate) with potassium hydroxide (11.3 g, 0.20 mol) in xylene (10 mL) followed by neutralization. The crude product was separated by silica gel column chromatography with *n*-hexane/THF (85/15 v/v) to give a light yellow solid (*S*),(*S*)-**4** (3.07 g, 70.9% yield from (*S*),(*S*)-**3**). Anal. Calcd for $C_{38}H_{40}O_2Si_3$: C, 74.44; H, 6.58. Found: C, 74.21; H, 6.55. ^{1}H NMR: δ 0.06 (s, 6H, SiCH_3), 0.55−0.58 (m, 4H, $CH_2Si(CH_3)_2$), 1.12−1.16 (m, 4H, CH_2SiNpPh), 1.71 (s, 2H, Si*OH*), 7.31−8.11 (m, 24H, naphthyl and phenyl). ^{13}C NMR: δ −4.58, 5.68, 7.91, 125.07, 125.56, 126.03, 128.00, 128.50, 128.93, 129.83, 130.71, 133.45, 133.95, 134.27, 135.08, 137.00, 137.05. ^{29}Si NMR: δ −1.17, 6.65. IR (neat): 3380 (ν(Si−OH)), ν 3053−2884, 1590, 1506, 1428, 1320, 1246, 1217, 1147, 1114, 1056 (ν(Si−O−C)) cm^{-1}. $[\alpha]^{25}_{D} = 3.7°$ (*c* 1.58, $CHCl_3$).

Poly[oxy{(*S*)-(1-naphthyl)phenylsilylene}ethylene(dimethylsilylene)ethylene{(*S*)-(1-naphthyl)phenylsilylene}oxydimethylsilylene] [(*S*),(*S*)-5]. (*S*),(*S*)-**5** was synthesized according to Scheme 2. In a 10 mL test tube under nitrogen atmosphere, (*S*),(*S*)-**4** (0.49 g, 0.80 mmol) was heated with equimolar amounts of bis(dimethylamino)dimethylsilane at 50 °C. After being stirred for 48 h, the mixture was cooled to room temperature. Precipitation and purification

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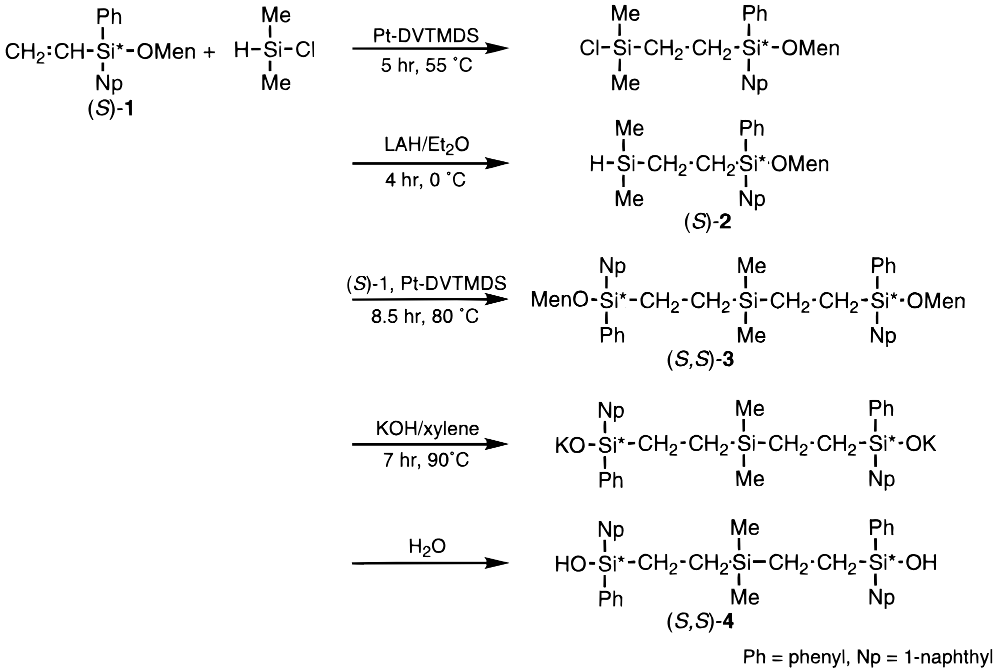
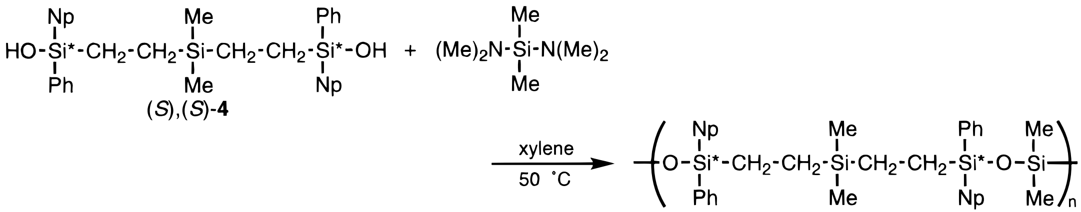
Scheme 1



(S)-1 (S)-2 (S,S)-3 (S,S)-4

Ph = phenyl, Np = 1-naphthyl

Scheme 2



(S),(S)-4 (S),(S)-5

by reprecipitation from THF into methanol afforded white polymeric materials (*S*),(*S*)-**5** (yield: 62.9%). SEC: M_n = 11 800, M_w/M_n = 1.84. ^{1}H NMR: δ −0.30 to −0.10 (two singlets, 12 H, SiCH_3), 0.30−0.50 (m, 4 H, CH_2Si(CH$_3$)$_2$), 0.90−1.10 (m, 4 H, CH_2SiNpPh), 6.95−8.00 (m, 24 H, naphthyl and phenyl). ^{13}C NMR: δ −4.53, 1.44, 6.03, 8.50, 124.87, 125.28, 125.56, 127.65, 128.58, 128.63, 129.35, 130.31, 133.24, 134.11, 134.18, 134.88, 136.83, 137.37. ^{29}Si NMR: δ −19.44, −10.82, 6.24. IR (neat): ν 3068−2911, 1590, 1506, 1428, 1320, 1260, 1217, 1147, 1114, 1044 (ν(Si−O−C)) cm^{-1}. $[\alpha]^{25}_D$ = −5.7° (*c* 1.59, CHCl$_3$).

Atactic poly[oxy{(1-naphthyl)phenylsilylene}ethylene(dimethylsilylene)ethylene{(1-naphthyl)phenylsilylene}oxydimethylsilylene] (*ata*-**5**) was obtained from racemic-**4**, *rac*-**4**. SEC: M_n = 14300, M_w/M_n = 1.98.

Results and Discussion

Preparation of (*S*),(*S*)-4 and Determination of Its Optical Purity. Polyaddition and polycondensation reactions are sometimes accompanied by the formation of low molecular weight cyclic compounds as side products. In such a case, degree of polymerization does not reach high enough for a polymer to develop the intrinsic properties. To avoid such cyclization during the polymerization, the structure of the monomer (*S*),(*S*)-**4** was designed to separate the telechelic functional groups by a long spacer group.

Since it is established that hydrosilylation does not affect the configuration of vinyl-attached chiral silicon atom,[8] hydrosilylation is utilized to elongate the length of the molecules to obtain (*S*),(*S*)-**3**. The menthoxy groups of (*S*),(*S*)-**3** were converted into silanolate by the careful treatment with excessive amounts of KOH. Telechelic bis(silanol) was obtained by the neutralization of the potassium salt with dilute hydrochloric acid to avoid the condensation of the formed silanol. HPLC study verified that (*S*),(*S*)-**4** with optical purity higher than 99% was obtained from (*S*)-**1** (>99% ee) as shown in Figure 1. The retention of stereochemistry of the silicon chiral center in the hydrolysis process of menthoxysilane with potassium hydroxide was confirmed.[3,9]

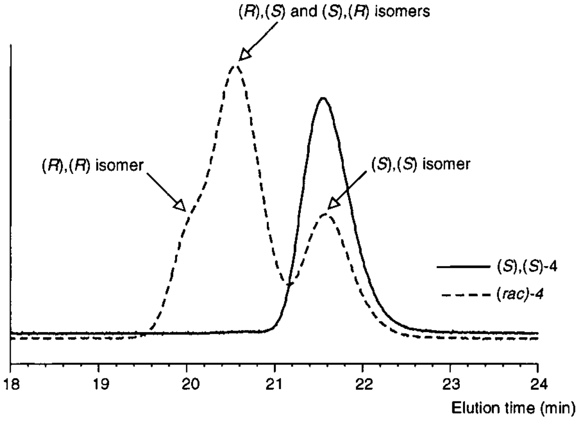


Figure 1. HPLC chromatograms of (*S*),(*S*)- and *rac*-**4** on optically active stationary phase with *n*-hexane/2-propanol = 10/1. Flow rate = 0.4 mL/min; column temperature = 35 °C.

Synthesis and Characterization of (*S*),(*S*)-5. Since dichlorosilane is too sensitive to moisture to handle without decomposition, bis(dimethylamino)dimethylsi-

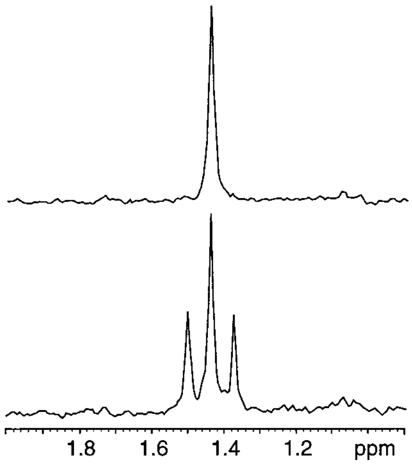


Figure 2. ^{13}C NMR of O−Si(CH_3)$_2$−O region: (upper) (*S*),(*S*)-**5**; (lower) *ata*-**5**.

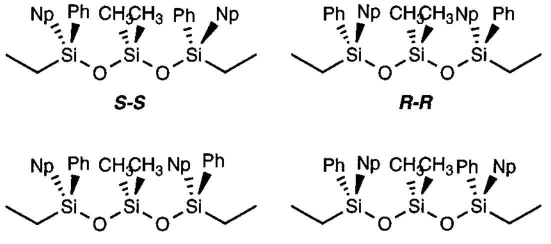


Figure 3. Four possible dyad sequences of *ata*-**5**.

lane was selected as a component in the polycondensation. It is known that aminosilane reacts more smoothly than chlorosilane in the condensation with silanol without the cleavage of the already formed polymer chain. [10,11] SEC showed the polymer produced with bis(dimethylamino)dimethylsilane had high molecular weight of unimodal distribution, contrary to the point that multimodal distribution is often observed when the polymer is synthesized with dichlorodimethylsilane.

This condensation reaction was supposed not to affect the stereochemistry of the chiral silicon atoms of the bis(silanol);[12] thus, the stereoregularity of the polymer depends on the optical purity of the monomer. As optical purity of the (*S*),(*S*)-**4** used for the polymerization was >99% de, the polymer was considered almost completely stereoregular. The ^{13}C NMR of Si(CH_3)$_2$ derived from the bis(dimethylamino)dimethylsilane component obviously reflected the stereoregularity of the polymer (Figure 2). The achiral Si(CH_3)$_2$ unit sandwiched by two oxygen atoms connected to two asymmetric silicon centers in this polymer can recognize different combination of configurations of neighboring asymmetric silicon atoms, and functions as a stereochemical probe as previously reported for poly[(oxydimethylsilylene)ethylene-(5*S*)-(1-naphthyl) phenylsilylene].[3,4] Three peaks are observed in the polymer *ata*-**5** from *rac*-**4**. Two peaks correspond to methyl groups between *R*−*S* (or *S*−*R*), and one peak corresponds to methyl groups between *R*−*R* (or *S*−*S*) configurational silicon centers as represented in Figure 3. *R*−*S* and *S*−*R* configurations are stereochemically nonequivalent for the two Si(CH_3)$_2$ carbon atoms, thus they should give two singlets. (*S*),(*S*)-**5** from optically pure (*S*),(*S*)-**4** shows only one singlet, which correspond to either *S*−*S* or *R*−*R* configuration of the asymmetric centers. Though it is not possible to distinguish if the polymer is either (*S*),(*S*)- or (*R*),(*R*)-diisotactic only by the result of ^{13}C NMR, it is reasonable to consider that the polymer is (*S*),(*S*)-diisotactic as discussed above.

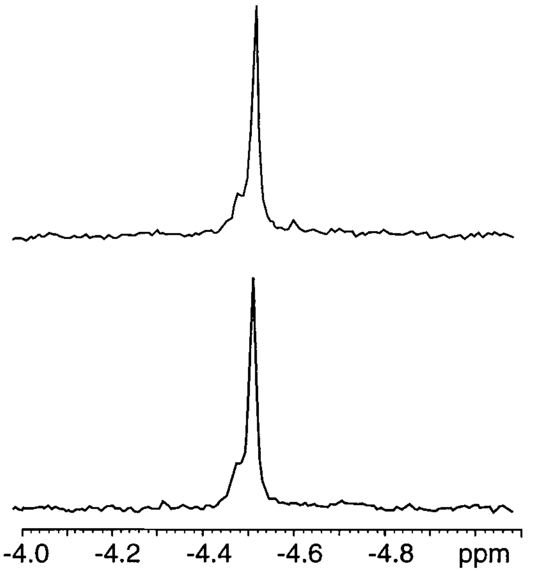


Figure 4. ^{13}C NMR of CH_2−Si(CH_3)$_2$−CH_2 region: (upper) (*S*),(*S*)-**5**; (lower) *ata*-**5**.

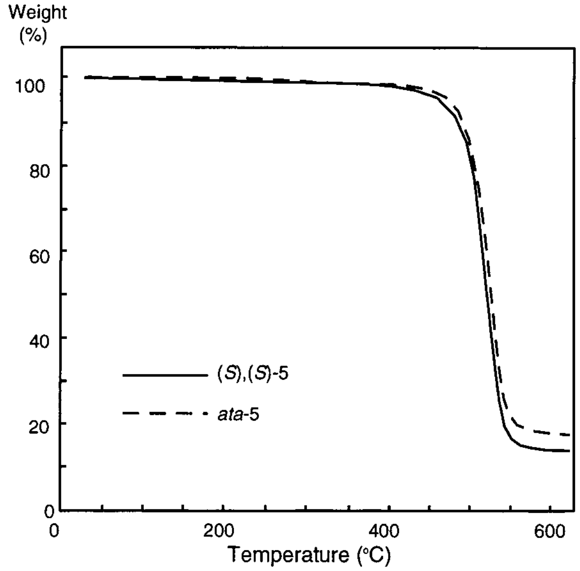


Figure 5. TGA thermograms of (*S*),(*S*)- and *ata*-**5**.

On the other hand, Si(CH_3)$_2$ sandwiched by two methylene groups did not split in the ^{13}C spectrum; therefore, it does not work as an efficient stereochemical probe (Figure 4). The two methyl groups are too much apart from the asymmetric centers. MM2 calculation also supported this consideration. Inter-silicon atom distance of *Si*(CH_3)$_2$−CH_2CH_2−*Si*NpPh is actually longer than that of *Si*(CH_3)$_2$−O−*Si*NpPh (4.12−4.66 vs 3.12−3.15 Å).[13] (*S*),(*S*)-**5** showed optical activity [$[\alpha]^{25}_D$ = −5.7° (*c* 1.59, $CHCl_3$)] as expected. However, CD spectrum showed no activity in cyclohexane, 1,2-dichloroethane or methanol.

Thermal properties of the polymers were evaluated using DSC and TGA. T_g of (*S*),(*S*)-**5** was 42.3 °C, which is a little different from that of *ata*-**5** (41.3 °C). TGA also showed similar behavior (Figure 5). Both polymers were stable up to 450 °C and then showed a sharp weight loss around 500 °C. Ten percent weight loss temperatures and pyrolysis residues at 600 °C of (*S*),(*S*)-**5** and *ata*-**5** were 487 and 492 °C and 13% and 17% of the initial weight, respectively. Stereoregularity of the polymer **5** had only a small influence on its thermal properties.

Conclusion

A new optically pure (>99%) organosilicon compound, (1*S*),(7*S*)-1,7-di(1-naphthyl)-1,7-diphenyl-4,4-dimethyl-1,4,7-trisilaheptane-1,7-diol was prepared. This bifunctional bis(silanol) was used as the monomer to synthesize optically active and diisotactic poly[oxy{(*S*)-(1-naphthyl)phenylsilylene}ethylene(dimethylsilylene)ethylene{(*S*)-(1-naphthyl)phenylsilylene}-oxydimethylsilylene] by polycondensation with bis(dimethylamino)dimethylsilane. This polymer with the optical activity induced by main chain asymmetric silicon units proved to be optically pure (>99%) and highly stereoregular (diisotacticity > 99%). Stereoregular and atactic polymers showed similar thermal properties.

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