Synthesis and Polymerization of an Optically Active Bifunctional Disiloxane. 1. Preparation of Optically Active and Highly Stereoregular Poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] by Polyaddition via Hydrosilylation

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Received March 24, 1998; Revised Manuscript Received June 9, 1998

ABSTRACT: A new optically active (>99% ee) organosilicon compound, 1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane was prepared. This bifunctional disiloxane was used as the monomer to synthesize optically active and isotactic poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] via hydrosilylation in the presence of the platinum−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex. This polymer with the optical activity induced by main chain asymmetric silicon units proved to be optically pure (>99% ee) and highly stereoregular (isotacticity > 99%).

Introduction

Optical activity can be observed only in chiral molecules both in low and high molecular weight compounds.[1] The optical activity of a macromolecule could be induced by its configurational or conformational chirality or by both. Most of the conformation-induced chirality is only stable in the crystalline state or in solution at very low temperature, except in some cases in which the chiral conformations, usually with excessive one-handed sense, can be stabilized by rigid structure[2] or bulky substituents[3] even in solution at room temperature. The optical activity derived from asymmetric configuration of polymer chain is usually extremely low, e.g., isotactic vinyl polymers, because an appreciable contribution to chiroptical properties is conceivable only for asymmetric centers close to the chain ends, the concentration of which decreases with increasing molecular weight. Namely, isotactic vinyl polymers are pseudo-asymmetric, having a mirror plane in the polymer chain, and do not show optical activity. Thus, to prepare polymers capable of displaying intrinsic and appreciable chiroptical properties, one of the methods is to synthesize a polymer consisting of absolutely nonsymmetric optically active sequence (the shortest absolutely nonsymmetric sequence is the hexad: mrmrr). This has not yet been succeeded. A more practical one is to prepare polymers containing optically active stereorepeating unit of the type −A−X*−B− (X*, chiral center; A ≠ B) from optically active monomers via polymerization which proceeds without racemization of the chiral center X* or by stereoselective polymerization of racemic or prochiral monomers using optically active catalysts or initiators. The chiral center X* can be an enantiomeric unit, a diastereomeric unit, or a C_2 symmetric structure, etc. Indeed, a number of optically active polymers were afforded in this way.[1]

Polycarbosiloxanes of the general structure **I** (Figure 1), have attracted most of the attention in past 40 years, because of the favorable combination of good properties of polycarbosilanes and polysiloxanes.[4,5] In the simplest case, when subsituents R^1 and R^2 are different (R^3 = R^4), the silicon atom Si^1 is chiral, which would render the polymer optically active if this silicon atom is of enantiomeric excess. A plausible and efficient route to form this chiral moiety is to polymerize optically active silicon compounds by a highly stereospecific strategy. In comparison to carbon compounds, however, optically active silicon compounds do not exist in nature, and optically active polymers induced by main chain asymmetric silicon atom have not been reported yet, although some optically active silicon-containing polymers with the optical activity derived from asymmetric carbon atoms were prepared.[6,7] Among the limited optically active organosilicon compounds, (*S*)-(1-naphthyl)phenylvinyl-(−)-menthoxysilane ((*S*)-**1**) and its derivatives ≡Si*X[8,9] is of our interest, because they bear two functional groups, vinyl and X, that make them possible to be reacted with some other functional groups and then applied for polymer synthesis (Figure 2).

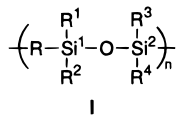

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Figure 1. General structure of a polycarbosiloxane.

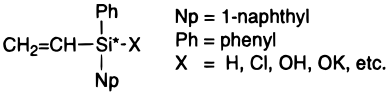


Figure 2. Examples of bifunctional optically active vinylsilanes.[8]

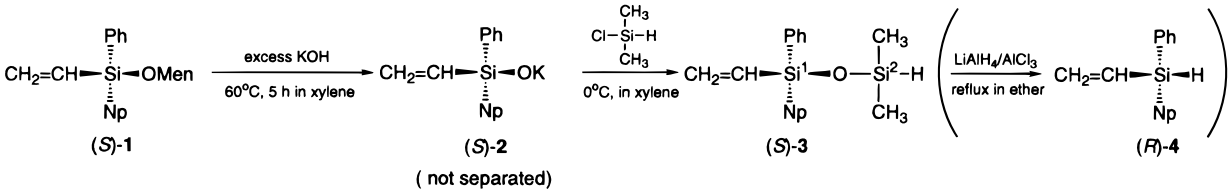
In this paper, we prepared an optically pure (>99% ee) bifunctional (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane ((*S*)-**3**) from (*S*)-**1** and synthesized optically active poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] ((*S*)-**5**), via hydrosilylation[10] of (*S*)-**3**, successfully.

Experimental Section

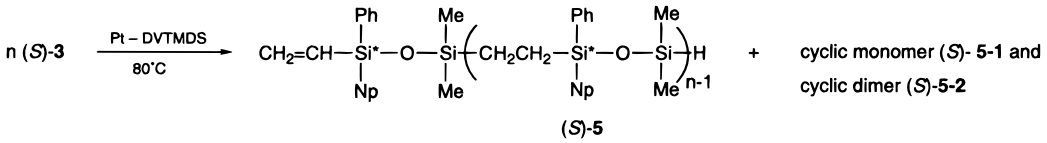
Analytical Methods. The 500 MHz ^{1}H and ^{1}H−^{1}H COSY, 75.3 MHz ^{13}C and ^{1}H−^{13}C COSY, and 79.6 MHz ^{29}Si NMR

S0024-9297(98)00463-X CCC: $15.00
Published on Web 08/01/1998

Scheme 1



Scheme 2



spectra were obtained in $CDCl_3$ on Varian 500 MHz Unity plus, 300 MHz Gemini 2000, and 400 MHz Unity INOVA spectrometers, respectively. Chemical shifts are reported in ppm, relative to $CHCl_3$ (δ 7.26) in ^{1}H NMR, $CDCl_3$ (δ 77.00) in ^{13}C NMR, and tetramethylsilane (δ 0.00) in ^{29}Si NMR. IR spectra were obtained on a JASCO VALOR-III spectrophotometer. Mass spectra were taken on Shimadzu QP-5000 mass spectrometer. Specific optical rotations were measured with a JASCO DIP-370S digital polarimeter. Size exclusion chromatography (SEC) and HPLC analyses 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) with *n*-hexane as an eluent, respectively.

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.[11]

(1*S*)-1-(1-Naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane ((*S*)-3). The synthetic route to monomer (*S*)-**3** is shown in Scheme 1. The starting optically pure (*S*)-(1-naphthyl)phenylvinyl-(−)-menthoxysilane ((*S*)-**1**) (>99% de) was prepared similarly to the literature.[8] $[\alpha]^{25}_D = -41.4°$ (*c* 1.92, pentane) (lit.:[8] $[\alpha]^{25}_D = -43.6°$). Mp: 91−92 °C. (*S*)-**1** (4.14 g, 0.01 mol in 30 mL of xylene) was converted to potassium silanolate (*S*)-**2** by heating with KOH (5.61 g, 0.10 mol) and reacted with dimethylchlorosilane (1.89 g, 0.02 mol). Excessive dimethylchlorosilane and solvent were removed under reduced pressure, and the formed yellowish solid was extracted with dry *n*-hexane. The product was separated by silica gel column chromatography with anhydrous *n*-hexane/CH_2Cl_2 (5/1 v/v) to give a viscous colorless liquid (*S*)-**3** (3.17 g, yield 94.7%). Bp: 127 °C (0.12 mmHg). Purity: 98.0% (by GC). ^{1}H NMR: δ 0.18 (d, 6 H, SiC*H*$_3$, J = 2.8 Hz), 4.86 (sept, 1 H, Si*H*, J = 2.8 Hz), 5.88 (dd, 1 H, vinyl, J_1 = 3.7 Hz, J_2 = 20.1 Hz), 6.24 (dd, 1H, vinyl, J_1 = 3.7 Hz, J_2 = 14.6 Hz,^{1}H), 6.61 (dd, 1 H, vinyl, J_1 = 14.6 Hz, J_2 = 20.1 Hz), 7.40−8.09 (m, 12H, naphthyl and phenyl). ^{13}C NMR: δ 0.64, 125.08, 125.57, 125.77, 127.92, 128.82, 129.02, 129.87, 130.84, 133.41, 133.72, 135.55, 135.92, 135.98, 136.34, 137.02. ^{29}Si NMR: δ −20.29, −3.41. IR (neat): ν 3176−2901, 2128 (ν_{Si-H}), 1591 ($\nu_{Si-CH=CH_2}$), 1252, 1066 (ν_{SiOSi}), 906 ($\delta_{CH=CH_2}$) cm^{-1}. MS: *m*/*e* 333 (M − 1), 319 (M − methyl), 307 (M − vinyl), 257 (M − phenyl), 207 (M − naphthyl). $[\alpha]^{25}_D = 3.7°$ (*c* 1.61, 1,4-dioxane).

Racemic 1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane ((*rac*)-**3**) was prepared from racemic 1-naphthylphenylvinylmethoxysilane ((*rac*)-**1**) by the same procedure described above.

Cleavage of (*S*)-3 by AlH_3 (See Scheme 1). To $AlCl_3$ (0.20 g, 1.5 mmol) dissolved in anhydrous ether (10 mL) in a 30 mL flask was added dropwise the 1 M $LiAlH_4$ ether solution (4.5 mL, 4.5 mmol). After the solution was stirred for 30 min, (*S*)-**3** (0.334 g, 1.0 mmol) was added and the new solution was heated to reflux. ^{1}H NMR analysis showed that 1-naphthylphenylvinylsilane ((*R*)-**4**) was generated and the conversion was about 64% after 8 h.

Poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] ((*S*)-5). Polymer (*S*)-**5** was synthesized according to Scheme 2. In a 5 mL one-necked flask under argon atmosphere, (*S*)-**3** (0.453 g, 1.35 mmol) was heated to 80 °C in the presence of Pt−DVTMDS (6.8×10^{-5} mmol of Pt, 6.8 μL in 0.01 M benzene solution). After the mixture was stirred for 5 h, when the reaction mixture became very viscous, xylene (0.453 g) was added. When there was no more distinct reaction occurring (by analyzing Si−H by IR), the mixture was cooled to room temperature. Removing the solvent gave a colorless to yellowish transparent solid. Reprecipitation from $CHCl_3$ into methanol afforded white polymeric materials (*S*)-**5** (yield: 37.8%). SEC: M_n = 2920, M_w/M_n = 1.57. ^{1}H NMR: −0.33 to 0.05 (br, 6 H, SiC*H*$_3$), 0.30−0.50 (br, 2 H, −CH$_2$C*H*$_2$-Si(CH$_3$)$_2$−), 0.85−1.18 (br, 2 H, −C*H*$_2$CH$_2$Si(CH$_3$)$_2$−), 6.93−8.14 (br, 12 H, naphthyl and phenyl). ^{13}C NMR: δ −0.56, −0.43, 7.72, 9.52, 124.93, 125.37, 125.57, 127.72, 128.70, 128.79, 129.36, 130.35, 133.34, 134.09, 134.64, 134.71, 135.25, 136.92, 137.80. ^{29}Si NMR: δ −23.26 (minor), −10.70 (major), −3.19 (minor), 10.42 (major). IR (neat): ν 3068−2874, 1254, 1066 (ν_{SiOSi}) cm^{-1}. $[\alpha]^{25}_D = 2.6°$ (*c* 1.88, 1,4-dioxane), 2.2° (*c* 1.18, $CHCl_3$).

Atactic poly[{1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] (**5a**) was obtained from (*rac*)-**3**. SEC: M_n = 2400, M_w/M_n = 2.11.

Results and Discussion

Preparation of (*S*)-3 and Determination of Its Optical Purity. Two diastereoisomers of 1-naphthylphenylvinyl-(−)-menthoxysilane, (*S*)-**1** and (*R*)-**1**, were separated successfully by HPLC on an optically active stationary phase shown in Figure 3a, and thus the optical purity of (*S*)-**1** was determined to be more than 99% de (Figure 3b), which was also determined by diastereomeric splitting of methyl protons of the isopropyl group in the menthoxy group in the ^{1}H NMR spectrum.[12] The reaction to prepare the optically active bifunctional monomer (*S*)-**3** (Scheme 1) was held without separating the intermediate (*S*)-**2**. This method not only simplified the procedure but also minimized the possible racemization. (*S*)-**3** is sensitive to water in the presence of acid or base; therefore purification of (*S*)-**3** was done under anhydrous condition or by distillation.

The stereospecificity of the reactions in Scheme 1 is vitally important for obtaining the monomer (*S*)-**3** with high optical purity. According to Sommer,[13] reactions of optically active 1-naphthylphenylmethylalkoxysilane (MePhNpSi*OR) with KOH proceeded with high stereospecificity. Corriu also showed that 1-naphthylphenylvinylsilanol (ViPhNpSi*OH) obtained from (*S*)-**1** by

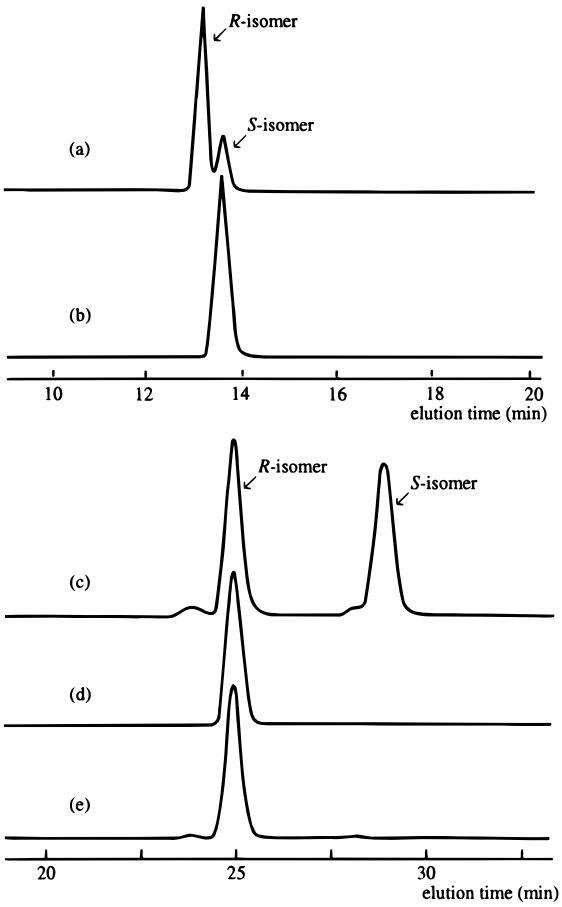
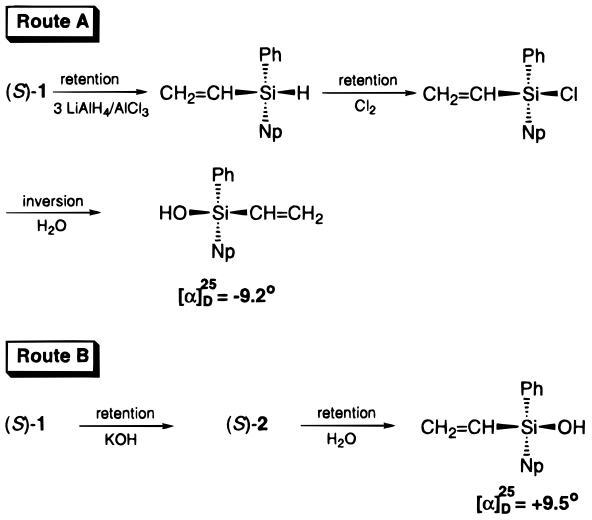


Figure 3. HPLC chromatograms on optically active stationary phase:[a] (a) a mixture of (*R*)-**1** and (*S*)-**1** rich in the *R*-isomer; (b) (*S*)-**1**; (c) (*rac*)-**4**;[b] (d) (*R*)-**4**;[b] (e) (*R*)-**4** from Scheme 1. Footnote key: [a]flow rate 0.6 mL/min, column temperature 35 °C, eluent *n*-hexane; [b]prepared according to the literature.[8]

Scheme 3



route B (in Scheme 3) had a higher optical rotation (+9.5°) than by route A (−9.2°).[8] Every step in route A is confirmed to be highly stereospecific because the reduction of (*S*)-**1** results in 100% retention according to our HPLC analysis of resulting (*R*)-1-naphthylphenylvinylsilane ((*R*)-**4**) (Figure 3d), and the following chlorination and hydrolysis are also reported to be highly stereospecific.[13] Therefore the reaction of (*S*)-**1** with KOH (route B in Scheme 3 and the first step in Scheme 1) must proceed highly stereospecifically. The

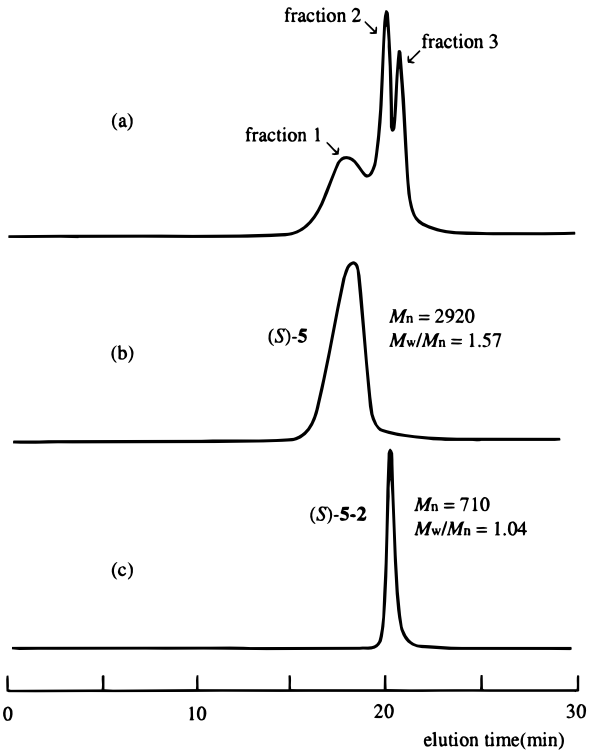


Figure 4. SEC chromatograms of (a) product mixture from Scheme 2, (b) polymer (*S*)-**5**, and (c) cyclic dimer (*S*)-**5**−**2**.

second step in Scheme 1, a nucleophilic reaction of ≡Si*OK ((*S*)-**2**) with Cl*Si*≡, should not change the chirality of the asymmetric silicon atom of (*S*)-**2**. Thus (*S*)-**3** is assumed to be of high optical purity. Attempts to determine the actual optical purity of (*S*)-**3** by HPLC failed. However the optical purity of (*S*)-**3** could be estimated by analyzing the optical purity of reduced product (*R*)-**4** in Scheme 1. Although the reduction of (*S*)-**1** (100% retention) and some other ≡Si*OR was proved to be a high retention procedure,[13] stereochemistry studies on the reduction of optically active disiloxane compounds were seldom reported. The only example of reducing optically active 1,3-bis(1-naphthyl)-1,3-diphenyl-1,3-dimethyl-1,3-disiloxane to 1-naphthylphenylmethylsilane showed an unsatisfactory result (86% retention).[14] Fortunately, HPLC analysis of (*R*)-**4** produced from (*S*)-**3** showed that optical purity of (*R*)-**4** is >99% ee (Figure 3e), which means that (*S*)-**3** must be almost optically pure (>99% ee) and the stereospecificity of reduction of (*S*)-**3** in Scheme 1 is close to 100% retention.

Synthesis of *(S)*-5. The SEC trace of the hydrosilylation product mixture of (*S*)-**3** (Scheme 2) exhibited distinctly three peaks (Figure 4a). Three fractions, after separation, proved to be polymer (*S*)-**5**, cyclic monomer (*S*)-**5**−**1** (26.3%), and cyclic dimer (*S*)-**5**−**2** (35.9%), respectively (detailed characterization of the cyclic compounds will be presented in another paper).

^{1}H, ^{13}C, and ^{29}Si NMR spectra of (*S*)-**5** are shown in Figure 5. Assignment of the signals was made on the basis of ^{1}H−^{1}H and ^{1}H−^{13}C COSY and DEPT NMR analyses. In general, hydrosilylation between ≡Si−CH=CH_2 and ≡Si−H in Scheme 2 may occur in two possible ways: α-addition and *β*-addition, which would result in two kinds of structures of main chain alkylene groups: methylmethylene (≡Si*CH(CH$_3$)*Si≡) and ethylene (≡SiCH_2CH_2Si≡). ^{1}H NMR spectrum (Figure 5a) showed broad and complicated signals because the

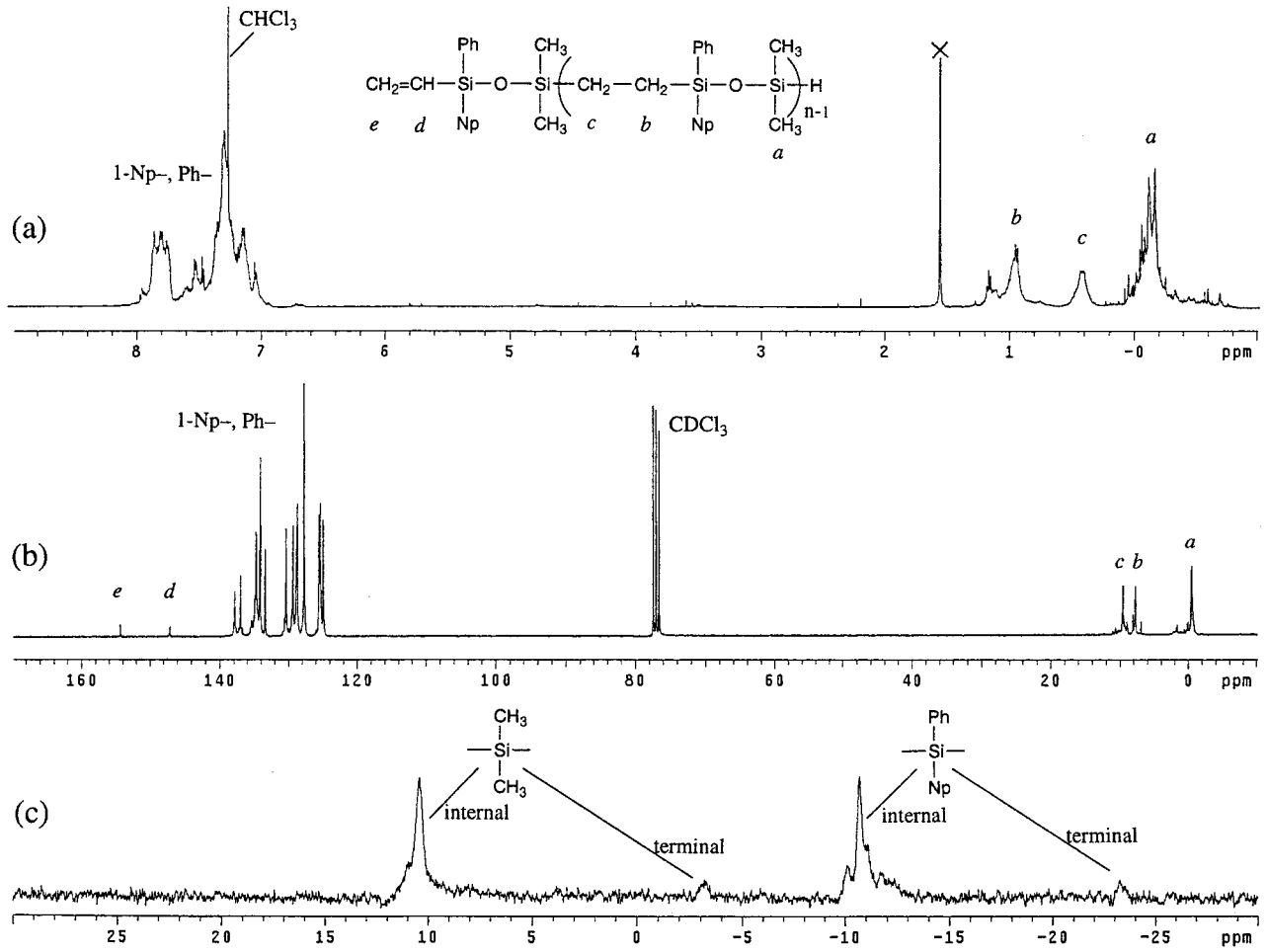


Figure 5. ^{1}H (a), ^{13}C (b), and ^{29}Si (c) NMR spectra of (*S*)-**5**.

molecular weight of this polymer is not high and some cyclic structure may be comprised. Aliphatic protons of $Si(CH_3)_2$ and $-Si^*CH_2CH_2Si-$ appeared as peaks *a*, *b*, and *c*, respectively. The DEPT NMR spectrum of (*S*)-**5** confirmed the above assignment and showed clearly that there was no observable CH carbon in the main chain alkylene region, indicating polymer (*S*)-**5** is formed predominantly in β-addition (>99%). The similar result was reported on the hydrosilylation between 1,3-dihydridotetramethyldioxane (DHTMDS) and 1,3-divinyltetramethyldisiloxane (DVTMDS) in the presence of Pt−DVTMDS catalyst, which gave a polymer with almost β-addition units.[15] Signals at around 1.21 ppm (on the left of peak *b*) are considered to be from the penultimate units or from some cyclic structures. The ^{13}C NMR spectrum (Figure 5b) showed rather clear signals. Peaks at −0.56 and −0.43 ppm are carbon atoms of $Si(CH_3)_2$, while peaks at 7.7 and 9.5 ppm are attributed to the main chain ethylene. Some small signals at 1.65, 6.93, 8.10, 9.02, and 9.68 ppm may have arisen from the above-mentioned reason in ^{1}H NMR. Two small peaks at 147.1 and 154.3 ppm were assigned to the terminal vinyl group on the basis of the $^{1}H-^{13}C$ COSY result. The ^{29}Si NMR spectrum (Figure 5c) exhibited basically four signals which are two internal silicon atoms (−10.7 and 10.4 ppm) and two terminal silicon atoms (−23.3 and −3.2 ppm, close to that of monomer (*S*)-**3**, −20.3 and −3.4 ppm). Some splitting of signals in these NMR spectra is caused probably by small amounts of cyclic structures, on which the details will be discussed in another report.

Optical Activity and Stereoregularity of *(S)*-5. Whether polymer (*S*)-**5** is optically active and stereoregular depends on not only the regiospecificity but also the stereospecificity of the hydrosilylation reaction in Scheme 2. Although no study on the stereochemistry of vinyl-attached asymmetric silicon atom in a hydrosilylation reaction has been reported, according to the generally accepted mechanism[16,17] and our result on allyl-substituted silicon compounds,[12] we can assume that chirality of the asymmetric silicon atom of (*S*)-**3** would not be changed during the hydrosilylation; i.e., (*S*)-**5** should have the same optical purity as that of (*S*)-**3** (>99% ee). Polymer (*S*)-**5** showed optical activity ($[\alpha]^{25}_{D}$ = 2.6° (*c* 1.88, 1,4-dioxane), 2.2° (*c* 1.88, $CHCl_3$)) as expected, which is considered to be induced by the chirality of the asymmetric silicon atom and not by the asymmetric conformation.

To study the stereochemical structure of polymer (*S*)-**5** by NMR analysis, an atactic polymer **5a** was prepared from racemic monomer (*rac*)-**3** for comparison. No appreciable difference was observed in the ^{1}H and ^{29}Si NMR spectra of **5a** and (*S*)-**5**. Their ^{13}C NMR spectra of the $Si(CH_3)_2$ region (Figure 6), however, showed interestingly different splitting patterns. It is clear that atactic **5a** showed three peaks (−0.427, −0.503, and −0.564 ppm), while (*S*)-**5** showed mainly two peaks (−0.427 and −0.564 ppm).

There are four possible types of dyads of this polymer depending on the asymmetric silicon centers: *S*−*S*, *S*−*R*, *R*−*S*, and *R*−*R* (represented in Figure 7a). Two methyl carbons in both *S*−*S* (or *R*−*R*) and *S*−*R* (or

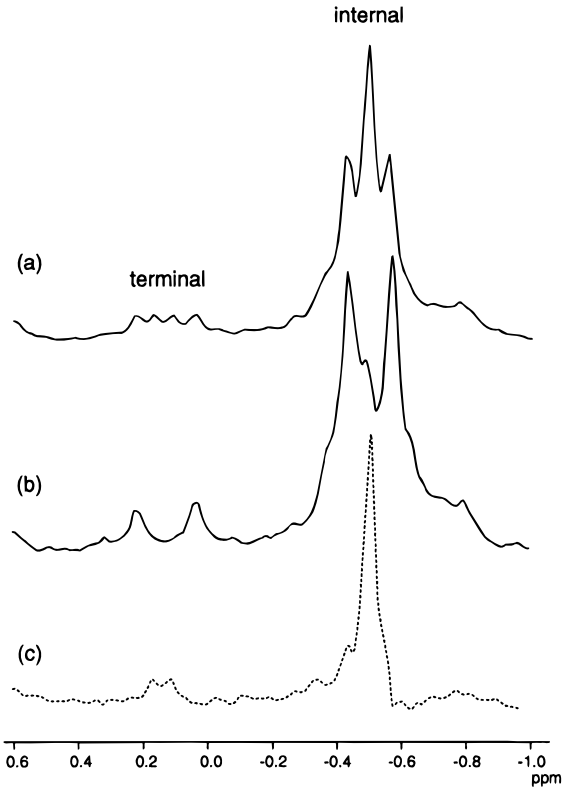


Figure 6. ^{13}C NMR spectra of the $Si(CH_3)_2$ region of (a) atactic **5a**, (b) isotactic (*S*)-**5**, and (c) difference spectrum, 2 × (a) − (b).

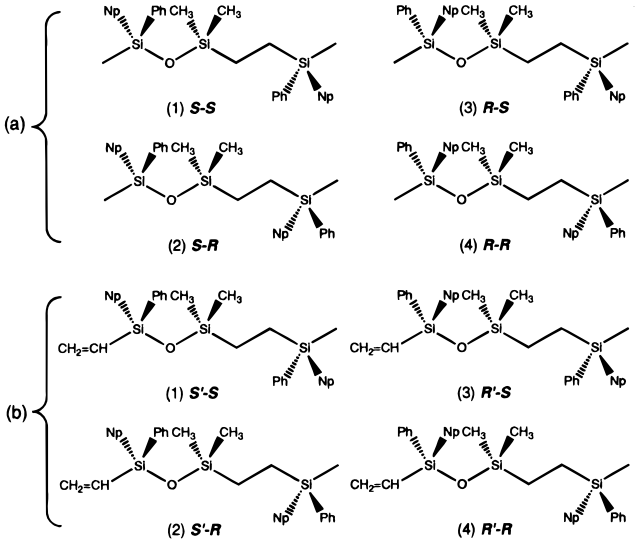


Figure 7. Possible dyads of atactic polymer **5a** of (a) internal dyads and (b) terminal dyads with a vinyl group.

R−*S*) dyad are located in different environments and therefore should have different chemical shifts. Apparently, the difference is big enough in *S*−*S* (or *R*−*R*) dyad to actually give two peaks. On the contrary, in the case of the *S*−*R* (or *R*−*S*) dyad, two methyl groups are in very similar environments, so that their carbon resonance appear at almost same position; i.e., methyl groups of *S*−*R* and *R*−*S* dyads appear as one inseparable peak by 75.3 MHz ^{13}C NMR (see the following discussion on terminal dyads). $Si(CH_3)_2$ in the atactic polymer, therefore, would be split into three peaks (the central peak represents the *S*−*R* and *R*−*S* dyads; two side peaks represent *S*−*S* and *R*−*R* dyads) in the ^{13}C NMR spectrum, with an intensity of 1:2:1. While the isotactic polymer, containing only the *S*−*S* (or *R*−*R*) dyad, would show two peaks of methyl carbons, the syndiotactic polymer would show only one (*S*−*R* and *R*−*S* dyads). (*S*)-**5** showed two distinct peaks of methyl carbons, indicating polymer (*S*)-**5** is highly isotactic. A minor shoulder at −0.486 ppm is seen on the right side of the left peak, which seems to be derived from the *S*−*R* and *R*−*S* dyads, biased from the position of methyl carbons of *S*−*R* and *R*−*S* dyads (−0.503 ppm). A difference spectrum (Figure 6c),[18] processed by subtracting one of (*S*)-**5** (Figure 6b) from two of **5a** (Figure 6a), showed a peak at −0.442 ppm on the left side of the major peak (*S*−*R* and *R*−*S*), which, being at neither the *S*−*S* (or *R*−*R*) dyad position nor the *S*−*R* and *R*−*S* dyads positions, is assumed to be due to the terminal unit (≡SiH terminated), penultimate units, or the cyclic structures.

It is noteworthy that on the left of the major methyl carbon region, there are obviously four peaks in atactic **5a** and two peaks in isotactic (*S*)-**5** (Figure 6a,b). These peaks were assigned most likely to be the terminal $Si(CH_3)_2$ of vinyl terminated chain end (Figure 7b) by examining the integral ratio of these peaks to vinyl peaks (the ratio is close to 1). Two of the methyl groups of terminal *S*′−*S* dyad (or *R*′−*R*) in the isotactic polymer are in different environments and so split into two peaks as explained by the internal units. In the case of the atactic one, in comparison with the internal units, two of the methyl groups of the terminal syndiotactic dyads (*S*′−*R* or *R*′−*S*) seem to be in different environments (e.g., more unsymmetrical) and thus showed totally four peaks together with the two isotactic dyad peaks. The difference spectrum (Figure 6c) of (*S*)-**5** and **5a** actually showed two closer peaks of *S*′−*R* and *R*′−*S*. Above ^{13}C NMR analysis fully proved the complete retention of asymmetric silicon atoms in polymerization. Thus, the high regiospecificity and stereospecificity of hydrosilylation conferred polymer (*S*)-**5** with high optical purity (>99% ee) and stereoregularity (isotacticity > 99%).

The achiral $Si(CH_3)_2$ unit in this polymer can recognize different configurations of both neighboring asymmetric silicon atoms and functions as a "stereochemical probe".

Conclusion

This study showed a convenient way to synthesize poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene]. The intervening $Si(CH_3)_2$ unit worked as a "stereochemical probe" to detect and provide information about the configuration of the main chain, and this polymer was proved to be optically pure (>99% ee) and highly stereoregular (isotacticity > 99%).

Acknowledgment. This work was partially supported by a grant in aid for Scientific Research (08455438), a grant in aid for Scientific Research in Priority Areas, "New Polymers and Their Nano-Organized Systems" (10126222), and a grant in aid for Scientific Research in Priority Areas (10133220) from the Ministry of Education, Science, Sports, and Culture of Japan.

References and Notes

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(18) The difference spectrum was obtained by an interactive add/subtract program named the *addi* program in the Varian NMR spectrometer system. First, a difference spectrum of spectrum a − b was obtained as the usual way by adjusting intensities, phases, and scales of two spectra finely. Then another spectrum a was added to above difference spectrum; thus, a difference spectrum of 2 × (a) − (b) (Figure 7c) was obtained.

MA980463D