

Polymerization of 1,1,2-Trimethylsilacyclobutane

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ABSTRACT: Polymerizations of 1,1,2-trimethylsilacyclobutane by phenyllithium and platinum complexes were studied. In polymerization by phenyllithium, the initiation reaction was nucleophilic attack of the carbanion on silicon atom of the silacyclobutane ring proved by the existence of terminal phenyl-silyl linkages in the polymer by ^1H NMR. Ring-opening was regioselective 1,4-. Polymers had reasonable molecular weights calculated from the molar ratio of the monomer to the initiator. Polymers with similar molecular weight were obtained even with small amounts of a platinum complex as catalyst. However, signals assignable to the olefinic protons of the polymer terminal were seen in ^1H NMR. Extensive chain transfer seems to have occurred. Number average molecular weight was estimated by ^1H NMR assuming that the polymer chain has one terminal double bond. The polymers obtained by both methods had head to tail regular structure.

KEY WORDS Silacyclobutane / Ring-Opening Polymerization / Living Polymerization / Regioselectivity / Reaction Mechanism / Chain Transfer / Isomerization /

Silicon-containing polymers have been given much attention, since they exhibit unique properties such as oxygen permeability, semiconductivity, heat-stability.¹ Polycarbosilanes, whose main chain is comprised of carbon and silicon atoms, have been studied mainly as precursors for ceramic materials.² One method to obtain polycarbosilane is the ring-opening polymerization of silacyclobutanes. Until now, there have been considerable reports on the polymerization of 1,1-dimethylsilacyclobutane (DMSB) using platinum complexes^{3–6} or alkyllithiums,^{7–12} although the reaction mechanism of polymerization has not been fully proved. For precision control of the structure of silicon-containing polymers, in addition to molecular weight, it is necessary to control the stereoregularity of the main chain.

Matsumoto reported the living nature of anionic polymerization of DMSB in *n*-hexane–tetrahydrofuran (THF) mixed solvent,¹³ and synthesized a block copolymer of controlled architecture.¹⁴ Although there are many reports on the control of stereochemistry of main chain by ring-opening polymerization of cyclic monomers,¹⁵ like propylene oxide and α -amino acid NCA, there are no reports on the stereoregular polymers containing silicon atoms in the main chain. We have been interested in the control not only of the molecular weight but stereoregularity of silicon-containing polymers, and recently reported the synthesis of stereoregular poly(methylphenylsilylenetrimethylene) by polyaddition of optically active allyl-methylphenylsilane in the presence of platinum catalyst.¹⁶

Stereospecific living ring-opening polymerization of optically active silacyclobutanes is considered suitable to control molecular weight and stereoregularity of polycarbosilanes. To realize this, it is necessary to elucidate not only the living nature of the polymerization but also the stereochemical aspects of the ring-opening of the silacyclobutane ring. Since data on the polymerization of DMSB do not tell anything about the regio- and stereochemical aspects of the ring-opening, a

methyl group was introduced at 2-position of the ring to probe the regioselectivity in the ring-opening. As a preliminary result, we herein report the polymerization of 1,1,2-trimethylsilacyclobutane (TMSB) with alkyllithium or transition metal complex, and elucidation of the structure of the formed polymer.

EXPERIMENTAL

General

^1H and ^{13}C - $\{^1\text{H}\}$ NMR, ^1H - ^1H COSY and DEPT, ^{13}C - ^1H COSY and ^{29}Si NMR spectra were recorded on Varian NMR spectrometers model Gemini 2000 (300 MHz for ^1H , 75.4 MHz for ^{13}C), Unity Plus 500 (500 MHz for ^1H , 125 MHz for ^{13}C), and Unity INOVA 400 (79.5 MHz for ^{29}Si), respectively. Chemical shifts were given in ppm relative to CHCl_3 (7.26 ppm for ^1H , 77.0 ppm for ^{13}C) and tetramethylsilane (0.00 ppm for ^{29}Si) as internal standards in CDCl_3 . Mass spectra (MS) were measured on a SHIMADZU QP-5000 spectrometer. Gas chromatography analysis was made on a Yanaco GLC model G6800. Molecular weights of the polymers were estimated by a JASCO gel permeation chromatograph (GPC) model 980 at 40°C equipped with Shodex KF-800P (precolumn), KF-801 (exclusion molecular weight, polystyrene $M_n = 1.5 \times 10^3$), and KF-804 (exclusion molecular weight, polystyrene $M_n = 4.0 \times 10^5$) columns using THF as an eluent (1 mL min⁻¹). The molecular weight was calibrated using standard polystyrenes.

Synthesis

DMSB and TMSB were synthesized similarly to the reported procedure.¹⁷

A mixture of (1-methyl-2-propenyl)dimethylphenylsilane (**1**) and (2-butenyl)dimethylphenylsilane (**2**, *trans*; **3**, *cis*) as model compounds were synthesized as previously.¹⁸ Three peaks were seen in GC-Mass chromatogram whose fragment patterns were the same. These compounds had the molecular formulae $\text{C}_4\text{H}_7(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}$. **1**:**2**:**3** = 42.3 : 35.0 : 22.7 (estimated by GLC).

Yield: 27%. bp 70–71°C (5 mmHg). The protons of

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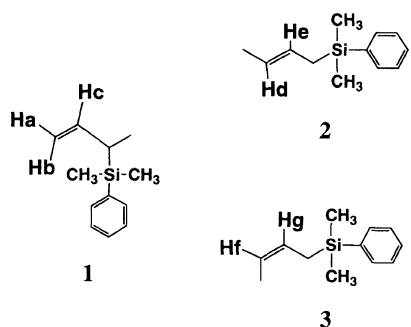


Figure 1. Designation of protons of the model compounds.

the model compounds are indicated in Figure 1.

^1H NMR δ 0.26 (s, 6H \times 0.35, Si(CH₃)₂ of **2**), 0.27 (s, 6H \times 0.42, Si(CH₃)₂ of **1**), 0.28 (s, 6H \times 0.23, Si(CH₃)₂ of **3**), 1.06 (d, 3H \times 0.42, $J = 7.0$ Hz, CH₂ = CHCHCH₃ of **1**), 1.51 (d with fine coupling, 3H \times 0.23, $J = 6.0$ Hz, CH₃CH = CH of **3**), 1.62–1.66 (m, 3H \times 0.35, CH₃CH = CHCH₂ and 2H \times 0.35, CH₃CH = CHCH₂ of **2**), 1.72 (d with fine coupling, 2H \times 0.23, $J = 8.0$ Hz, CH₃CH = CHCH₂ of **3**), 1.86 (m, 1H \times 0.42, CH₂ = CHCHCH₃ of **1**), 4.81 (dt, 1H \times 0.42, $J_1 = 2.0$ Hz, $J_2 = 17.5$ Hz, H_b), 4.87 (dt, 1H \times 0.42, $J_1 = 2.0$ Hz, $J_2 = 10.5$ Hz, H_a), 5.25–5.32 (m, 1H \times 0.35, H_d), 5.35–5.47 (m, 1H \times 0.42, H_e and 2H \times 0.23, H_f, H_g), 5.86 (m, 1H \times 0.23, H_c), 7.34–7.37, 7.50–7.54 (m, 5H, aromatic protons). ^{29}Si NMR δ –4.42 (**2**, 0.35), –3.65 (**3**, 0.23), –2.00 (**1**, 0.42). MS (m/z): 190 (M⁺), 175 (M⁺ – CH₃), 135 (M⁺ – C₄H₇), 113 (M⁺ – C₆H₅).

Reaction of TMSB with Excess Phenyllithium

To a solution of phenyllithium (1.02 M cyclohexane–diethyl ether solution, 11.2 mL, 11.4 mmol) in THF (8.4 mL) was slowly added TMSB (1.09 g, 9.54 mmol) in THF (4.2 mL) for 2 h at –40°C. The reaction mixture was stirred for 2 h at the temperature after addition and stopped with methanol. A volatile main product (bp 86–88°C/8 mmHg) was obtained by distillation under reduced pressure in 45% yield (0.83 g).

^1H NMR δ 0.25 (two s, 6H, Si(CH₃)₂), 0.77 (m, 1H, SiCH), 0.90 (t, 3H, $J = 7.5$ Hz, CH₂CH₃), 0.94 (d, 3H, $J = 7.0$ Hz, CHCH₃), 1.12, 1.55 (m, 2H, CH₃CH₂), 7.33–7.36, 7.49–7.51 (m, 5H, aromatic protons). ^{13}C NMR δ –5.00 (SiCH₃), –4.90 (SiCH₃), 13.32 (CHCH₃ or CH₂CH₃), 13.43 (CHCH₃ or CH₂CH₃), 21.15 (SiCH), 24.48 (CH₃CH₂), 127.66, 128.75, 134.01, 139.05 (four aromatic carbons). ^{29}Si NMR δ –0.30. MS (m/z): 177 (M⁺ – CH₃), 135 (M⁺ – C₄H₉), 115 (M⁺ – C₆H₅).

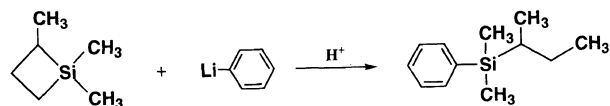
This compound was identified as 1-methylpropyldimethylphenylsilane. By analyzing the reaction mixture using GC–MS, two other products were identified.

2,3,6,6,7-Pentamethyl-2-Phenyl-2,6-Disilanonane. MS (m/z): 291 (M⁺ – CH₃), 249 (M⁺ – C₄H₉), 229 (M⁺ – C₆H₅), 135 (M⁺ – C₄H₈Si(CH₃)₂C₄H₉).

2,3,6,6,7,10,10,11-Octamethyl-2-Phenyl-2,6,10-Trisilatridecane. MS (m/z): 405 (M⁺ – CH₃), 363 (M⁺ – C₄H₉), 249 (M⁺ – C₄H₈Si(CH₃)₂C₄H₉).

Polymerization of TMSB

By Phenyllithium. To cyclohexane–diethyl ether solution of phenyllithium (0.91 M, 0.38 mL, 0.35 mmol) in



Scheme 1. Initiation reaction of TMSB by phenyllithium.

THF (2.2 mL), TMSB (0.80 g, 7.00 mmol) was added at –40°C under argon atmosphere, and the stirring was commenced. After 1 h, the reaction was quenched with 1 N–HCl (5 mL), and extracted with chloroform (15 mL \times 3). Polymer was obtained from chloroform solution by removing volatile materials under reduced pressure. Yield: 0.75 g (94%).

^1H NMR δ –0.08, –0.07 (two s, 6H, each H_E), 0.34, 0.73 (two m, 2H, each H_A), 0.55 (m, 1H, H_C), 0.92 (d, 3H, $J = 7.2$ Hz, H_D), 1.08, 1.50 (two m, 2H, each H_B), 7.33 (m, 3 \times 0.05H, H_O, H_P), 7.48 (m, 2 \times 0.05H, H_m). ^{13}C NMR δ –5.08, –5.02 (each C_E), 12.91 (C_A), 13.63 (C_D), 22.26 and 22.31 (C_C), 25.91 (C_B), 127.66 (C_m), 128.73 (C_p), 133.98 (C_o), 139.09 (C_i). ^{29}Si NMR δ 4.86.

The assignments were made based on the data by DEPT, ^{13}C – ^1H COSY, ^1H – ^1H COSY spectra. In ^1H NMR of the polymer, extra weak singlet at 0.25 ppm and multiplets at 7.33 and 7.44 ppm were observed. The peaks were assignable to terminal Si(CH₃)₂ and Ph protons of initiated terminal [PhSi(CH₃)₂–], respectively.

By 1,3-Divinyl-Tetramethyldisiloxaneplatinum(0) (Pt-DVTMDS). To TMSB (0.60 g, 5.25 mmol), a toluene solution of PtDVTMDS (0.01 M, 0.02 mL, [M]/[cat] = 3.0 \times 10⁴)¹⁶ was added at 80°C, and stirred for a given time. The resulting reaction system was dissolved in small amounts of THF and poured into large excess methanol to precipitate the polymer. Yield: 0.55 g (91%).

In ^1H NMR of the polymer, instead of Si(CH₃)₂ and phenyl protons of initiated terminal [PhSi(CH₃)₂–] in anionically obtained polymer, multiplet signals at 5.2–6.2 ppm assignable to olefin proton (2 \times 0.04H), were observed besides the assignable peaks.

RESULTS AND DISCUSSION

Polymerization of TMSB by Phenyllithium

The reaction of TMSB and phenyllithium in 1:1.2 molar ratio gave 1-methylpropyldimethylphenylsilane, indicating that phenyllithium attacked the silicon atom of TMSB followed by 1,4-opening in the initiation reaction (Scheme 1).

Three compounds were founded in GC–MS of the volatile components of the reaction mixture in 78.1:19.0:2.9 ratio (Figure 2).

The presence of 2,3,6,6,7-pentamethyl-2-phenyl-2,6-disilanonane (dimer) and 2,3,6,6,7,10,10,11-octamethyl-2-phenyl-2,6,10-trisilatridecane (trimer) suggests that the propagation reaction is faster than the initiation reaction in THF.

The number average molecular weight, M_n , of the polymer obtained by phenyllithium was 3.3 \times 10³ ($M_w/M_n = 2.7$, [M]/[I] = 20, $M_{\text{calc}} = 2.4 \times 10^3$) by GPC analysis. When using *n*-butyllithium or methyllithium, polymers with $M_n = 3.0 \times 10^3$ ([M]/[I] = 20) and reason-

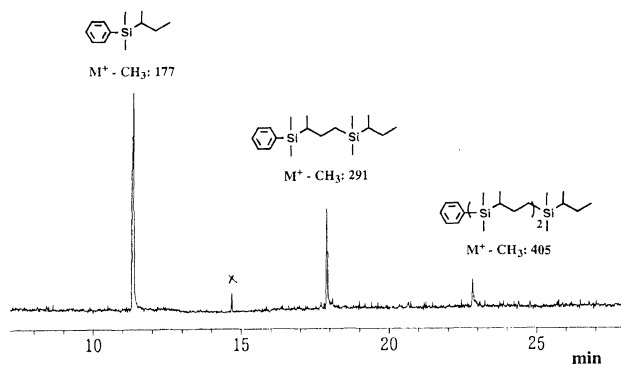


Figure 2. GC-MS chromatogram of the volatile components in the reaction of TMSB with phenyllithium in 1.0:1.2 molar ratio.

ably narrower molecular weight distribution ($M_w/M_n = 1.4\text{--}2.0$) were obtained. In contrast to hexane-THF mixed solvent suggested by Matsumoto,^{13,14} our polymerization solvent, pure THF, gave polymers of rather wide molecular weight distribution.

^1H and ^{13}C NMR spectra of the polymer are shown in Figure 3.

All major signals were assigned to the protons or carbons in the repeating unit, and supported by DEPT, $^1\text{H}\text{--}^1\text{H}$ COSY, $^{13}\text{C}\text{--}^1\text{H}$ COSY spectra. The DEPT spectrum of the polymer indicated that two CH_3 carbons (C_D , C_E), two CH_2 carbons (C_A , C_B) and one CH carbon (C_C) were present in the repeating unit of the polymer. Only one sharp peak is seen at around 5.0 ppm in the ^{29}Si spectrum. Based on these data, it was concluded that polymerization of TMSB by phenyllithium gave head to tail regular structure. In ^1H NMR of the polymer, the initiator fragment phenyl group was proved to be attached to the silicon atom of the polymer terminal. The degree of polymerization calculated from the ratio of phenyl proton and SiCH_3 proton in the repeating unit was 20.2. The initiator efficiency was 99% from the ratio of $[\text{M}]/[\text{I}]$ and M_n estimated by ^1H NMR.

The correlated proton and carbon chemical shifts in the $^{13}\text{C}\text{--}^1\text{H}$ COSY spectrum are: $^1\text{H} - 0.08$ and -0.07 ; $^{13}\text{C} - 5.08$ and -5.02 (SiCH_3), $^1\text{H} 0.34$ and 0.73 ; $^{13}\text{C} 12.91$ (SiCH_2), $^1\text{H} 0.55$; $^{13}\text{C} 22.26$ and 22.31 (SiCH), $^1\text{H} 0.92$; $^{13}\text{C} 13.63$ (CHCH_3), $^1\text{H} 1.08$ and 1.50 ; $^{13}\text{C} 25.91$ (SiCH_2CH_2).

According to the enlarged spectra, the SiCH_3 protons (H_E) and carbons (C_E) are split into two singlets. The two CH_2 protons of the repeating unit (H_A and H_B) are also split into two multiplets. There is the possibility that the splittings are caused by diad tacticity. However, if such splitting is caused by diad tacticity, the only one pair of signals for each repeating methylene protons strongly suggests the polymer being isotactic, which should not be the case for the polymerization of racemic monomer. These splittings are considered enantiotopic by the presence of neighboring asymmetric center (C_C). The SiCHCH_3 carbon (C_C) also split into two singlets of equal intensity. This splitting might be caused by triad tacticity, but details are not clear at present, since this carbon should split into three singlets instead of two, if this carbon reflects the triad tacticity.

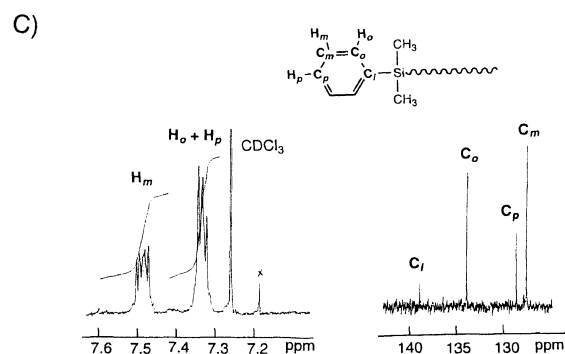
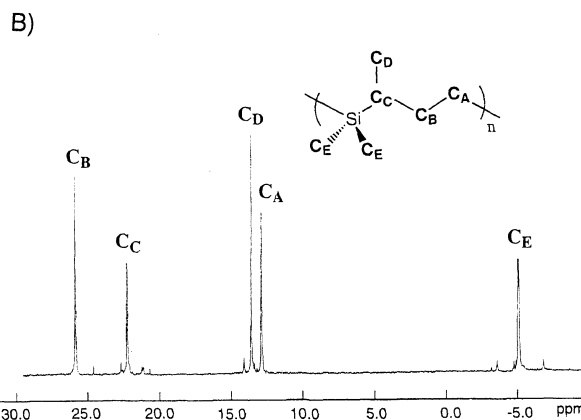
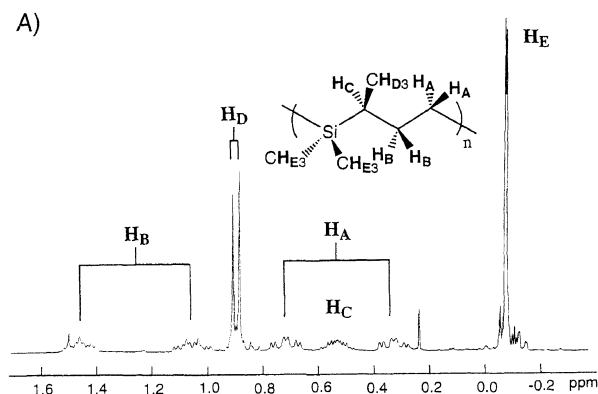


Figure 3. NMR spectra of poly(TMSB) produced by phenyllithium, A) ^1H , main chain; B) ^{13}C , main chain; C) ^1H and ^{13}C , terminal aromatic region (at room temperature in CDCl_3 ; ^1H , 300 MHz; ^{13}C , 75.4 MHz).

Polymerization by Transition Metal Complex

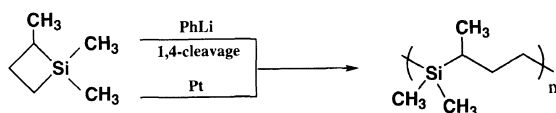
The results of polymerization of dimethylsilacyclobutane derivatives using transition metal complexes are summarized in Table I.

The fate of the monomer was followed by ^1H NMR for determination of conversion. The number average molecular weights of the polymer were $3.7\text{--}4.7 \times 10^3$ ($M_w/M_n = 1.5\text{--}1.6$). The polymerization of DMSB using platinum complex gives high molecular weight polymer,¹⁹ for example, $M_n = 1.1 \times 10^5$ with PtDVTMDS which were also included in the Table. In contrast to the polymerization of DMSB, lower molecular weight materials were formed in the polymerization of TMSB. This suggests the existence of chain transfer reaction, although, molecular weight distribution is reasonably narrow. The rhodium complex did not show activity even

Table I. Polymerization of silacyclobutanes by transition metal catalysts^a

Run	Monomer	Cat	Conv./% ^b	$M_n^c/10^3$	M_w/M_n^c	$M_{n,NMR}^b/10^3$	Yield/%
1	TMSB	PtDVTMDS	Quant.	3.7	1.5	2.8	91
2		PtDVTMDS ^d	0	—	—	—	—
3		H ₂ PtCl ₆	Quant.	4.7	1.6	3.3	95
4	DMSB	Ph(PPh ₃) ₃ Cl	0	—	—	—	—
5		PtDVTMDS ^c	Quant.	110	1.3	—	94

^a In bulk, for 17 h, at 80°C, [M]/[Cat]=3.0 × 10⁴. ^b Estimated by ¹H NMR. ^c Estimated by GPC using standard polystyrene. ^d At room temperature. ^e In toluene, [M]=5.0 M, for 30 min.



Scheme 2. Head to tail regular structure of poly(TMSB) by phenyllithium and Pt complex.

at 80°C.

The major peaks of ²⁹Si, ¹³C, ¹H NMR spectra were the same as those of the polymers obtained by phenyllithium. The polymers obtained by two different procedures had the same head to tail regular structure (Scheme 2).

In the ¹H NMR spectrum, multiplets at 5.20–5.85 ppm assignable to the olefin protons were seen (Figure 4B). The olefinic protons consisted of basically three protons reflecting the structure at 5.21–5.46, 5.52–5.53 (two singlets), and 5.56–5.86 ppm in the ratio of 63.4:2.6:18.0. To elucidate the origin and structures of the double bonds formed by platinum complexes, which must have strong correlation with the reaction mechanism, the structures of the double bonds were studied by comparison with model compounds.

The majority of the olefinic protons of the polymer terminal appeared at quite similar positions with inner olefinic protons of the model compounds (2, 3) (Figure 4A) at 5.21–5.46 ppm. These olefinic protons are considered to be the inner type 6 in Scheme 3 (two protons). The singlets at 5.52 and 5.55 are tentatively assigned to olefinic proton of *cis* and *trans* form of the terminal type 5 (one proton each). The signals at 5.57 and 5.93 (*J*=18.0 Hz), and multiplets at 5.71–5.86 are assignable to terminal vinyl protons of the type 4.

The polymer by anionic procedure did not show such signals. The presence of the inner olefinic signals suggests that these olefinic bonds were formed by chain transfer reaction in the polymerization through the β-elimination of the propagating end, and that isomerization of the terminal olefin to inner olefin might have occurred.

Lappert reported that the reaction of TMSB with [Fe₂(CO)₉] gave 1-ferro-1,1,1,1-tetracarbonyl-2,2,3-trimethyl-2-silacyclopentane by steric hindrance.²⁰ Tanaka reported that the polymerization of silacyclobutane proceeded through 1-platina-2-silacyclopentane intermediate.¹⁹ Although it is not clear which bond of 1,2- or 1,4- is cleaved in the polymerization of TMSB by platinum catalyst, the silacyclobutane ring must open at 1,2- or 1,4-bond selectively to give head-tail controlled polymer structure. It may be reasonable to assume 1-platina-2,2,3-trimethyl-2-silacyclopentane is formed as the intermediate which gives growing end through

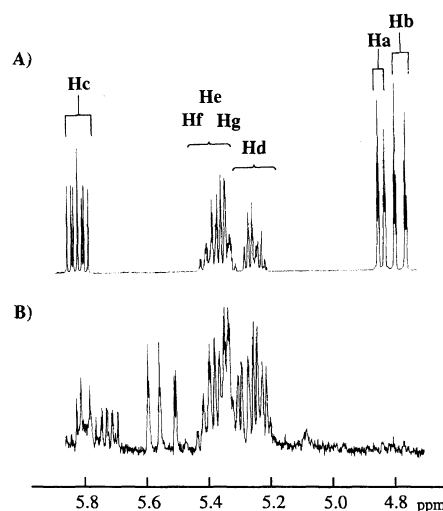


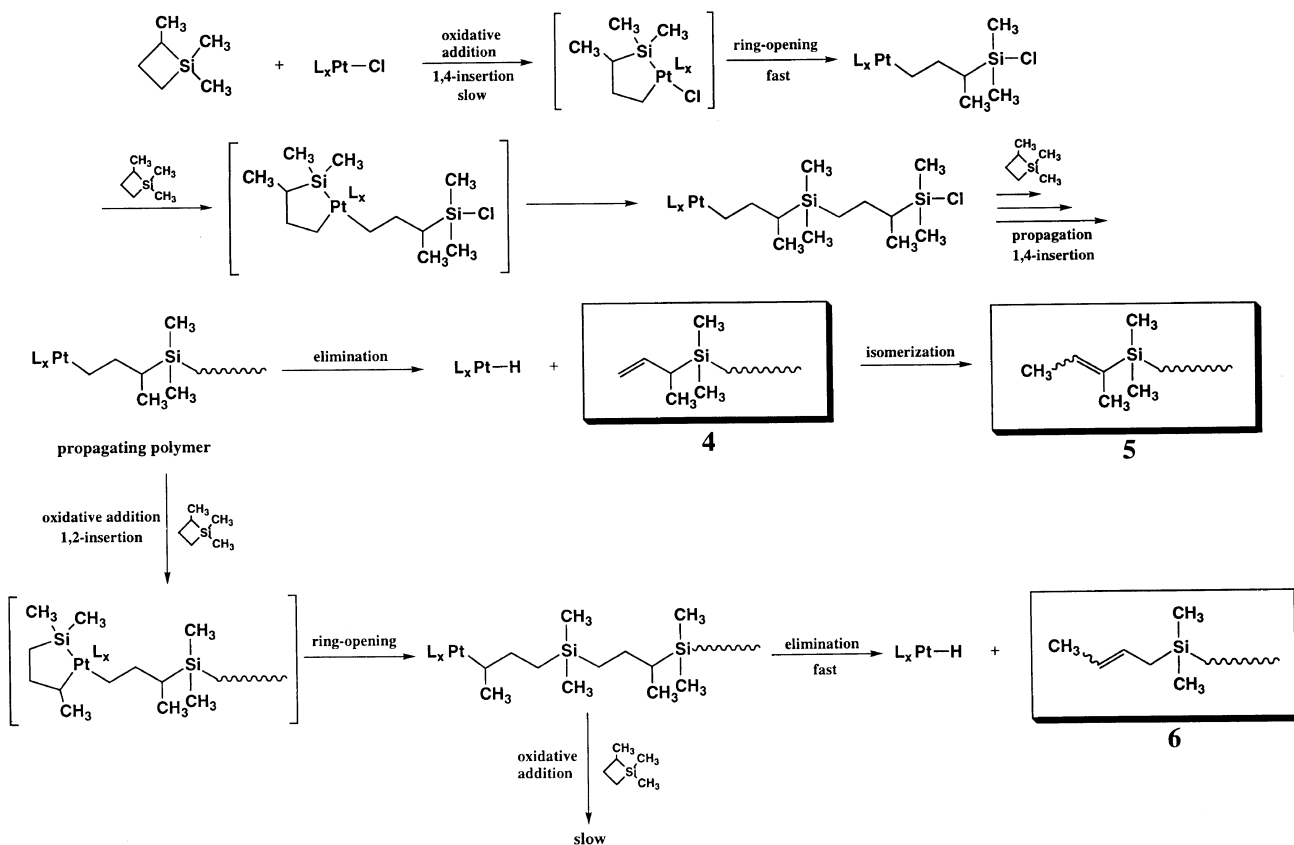
Figure 4. Olefinic region of ¹H NMR spectra A) mixture of 1, 2, and 3, B) poly(TMSB) by H₂PtCl₆ (500 MHz, at room temperature in CDCl₃).

1,4-cleavage of the ring. The polymerization is considered to proceed according to following mechanism: 1) oxidative addition of TMSB to the Pt complex to form platinasilacyclopentane ring (slow), followed by ring-opening (fast) (initiation reaction), 2) repeated formation of platinasilacyclopentane ring and ring-opening (propagation reaction), 3) elimination of platinum hydride (chain transfer reaction) to give the structures 4 and 6. Isomerization from 4 to 5 may occur thermally and catalytically. When the insertion of TMSB to the growing end occurs in the 1,2-mode, the formed propagating end might be less reactive than that formed *via* 1,4-addition because of the steric factor, and elimination of platinum hydride which gives inner olefinic terminal 6 might be preferred over propagation reaction. The major chain transfer reaction may occur by this reaction path, and the butenyl terminal would be produced mainly in the polymer.

From the ratio of terminal olefinic protons (2H for 6, 1H for 5, and 3H for 4) and Si(CH₃)₂ (6H), the degree of polymerization was estimated (Table I). Number average molecular weights estimated by ¹H NMR were considerably smaller (25–30%) than by GPC.

CONCLUSIONS

Polymerizations of TMSB were carried out with phenyllithium and Pt complexes. Polymers had controlled head to tail structure. 1,4-Bond of the monomer was selectively cleaved in the anionic polymerization by phenyllithium. In polymerization by Pt complexes,



Scheme 3. Polymerization mechanism by the Pt complex.

propagation reaction is the selective oxidative addition of the monomer to the Pt complex in either 1,2- or 1,4-bond. Frequent chain transfer reaction occurred through 1,2-insertion to give 2-butenyl terminal.

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