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Synthesis and Polyaddition Reaction of Optically Active Methylphenylpropargylsilane

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Ring-opening polymerization of silacyclobutane or disilacyclobutane derivatives and polyaddition reaction of hydrosilyl compounds with unsaturated compounds have been conducted to prepare a variety of polycarbosilanes.[1−3] We have reported the stereoregular poly[(methylphenylsilylene)(trimethylene)] synthesized from optically active allylmethylphenylsilane via a self-polyaddition reaction.[3] The stereoregularity of the polymer estimated by ^{1}H NMR indicated that this polymerization proceeded through β-selective hydrosilylation in which the stereochemistry of the silicon atom was retained, but the optical activity itself was lost in the resulting polymer since the silicon atoms in the formed polymer are not chiral any more. To keep the configurational optical activity derived from the chiral silicon atom, it is necessary to distribute the optically active silicon moiety connected with different constitutional units in the polymer chain. Here, we report the synthesis and polymerization of optically active (*R*)-methylphenylpropargylsilane, (*R*)-**5** to obtain optically active polycarbosilane, poly[(*R*)-**5**]. Such stereoregular and optically active unsaturated polycarbosilanes will find potential applications as reactive polymer precursors for the synthesis of variety of new optically active branched polymers, typically star-type, comb-shaped, and hyperbranched polymers.

(*R*)-Methylphenyl(1-naphthyl)-(+)-menthoxysilane, (*R*)-**1** (>99% de), was obtained by optical resolution in a manner similar to the (*S*)-isomer using (−)-menthol as the chiral resolving agent.[4,5] The reaction of methylphenylbromo-(+)-menthoxysilane, (*R*)-**2**[5] (74% de), with propargylmagnesium bromide in the presence of HgCl$_2$ gave a mixture of (*S*)-methylphenylpropargyl-(+)-menthoxysilane, (*S*)-**3** (19%, 56% de), and (*S*)-allenylmethylphenyl-(+)-menthoxysilane, (*S*)-**4** (66%, 73% de).[6] According to Sommer, the brominative cleavage of the silicon−naphthyl bond proceeded with inversion of the stereochemistry of the silicon atom. It was also shown that alkylation of silyl bromide with alkyllithium or a Grignard reagent in ether proceeded with inversion of the sterochemistry.[7] Although the formation of side product **4** was noticeable, since almost the same reaction conditions were employed in our synthesis using propargylmagnesium bromide, products **3** and **4** are considered to have the (*S*)-configuration. The reason that the de of (*S*)-**3** is lower than that of (*S*)-**4** is not clear at present. The reduction of (*S*)-**1** with lithium aluminum hydride was reported to proceed with retention of the stereochemistry of the silicon atom.[8] We analyzed the optical purity of methylphenylnaphthylsilane, the reduced product from (*R*)-**1**, by HPLC on an optically active stationary phase, and concluded that retention of the sterochemistry of the silicon atom in the reduction of the silicon−menthoxy bond of **1** took place.[9] We also showed retention of stereochemistry in the reduction of phenylnaphthylvinylmenthoxysilane by HPLC[10] and of allylmethylphenylmenthoxysilane through analysis of the polymer by ^{1}H NMR.[3] HPLC of (*R*)-**5**, the reduced product of (*S*)-**3** (56% de by ^{1}H NMR) is shown in Figure 1. The chromatograms indicated that (+)-**5** was obtained by the reduction of (*S*)-**3**. The area ratio of the two peaks indicates that the product is 56% ee. It is reasonable to consider that the reduction reaction proceeded with the retention of silicon sterochemistry to give (*R*)-(+)-**5** (34%, 56% ee, $[\alpha]^{23}_{D}$ +38.3 (*c* 2.17, hexane)) (Scheme 1).[8−11]

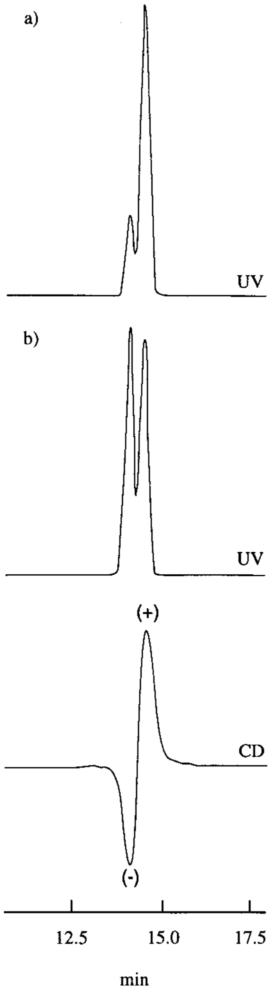

Figure 1. HPLC chromatograms of **5** on optically active stationary phase: (a) (*R*)-(+)-**5** from (*S*)-**3** (UV detection); (b) *rac*-**5** (UV, and CD detection) (eluent, hexane; column, Chiralcel OD; vertical axis in arbitrary unit).

Polyaddition reactions of (*R*)-**5** and *rac*-**5** using platinum 1,3-divinyl-1,1,3,3-tetramethyl-1,3-disiloxane (Pt−DVTMDS) as a catalyst gave polymers. Polymers were characterized by ^{1}H NMR, ^{13}C NMR, and SEC measurements.[12] Molecular weights were estimated by SEC using a polystyrene standard. Although the terminal methyne carbon of the propargyl group was observed

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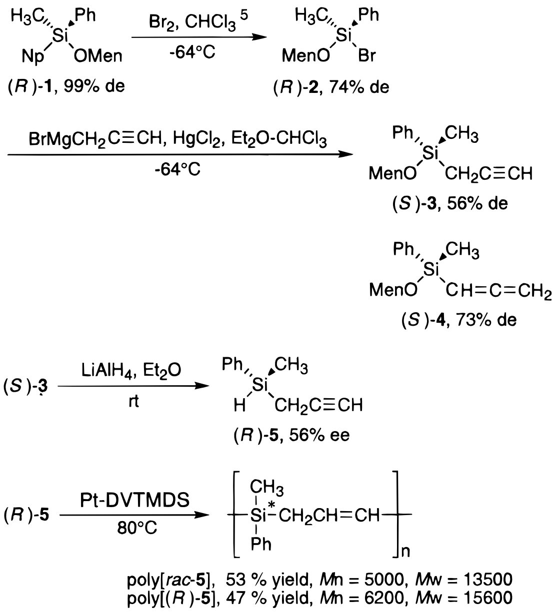
Scheme 1



at 68.1 ppm, the accurate molecular weight could not be estimated by ^{13}C NMR. Chloroplatinic acid is not an effective catalyst. Polymerization of *rac*-**5** by [Rh(COD)$_2$]BF$_4$/2PPh$_3$ resulted in the formation of only low molecular weight products.

Poly[(*R*)-**5**] obtained by Pt–DVTMDS showed optical activity ($[\alpha]^{23}_{D}$ −2.74 (*c* 3.43, CHCl$_3$)). This is the first example of an optically active polycarbosilane, poly[(methylphenylsilylene)(2-propenylene)]. The low optical activity of the polymer, compared with the monomer (*R*)-**5** in which hydrogen and propargyl together with methyl and phenyl groups are attached to the asymmetric silicon atom, seems to be because the asymmetric environment around the silicon atom, to which allyl and 1-propenyl are attached, becomes close to an achiral environment after the polymerization.

Although hydrosilylation of propargyl group could proceed in α- or *β*-addition mode, the polymers were formed selectively through *β*-addition, elucidated by ^{1}H NMR, ^{13}C NMR, and DEPT spectra, just as with the allylsilane.[3,5] ^{1}H NMR spectra of the orefinic region of the products by Pt–DVTMDS and [Rh(COD)$_2$]BF$_4$/2PPh$_3$ catalysts are shown in Figure 2.

Basically, four signals were observed from 5.4 to 6.2 ppm for the polymers by Pt–DVTMDS (Figure 2b,c), and two kinds by [Rh(COD)$_2$]BF$_4$/2PPh$_3$ at 5.6 (J = 18 Hz) and 6.2 ppm (Figure 2a). These signals can be assigned to cis or trans vinylene protons.

It is known that the hydrosilylation of the carbon–carbon triple bond by [Rh(COD)$_2$]BF$_4$/2PPh$_3$ proceeds in the syn addition mode.[13] The coupling constant (J = 18 Hz) indicated that the olefin protons in the oligomers by [Rh(COD)$_2$]BF$_4$/2PPh$_3$ are trans vinylene protons formed through syn addition (Figure 2a). The signals at 5.4, 5.7 ppm produced by Pt–DVTMDS were assigned to cis vinylene protons. However, the signals are not sharp, and moreover, the ratio of cis and trans vinylene protons in the polymers by platinum catalyst was 2:1 for poly[(*R*)-**5**]obtained from (*R*)-**5** of 58% ee (Figure 2b), and 1:1 for poly[*rac*-**5**] (Figure 2c). Influences not only by the configuration of silicon atom but also by the geometry of the double bond in the main chain are conceivable. Further study is needed to elucidate the precise structure of the polymer and reaction mechanism and to evaluate the absolute optical activity of the polymer derived from the configuration of silicon atom of single geometry of the olefinic bond in the main chain.

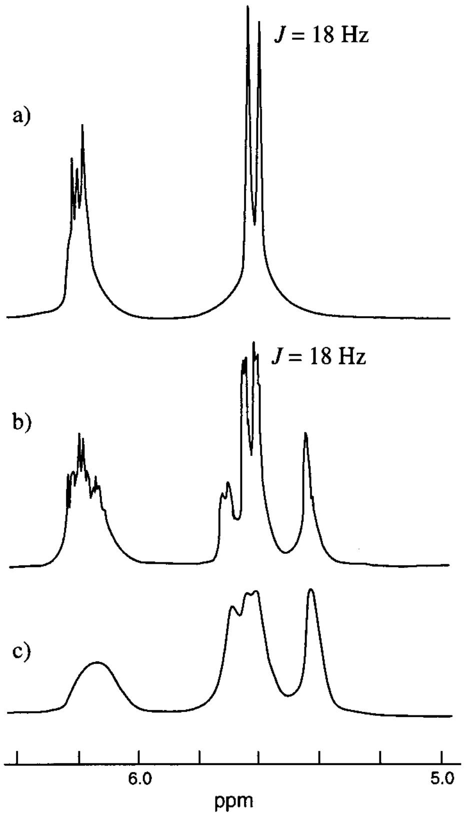


Figure 2. ^{1}H NMR spectra of olefin region of the poly[(*R*)-**5**]: (a) oligomers from *rac*-**5** by [Rh(COD)$_2$]BF$_4$/2PPh$_3$; (b) poly[(*R*)-**5**] from (*R*)-**5** by Pt–DVTMDS; (c) poly[*rac*-**5**] from *rac*-**5** by Pt–DVTMDS.

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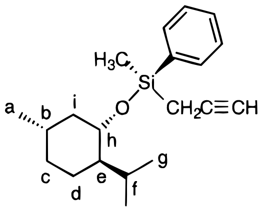
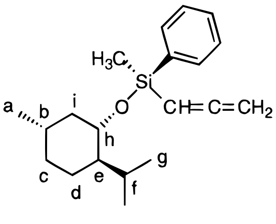
(6) To a solution of (*R*)-**1** (8.05 g, 20.0 mmol, 99% de) in CHCl$_3$ (140 mL) was added Br$_2$ in CHCl$_3$ (1.00 M, 20.0 mmol) at

−64 °C, and the resulting mixture was stirred for 1.5 h. To a solution of excess propargylmagnesium bromide in Et_2O (50 mL) in the presence of 0.18 mol % $HgCl_2$ was added the solution of (*R*)-**2** (74% de) prepared above, and stirred for 6.5 h at −64 °C. Water was added, and the system was extracted with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude liquid products were purified by silica gel column chromatography (hexane/$CHCl_3$ = 2/1) to afford (*S*)-**3** (1.23 g, 19%, 56% de) and (*S*)-**4** (4.17 g, 66%, 73% de).[14] The de was estimated by ^1H NMR from the integral ratio of $SiCH_3$ signals split by the connection to (+)-menthoxy group. (*S*)-**3**: ^1H NMR (500 MHz, $CDCl_3$) δ 0.53, 0.54 (two s, 3H, $SiCH_3$), 0.65 (d, 3H, J = 6.7 Hz, *H*g), 0.80−0.94 (m, 8H, *H*a, *H*c, *H*g), 1.00−1.10 (m, 1H, *H*i), 1.16−1.23 (m, 1H, *H*e), 1.26−1.36 (m, 1H, *H*b), 1.56−1.64 (m, 2H, *H*d), 1.78−1.92 (m, 4H, $CH_2{-}C{\equiv}CH$, *H*i), 2.16−2.26 (m, 1H, *H*f), 3.51−3.57 (m, 1H, *H*h), 7.36−7.43, 7.62−7.66 (m, 5H, Ar*H*). (*S*)-**4**: ^1H NMR (500 MHz, $CDCl_3$) δ 0.47, 0.49 (two s, 3H, $SiCH_3$), 0.65, 0.69 (2d, 3H, J = 6.9 Hz, *H*g), 0.80−0.92 (m, 8H, *H*a, *H*c, *H*g), 1.00−1.12 (m, 1H, *H*i), 1.17−1.24 (m, 1H, *H*e), 1.26−1.40 (m, 1H, *H*b), 1.56−1.64 (m, 2H, *H*d), 1.88−1.94 (m, 1H, *H*i), 2.18−2.26 (m, 1H, *H*f), 3.49−3.57 (m, 1H, *H*h), 4.42 (dd, 2H, J = 7.5, 1.0 Hz, $SiCH{=}C{=}CH_2$), 5.12 (t, 1H, J = 6.5 Hz, $SiCH{=}C{=}CH_2$), 7.35−7.42 (m, 3H, Ar*H*), 7.60−7.64 (m, 2H, Ar*H*).



(*S*)-**3**



(*S*)-**4**

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(11) A solution of (*S*)-**3** (1.11 g, 3.55 mmol, 56% de) in Et_2O (5 mL) was added to a suspension of $LiAlH_4$ (0.16 g, 4.21 mmol) in Et_2O (4 mL) at room temperature, and stirred for 6.5 h. The reaction was stopped by the addition of water (0.25 mL), and the mixture poured into 1N HCl solution, and extracted with Et_2O. Purification by silica gel column chromatography (hexane) afforded (*R*)-**5** (0.194 g, 34% yield, 56% ee). The ee of (*R*)-**5** was estimated by HPLC on an optically active stationary phase (cellulose carbamates,[15] Daicel Chem. Ind., Chiralcel OD, 0.46 cm o.d. × 25 cm; eluent, hexane; flow rate, 0.5 mL/min; pressure, 7 kg/cm^2; separation factor, 1.11). ^1H NMR (500 MHz, $CDCl_3$): δ 0.49 (d, 3H, J = 3.5 Hz, $SiCH_3$), 1.79, 1.84 (two t (dd) each, J_1, J_2 = 3.0 Hz, J_3 = 16.5 Hz, 2H, $SiCH_2$), 1.89 (t (dd), 1H, J = 3.0 Hz, $C{\equiv}CH$), 4.49 (sext, J = 3.5 Hz, 1H, Si*H*), 7.36−7.43, 7.59−7.60 (m, 2H, Ar*H*). $[\alpha]^{23}_{D}$ +38.3 (*c* 2.17, hexane).

(12) Polymerization of **5** was typically carried out in bulk at 80 °C for 48 h using 5 mmol % platinum 1,3-divinyl-1,1,3,3-tetramethyl-1,3-disiloxane (Pt−DVTMDS) catalyst under argon atmosphere. The obtained polymer was recovered by precipitating into MeOH and purified by repeated precipitation from $CHCl_3$ into MeOH. The molecular weights were estimated by SEC (polystyrene standard). Poly[*rac*-**5**] (53% yield): M_n = 5000, M_w = 13 500; ^1H NMR (500 MHz, $CDCl_3$) δ 0.18−0.48 (m, 3H, $SiCH_3$), 1.74−2.10 (broad s, 2H, $SiCH_2$), 5.34−5.52, 5.67−5.84 (two broad s, 1H, cis $-CH{=}CH$-), 5.52−5.67, 5.98−6.25 (two m, 1H, trans $-CH{=}CH-$), 7.05−7.30, 7.35−7.65 (m, 2H, Ar*H*). Poly[(*R*)-**5**] (47% yield): M_n = 6200, M_w = 15 600; ^1H NMR signals are more complicated than those for poly[*rac*-**5**]; $[\alpha]^{23}_{D}$ −2.74 (*c* 3.43, $CHCl_3$); UV λ_{max} (hexane) 222 nm.

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