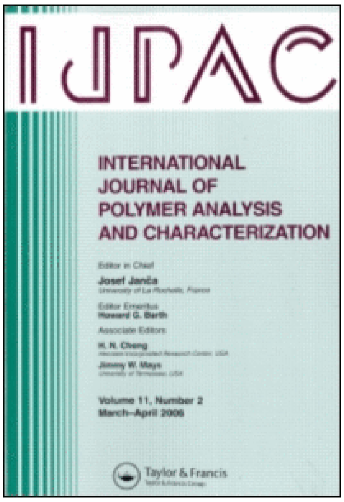

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Yusuke Kawakami[a]; Ichiro Imae[a]
[a] Graduate School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), Ishikawa, Japan

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Analysis of Terminal Group and Stereochemistry of Silicon-Containing Compounds and Polymers by NMR

YUSUKE KAWAKAMI* and ICHIRO IMAE

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

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^{1}H, ^{13}C and ^{29}Si NMR spectroscopy was used to study the terminal structures, stereoregularity, and optical activity of silicon-containing polymers. In the ring-opening polymerization of 1,1,2-trimethylsilacyclobutane using a platinum catalyst, extensive chain transfer reactions occurred. The five-membered cyclic carbosiloxane could be easily polymerized by phenyllithium to give a high-molecular-weight polymer through regioselective ring-opening. Polymerization of optically active allylsilane, vinylsiloxane, and cyclic carbosiloxane gave highly isotactic poly(carbosilane) and poly(carbosiloxane).

Keywords: NMR; Poly(carbosiloxane); Poly(carbosilane);
Ring-opening polymerization; Tacticity

INTRODUCTION

The increasing interests in recent years in silicon-containing polymers as electronic and optical materials, ceramics precursors, and other applications[1] have spurred the development of silicon-containing polymers with well-controlled molecular weights and molecular weight distributions, as well as well-controlled microstructures.[2,3] Weber,[4] Interrante,[5] and Bacqué[6] reported the evaluation of the tacticity of

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* Corresponding author.

poly(silylenemethylene) such as poly(ethoxymethylsilylenemethylene) by ^{1}H NMR at 500 MHz (^{13}C NMR at 125.7 MHz), but definite identification was not made. Rinaldi[7] evaluated the stereoregularity of poly(hydrophenylsilylenetrimethylene) by ^{1}H/^{13}C/^{29}Si triple-resonance 3D-NMR at 600 MHz and pulse field gradient technique. However, only limited information has been obtained so far on the stereoregularity of these polymers. The stereospecific ring-opening polymerization (ROP) of cyclic silicon compounds[8] is the most promising method to obtain these polymers.[9] Nevertheless, it is not easy to perform such polymerizations. It is useful to have practical methods to prepare polymers capable of displaying intrinsic and appreciable chiroptical properties. One possible way is to prepare polymers containing optically active stereorepeating unit of the type $-A-X^*-B-$ (X^* = chiral center; $A \neq B$) from optically active monomers via polymerization which proceeds without racemization of the chiral center X^*.

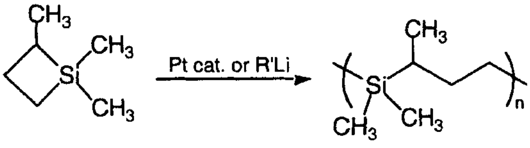
In order to extend the actual applications of these polymers, it is important to establish both analytical methods to elucidate the functional and stereochemical structures of these polymers, and practical synthetic methods to obtain stereoregular and/or optically active polymers. In this article, we report the terminal group determination and elucidation of stereochemical structure of silicon-containing polymers by NMR.

EXPERIMENTAL

The NMR spectra were obtained in $CDCl_3$ on the following spectrometers: 750 MHz ^{1}H NMR on a Varian spectrometer, 500 MHz ^{1}H and ^{1}H–^{1}H COSY on 500 MHz UNITY *plus*, 75.3 MHz ^{13}C and ^{1}H–^{13}C COSY on 300 MHz Gemini 2000, and 79.6 MHz ^{29}Si NMR on 400 MHz UNITY INOVA spectrometers. 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. Specific optical rotations were measured with a JASCO DIP-370S digital polarimeter. HPLC analyses on an optically active stationary phase were performed on a JASCO HPLC using a DaicelCHIRALCEL® OD column (cellulose carbamate derivative) with hexane as the eluent.

RESULTS AND DISCUSSION

Polymerization Mechanism of 1,1,2-Trimethylsilacyclobutane (TMSB) (1)



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The polymers were obtained by platinum catalyst (Pt catalyst) or phenyllithium (PhLi). The major peaks of the ^{29}Si, ^{13}C and ^{1}H NMR spectra were the same for both polymers. As an example, only one sharp peak is seen at around 5.0 ppm in the ^{29}Si spectrum as shown in Figure 1. This fact proves the existence of only one kind of silicon atom in the repeating unit. ^{1}H and ^{13}C NMR spectra also support the regular head-to-tail structure. The DEPT spectrum indicates the existence of two kinds of CH_3 and CH_2, and one kind of CH carbons in the regular repeating unit of the polymer.

However, when the ^{1}H NMR spectra are carefully examined, distinct differences were noticed for the polymers obtained by the Pt catalyst and by PhLi. In the spectrum of the polymer made by the Pt catalyst,

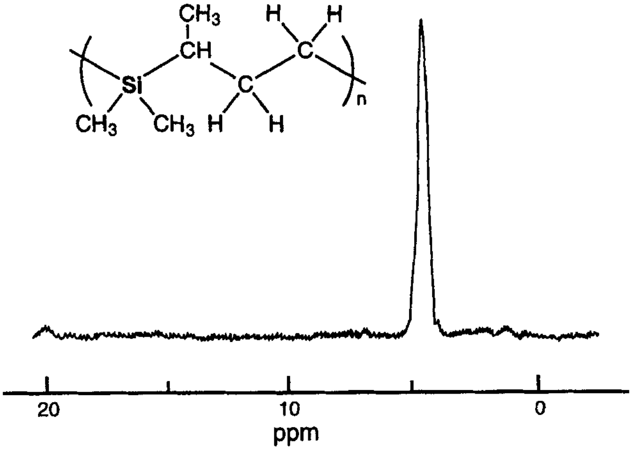


FIGURE 1 ^{29}Si NMR spectrum of poly1.

multiplets at 5.20–5.85 ppm assignable to the olefinic protons were seen (Figure 2(b)). The olefinic protons consisted of basically three kinds of protons reflecting the structure at 5.21–5.46, 5.52–5.53 ppm (two singlets), and 5.56–5.86 ppm in the ratio of 63.4 : 2.6 : 18.0. The majority of the olefinic protons at the polymer terminal appeared at rather similar positions as the inner olefinic protons of the model compounds (**3**, **4**)

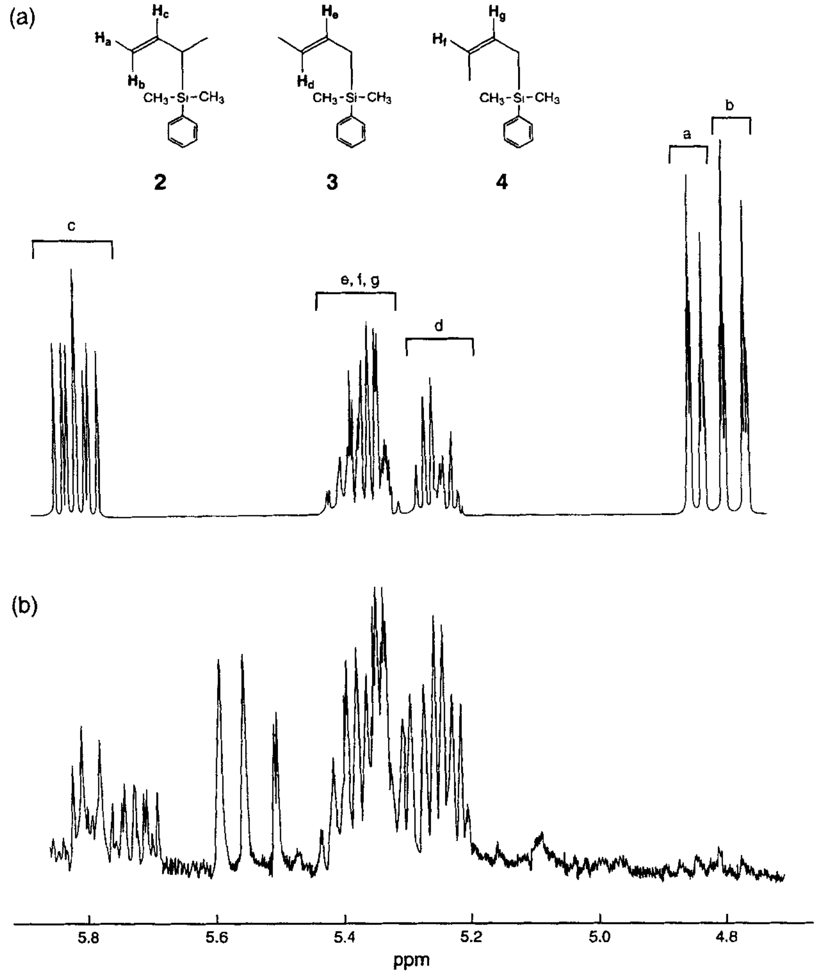


FIGURE 2 ^{1}H NMR spectra of (a) model compounds **2–4** and (b) **poly1** obtained by Pt catalyst.

(Figure 2(a)) at 5.21–5.46 ppm. These olefinic protons are considered to originate from the inner protons in compound **7** in Scheme 1 (two protons). The singlets at 5.52 and 5.55 are tentatively assigned to olefinic proton of *cis* and *trans* forms of the terminal type **6** (one proton each). The signals at 5.57 and 5.93 ($J = 18.0\,\text{Hz}$), and multiplets at 5.71–5.86 are assignable to terminal vinyl protons of the type **5**.

A simplified polymerization mechanism can be described as follows:

(1) Oxidative addition of **1** to the Pt (0) complex to form platinasilacyclopentane ring, followed by β-elimination to form a platinum(II) hydride species which acts as an initiator. Note that the oxidative addition could occur in 1,2- or 1,4-insertion mode. The 1,4-mode might be preferred.

(2) Coordination of the monomer to the platinum hydride species followed by 1,4-ring-opening by the attack of the platinum hydride bond as a nucleophile (initiation reaction).

(3) Repeated coordination of **1** to give platinasilacyclopentane ring nd 1,4-ring-opening (propagation reaction) to give regular repeating unit.

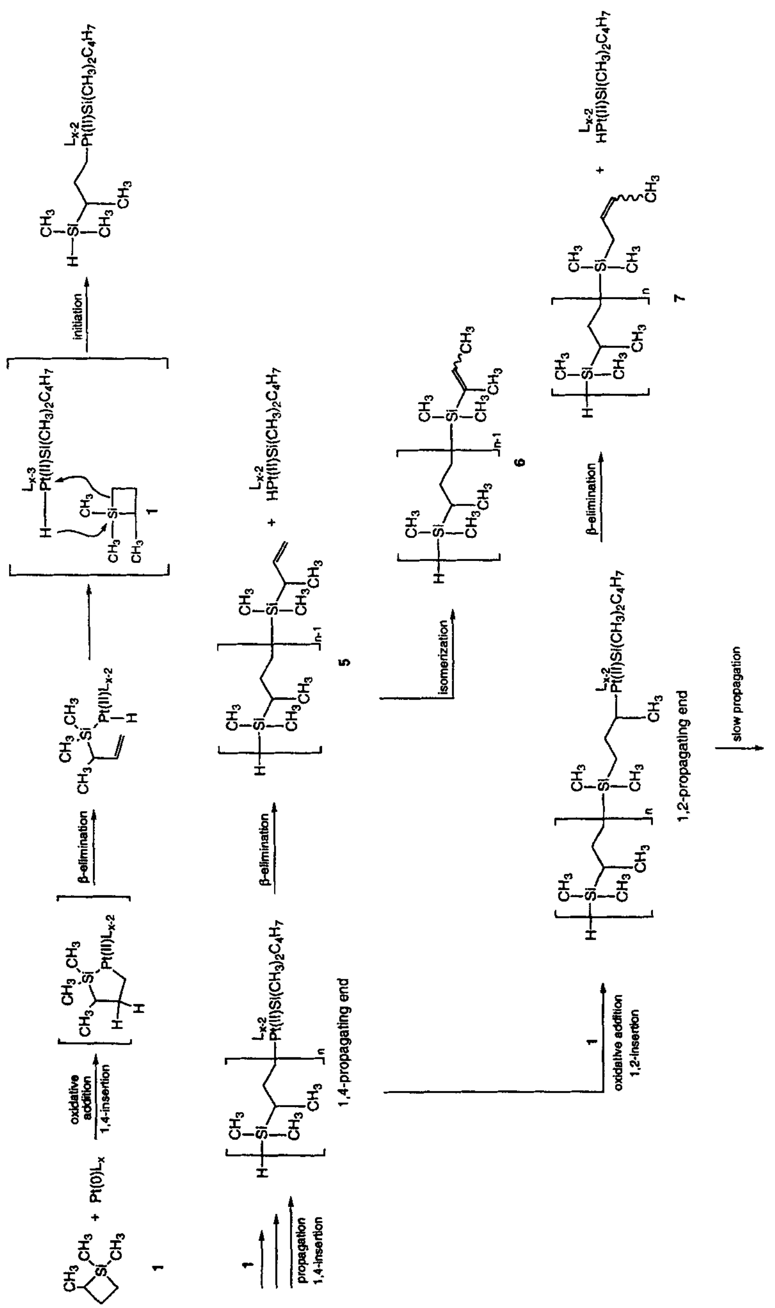
(4) Elimination of platinum hydride (chain transfer reaction) to give the structures **5**, which may isomerize to **6**, and **7** after 1,2-insertion of monomer. Note that the 1,2-propagation is slow because of the steric factor.

The situation with PhLi is different. PhLi opened **1** selectively by 1,4-mode. No olefinic signals were observed in the ^{1}H and the ^{13}C NMR spectra of the polymer. The phenyl group in the initiator fragment was shown to be attached to the silicon atom of the polymer terminal (Figure 3(a) and (b), Scheme 2).

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 estimated by ^{1}H NMR to be 99% from the ratio of $[M]/[I]$ and from M_n.

Polymerization Mechanism of 2-Oxa-1-naphthyl-1-phenyl-3,3-dimethyl-1,3-disilacyclopentane (8)

The attack of a nucleophile could possibly occur on the $Si(\text{Me})_2$ or $Si(\text{NpPh})$ of **8**, that would thus result in the formation of **9** and **9′**


1
Pt(0)Lx
oxidative addition
1,4-insertion
β-elimination
initiation
Pt(II)Lx-2
Lx-3
Pt(II)Si(CH3)2C4H7
Lx-2
propagation
1,4-insertion
1,4-propagating end
HPt(II)Si(CH3)2C4H7
5
isomerization
6
β-elimination
7
oxidative addition
1,2-insertion
1,2-propagating end
slow propagation
n
n-1

SCHEME 1

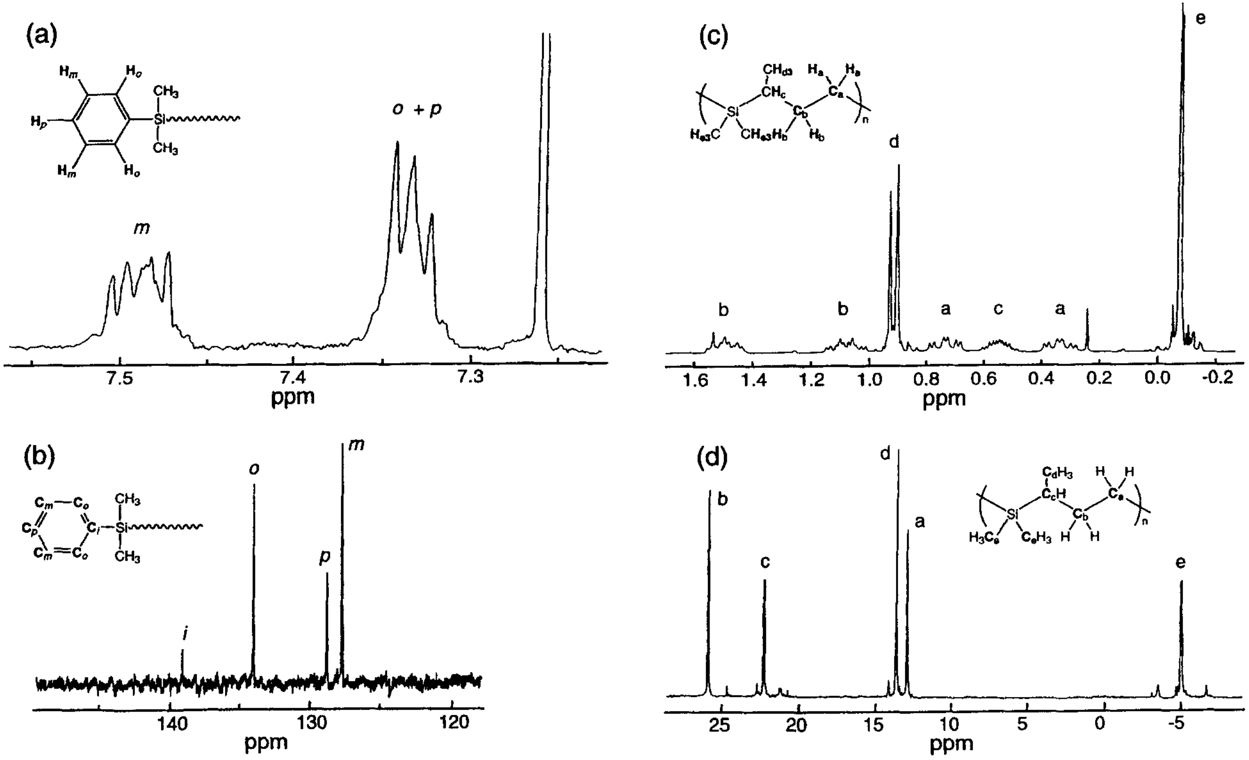
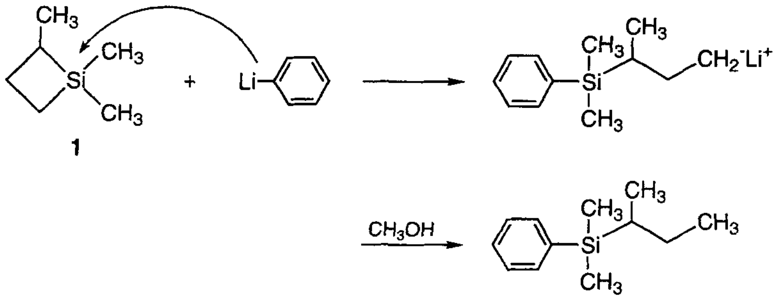


FIGURE 3 The 300 MHz ^1H and 75.4 MHz ^{13}C NMR spectra of **poly1**. (a) ^1H, terminal aromatic, (b) ^{13}C, terminal aromatic, (c) ^1H, main chain (enlarged), and (d) ^{13}C, main chain.

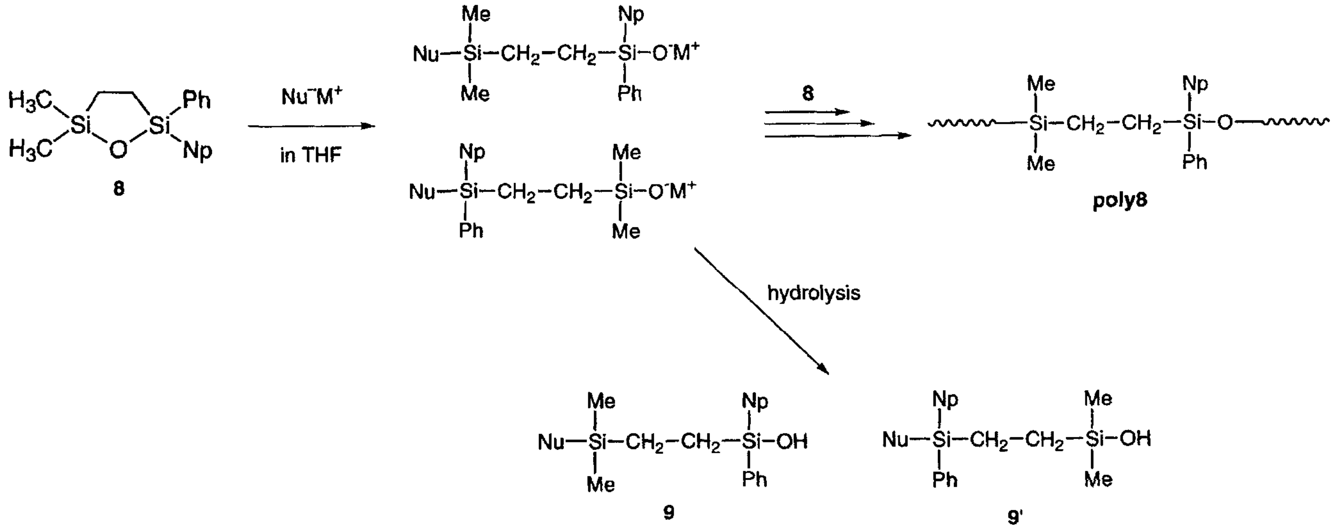


SCHEME 2

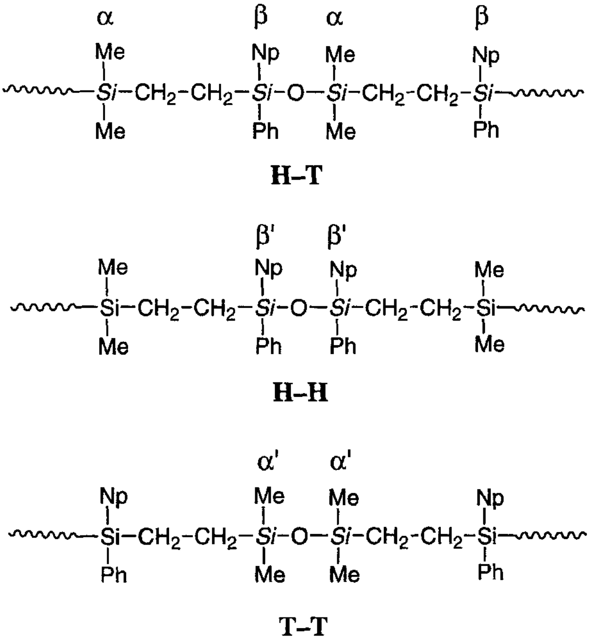
in the initiation step (Scheme 3), and the formation of three kinds of disiloxane linkage, that is, the head-to-tail (H–T), head-to-head (H–H), and tail-to-tail (T–T) structures in the propagation step (shown in Figure 4).

Anionic ROP of **8** by PhLi was studied. The two major peaks at −1.2 and −0.9 ppm in Figure 5(a) are assigned to be the *Si*(NpPh)OH and *Si*(Me)$_2$Ph of **9**, respectively, referring to the chemical shift of the model compound **11** (Table I), and the fact that, when the initiator was changed to MeONa, the peak at lower field (−0.9 ppm) disappeared, while the peak at higher field (−1.2 ppm) remained (Figure 5(c)). A very small peak at 18.5 ppm in Figure 5(a) is considered to be the *Si*(Me)$_2$OH of **9′**, judging from the chemical shifts of the model compounds **10**, **14**, and **15**. The integral ratio of *Si*(NpPh)OH and *Si*(Me)$_2$OH is about 92:8. Therefore, it can be concluded that the initiation step of the polymerization using PhLi as an initiator is highly regioselective; *i.e.*, PhLi predominantly attacked the silicon atom of *Si*(Me)$_2$ rather than the *Si*(NpPh).

In the ^{29}Si NMR spectrum of **poly8** prepared by PhLi (Figure 5(b)), the major signals at −10.7 and 10.4 ppm can be undoubtedly assigned to the H–T structure by reference to the structure of **poly[(*S*)-22]** obtained by polyaddition, on which comments will be made later. Identification of the minor peaks at −8.4, −1.9, −1.2, and 8.1 ppm is also important because these peaks may reveal the structural sequence of this polymer and the mechanism of polymerization. The two peaks at −1.9 and −1.2 ppm of **poly8** clearly correspond to the peaks at −1.2 and −0.9 ppm of the initial product **9** (Figure 5(a)) and are therefore



SCHEME 3



H–T

H–H

T–T

FIGURE 4 Head-to-tail, head-to-head, and tail-to-tail structures of **poly8**.

assigned to be the chain end *Si*(NpPh)OH and the initial terminal *Si*(Me)$_2$Ph, respectively. Because there is no visible chain end, *Si*(Me)$_2$OH, in **poly8** (Figure 5(b)), the propagation step of the polymerization seems to proceed highly regioselectively to give the *Si*(NpPh)OH chain end.

Based on the model compounds **12–15** (in Table I), the peaks at −8.4 and 8.1 ppm of **poly8** were ascribed to the H–H and T–T structure, respectively. Consequently, the H–T content of **poly8** is calculated to be 98.7%. The counter cation of the initiator greatly influences the H–T content of the polymer formed, following the order of Li^+: 97.6% > Na^+: 89.4% > K^+: 79.2% (at 10 min). A lower polymerization temperature leads to a higher H–T content; for example, in the case of Li^+, 0°C: 98.7% > 20°C: 97.6%.

The calculated M_n of **poly8** based on the ^{29}Si NMR spectrum is about 20 800, which is quite consistent with the value calculated from the monomer/initiator ratio and the polymer yield.

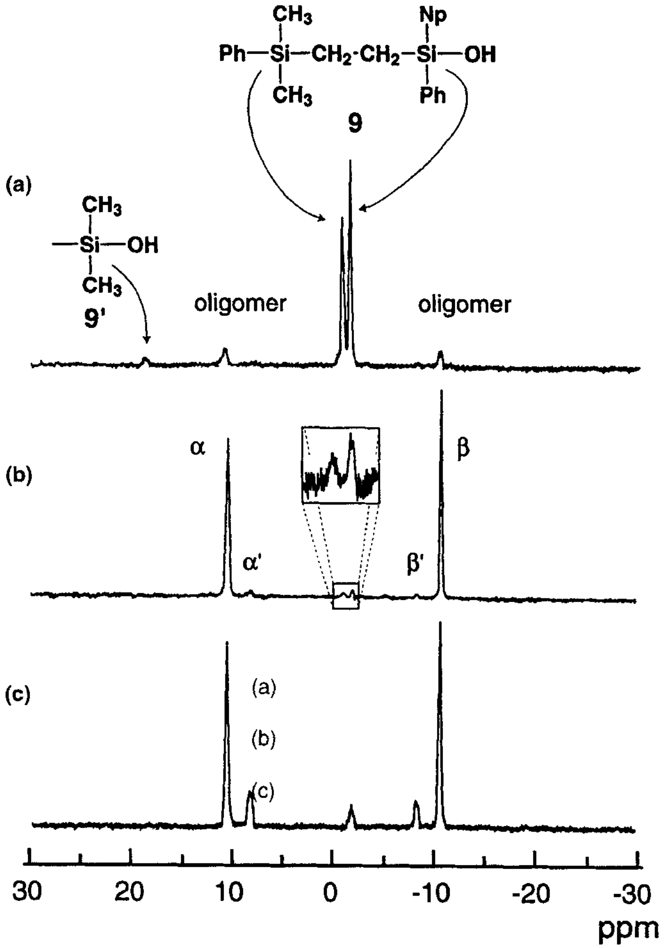
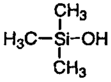
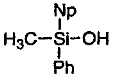
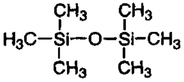
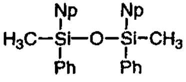
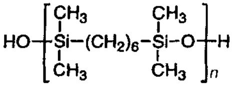
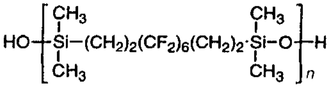


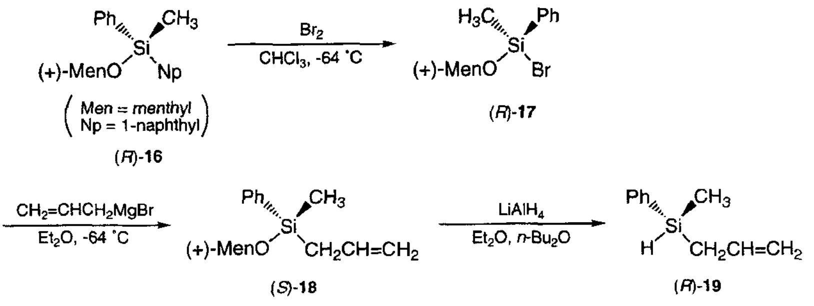
FIGURE 5 ^{29}Si NMR spectra of (a) the mixture of **9** and **9′**, (b) **poly8** by PhLi, and (c) **poly8** by MeONa.

Evaluation of Stereoregularity of Poly(carbosilane)s and Poly(carbosiloxane)s

According to the enlarged spectra of **poly1** (Figure 3(a)), 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. These splittings are considered enantiotopic due to the presence

TABLE I ^{29}Si NMR chemical shifts of model silicon compounds

Compounds	 $H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-OH$ **10**	 $H_3C-\overset{Np}{\underset{Ph}{Si}}-OH$ **11**	 $H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$ **12**	 $H_3C-\overset{Np}{\underset{Ph}{Si}}-O-\overset{Np}{\underset{Ph}{Si}}-CH_3$ **13**	 $HO-\left[\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-H$ **14**	 $HO-\left[\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_2(CF_2)_6(CH_2)_2\cdot\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-H$ **15**
Chemical shifts of signals in ^{29}Si NMR (ppm)	16.5	−0.9	7.3	−8.4	SiOH: 18.0	SiOH: 17.5
					SiOSi: 7.3	SiOSi: 8.4



SCHEME 4

of neighboring asymmetric center (C_c). The SiCHCH$_3$ carbon (C_c) was also split into two singlets of equal intensity.

Stereoregular and/or optically active poly(carbosilane)s and poly(carbosiloxane)s were synthesized starting from optically active (*R*)-**19**, (*S*)-**22** and (*S*)-**8**.[10,11] Optically active allylmethylphenylsilane (*R*)-**19** was synthesized according to Scheme 4.[11]

Methyl(1-naphthyl)phenyl-(+)-menthyloxysilane, (*R*)-**16**, or methyl (1-naphthyl)phenyl-(−)-menthyloxysilane, (*S*)-**16**, is a useful and versatile starting material in the synthesis of a variety of optically active silicon compounds.[11–14] Its optical purity can be determined by diastereomeric splitting in ^{1}H NMR and HPLC on an optically active stationary phase (Figure 6).[11] By recrystallization of methyl(1-naphthyl)phenyl-(+)-menthyloxysilane, (*R*)-**16** (diastereomer excess (d.e.) > 99%), is predominantly obtained as a crystalline material. The optical purity of methyl(1-naphthyl)phenylsilane can also be determined by HPLC.

The d.e. of (*R*)-**17** is estimated by the split signals at 0.62 and 0.79 ppm to be 76.5% from (*R*)-**16** (with d.e. of 78.9%). The d.e. of allylated product (*S*)-**18** is estimated by the signals at 0.60 and 0.63 ppm. Reduction by lithium aluminum hydride gives (*R*)-**19** having $[\alpha]_D^{26} = +24.0$ (*c* 1.00, pentane). The enantiomer excess (e.e.) of (*R*)-**19** could not be estimated at this point. Recently, we found that the introduction of methoxy group at 4-position of naphthyl group improved the d.e. of (*R*)-**17** up to 91%.[15]

The 500 MHz ^{1}H NMR spectra of the **poly[(*R*)-19]** are shown in Figure 7. The methyl signals at 0.120, 0.125, and 0.131 ppm were

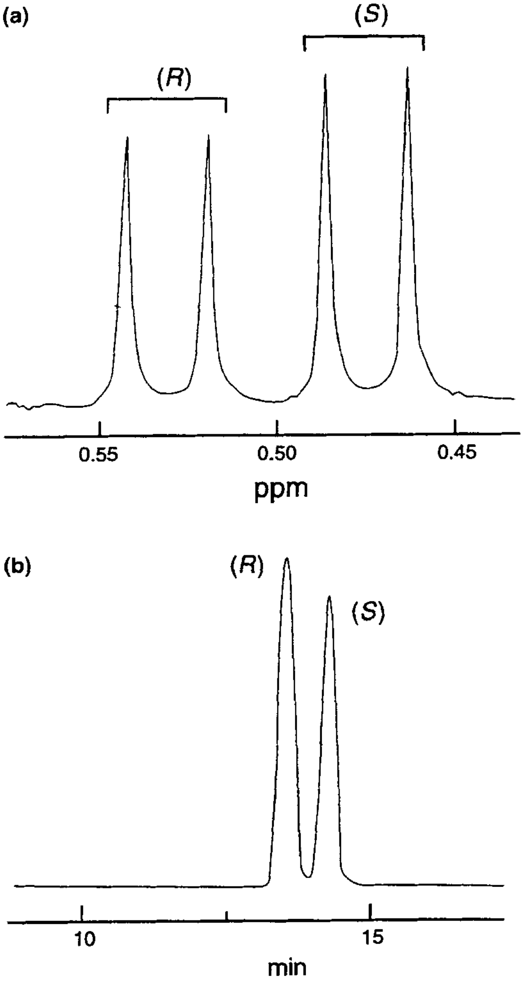


FIGURE 6 ^{1}H NMR spectrum and HPLC of *rac*-**16**.

assigned to syndiotactic (S), heterotactic (H), and isotactic (I) triad, respectively.[10,11] The calculated concentration of each triad starting from the optically active monomer with 76.5% e.e. (assuming complete retention of Si stereochemistry in the reduction and in the polymerization) is S : H : I = 1.0 : 2.0 : 6.6 (run 3 in Table II). The actual concentration of each triad evaluated was 1.0 : 2.0 : 7.0. The ratio was 1.0 : 2.0 : 3.5 starting from (*S*)-**18** with 60.8% e.e. (run 2). These facts

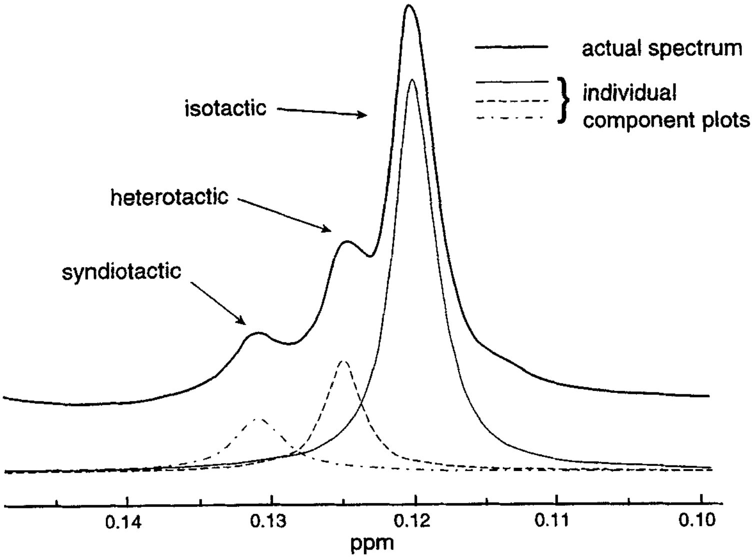


FIGURE 7 The 500 MHz ^{1}H NMR spectra of CH_3 region of **poly[(*R*)-19]**.

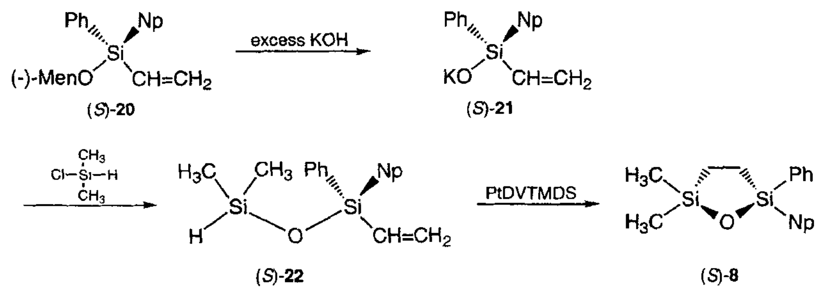
TABLE II Tacticity of poly(methylphenylsilylenetrimethylene)

Run	*d.e. of* (*S*)-**18** (%)	$[\alpha]_D^{26}$ *of* (*R*)-**19**[a] (*e.e.*[b]) (degree) (%)	*I*:*H*:*S* *Calcd.*	*Obs.*	*e.e. of* (*R*)-**19**[c] (%)
1[d]	—	— (0)	1.0 : 2.0 : 1.0	1.0 : 2.0 : 1.0	—
2	60.8	21 (67)	3.3 : 2.0 : 1.0	3.5 : 2.0 : 1.0	61
3	76.5	24 (76)	6.6 : 2.0 : 1.0	7.0 : 2.0 : 1.0	77

[a] *c* 1.00, Pentane; [b] calculated value assuming optically pure (*R*)-**19** has the optical rotation of $[\alpha]_D^{26}$ = 31.4; [c] estimated from triad tacticity; [d] racemic monomer.

proved that there was no racemization in the reduction step to synthesize (*R*)-**19** and in polymerization. These facts also confirmed that the e.e. of (*R*)-**19** having $[\alpha]_D^{26} = +24.0$ is 76.5%. Optically pure compound might show $[\alpha]_D^{26} = +31.4$. This value is little larger than the recently reported value (−28.89).[16]

Although the optical activity of the starting monomer influences in the isotacticity of the polymer formed via selective β-addition, the optical activity itself is lost in the polymer since the polymer formed is *pseudo*-asymmetric. In order to retain the optical activity from the optically active monomer in the resulting polymer, it is necessary to



SCHEME 5

distribute such optically active repeating unit connected with different constitutional unit in the polymer chain. Optically active poly[oxy-(naththylphenylsilylene)ethylene-(dimethylsilylene)]s were obtained from (*S*)-**22** and (*S*)-**8**, synthesized according to the Scheme 5.[17] The e.e. of (*S*)-**20** was confirmed by diastereomeric splitting in the ^{1}H NMR spectrum, and those of (*S*)-**22** and (*S*)-**8** were found to be close to 100% by chemical transformations and by HPLC analysis.

^{13}C NMR spectra of Si(CH$_3$)$_2$ methyl groups in the polymer main chain obtained by polyaddition of racemic and (*S*)-**22** and by ROP of (*S*)-**8** are shown in Figure 8. The atactic polymer, from the racemic monomer, showed three peaks (−0.427, −0.503 and −0.564 ppm, Figure 8(a)), while **poly[**(*S*)-**22]** showed mainly two peaks (−0.427 and −0.564 ppm, Figure 8(b)).

There are four possible types of diads for this polymer depending on the asymmetric silicon centers: *S–S*, *S–R*, *R–S* and *R–R* (Figure 9). The two methyl carbons in the *S–S* (or the *R–R*) diad are located in quite different environments and therefore have two chemical shifts. In the case of the *S–R* (or the *R–S*) diad, the two methyl groups are in very similar environments, and their carbon resonances will appear at the same position, *i.e.*, as one NMR peak. In atactic polymer, therefore, Si(CH$_3$)$_2$ would be split into three peaks (the central peak representing the *S–R* and *R–S* diads and two side peaks represent the *S–S* and the *R–R* diads) in the ^{13}C NMR spectrum, with an intensity of 1 : 2 : 1. In contrast, pure isotactic polymer, containing only the *S–S* (or the *R–R*) diad, would show two peaks for methyl carbons, and pure syndiotactic polymer only one peak for the *S–R* and *R–S* diads.

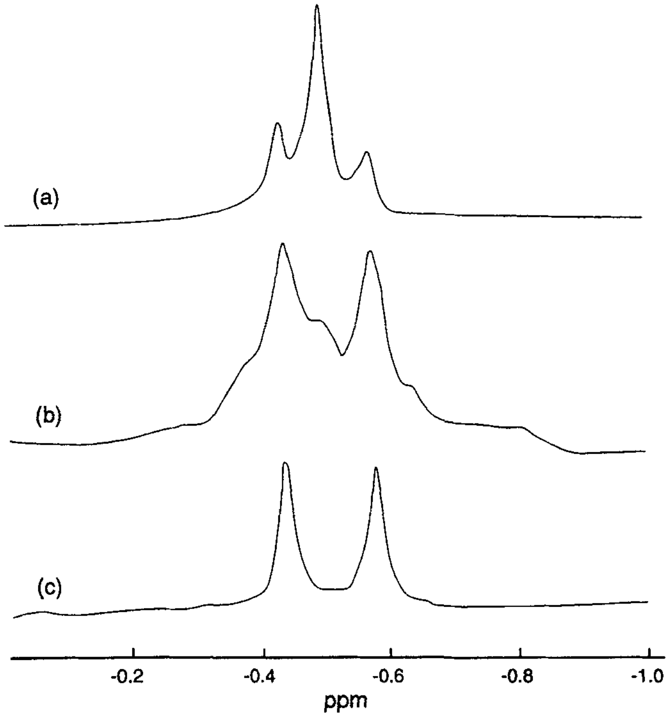


FIGURE 8 The 75.4 MHz ^{13}C NMR spectra of Si(CH$_3$)$_2$ of (a) **poly[*rac*-22]**, (b) **poly[(*S*)-22]**, and (c) **poly[(*S*)-8]**.

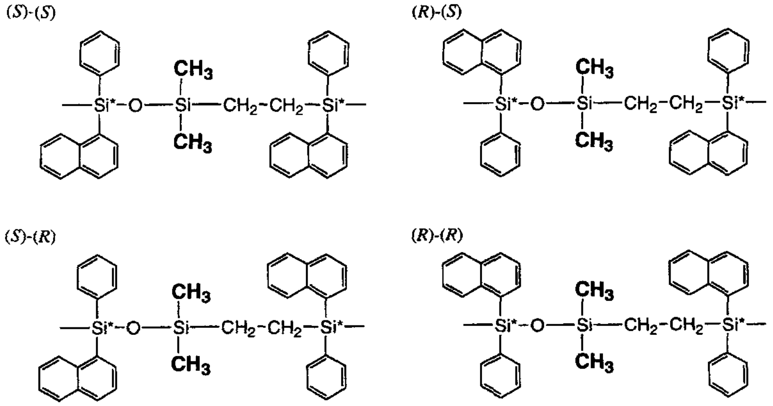


FIGURE 9 Diad sequences of poly[oxy(naphthylphenylsilylene)ethylene(dimethylsilylene)].

Since the present polymer showed two peaks for methyl carbons, the polymer is highly isotactic. The ROP of (*S*)–**8** using PhLi as an initiator gave a polymer in high yield with a higher molecular weight and a narrow molecular weight distribution.[18]

CONCLUSION

^1H, ^{13}C and ^{29}Si NMR spectroscopy was used to elucidate the terminal structure and the tacticity of these polymers. It was found that, in the ROP of **1** by platinum catalyst, extensive chain transfer reactions have occurred. The five-membered cyclic carbosiloxane **8** could be easily polymerized by phenyllithium to give a high-molecular-weight polymer through regioselective ring-opening. Polymerization of optically active allylsilane (*R*)-**19**, vinylsiloxane (*S*)-**22**, cyclic carbosiloxane (*S*)-**8** gave highly isotactic poly(carbosilane) and poly(carbosiloxane).

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