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Separation of Optically Active Ethynylsilane Derivatives and Their Polymerization by Transition-Metal Catalysts

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ABSTRACT: Optically pure (−)-(4-bromophenyl)ethynylmethyl(1-naphthyl)silane [**(−)-1**], (−)-1,2-diethynyl-1,2-dimethyl-1,2-di(1-naphthyl)disilane [**(−)-2**], and (+)-1,2-diethynyl-1,2-dimethyl-1,2-diphenyldisilane [**(+)-3**] were separated by a chromatographic technique on an optically active stationary phase. Polymerization via Heck reaction or dimerization of bis(ethynyl) groups of these compounds gave optically active polymers. The structures of the polymers were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies. Poly(**1**) and poly(**2**) have regular chemical structure. In poly(**3**), (*E*)-ene−yne is mixed with (*E*)-ene−(*E*)-ene and yne−yne structures. All the polymers are considered stereoregular concerning the configuration of the silicon atoms. The optical properties in solution were measured. Although the electronic absorption and fluorescence spectra of optically active polymers did not change compared with those of racemic polymers, the circular dichroism spectra showed a negative Cotton effect.

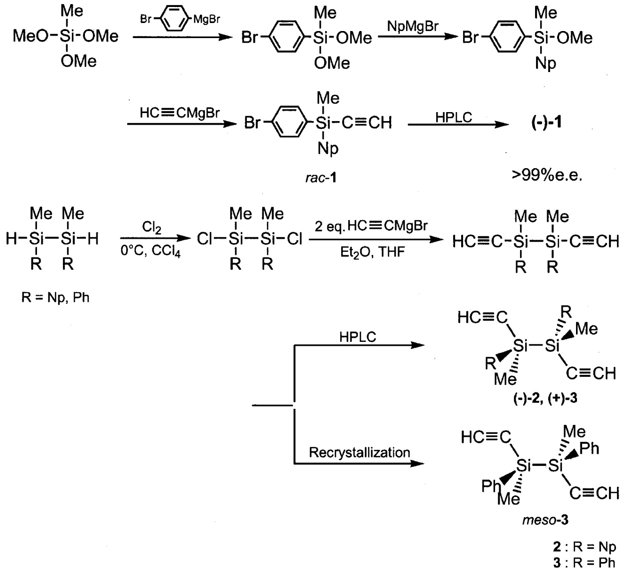
Introduction

There has been much attention given to organosilicon polymers such as polysilanes and polycarbosilanes as functional materials, such as photoresists, semiconductors, and hole-transporting materials. Among these polymers, those having an oligosilane unit sandwiched by a carbon−carbon conjugated system are especially interesting to elucidate electrical and optical properties of the polymers arising from $\sigma-\pi$ conjugation. Ishikawa, Corriu, and West reported the preparation of such disilane-containing polymers through dimerization or palladium-catalyzed Heck coupling reaction of ethynylsilyl compounds, and mentioned their electrical and optical properties.[1−5] However, characterization of the polymer structure is not well-done, which makes it difficult to understand their properties on the basis of the chemical structure.

Meanwhile, we have developed a stereospecific synthesis of optically active silicon compounds to obtain stereoregular and/or optically active poly(carbosilane)s,[6,7] poly(carbosiloxane)s,[8,9] and poly(siloxane)s.[10] These reactions contribute very much to the clarification of the polymer structure and stereochemical pathway of the reaction. If the chirality of the silicon atoms is controlled, characterization of the polymer by spectroscopic methods will become easier compared with that of the racemic polymer, and unambiguous identification of the structure might be made. However, no such stereoregular poly(carbosilane)s conjugated with a π-system have been reported.

In this paper, we describe the separation of optically pure (−)-(4-bromophenyl)ethynylmethyl(1-naphthyl)silane, (−)-1,2-diethynyl-1,2-dimethyl-1,2-di(1-naphthyl)disilane, and (+)-1,2-diethynyl-1,2-dimethyl-1,2-diphenyldisilane on optically active stationary phases,[11] and structural analyses of the polymers obtained via Heck reaction or dimerization of ethynyl functions.

Scheme 1. Synthesis and Separation of Optically Active (−)-1, (−)-2, and (+)-3



Experimental Section

General Procedures. NMR spectra (500 MHz, ^{1}H; 125.7 MHz, ^{13}C; 99.3 MHz, ^{29}Si) were obtained in $CDCl_3$ on a Varian 500 MHz spectrometer, model Unity INOVA. Chemical shifts are reported in parts per million relative to the peaks for $CHCl_3$ (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 HPLC analysis were performed on a JASCO HPLC apparatus, model GULLIVER, with a combination of Shodex KF-803L (30 cm, exclusion limit $M_n = 7 \times 10^4$, polystyrene) and KF-804 (30 cm, exclusion limit $M_n = 4 \times 10^5$, polystyrene) columns (linear calibration down to $M_n = 100$) using tetrahydrofuran (THF; 1 mL/min) as the mobile phase for molecular weight analysis, and with a CHIRALCEL OD (25 cm, cellulose tris(3,5-dimethylphenyl)-carbamate coated on silica gel, Daicel) column with hexane/2-propanol (100:0 to 1500:1 v/v) as the mobile phase at 35 °C (0.4 mL min^{-1}, 9−11 kg cm^{-2}) detected by UV (254 nm) and circular dichroism (CD; 254 nm) for optical purity analysis. Separation by HPLC was performed on a CHIRALCEL OD column (25 cm × 2 cm) with hexane/2-propanol (100:0 to 750:1 v/v) as the mobile phase (4.0 mL min^{-1}, 16−20 kg cm^{-2}). High-resolution mass spectra were taken on a Bruker DALTONICS

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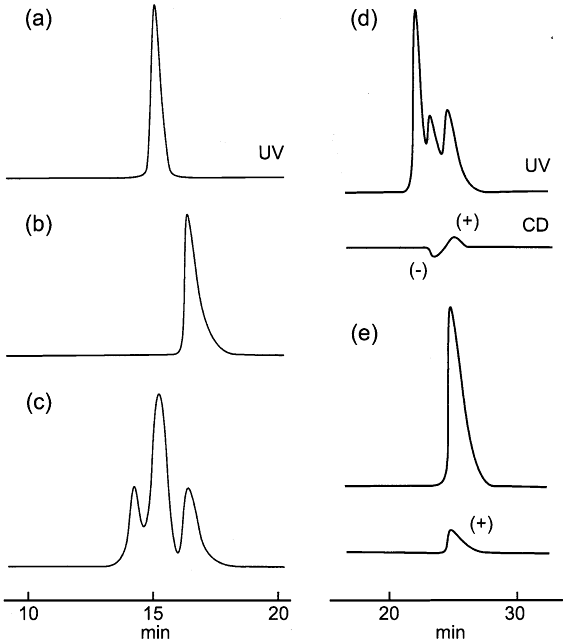


Figure 1. HPLC chromatograms of (a) *meso*-**2**, (b) **(−)-2**, (c) diastereomeric **2** (*n*-hexane:2-propanol = 100:1), (d) diastereomeric **3**, and (e) optically pure **(+)-3** (*n*-hexane:2-propanol = 1500:1).

Bio-Apex 70E. Electronic absorption, fluorescence, and circular dichroism spectra were obtained on a JASCO V-570 UV/VIS/near-IR spectrometer, JASCO FP-6500 spectrofluorometer, and JASCO J-720 spectropolarimeter, respectively.

Materials. Synthetic routes and chromatograms of the monomers are shown in Scheme 1 and Figure 1.

(−)-(4-Bromophenyl)ethynylmethyl(1-naphthyl)silane [(−)-1]. Dropwise addition of a solution of 4-bromophenylmagnesium bromide (105 mmol) in diethyl ether (120 mL) to a solution of methyltrimethoxysilane (13.62 g, 100 mmol) in diethyl ether (100 mL) afforded (4-bromophenyl)dimethoxymethylsilane (15.62 g, 60 mmol). Naphthylation (naphthylmagnesium bromide in THF) and ethynylation (ethynylmagnesium bromide in THF) gave (4-bromophenyl)ethynylmethyl(1-naphthyl)silane (5.97 g, 17% yield). Optically pure **(−)-1** was separated by preparative HPLC (750:1)

: ^{1}H NMR δ 0.86 (s, 3H, SiCH_3), 2.74 (s, 1H, SiC≡CH), 7.40−8.06 (m, 11H, naphthyl and phenyl protons); ^{13}C NMR δ −1.19 (SiCH$_3$), 86.63 (SiC≡CH), 97.42 (SiC≡CH), 124.85, 125.12, 125.72, 126.10, 128.20, 129.01, 130.99, 131.25, 131.29, 133.41, 133.88, 135.61, 136.08, 136.49 (naphthyl and phenyl carbons); ^{29}Si NMR δ −25.23; HRMS *m*/*z* found 352.0128, calcd for $C_{19}H_{15}SiBr$, M, 352.0106; $[\alpha]^{25}_D = -8.80°$ (*c* 1.00, $CHCl_3$).

(−)-1,2-Diethynyl-1,2-dimethyl-1,2-di(1-naphthyl)disilane [(−)-2]. To a cooled solution of 1,2-dimethyl-1,2-diphenyldisilane[12] (9.59 g, 39.5 mmol) in CH_2Cl_2 (40 mL) at −20 °C was added trifluoromethanesulfonic acid (80 mmol), and the solution was warmed to room temperature over 40 min and stirred for 30 min. Naphthylation at −20 °C, followed by distillation of the residue after the removal of volatile materials by heating to 200 °C at 2.2 mmHg gave 1,2-dimethyl-1,2-di(1-naphthyl)disilane (9.12 g, 67% yield).

Passing excess chlorine gas over 1,2-dimethyl-1,2-dinaphthyldisilane in CCl_4 gave 1,2-dichloro-1,2-dimethyl-1,2-dinaphthyldisilane without cleavage of the Si−Si bond. Ethynylation afforded diastereomeric **2** (5.56 g, 14.2 mmol, 57% yield). Pure isomers, **(−)-2** and *meso*-**2**, were separated by preparative chromatography (100:1) by recycling three times (Figure 1a−c). Data for (−)-**2**: ^{1}H NMR δ 0.75 (s, 6H, SiCH_3), 2.83 (s, 2H, SiC≡CH), 7.10−7.95 (m, 14H, naphthyl protons); ^{13}C NMR δ −2.51 (SiCH$_3$), 86.64 (SiC≡CH), 98.72 (SiC≡CH), 125.10, 125.39, 125.45, 128.29, 128.53, 130.38, 131.54, 133.07, 134.89, 136.58 (naphthyl carbons); ^{29}Si NMR δ −36.89; HRMS *m*/*z* found 390.1273, calcd for $C_{26}H_{22}Si_2$, M, 390.1260; $[\alpha]^{25}_D = -26.53°$ (*c* 1.01, $CHCl_3$). Data for *meso*-**2**: ^{1}H NMR δ 0.72 (s, 6H, SiCH_3), 2.65 (s, 2H, SiC≡CH), 7.27−8.12 (m, 14H, naphthyl protons); ^{13}C NMR δ −2.33 (SiCH$_3$), 86.45 (SiC≡CH), 98.75 (SiC≡CH), 125.20, 125.51, 125.60, 128.69, 128.72, 130.46, 131.77, 133.24, 134.98, 136.75 (naphthyl carbons).

(+)-1,2-Diethynyl-1,2-dimethyl-1,2-diphenyldisilane [(+)-3]. Similar chlorination of 1,2-dimethyl-1,2-diphenyldisilane and ethynylation afforded diastereomeric **3** (69% yield). After recrystallization two times from ethanol, *meso*-**3** was isolated[1e] as a pure isomer. Optically active antipode **(+)-3** was separated with hexane/2-propanol (750:1) as the mobile phase. By recycling five times, optically pure disilane was isolated (Figure 1d,e). Data for (+)-**3**: ^{1}H NMR δ 0.57 (s, 6H, SiCH_3), 2.68 (s, 2H, SiC≡CH), 7.28−7.52 (m, 10H, phenyl protons); ^{13}C NMR δ −4.42 (SiCH$_3$), 85.48 (SiC≡CH), 97.71 (SiC≡CH), 127.89, 129.44, 133.19, 134.35 (phenyl carbons); ^{29}Si NMR δ −38.63; $[\alpha]^{26}_D = +8.17°$ (*c* 2.33, $CHCl_3$).

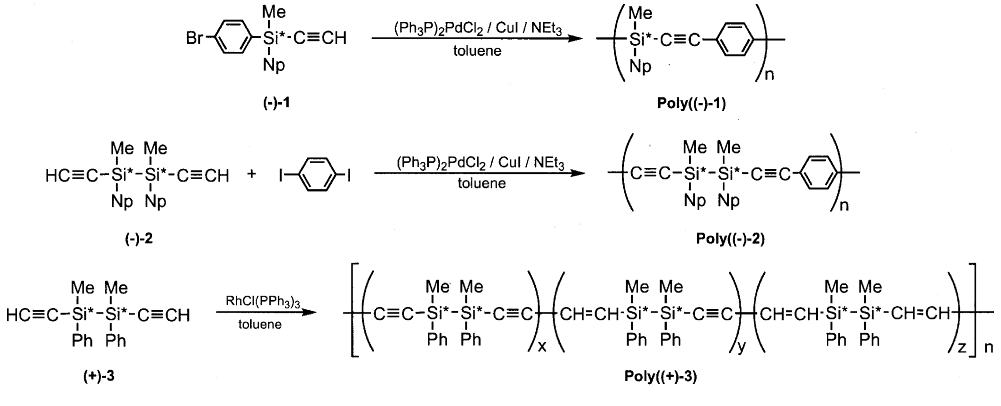
(*R*)-Ethynylmethyl(1-naphthyl)phenylsilane was synthesized as a model compound to study regio- and stereoselectivity in the dimerization of an ethynyl group from (*S*)-methyl(1-naphthyl)phenylchlorosilane[13] (1.13 g, 4.0 mmol, 99% ee). Optically pure compound was separated with hexane as the mobile phase from the crude product with 60% ee:

^{1}H NMR δ 0.88 (s, 3H, SiCH_3), 2.73 (s, 1H, SiC≡CH), 7.34−8.14 (m, 12H, naphthyl and phenyl protons); IR (KBr) 2035 (γ (C≡CH)) cm^{-1}; HRMS *m*/*z* found 272.1026, calcd for $C_{19}H_{16}Si$, M, 272.1021; $[\alpha]^{27}_D = +6.00°$ (*c* 1.00, $CHCl_3$).

Polymerization. Polymerization schemes are shown in Scheme 2.

Polymerization by Heck Reaction. A typical procedure is given. 1,4-Diiodobenzene (0.33 g, 1 mmol), **2** (0.39 g, 1 mmol), $(Ph_3P)_2PdCl_2$ (35.1 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol), triethylamine (1.5 mL), and toluene (10 mL) were placed in a flask and stirred at 80 °C for 2 days. The resulting solution was filtered, concentrated, and purified by reprecipitation from $CHCl_3$ into methanol two times. Data for poly((−)-**1**): M_w = 4900; M_n = 3300; ^{1}H NMR δ 0.88 (s, 6H, SiCH_3), 7.23−8.17 (m, 11H, naphthyl and phenylene protons); ^{13}C NMR δ −1.09 (SiCH$_3$), −1.00 (SiCH$_3$ terminal), 91.56 (SiC≡C−), 109.11

Scheme 2. Polymerization of (−)-1, (−)-2, and (+)-3



($\mathrm{SiC}{\equiv}C-$), 123.81, 125.10, 125.63, 125.99, 126.01, 128.41, 128.91, 131.04, 131.08, 131.22, 131.40, 131.45, 131.56, 131.90, 132.10, 133.41, 134.43, 135.51, 136.19, 136.62, 137.12 (naphthyl and phenylene carbons); ^{29}Si NMR δ −25.73 (half-height peak width 2.28 Hz), −25.60 (terminal); $[\alpha]^{25}_{\mathrm{D}} = +11.40°$ (*c* 1.00, $\mathrm{CHCl_3}$); yield 76%. Data for poly(*rac*-**1**): $M_w = 4000$; $M_n = 2800$; ^{29}Si NMR δ −25.73 (half-height peak width 3.76 Hz), −25.60 (terminal); yield 48%. Data for

poly((−)-**2**): $M_w = 13000$; $M_n = 5900$; ^{1}H NMR δ 0.84 (s, 6H, $\mathrm{SiC}H_3$), 7.08−8.22 (m, 18H, naphthyl and phenylene protons); ^{13}C NMR δ −2.25 ($\mathrm{Si}CH_3$), 93.39 ($\mathrm{SiSi}C{\equiv}\mathrm{C}-$), 110.05 ($\mathrm{SiSiC}{\equiv}C-$), 123.27, 125.18, 125.40, 125.45, 128.59, 128.64, 130.30, 131.73, 131.82, 131.93, 132.37, 133.19, 134.92, 135.20, 136.78 (naphthyl and phenylene carbons); ^{29}Si NMR δ −36.95; $[\alpha]^{25}_{\mathrm{D}} = -80.20°$ (*c* 1.00, $\mathrm{CHCl_3}$); yield 78%.

Data for poly(*diastereo*-**2**): $M_w = 15300$; $M_n = 6000$; yield 71%. Data for poly(*meso*-**2**): $M_w = 19600$; $M_n = 8300$; yield 73%.

Polymerization by Dimerization. Typically, a solution of 0.185 g (0.64 mmol) of **3** and 5 mol % chlorotris(triphenylphosphine)rhodium(I) in 0.6 mL of toluene was stirred for 2 days at room temperature. The residue was reprecipitated twice from chloroform to 2-propanol to give 33.6 mg (18% yield) of poly(**3**).[1c]

Data for poly((+)-**3**): $M_w = 17300$; $M_n = 5400$; ^{1}H NMR δ 0.48−0.59 (m, 6H, $\mathrm{SiC}H_3$), 6.05 (d, 1H, $J = 19.0$ Hz, olefinic protons), 6.68 (d, 1H, $J = 19.0$ Hz, olefinic protons), 7.06−7.74 (m, 10H, phenyl protons); ^{13}C NMR δ −5.76, −5.52, −3.91, −3.77 ($\mathrm{Si}CH_3$), 91.19, 91.34, 91.42, 91.57 ($\mathrm{SiSi}C{\equiv}\mathrm{C}-$), 109.61, 109.71, 109.77, 109.88 ($\mathrm{SiSiC}{\equiv}C-$), 125.79, 125.83, 125.90, 125.93 ($\mathrm{SiSi}C{=}\mathrm{C}-$), 127.72, 127.87, 127.92, 128.02, 128.59, 129.23, 134.09, 134.36, 134.45, 134.64, 134.71, 133.19, 134.87 (phenyl carbons), 142.55, 142.59, 142.75, 142.79 ($\mathrm{SiSiC}{=}C-$); ^{29}Si NMR δ −39.29 ($\mathrm{Si}\mathit{Si}\mathrm{C}{\equiv}\mathrm{C}-$), −26.25 ($\mathrm{Si}\mathit{Si}\mathrm{C}{=}\mathrm{C}-$). Data for poly(*meso*-**3**): $M_w = 22600$; $M_n = 8200$; yield 62%. Data for poly(*diastereo*-**3**): $M_w = 12300$; $M_n = 5600$; yield 59%.

Results and Discussion

A model reaction to obtain poly(**1**) or poly(**2**) from ethynylsilanes and haloaryl compounds, by treatment of a toluene solution of *meso*-**3**[1c] with iodobenzene under the Heck condition, afforded 1,2-dimethyl-1,2-diphenyl-1,2-bis(2-phenylethynyl)disilane. Only one isomer was produced, evidenced by HPLC, which suggests that the reaction has proceeded with retention of stereochemistry of the asymmetric silicon center.

Poly(**1**) and poly(**2**) obtained from *rac*-**1**, **(−)-1**, diastereomeric **2**, *meso*-**2**, and **(−)-2** were light-yellow, and soluble in common organic solvents such as toluene, THF, and $\mathrm{CHCl_3}$. In the ^{13}C NMR spectrum of poly(**1**), the signal at 91 ppm is assigned to the ethynyl carbon adjacent to the silicon atom, and the signal at 109 ppm to the ethynyl carbon bonded to phenylene groups. No dimerization of the ethynyl group was observed. In the ^{29}Si NMR spectra shown in Figure 2, two peaks (−25.73 and −25.60 ppm) were observed.

The signal at −25.73 ppm is assigned to the internal silicon atom of the polymer chain, and the signal at −25.60 ppm to the terminal silicon atom. The terminal signals were observed because of the low molecular weight of the product. Thus, poly(**1**) is determined as poly[{methyl(1-naphthyl)silylene}(ethynylene)(1,4-phenylene)]. However, unfortunately, no definite peak separation which reflects the stereoregularity of the polymer was observed in the NMR spectra of poly(*rac*-**1**) and poly((−)-**1**). The half-height peak width at −25.73 ppm in the ^{29}Si spectrum measured after deconvolution was narrower for poly((−)-**1**) (2.28 Hz) than that of poly(*rac*-**1**) (3.76 Hz). This probably suggests that poly((−)-**1**) is isotactic because the model reaction proceeded with 100% retention of configuration at the silicon atom.

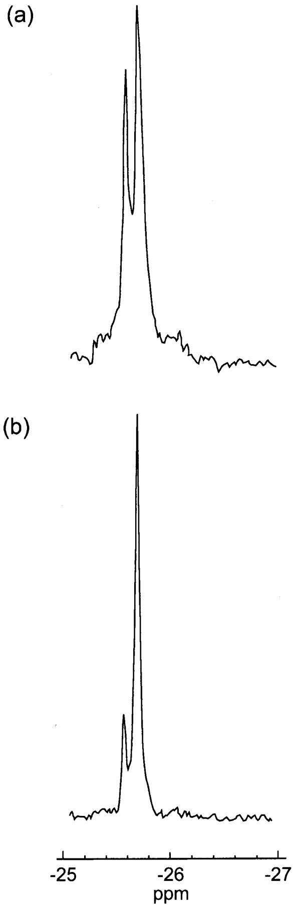


Figure 2. ^{29}Si NMR spectra of (a) poly(*rac*-**1**) and (b) poly((−)-**1**).

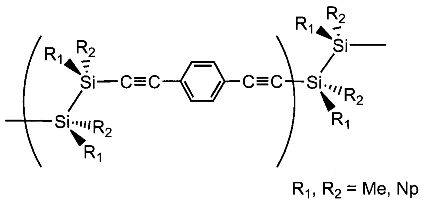
Poly((−)-**1**) showed optical activity ($[\alpha]^{25}_{\mathrm{D}} = +11.40°$ (*c* 1.00, $\mathrm{CHCl_3}$)).

The ^{1}H NMR spectra of poly(**2**) show two singlet peaks assignable to methyl protons and multiplet peaks assignable to 1-naphthyl and phenylene protons in the ratio 3:3:14:4. The ^{13}C NMR spectra show peaks of the methyl carbon, ethynylene carbon, and aromatic carbons. In the ^{29}Si NMR spectra, only one peak could be observed. Although the two silicon atoms could not be distinguished, the chemical structure of poly(**2**) is assigned as poly[{1,2-di(1-naphthyl)-1,2-dimethyldisilanylene}(ethynylene)(1,4-phenylene)(ethynylene)] as shown in Scheme 2. Poly(**2**) has a high enough molecular weight; therefore, no terminal signal was observed. However, no definite difference was observed in the ^{29}Si spectra among poly(*diastereo*-**2**), poly(*meso*-**2**), and poly((−)-**2**).

The splitting pattern of poly(**2**) should reflect the relation of configuration of two successive disilane units. There are six distinguishable stereochemical relations concerning two successive disilane units for poly(*diastereo*-**2**), as shown in Figure 3.

The information about the stereochemistry of the disilane unit in the polymer could be obtained by the analysis of the ^{1}H and ^{13}C signals of the $\mathrm{Si}CH_3\mathrm{Np}$ unit. Two peaks were observed for the methyl proton of poly(*diastereo*-**2**) as shown in Figure 4a.

The peak at 0.84 ppm should be assigned to the signal of the *R*−*R* disilane unit (Figure 4c), and the signal at 0.75 ppm to the *R*−*S* (*S*−*R*) unit. The ^{13}C NMR methyl signal showed a trend similar to that of the ^{1}H NMR



(i) ***R-R*** - π-conjugation - ***R-R***

(ii) ***R-R*** - π-conjugation - ***R-S***

(iii) ***R-R*** - π-conjugation - ***S-R***

(iv) ***R-R*** - π-conjugation - ***S-S***

(v) ***R-S*** - π-conjugation - ***R-S***

(vi) ***R-S*** - π-conjugation - ***S-R***

Figure 3. Stereochemical relations concerning two successive disilane units of poly(*diastereo*-**2**) (*R* and *S* indicate the absolute configuration of the silicon atom).

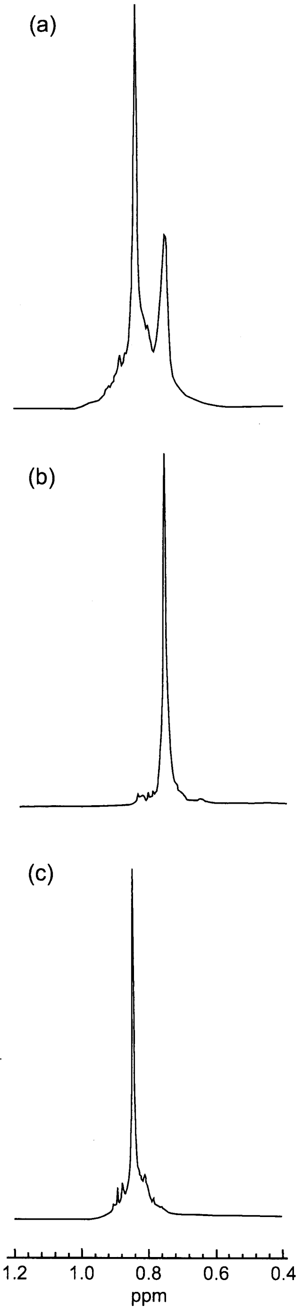


Figure 4. ^{1}H NMR spectra of SiCH_3 of (a) poly(*diastereo*-**2**), (b) poly(*meso*-**2**), and (c) poly((−)-**2**).

spectrum; namely, two peaks were observed in poly(*diastereo*-**2**) (Figure 5a).

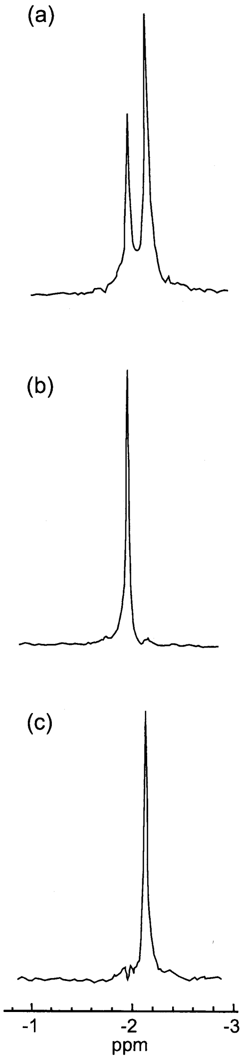


Figure 5. ^{13}C NMR spectra of SiCH_3 of (a) poly(*diastereo*-**2**), (b) poly(*meso*-**2**), and (c) poly((−)-**2**).

The peak of SiCH_3Np at −2.27 ppm could be assigned to the *R*−*R* disilane unit, and that at −2.09 ppm to the *R*−*S* (*S*−*R*) disilane unit. The ^{1}H and ^{13}C NMR analysis of poly((−)-**2**) proved the complete retention of asymmetric silicon atoms in the polymerization. It is important to note that the areas of the two peaks of poly(*diastereo*-**2)** are not equal. The ratio of the *R*−*R* (*S*−*S*) and *R*−*S* (*S*−*R*) disilane units in poly(*diastereo*-**2**) is roughly estimated to be 60:40 by ^{13}C NMR. In comparison with poly(**1**), it is possible to observe an environmental difference around the Si atom of poly(**2**) by NMR spectroscopy. In the ^{1}H NMR spectrum of poly(*diastereo*-**2**), two doublet signals were observed at 8.28 and 8.14 ppm for one of the naphthyl protons (Figure 6a). Poly(*meso*-**2**) showed the signal at 8.28 ppm (Figure 6b), and poly((−)-**2**) the signal at 8.14 ppm (Figure 6c). The peaks of poly(*diastereo*-**2**) at 8.28 and 8.14 ppm are reasonably considered to reflect the relative concentration of the meso and racemo diads of the disilane units. The ratio is estimated to be (*R*−*R* + *S*−*S*):(*R*−*S* + *S*−*R*) = 69:31. If the polymerization proceeds statistically, these signals must be equal. This means racemo diads are more contained in the isolated poly(*diastereo*-**2**). It is reasonable to consider that the fractions which contain more racemo diads would be less soluble in methanol, precipitated, and separated as the product. Some stereoselection should be occurring in the polymerization.

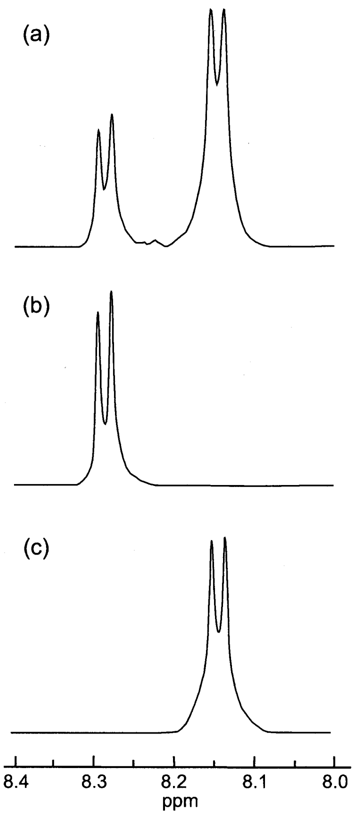


Figure 6. ^{1}H NMR spectra of SiNp-*H* of (a) poly(*diastereo*-**2**), (b) poly(*meso*-**2**), and (c) poly((−)-**2**).

Poly((−)-**2**) is considered optically pure (>99%).

It is not clear at this point whether a successive relation among *R*−*R*, *S*−*S*, *R*−*S*, and *S*−*R* can be distinguished or not. Precise analysis of the regularity concerning the two successive disilane units can be obtained by the analysis of the ethynyl carbon directly attached to the silicon atom.

The ^{13}C NMR spectra of poly(*meso*-**2**) and poly((−)-**2**) showed ethynylene carbon signals at 93.17 and 110.16 ppm and at 93.40 and 110.06 ppm, respectively. Peaks around 93 ppm are assigned to the ethynylene carbon directly attached to the silicon atom (SiSi*C*≡C, α-carbon), and the peaks around 110 ppm to the ethynylene carbon adjacent to the *p*-phenylene ring (SiSiC≡*C*−Ar−, β-carbon). Poly(*diastereo*-**2**) showed two broad multiplet signals at around 93 ppm in different strengths, namely, at 93.44, 93.39 (shoulder), 93.27, and 93.23 (shoulder) ppm, and two signals at around 110 ppm. The β-carbon signals around 110 ppm are not well separated. The ^{13}C peaks of the α-carbon around 93 ppm are shown in Figure 7.

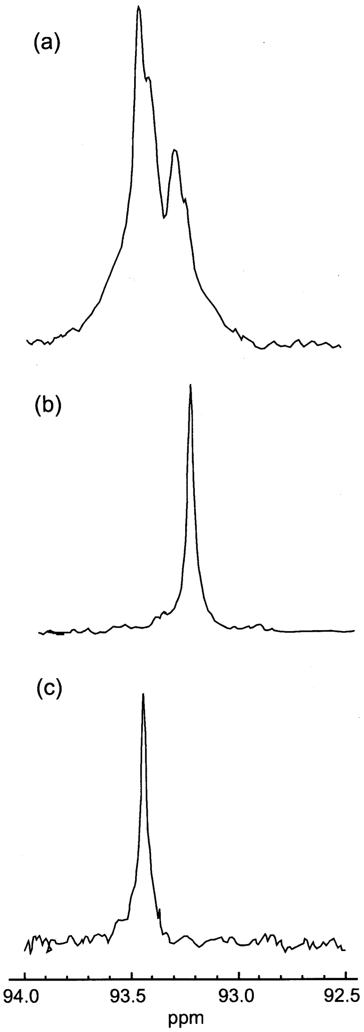


Figure 7. ^{13}C NMR spectra of Si*C*≡C of (a) poly(*diastereo*-**2**), (b) poly(*meso*-**2**), and (c) poly((−)-**2**).

The shoulder peaks at 93.39 and 93.23 ppm are assigned to the α-carbon signals of the racemo relation i and the meso relation v (mirror relation) + vi (center of symmetry) (Figure 3). The α-carbon signals of relation iv (center of symmetry) seem to appear at slightly lower field than that of relation i around 93.44 ppm. The peaks of the two α-carbons in relations ii and iii are not equal, and seem to slightly downfield shift from the signals related to the racemo (93.39 ppm) or meso (93.23 ppm) disilane unit, and appear around 93.44 and 93.27 ppm, respectively. Thus, the signals at 93.44 and 93.27 ppm are considered as overlapped signals of α-carbons attached to the racemo and meso units in relations ii−iv. To confirm the assignment, signals of poly(**2**) obtained from the monomer with the stereoisomer ratio *RR*:*SS*:*RS*:*SR* = 43:43:7:7 were analyzed. The crude polymer showed three peaks (93.44, 93.39, and 93.27 ppm) reflecting the small theoretical concentration of the α-carbon of relation vi; namely, the signal at 93.23 ppm was weak. This peak ratio was roughly determined as 8:2:1:0 after deconvolution of the peaks at 93.44, 93.39, 93.27, and 93.23 ppm. This fact partially guarantees the appropriateness of the above assignment. After reprecipitation, the signal at 93.27 ppm became even weaker than the crude polymer.

If the polymerization proceeds statistically, the four signals in Figure 7a must be in a ratio of 2:1:1:2. However, the peaks originating from the racemo relation were strong, and those originating from the meso relation were weaker than the calculated value. This indicates nonstatistical distribution of the disilane diad in the isolated polymer. However, the precise concentration of the successive diad of poly(*diastereo*-**2**) could not be estimated quantitatively because of the signal overlap.

To examine the more complicated case of a $\sigma-\pi$ conjugated polymer, the polymer was synthesized via dimerization reaction of ethynyl functions. A model reaction of polymerization by dimerization was studied by the treatment of a toluene solution of (*R*)-ethynylmethyl(1-naphthyl)phenylsilane with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) at room temperature for 24 h, which afforded 1,4-bis(methyl(1-naphthyl)phenylsilyl)but-1-en-3-yne in 84% yield. The coupling constants (J = 19.0 Hz) of the olefinic protons at δ 6.11 and 7.02 in the ^{1}H NMR clearly indicate the compound has an E configuration of the olefinic group. On HPLC analysis, only one stereoisomer was observed. The product is reasonably considered an (R,R) isomer. The dimer from *rac*-ethynylsilane showed four peaks assignable to the (R,R), (R,S), (S,R), and (S,S) isomers in equal quantities. The reaction is considered to proceed with retention of the stereochemistry of the asymmetric silicon centers.

To study the structure of poly(**3**), poly((+)-**3**), poly(*meso*-**3**), and poly(*diastereo*-**3**) were prepared from (+)-**3**, *meso*-**3**, and diastereomeric **3**, respectively, for comparison. In the ^{1}H NMR spectra of poly(*meso*-**3**), olefin protons were observed as doublets at 6.05 (d, 1H, J = 19.0 Hz) and 6.68 (d, 1H, J = 19.0 Hz) ppm. The appearance of two peaks for the olefin protons with *trans*-coupling indicates that the polymers have ene−ene and ene−yne structures with (E)-configuration concerning the C=C bond. In the ^{13}C NMR spectra, two olefin and two ethynylene carbons were observed at 125 (SiSi*C*=C−) and 142 (SiSiC=*C*−) ppm and and at 91 (SiSi*C*≡C−) and 110 (SiSiC≡*C*−) ppm, respectively. The signal of the ethynylene carbon at 110 ppm (SiSiC≡*C*−) split into two peaks (109.82 and 109.91 ppm), which also indicates that the polymer has yne−yne and yne−ene structures. The olefin carbon at 142 ppm (SiSiC=*C*−) also split into two peaks (142.50 and 142.82 ppm), which indicates that the polymer has ene−ene and ene−yne structures. Thus, it is concluded that the polymer has three kinds of basic structure, yne−yne, (E)-ene−yne, and (E)-ene−(E)-ene, similar to those reported by Ishikawa and as shown in Scheme 2.[1b,c]

Whether poly((+)-**3**) has regular structure or not depends on the stereo- and regiospecificity of the dimerization reaction. Chemical shifts of poly(**3**) are determined by the geometrical structure of carbon 4 units formed by dimerization, namely, (E)-ene−(E)-ene, (E)-ene−yne, and yne−yne structure, and the configuration of asymmetric silicon centers. The ^{29}Si NMR spectra of poly(**3**) are shown in Figure 8.

In poly(**3**), silicon atoms are attached to an ene or yne carbon, and the ene or yne group is further attached to an ene or yne group. The ^{29}Si chemical shifts are considered to be determined principally by which carbon of the C_4 unit formed by dimerization the silicon atom is attached to, which will be further split by the stereochemistry of the disilane unit (meso, racemo). This is also true for silicon atoms attached to an olefinic carbon. Such possible structures with a *meso*-disilane unit are shown in Table 1.

In the spectra, the signal of *Si*C≡C adjacent to the yne−yne [R^1 = yne] and yne−ene [R^2 = ene] structures of poly(*meso*-**3**) appeared as two peaks (−38.98 and −39.12 ppm). The signal at −39.12 ppm is assigned to the silicon atom attached to the yne−yne C_4 unit, and the signal at −38.98 ppm to that attached to the yne−ene C_4 unit at present, taking the magnetic anisotropy effect into account. The ratio of the yne−yne and yne−ene is roughly estimated to be 60:40. These signals appeared as broad and at a little higher field than the peaks for poly((+)-**3**). The signal was not separated for the silicon atom attached to yne−yne and yne−ene structures. The signal of *Si*C=C in the ene−ene and ene−yne structures appeared as one peak (−26.12 ppm) for poly(*meso*-**3**) (Figure 8b). A shoulder signal was observed for poly((+)-**3**) (Figure 8c). Some distinction was made by the difference between the structures of the C_4 units, but the difference between the ene−ene and ene−yne structures of the C_4 unit could not be clearly distinguished. There may be influences by higher order regularity on the broadness of these two peaks. The ratio of the peaks at −39 and −26 ppm of poly(*meso*-**3**) is roughly 1:1, which, with the 60:40 ratio of yne−yne and yne−ene structures, strongly indicates that the ratio of the ethynylene and olefin carbons attached to the silicon atom is roughly 1:1.

The signals for the silicon atoms adjacent to the carbon−carbon double bond appeared as only one peak, and did not give any information about the ratio of the concentration of the ene−yne and ene−ene structures. In poly(*diastereo*-**3**), the signal for each silicon atom was observed as two peaks (*Si*C=C, −26.11 and −26.23 ppm; *Si*C≡C, −39.00 and −39.27 ppm) (Figure 8a). These peaks are basically overlapped signals of poly((+)-**3**) and poly(*meso*-**3**).

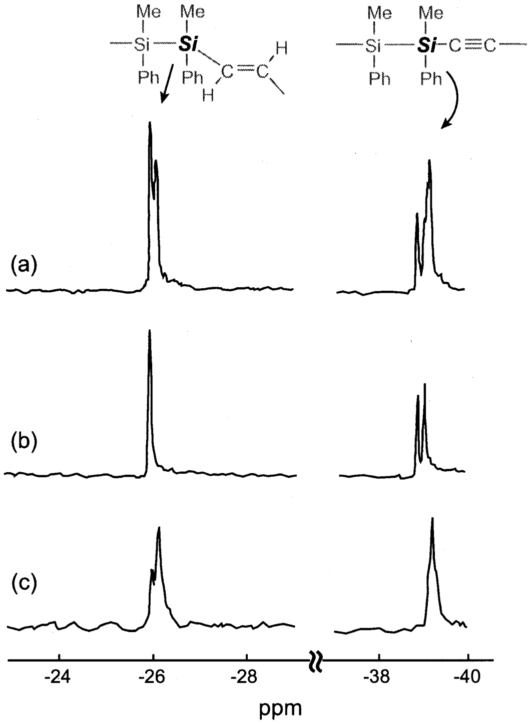
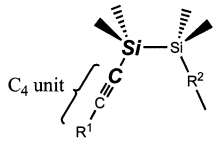


Figure 8. ^{29}Si NMR spectra of (a) poly(*diastereo*-**3**), (b) poly(*meso*-**3**), and (c) poly((+)-**3**).

Table 1. Structure of $-R^{1-}C{\equiv}C-[meso\text{-}Si-Si]-R^{2-}$ and the Chemical Shifts of Silicon and Carbon Atoms (Indicated)



substituent		chemical shift of Si (ppm)		chemical shift of C (ppm)	
R^1	R^2	poly(meso-**3**)	poly((+)-**3**)	poly(*meso*-**3**)	poly((+)-**3**)
yne	yne	[a] 39.12	∼**39**[a]	01/16	91.19
yne	ene			91.30	91.34
ene	yne			91.45	91.42
ene	ene			91.57	91.57

[a] Not separated.

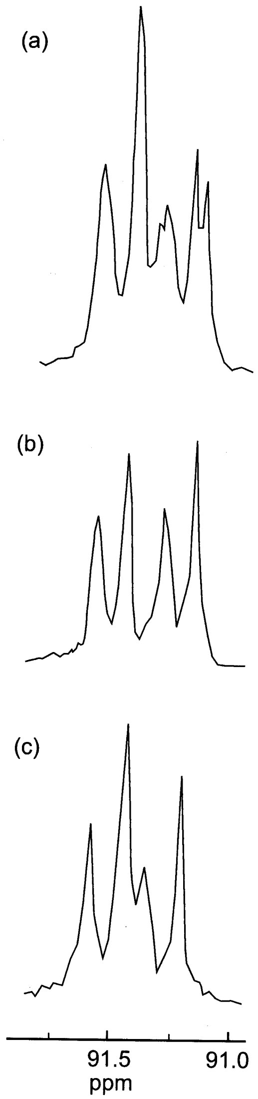


Figure 9. ^{13}C NMR spectra of Si*C*≡C of (a) poly(*diastereo*-**3**), (b) poly(*meso*-**3**), and (c) poly((+)-**3**).

In the ^{13}C NMR spectra, the signal for the ethynylene carbon of poly(*meso*-**3)** not directly adjacent to the silicon atom (SiC≡*C*) was observed at 109 ppm as two peaks. The signal for the ethynylene carbon adjacent to the silicon atom (Si*C*≡C) was observed around 91 ppm, split into four peaks, and gave more information about the structure of the polymers. Analysis of the structures of poly(**3**) was made using the signal of Si*C*≡C.

The signal for the ethynylene carbon attached to the silicon atom should ideally split into eight peaks reflecting the chemical structure, and that for the ene carbon into four peaks, for poly(*meso*-**3**). The chemical shift of the ethynylene carbon (Si*C*≡C) is considered to reflect the structure of consecutive $-R^{1}-C{\equiv}C-Si-Si-R^{2}-$ units (R^1, R^2 = yne or ene shown in Table 1). The ^{13}C NMR spectra of poly(**3**) are shown in Figure 9.

In the spectrum of poly(*meso*-**3**), the signal of the ethynylene carbon with R^1 = yne and R^2 = yne is considered to appear at 91.16 ppm, and that of the ethynylene carbon with R^1 = yne and R^2 = ene at 91.30 ppm. The signals of the ethynylene carbon with R^1 = ene and R^2 = yne will appear at 91.45 ppm, and that of the ethynylene carbon with R^1 = ene and R^2 = ene at 91.57 ppm, respectively. Poly((+)-**3**) also showed four peaks at 91.57, 91.42, 91.34, and 91.19 ppm (Figure 9c). The assignments are similar to those of poly(*meso*-**3**). Atactic poly(*diastereo*-**3**) showed six peaks at 91.42, 91.55, 91.13, 91.17, 91.29, and 91.32 ppm (Figure 9a). The signals are basically overlapped peaks of poly(*meso*-**3**) and poly((+)-**3**). Although complete analysis could not be made, detailed structural analysis of poly(**3**) became possible with the aid of optically active poly((+)-**3**).

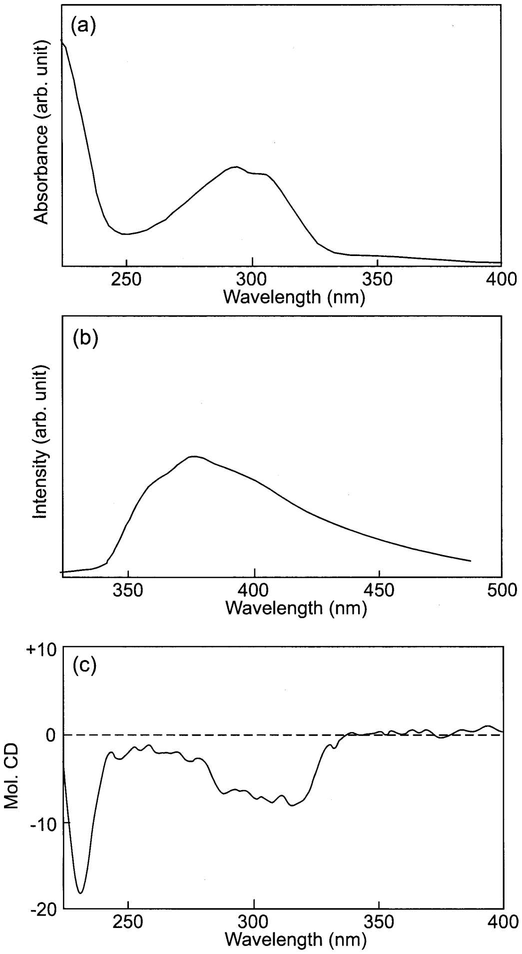


Figure 10. Electronic absorption (a), fluorescence (b), and circular dichroism (c) spectra of poly((−)-**2**) in cyclohexane.

The optical properties of the polymer were investigated. Typical spectra are shown for poly((−)-**2)** in Figure 10. The electronic absorption spectrum showed two absorption maxima at around 300 and 225 nm, which are ascribed to the absorptions of the $\pi-\pi^*$ transition of the pendant naphthyl group and the transition of the $\sigma-\pi$-conjugated backbone system, respectively. In the fluorescence spectrum, a broad peak was observed around 375 nm, when the polymer was excited at 265 nm. These spectra in cyclohexane did not differ remarkably between optically active and racemic polymers. However, negative Cotton effects at both absorption bands were observed in the circular dichroism spectra of optically active polymers, but not for racemic polymers. Recently, we reported that Cotton effects of optically pure oligosilanes having chiral centers on the silicon atoms are well-related to their crystal structures by X-ray analysis.[14] The stereochemistry of the disilane units in poly((−)-**2**) can be assumed an *S*,*S* relationship. The optical properties of the polymer in the solid film state are under study.

Conclusion

Polymerization of optically pure **(−)-1** and **(−)-2** via Heck reaction gave polymers with regular chemical structure, while the polymer from dimerization of **(+)-3** had a mixture of (*E*)-ene−yne, (*E*)-ene−(*E*)-ene, and yne−yne structures.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the polymers from optically pure monomers showed sharper signals compared with those of the polymers from racemic monomers, suggesting that the polymers from optically pure monomers are highly stereoregular. The optically active polymers showed negative Cotton effects in the wavelength region of both the σ-main chain and π-side chain, reflecting their stereochemical structures.

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