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# Articles

## Synthesis of Stereoregular and Optically Active Poly[{methyl(1-naphthyl)silylene}(*o*-phenylene)methylene] by Platinum-Catalyzed Ring-Opening Polymerization

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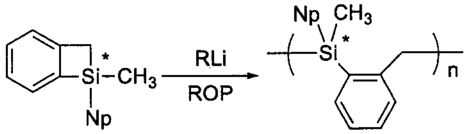
ABSTRACT: Reaction of 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene (**1**) with platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (PDT) as catalyst (0.1 mol %) gave a polymer, possibly cyclic, with $M_n$ = 1 210 000, polydispersity index (PDI) = 1.77, and cyclic dimer produced via a reductive-elimination. Reaction of **1** with PDT in the presence of $Et_3SiH$ (**1**:$Et_3SiH$ = 1:1) gave 1-triethylsilyl-2-{methyl(1-naphthyl)silylmethyl}benzene (**2**), a dimer, 1-{methyl(1-naphthyl)(2′-triethylsilylphenylmethyl)silyl}-2-{methyl(1-naphthyl)silylmethyl}benzene (**3**), and a trimer, 1-{methyl(1-naphthyl)(2′-triethylsilylphenylmethyl)silyl}-2-[methyl(1-naphthyl)[2′-{methyl(1-naphthyl)silylmethylphenyl}]silylmethyl]benzene, in 54, 18, and 11% yield, respectively, through a regioselective ring-opening reaction, followed by the $\sigma$-bond metathesis process. The molecular weight of the formed polymers can be controlled by the amount of $Et_3SiH$. When optically pure **(+)-1** was used, **2** and **3** are proved to have enantiomer excess (ee) or optical purity (op) higher than 99%. These products are considered to be formed from the intermediate cyclic Pt complexes, which were formed by a regio- and stereoselective oxidative-addition of silicon-aryl bond of **(+)-1** to Pt, followed by a stereoselective $\sigma$-bond metathesis process. Pt-catalyzed ring-opening polymerization (ROP) of optically pure **(+)-1** provided an isotactic and optically pure polymer [$M_n$ = 356 000, PDI = 1.73, $[\alpha]^{27}_D$ = −33.5, *c* 1.11, $CHCl_3$].

### Introduction

Polycarbosilanes have various interesting features compared with ordinary hydrocarbon polymers, and potential applications as advanced materials such as ceramics precursors,[1] conductive polymers,[2] thermally stable polymers,[3] and liquid crystalline polymers[4] have been widely investigated. We reported that poly(methylsilylenetrimethylene) with a pendant {3-[(4-cyanobiphenyl-4′-yl)oxy]propyl}dimethylsiloxyl group shows a smectic liquid crystalline phase at room temperature.[5] Thus, ring-opening polymerization (ROP) of strained cyclic carbosilanes is an attractive way to obtain poly(carbosilane)s with well-controlled structures. Since ROP of a silacyclobutane[6] and a silacyclobutene[7] is a chain polymerization, ROP of an optically active silacyclobutane or silacyclobutene may give polymers with well-controlled stereoregularity, molecular weight, and distribution.

Recently we found that attack of an alkyllithium and a silyllithium occurs selectively on silicon and methylene carbon atom of 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene (**1**), respectively, accompanied by selective cleavage of the Si−methylene carbon bond of the ring in both cases.[8] On the basis of these results, we attempted anionic ROP of an optically pure **1** by *n*-butyllithium and methyldiphenylsilyllithium. In fact, formed polymers are optically active but do not have well-controlled stereochemical structures for the backbone (Scheme 1).[9] A better method to control the polymer structure is needed.

**Scheme 1. Anionic ROP of Optically Active 1**



1

**Poly-1**
**optically active, but not stereoregular**

On the other hand, several reports have appeared on transition-metal-catalyzed ROP of the strained cyclic carbosilane using Rh,[10] Pt,[6c,11,12] and Pd.[12] ROP of 1,1-diphenyl-2,3-benzosilacyclobut-2-ene, an analogue of **1**, with Pt complexes at 80 °C was reported by Watt and co-workers.[12] However, details concerning the structure of the obtained polymers and its polymerization mechanism were not reported. Furthermore, a more active catalyst, which works at a lower temperature, is preferable to control the stereoregularity of the polymer.

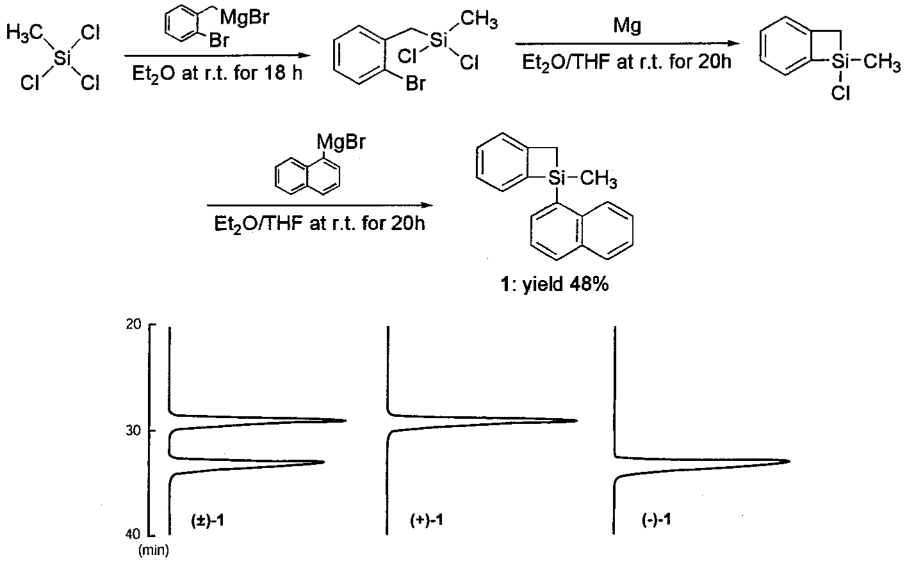
In this paper, regio- and stereochemical features of ring-opening reaction and polymerization behavior of **1** with platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (PDT) was investigated.

### Experimental Section

**Materials.** Solvents were dried by standard procedures and distilled before use. **1** was synthesized from $MeSiCl_3$ via three step reactions as shown in Scheme 2.[13] Optically pure **(+)-** and **(−)-1** were separated on HPLC with a cellulose tris(carbamate) column. PDT was synthesized as described in the literature.[14]

10.1021/ma011763p CCC: $22.00

**Scheme 2. Synthesis of 1 and Optical Separation**



**General Data.** NMR spectra (500 MHz $^1$H, $\delta_{CHCl_3}$ = 7.26 ppm; 125.7 MHz $^{13}$C, $\delta_{CHCl_3}$ = 77.00 ppm; 98 MHz $^{29}$Si, $\delta_{TMS}$ = 0.00 ppm) were obtained on a Varian NMR spectrometer model Unity INOVA, and chemical shifts are given in ppm from the standard. Mass spectra were obtained on a Shimadzu QP-5000. IR spectra were recorded on a JASCO VALOR-III. Optical rotation was measured on a JASCO digital polarimeter DIP-370S. Analytical and preparative size exclusion chromatography (SEC) and HPLC were performed on a JASCO chromatograph, model Gulliver 900. Combinations of Shodex KF-803 (exclusion limit, polystyrene $M_n = 7 \times 10^4$) and KF-804 ($M_n = 4 \times 10^5$) and KF-804 and KF-806L ($M_n = 2 \times 10^7$) styrogel columns were used for molecular weight analysis (0.8 cm $\phi \times$ 30 cm each), and two KF-2001 ($M_n = 1.5 \times 10^3$) and KF-2002 ($M_n = 5 \times 10^3$) for isolation of the products (2 cm $\phi \times$ 30 cm each). THF was used as an eluent at a flow rate of 1 mL/min for analysis and 2 mL/min for isolation of the products. A Daicel cellulose tris(carbamate) column (CHIRALCEL OD) was used for optical purity analysis (0.46 cm $\phi \times$ 25 cm) and optical separation (2 cm $\phi \times$ 25 cm). Hexane was used as an eluent at a flow rate of 0.4 mL/min for analysis and 4 mL/min for separation of stereoisomers.

**Polymerization and Oligomerization of 1 with PDT.** The solution of PDT in toluene was added all at once to **1** dissolved in toluene in the absence or presence of various amounts of Et$_3$SiH at room temperature. Polymerization of **1** (0.290 g, 1.12 mmol) in toluene (1 mL) with PDT (0.01 mol/L, 0.0011 mmol) in the absence of Et$_3$SiH was carried out for 42 h. After the volatile fractions were removed, the residue was dissolved in THF, and precipitated into hexane. The product was purified by reprecipitation into hexane. **Poly-1** (0.147 g) with $M_n$ = 1 210 000 and PDI = 1.77 was isolated as a white solid in a yield of 51%. Optically active polymer was obtained from optically pure **(+)-1** by the same procedure. **(−)-Poly-1** with $M_n$ = 356 000 and PDI = 1.73 was obtained in 45% yield.

**(−)-Poly-1 ([α]$^{28}$$_D$ = −33.5 *c* 1.11, CHCl$_3$).** $^1$H: 7.68−7.60 (br), 7.54−7.46 (br), 7.26−7.18 (br), 7.16−7.10 (br), 7.09−6.97 (br), 6.89−6.76 (br), 6.35−6.29 (br), 2.43−2.27 (br, C*H*$_2$), −0.30 to −0.42 (br, Si−C*H*$_3$) ppm . $^{13}$C: 145.61, 136.47, 135.85, 134.74, 133.28, 130.44, 130.13, 129.40, 128.68, 128.13, 125.55, 127.46, 126.04, 125.83, 124.66, 123.37, 24.20−22.29, −1.39 to −3.31 ppm. $^{29}$Si: −10.53 (CH$_2$−*Si*(CH$_3$)$_3$) ppm. IR (neat): 3053, 2971, 2870, 1588, 1467, 1429, 1259, 1145, 1110, 1068, 980, 826, 794, 776 cm$^{-1}$.[15]

The cyclic dimer of **1** was separated from the soluble fraction by silica gel column chromatography ($R_f$ = 0.05, hexane, 0.016 g).

**Cyclic Dimer of 1.** $^1$H: 8.04 (d, *J* = 7.5 Hz, 2H), 7.82 (m, 4H), 7.45−7.28 (m, 12H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 3.15−2.77 (two d, geminal *J* = 13.8 Hz, 4H), 0.76 (s, 6H)) ppm. $^{13}$C: 145.92, 137.23, 135.72, 135.12, 135.00, 134.73, 133.60, 133.17, 130.29, 129.69, 129.13, 128.12, 125.85, 125.39, 125.24, 124.35, 27.58, 3.13 ppm. $^{29}$Si: −6.98 (cyclic CH$_2$*Si*(CH$_3$)(Np)Ph) ppm. MS (*m*/*e*): 520 (*M*), 393 (*M* (520) − 127(Np)), 297, 245, 215, 185, 167. IR (neat): 3051, 2969, 2891, 2856, 1587, 1562, 1505, 1466, 1433, 1250, 1155, 1105, 810, 775, 746 cm$^{-1}$.

When 1, 2, and 5 mol % of Et$_3$SiH was used, **Poly-1** with $M_n$ = 27 200 and PDI = 2.04, $M_n$ = 18 500 and PDI = 2.43, and $M_n$ = 3810 and PDI = 1.89 were obtained in 48, 52, and 74% yields, respectively.

The reaction of **1** (0.104 g, 0.399 mmol) with PDT (0.01 mol/L, 0.0004 mmol) in the presence of an equivalent amount of Et$_3$SiH (0.0462 g, 0.399 mmol) was carried out for 18 h. **2** (0.0803 g, 0.214 mmol, 54%, $R_f$ = 0.25) was isolated as colorless oil by silica gel column chromatography with hexane as an eluent. Dimer **3** (0.0232 g, 0.0365 mmol, 18%) and trimer (0.0125 g, 0.0140 mmol, 11%) were isolated from the recovered solution by preparative SEC. **(+)-3** was obtained from **(+)-1**.

**2.** $^1$H: 8.08−8.05 (m, 1H), 7.93−7.87 (m, 2H), 7.76−7.73 (m, 1H), 7.51−7.39 (m, 4H), 7.20−7.02 (m, 3H), 4.89 (sext, 1H, $J_{CH_2-SiH}$ = 3.3, 4.5 Hz, $J_{CH_3-SiH}$ = 3.9 Hz, Si-*H*), 2.78−2.60 (two dd, 2H, $J_{CH_2-SiH}$ = 3.3, 4.5 Hz, geminal *J* = 14.4 Hz, C*H*$_2$−Si-(CH$_3$)(Np)H), 0.93−0.80 (m, 15H, C*H*$_3$C*H*$_2$), 0.47 (d, 3H, $J_{CH_3-SiH}$ = 3.9 Hz, Si−C*H*$_3$) ppm. $^{13}$C: 145.79, 137.09, 136.13, 134.59, 134.56, 134.48, 133.38, 130.36, 129.07, 128.90, 127.77, 126.06, 125.68, 125.28, 123.94, 23.64, 7.49, 4.30, −4.94 ppm. $^{29}$Si: 2.76 (Et$_3$*Si*), −15.45 ($J_{Si-H}$ = 192.7 Hz, CH$_2$*Si*(CH$_3$)(Np)H) ppm. MS (*m*/*e*): 376 (M), 347 (M − 29(C$_2$H$_5$)), 285, 260, 245, 215, 185, 171. IR (neat): 3054, 2954, 2910, 2874, 2133, 1587, 1467, 1429, 1254, 1146, 1107, 1023, 1002, 983, 888, 862, 850, 795, 778, 729 cm$^{-1}$.

**(+)-3 ([α]$^{25}$$_D$ = +19.8 *c* 0.82, CHCl$_3$).** $^1$H: 7.94−7.72 (m, 10H), 7.49−7.21 (m, 6H), 7.06−6.95 (m, 5H), 6.57 (m, 1H), 4.32 (sext, 1H, $J_{CH_2-SiH}$ = 3.3, 4.5 Hz, $J_{CH_3-SiH}$ = 3.9 Hz, Si*H*), 3.06−2.96 (two d, 2H, geminal *J* = 14.4 Hz, C*H*$_2$Si(CH$_3$)(Np)Ph), 2.60−2.42 (two dd, 2H, $J_{CH_2-SiH}$ = 3.3, 4.5 Hz, geminal *J* = 14.4 Hz, C*H*$_2$Si(CH$_3$)(Np)H), 0.93−0.88 (m, 6H, CH$_3$C*H*$_2$), 0.84−0.79 (m, 9H, C*H*$_3$CH$_2$), 0.49 (s, 3H, internal SiC*H*$_3$), −0.13 (d, 3H, $J_{CH_3-SiH}$ = 3.9 Hz, Si(C*H*$_3$)H) ppm. $^{13}$C: 146.22, 145.49, 137.12, 136.88, 136.71, 136.02, 135.92, 135.70, 135.55, 134.35, 134.28, 134.19, 133.72, 133.17, 130.30, 130.07, 129.60, 129.46, 129.04, 128.90, 128.50, 128.47, 127.68, 125.88, 125.80, 125.60, 125.54, 125.51, 125.30, 125.10, 124.49, 123.80, 23.49, 23.42, 7.49, 4.37, −2.29, −5.71 ppm. $^{29}$Si: 2.45 (Et$_3$*Si*), −9.78 (CH$_2$*Si*(CH$_3$)(Np)Ph), −14.85 ($J_{Si-H}$ = 192.7 Hz, CH$_2$*Si*(CH$_3$)-(Np)H) ppm. MS (*m*/*e*): 431 (M (636) − 205 (C$_{13}$H$_{21}$Si)), 297, 245, 215, 185, 171. IR (neat): 3054, 2955, 2910, 2874, 2130, 1587, 1467, 1429, 1254, 1146, 1107, 1023, 1002, 983, 887, 862, 852, 827, 795, 777, 730 cm$^{-1}$.[15]

**Table 1. Results of Pt-Catalyzed Polymerization of 1 in the Presence of $Et_3SiH$ in Toluene at Room Temperature**

| entry | [**1**]:[$Et_3SiH$] | time (h) | yield (%) | $M_n$[a] | PDI[a] | $[\alpha]^{28}_D$[b] |
|---|---|---|---|---|---|---|
| 1[c] | 100:0 | 0.7 | 21 | 977 000 | 1.69 | |
| 2[d] | 100:0 | 42 | 51 | 1 210 000 | 1.77 | |
| 3[d] | 100:1 | 42 | 48 | 27 200 | 2.04 | |
| 4[d] | 100:2 | 42 | 52 | 18 500 | 2.43 | |
| 5[d] | 100:5 | 42 | 74 | 3 810 | 1.89 | |
| 6[d,e] | 100:0 | 42 | 45 | 356 000 | 1.73 | −33.5 |

[a] Estimated by SEC (polystyrene standard). [b] $c = 1.11$, ($CHCl_3$). [c] In bulk. [d] 0.2 mol/L. [e] Optically pure (+)-**1** was used.

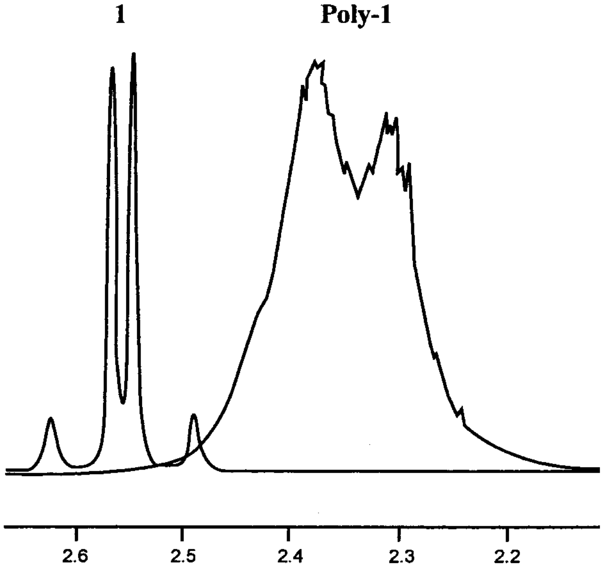


**Figure 1.** $^1H$ NMR spectra of **Poly-1** and **1** in the methylene region.

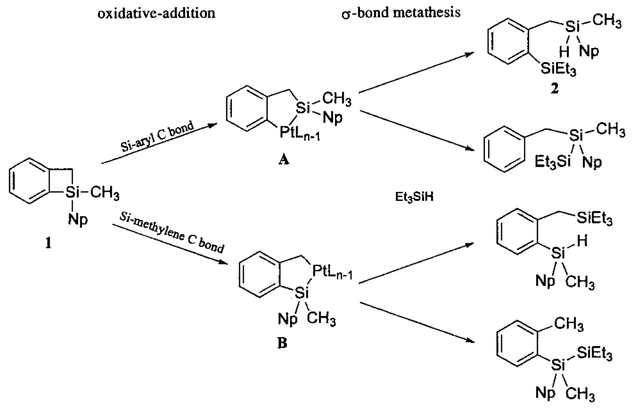
## Results and Discussion

**Polymerization of 1 with PDT.** The results of the polymerization are shown in Table 1.

When a catalytic amount of PDT was added to **1** in the bulk condition, the colorless system changed to pale yellow. Increase in the viscosity of the system was noticed after 15 min, and stirring could not be maintained after 40 min. **Poly-1** was obtained in 21% yield as a white solid. Starting **1** was recovered in 69% together with small amounts of cyclic dimer. $M_n$ and PDI value of **Poly-1** are estimated as 977 000 and 1.69 by SEC analysis. Solution polymerization of **1** in toluene was carried out for 42 h. The yield of **Poly-1**, possessing a monomodal molecular weight distribution with $M_n$ and PDI of 1 210 000 and 1.77, increased to 51%. In the $^1H$ spectra of **Poly-1** shown in Figure 1, signals assignable to methylene protons were observed at around 2.26−2.54 ppm as a little upfield shifted signal compared with **1**. This shift was caused by the disappearance of the strain of the ring of the monomer. In $^{29}Si$ spectra, the only one sharp signal was observed at −10.53 ppm, and assigned to the dialkyldiaryl-substituted silicon atom.[8] This indicates that the repeating unit of the polymer is precisely controlled as to the head-to-tail sequence. The cyclic dimer is considered to be formed by reductive-elimination from the cyclic intermediate shown in Scheme 4. The polymer is also considered to have a cyclic structure, without platinum in the molecule (see later discussion).

In Pt-catalyzed ROP of **1** in the presence of $Et_3SiH$, the molecular weights of the obtained polymers can be controlled by the amount of $Et_3SiH$. Polymerization of **1** in the presence of 1 mol % $Et_3SiH$ resulted in **Poly-1** in the yield of 48% with $M_n$ and PDI of 27 200 and 2.04. In the presence of 2 mol % and 5 mol % $Et_3SiH$, **Poly-1** with $M_n$ and PDI of 18 500 and 2.43 and of 3810 and 1.89 were obtained, respectively. The number-average molecular weight, $M_n$ of these polymers obtained in the presence of $Et_3SiH$ (1, 2, and 5 mol %) is reasonably consistent with the calculated values, 26 100, 13 100, and 5320 from $\{[\mathbf{1}][M_w(260)\text{ of }\mathbf{1}]/[Et_3SiH]\} + [M_w(116)$ of $Et_3SiH]$. These polymers are considered to be linear.

**Scheme 3. Expected Ring-Opened Products**



**Ring-Opening Behavior of 1 with PDT in the Presence of a $Et_3SiH$.** Analysis of ring-opened products provides important information on ROP behavior.[16] When **1** was reacted with PDT in the presence of the $Et_3SiH$ (**1**: $Et_3SiH$ = 1:1), **2**, **3**, and linear trimer were obtained as the products.

Oxidative-addition of **1** to Pt complex could occur at two different positions, namely, the silicon−aryl carbon bond and the silicon−methylene carbon bond. Trapping of this intermediate Pt complex, **A** or **B**, by σ-bond metathesis with $Et_3SiH$ will give four possible ring-opened products as shown in Scheme 3.

Only one product was obtained as the product with molecular weight 376. In the $^1H$ spectrum shown in Figure 2, the signal assigned to $CH_3$-SiH is observed a doublet ($J_{CH_3-SiH} = 3.9$ Hz) at 0.47 ppm. An apparent sextet signal at 4.85, 4.87, 4.88, 4.89, 4.90, and 4.92 ppm indicates the existence of Si-*H* coupled with five protons of methylene and methyl groups ($J_{CH_2-SiH} = 3.3$, 4.5 Hz and $J_{CH_3-SiH} = 3.9$ Hz). Two double doublet signals from 2.60 to 2.78 ppm were assigned to typical benzyl methylene proton, adjacent to the asymmetric silicon atom, coupled with Si−H ($J_{CH_2-SiH} = 3.3$, 4.5 Hz). The $^{29}Si$ spectrum showed a singlet at 2.76 ppm and a doublet ($J_{Si-H} = 192.7$ Hz) at −15.45 ppm indicating the existence of two kinds of silicon atoms in the compounds. The compound contains a *Si*−H function, but not an *Si*−Si function whose chemical shifts appear around −20 ppm.[8] In the IR spectrum, the absorption at 2133 $cm^{-1}$ assignable to Si−H was observed.

On the basis of these results, the product was concluded as **2** containing the structure of $PhCH_2Si(CH_3)(Np)H$.

In the HPLC analysis, two peaks were observed for **2** at retention times 21.7 and 27.4 min.

On the other hand, **2** {**(−)-2**} obtained from optically pure **(+)-1** appeared as only one peak at retention time 27.4 min, and its optical purity was determined as higher than 99%. The spectra of **(−)-2** ($[\alpha]^{25}_D = -16.3$ $c$ 1.26, $CHCl_3$) are same as those of **2**.

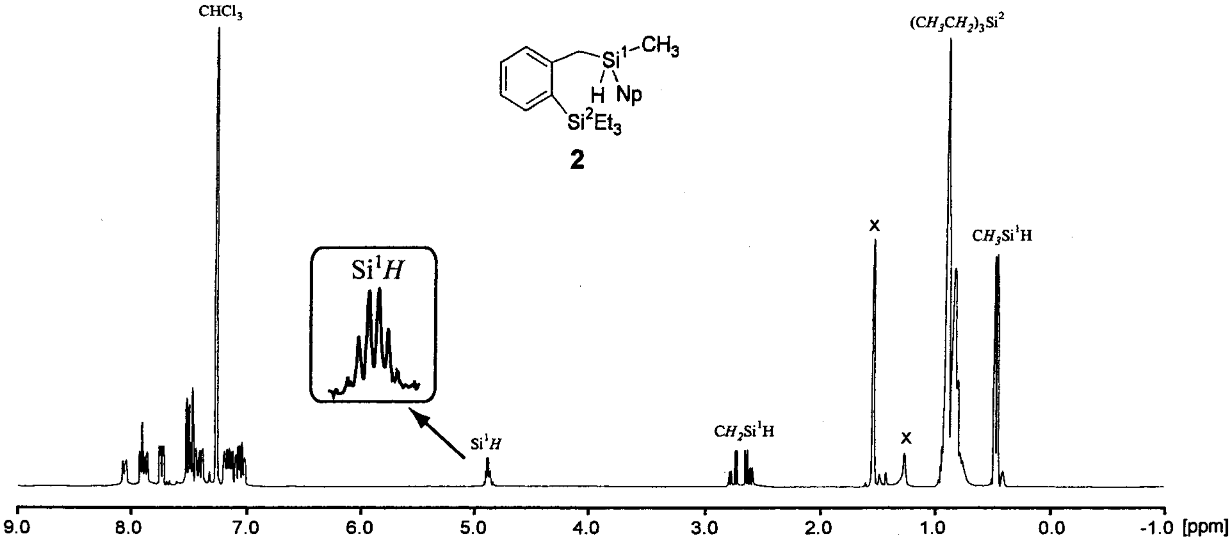
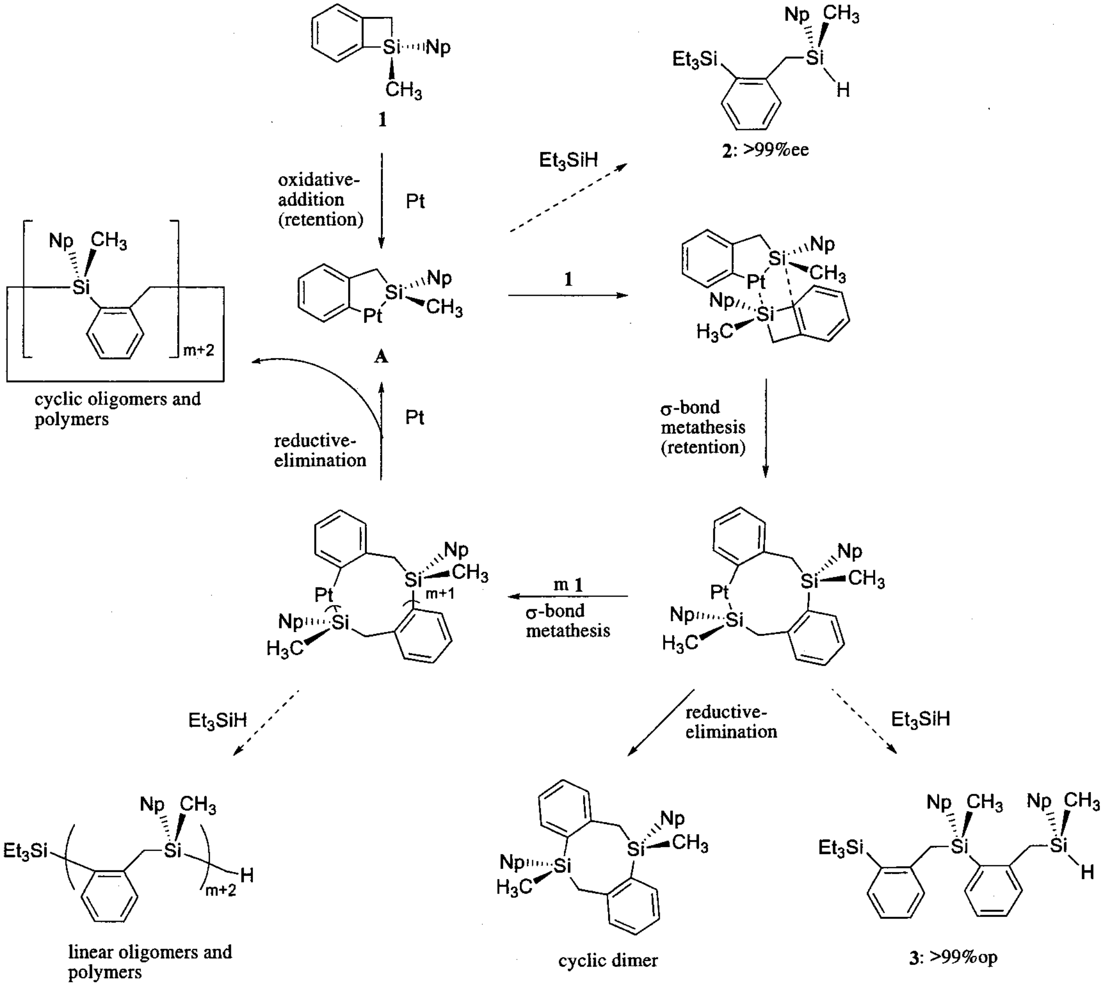


**Figure 2.** $^1$H NMR spectrum of **2**.

**Scheme 4. Possible Polymerization Mechanism of Polymer of 1 with PDT**



It was concluded that the first step of the polymerization is the formation of intermediate Pt complex **A** through regio- and stereoselective oxidative-addition of the Si−aryl carbon bond of the silacyclobutene ring of **1** to Pt, and **2** was obtained via a σ-bond metathesis process between complex **A** and Et$_3$SiH.

When the intermediate complex **A** is reacted further with **1**, ring-opened oligomer will be formed by successive ring opening and σ-bond metathesis process in the presence of Et$_3$SiH. Only one product was obtained as the dimer fraction [*m*/*e*: 431 {*M* (636) − Et$_3$Si(*o*-Ph)CH$_2$ (205)}]. The $^{29}$Si spectrum is same as that of **3**. The $^1$H and $^{13}$C NMR spectra of **(+)-3** reflect the diastereomeric environment of the nuclei.[15] The $^1$H spectrum of the product from optically pure **(+)-1** is shown in Figure 3. The spectrum showed an apparent sextet signal at 4.31, 4.33, 4.34, 4.35, 4.36, and 4.38 ppm assignable to Si-*H* and the two double doublet signals from 2.42 to 2.60

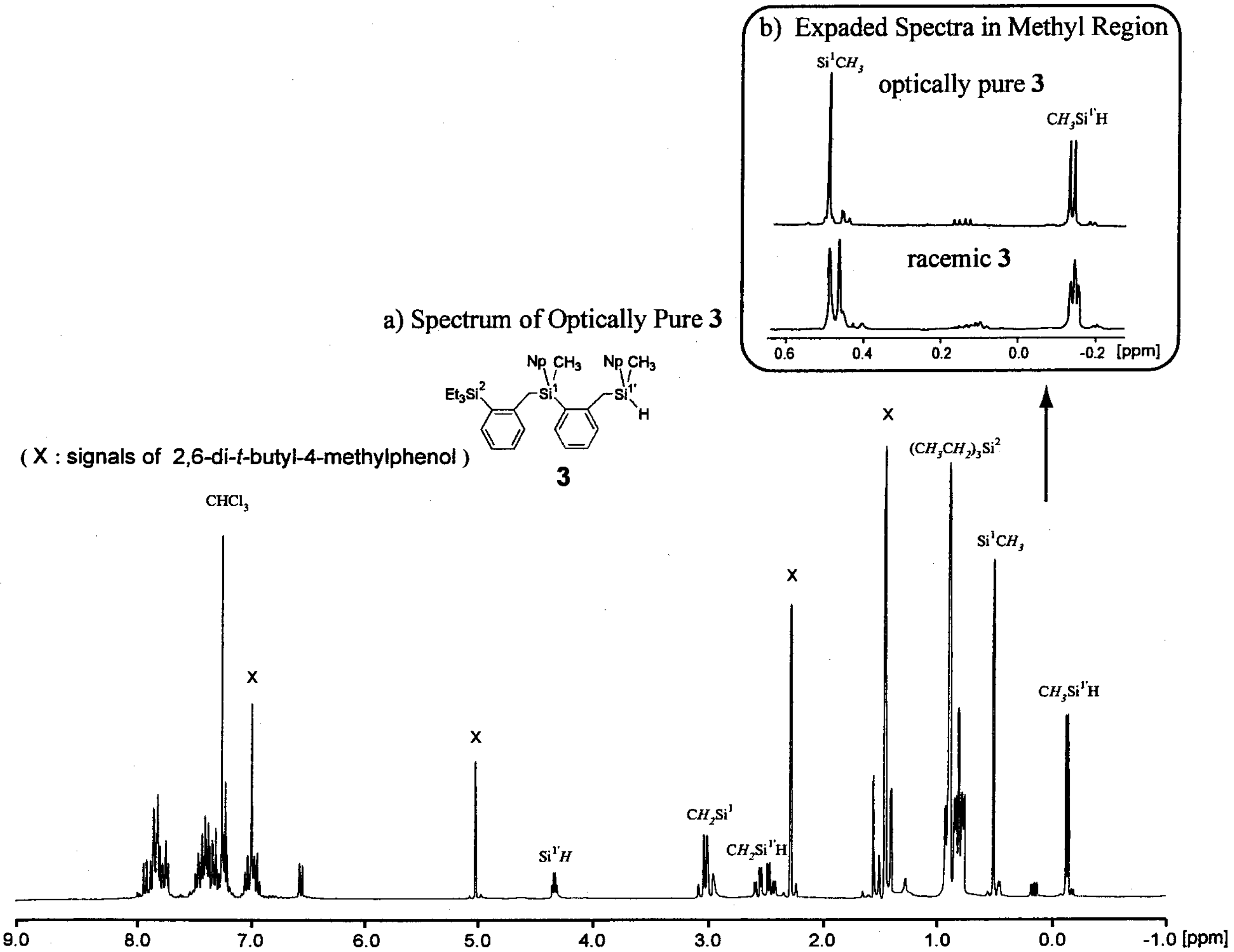


**Figure 3.** $^1$H NMR spectra of (a) optically pure **3** and (b) an expanded methyl region of optically pure **3** and racemic **3**.

ppm assignable to PhC$H_2$Si(CH$_3$)(Np)H similarly with **2**. Further, a new pair of doublet signals from 2.96 to 3.06 ppm with geminal coupling ($J$ = 14.4 Hz) were observed and assigned to methylene group adjacent to the asymmetric silicon atom of PhC$H_2$Si(CH$_3$)(Np)Ph. Relatively large coupling constant supports the existence of two aromatic groups on silicon atom.[8] In the $^{29}$Si spectrum of the product, in addition to the signals at +2.45 and −14.85 ppm indicating the presence of Et$_3$*Si* and PhCH$_2$*Si*(CH$_3$)(Np)H, similarly, in the case of **2**, a new signal at −9.78 ppm assignable to dialkyldiaryl-substituted silicon was observed.[8]

On the basis of these results, the product was identified as **3**. $^1$H spectrum of racemic **3** is more complicated because of the existence of diastereomers. In the spectrum, two singlets at 0.46 and 0.49 ppm of PhCH$_2$Si(C$H_3$)(Np)Ph, and two doublets at −0.15 and −0.13 ppm of PhCH$_2$Si(C$H_3$)(Np)H are observed, a fact, which indicates the occurrence of the diastereomers in the reaction of racemic **1**. Contrary to that only a singlet signal at 0.49 ppm of internal PhCH$_2$Si(C$H_3$)(Np)Ph and a doublet signal at −0.13 ppm of terminal PhCH$_2$Si(C$H_3$)(Np)H were observed for **3** obtained from optically pure **(+)-1**.

Optical purity of **3** was also estimated by HPLC. Contrary to the fact that four peaks were observed at retention times of 45.1, 48.1, 56.6, and 57.7 min in the HPLC chromatogram of racemic **3**, **3** obtained from **(+)-1** showed only one peak at retention time 56.6 min (Figure 4). The optical purity of the optically active **3** is higher than 99%.

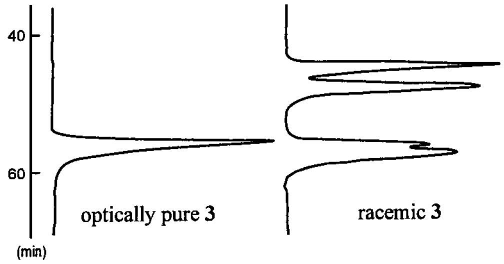


**Figure 4.** HPLC chromatograms of **3**.

It was concluded that **3** was formed through regio- and stereoselective oxidative-addition of **1** to intermediate complex **A**, followed by $\sigma$-bond metathesis of intermediate dimeric cyclic Pt complex with Et$_3$SiH as shown in Scheme 4.

**Reaction Mechanism of Polymerization and Stereochemistry of Polymers.** The Pt-catalyzed ROP mechanism of **(+)-1** was considered to proceed according to the reaction scheme shown in Scheme 4. Oxidative-addition of Si−aryl carbon bond in silacyclobutene ring to Pt gives the optically active intermediate Pt complex **A**. Further coordination of **1** to complex **A** and $\sigma$-bond metathesis will provide the cyclic dimer Pt complex. Pt-catalyzed ROP of **1** seems to proceed via a ring expansion mechanism. Reductive-elimination from the intermediate platinum complex gives cyclic polymers and oligomers. Preference of $\sigma$-bond metathesis over reductive-elimination gives polymers of higher molecular weight. Existence of Et$_3$SiH in the system results in the

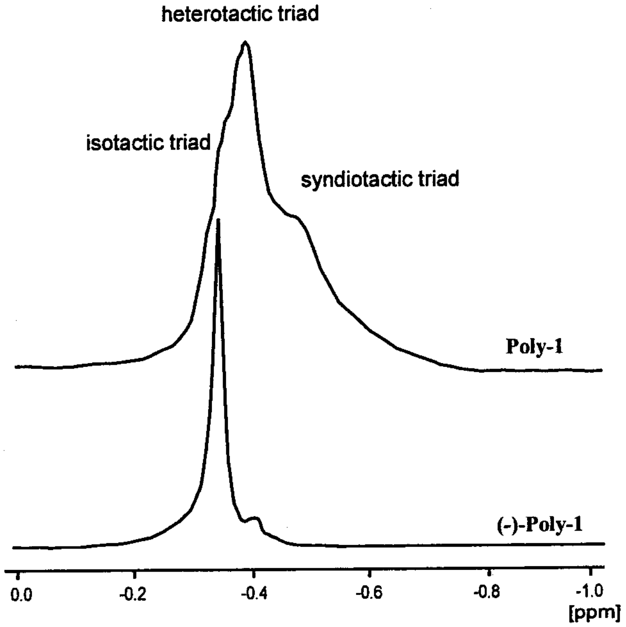


**Figure 5.** $^1$H NMR spectra of polymers in methyl region.

formation of linear products via $\sigma$-bond metathesis. All the reaction proceeds regio- and stereoselectively.

The Pt-catalyzed ROP of optically pure **(+)-1** in the absence of $Et_3SiH$ gave a polymer with monomodal molecular weight distribution with $M_n$ and PDI of 356 000 (lower than the racemic polymer) and 1.73 in 45% yield. The optical rotation of **(−)-Poly-1** is −33.5. $^{29}$Si of **(−)-Poly-1** is same as that of **Poly-1**. The $^1$H and $^{13}$C spectra of **(−)-Poly-1** reflect the diastereomeric environment of the nuclei.[15]

The $^1$H spectrum of **(−)-Poly-1** showed very sharp signals in comparison with **Poly-1** obtained from racemic **1** by the same method. **(−)-Poly-1** showed mainly one signal at −0.34 ppm in methyl region. This signal is considered reasonably assigned to isotactic triad (*I*) signal. The signal at −0.40 ppm should be assigned to heterotactic triad (*H*). Apparently no syndiotactic signal was observed. **Poly-1** from racemic **1** showed the highest peak at −0.40 ppm with two shoulder signals at −0.34 and −0.48 ppm (Figure 5). The signal at −0.48 ppm is reasonably assigned to syndiotactic triad (*S*). Higher order splitting may be included, reflecting pentad regularity.

As reported in our previous paper, the hydrosilylation, which includes the oxidative-addition step of Si−H to transition metal, with Pt complex stereoselectively proceeded via a retention stereochemistry of configuration of asymmetric silicon atom.[17] Regio- and stereoselective oxidative-addition of **1** to the platinum complex will give the optically active intermediate **A**. Following stereoselective $\sigma$-bond metathesis will result in optically active **2** and **3** of high optical purity as shown in Scheme 4. Although $\sigma$-bond metathesis at carbon-Pt bond of intermediate **A** is conceivable, it was reported that $\sigma$-bond metathesis proceeds at silicon-transition metal bond with retention stereoselectivity.[18] Polymers obtained in the absence of $Et_3SiH$ are considered to be cyclic, and those obtained in the presence of $Et_3SiH$, linear. There is almost no difference in NMR spectrum between the polymers obtained in the presence or absence of $Et_3SiH$.

If stereoregularity is determined by successive independent processes, *I*, *H*, and *S* are defined as $(1 + ee^2)^2/4$, $(1 - ee^4)/2$, and $(1 - ee^2)^2/4$, respectively, using ee.[19] Since the ee of **2** is 99%, the ratio of *I*, *H*, and *S* is calculated as 0.98, 0.02, and 0.00, respectively. This result approximately agrees with the observed result ($I$:$H$:$S$ = 0.95:0.05:0.00) by the $^1$H spectrum.

## Summary

Ring-opening polymerization of optically pure 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene, catalyzed by the Pt complex, gives optically pure and isotactic poly[methyl(1-naphthyl)silylene(*o*-phenylene)methylene]. These polymers are considered to be cyclic. In the presence of $Et_3SiH$, linear polymers are formed, from which the molecular weight can be controlled by the amount of $Et_3SiH$.

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**Supporting Information Available:** Text giving analytical data for **Poly-1** and racemic **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) If the stereoselection is controlled by independent ring-opening process of **1**, isotactic diad (*i*) and syndiotactic diad (*s*) are defined as successive independent probabilities, namely, $i = [(+)]^2 + [(-)]^2$ and $s = 2[(+)][(-)]$. When the (−)-configuration is preferred over the (+)-configuration in the polymer backbone, ee is defined as $ee = \{[(-)] - [(+)]\}/\{[(+)] + [(-)]\}$. Since the concentrations of (−) and (+)-isomers can be described as $[(-)] = (1 + ee)/2$ and $[(+)] = (1 - ee)/2$ using ee, *i* and *s* can be written as $i = \{(1 + ee)/2\}^2 + \{(1 - ee)/2\}^2$ and $s = 2\{(1 + ee)/2\}\{(1 - ee)/2\}$, namely, $i = (ee^2 + 1)/2$ and $s = (1 - ee^2)/2$, respectively, and *I*, *H*, and *S* as $(1 + ee^2)^2/4$, $(1 - ee^4)/2$, and $(1 - ee^2)^2/4$, respectively.

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