Synthesis of Poly(methylphenylsilylenetrimethylene) Rich in Isotacticity Characterized by 750 MHz ^{1}H NMR

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Introduction. Poly(carbosilane)s have been of interest as precursors to silicon carbide.[1] Two basic methods, namely, ring-opening polymerization of silacyclobutane,[2] disilacyclobutane,[3] or disilacyclopentane derivatives[4] and polyaddition of hydrosilyl compounds with (unsaturated alkyl)-substituted compounds,[5] have been conducted to prepare a variety of poly(carbosilane)s.[6] Polyaddition via hydrosilylation was first reported by Curry,[5a] and we reported the polyaddition of 1-allyl-3-hydrotetramethyldisiloxane,[7] which was prepared by alkylative cleavage of cyclic trisiloxane, D_3.[8] Recently, investigations focusing on thermal or liquid crystalline behavior of these polymers have been published.[9] It is very important to control the stereochemistry of the Si atom in the repeating units to correlate precisely such behavior with the primary structure of the polymers. However only limited information has been obtained so far on the stereoregularity of these polymers. Weber,[2b] Interrante,[3] and Bacqué[10] showed that tacticity of unsymmetrically substituted poly(silylenemethylene)s such as poly(methylethoxysilylenemethylene) can be evaluated by 500 MHz ^{1}H (125.7 MHz ^{13}C) NMR, but definite identification was not made. Recently Rinaldi reported the use of a 600 MHz ^{1}H/^{13}C/^{29}Si triple-resonance 3D-NMR and pulse field gradient technique to evaluate the stereoregularity of poly(hydrophenylsilylenetrimethylene) without making stereoregular polymers.[11] However, the actual synthesis of stereoregular silicon-containing polymers is also very important in order to study the properties of these polymers. We herein wish to report the first example of the synthesis of poly(methylphenylsilylenetrimethylene) rich in isotacticity by self-polyaddition of allylhydromethylphenylsilane, and definite and quantitative evaluation of triad tacticity by 750 MHz ^{1}H NMR.

Experimental Section. ^{1}H NMR spectra were recorded on Varian NMR spectrometers, models UNITY plus (750 MHz) and Gemini 2000 (300 MHz). ^{13}C (125.7 MHz) and ^{29}Si (79.5 MHz) NMR spectra were recorded on a model UNITY plus. The chemical shifts are given in ppm relative to $CHCl_3$ (7.26 ppm for ^{1}H), $CDCl_3$ (77.1 ppm for ^{13}C), and tetramethylsilane (0.00 ppm for ^{29}Si) as internal standards in $CDCl_3$ unless otherwise noted. IR spectra were recorded on a JASCO VALOR−III. Gel permeation chromatography (GPC) analyses were carried out on a JASCO GPC Model HLC 880 equipped with Shodex gels KF804 and KF801 (exclusion molecular weight, polystyrene 4.0×10^5 and 1.5×10^3, respectively) using tetrahydrofuran as an eluent at the flow rate of 1 mL/min. The molecular weight and the molecular weight distribution were estimated using standard polystyrene.

Allylmethylphenyl[(−)-bornyloxy]silane. A solution of allyllithium[12] prepared from tetraallyltin (3.48 g, 12.3 mmol) was reacted with methylphenyldi[(−)-bornyloxy]silane[13] (20.0 g, 46.9 mmol) in anhydrous ether (350 mL) at −40 °C for 24 h. A mixture of products (17.4 g), after treatment with phosphate buffer solution (pH 7.0) at 0 °C, was obtained by silica gel column chromatography (eluent, hexane; $R_f = 0.2$−0.3, methylphenyldi[(−)-bornyloxy]silane and allylmethylphenyl[(−)-bornyloxy]silane in 0.9:1.0 ratio; $R_f = 0$, (−)-borneol). ^{1}H NMR (500 MHz, $CDCl_3$) assignable to allylmethylphenyl-[(−)-bornyloxy]silane:δ 0.35, 0.36 (two s, 3H, SiCH_3), 0.74−0.90 (m, 9H, *H*f, *H*g, *H*h), 0.98 (t with fine coupling, 1H, J = 12.8 Hz, *H*c), 1.65−1.73 (m, 1H, *H*c), 1.13−1.33 (m, 2H, *H*b), 1.55−1.60 (m, 1H, *H*d), 1.78−1.90 (m, 2H, SiCH_2), 2.06−2.19 (m, 2H, *H*e), 4.00, 4.06 (two d with fine coupling, 1H, J = 9.5 Hz, *H*a), 4.86 (dd, J_1 = 11.6 Hz, J_2 = 3.2 Hz, 1H, *cis*-CH_2-CH=CH_2), 4.89 (dd, J_1 = 18.8 Hz, J_2 = 3.2 Hz, 1H, *trans*-CH_2-CH=CH_2), 5.76−5.85 (m, 1H, CH_2CH=CH_2), 7.32−7.41, 7.56−7.68 (m, 5H, phenyl protons); assignable to methylphenyldi[(−)-bornyloxy]silane: δ 0.31 (s, 3H, SiCH_3), 0.76, 0.80, 0.82, 0.84, 0.85 (s, 18H, *H*f, *H*g, *H*h), 1.01 (t with fine coupling, J = 12.8 Hz, 2H, *H*c), 1.63−1.73 (m, 2H, *H*c), 1.17 (t with fine coupling, J = 11.6 Hz, 2H, *H*b), 1.24 (t with fine coupling, J = 11.6 Hz, 2H, *H*b), 1.55−1.60 (m, 2H, *H*d), 2.06−2.19 (m, 4H, *H*e), 4.12, 4.16 (two d with fine coupling, J = 9.2 Hz, 2H, *H*a), 7.32−7.41, 7.62−7.68 (m, 10H, phenyl protons).

Optically Active Allylmethylphenylsilane. A mixture (17.4 g) of allylmethylphenyl[(−)-bornyloxy]silane and methylphenyldi[(−)-bornyloxy]silane was reduced by lithium aluminum hydride (1.32 g, 35 mmol) in ether (25 mL) by refluxing for 25 h. Silica gel column chromatography (eluent, hexane) gave chemically pure and optically active allylhydromethylphenylsilane as a colorless oil. Yield 0.81 g, 20% from methylphenyldi[(−)-bornyloxy]silane. $[\alpha]_D^{25} = -16.0°$ (*c* 0.50, pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.36 (d, J = 4.1 Hz, 3H, SiCH_3), 1.79−1.89 (m, 2H, SiCH_2), 4.39 (q, J = 3.1 Hz, 1H, Si*H*), 4.88 (dd, J_1 = 11.0 Hz, J_2 = 2.2 Hz, 1H, *cis*-CH_2-CH=CH_2), 4.91 (dd, J_1 = 14.9 Hz, J_2 = 2.2 Hz, 1H, *trans*-CH_2-CH=CH_2), 5.73−5.89 (m, 1H, CH_2CH=CH_2), 7.32−7.41, 7.50−7.57 (m, 5H, phenyl protons). IR (KBr plate, cm^{-1}) 3070 (aromatic C−H), 3000 (vinylic C−H), 2915 (saturated C−H), 2120 (Si−H), 1630 (C=C).

Polymerization. Polymerization was carried out in bulk at 80 °C for 12 h using 0.005 mol % 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum catalyst.[14] The obtained polymer was recovered by precipitating into methanol and purified by repeated reprecipitation from toluene into methanol. IR spectrometric analysis of the polymer indicated the disappearance of Si−H and C=C stretching vibrations. The molecular weight and its distribution of the polymer were estimated to be M_w = 25 000, M_n = 11 000, and M_w/M_n = 2.3. ^{1}H NMR (750 MHz, $CDCl_3$): δ 0.12−0.13 (three s, 3H, SiCH_3), 0.68−0.75 (m, 4H, SiCH_2), 1.25−1.32 (m, 2H, $SiCH_2CH_2$), 7.27−7.32, 7.34−7.39 (m, 5H, phenyl protons). IR (KBr pellet, cm^{-1}) 3070 (aromatic C−H), 2915 (saturated C−H).

Results and Discussion. Basically three ways have been reported for obtaining optically active silicon compounds (optical resolution,[15] diastereoselection in asymmetric reduction of carbonyl compounds by dihydrosilane,[16] and the diastereoselective alkylation of di(optically active alkoxy)silanes).[13] The last method was adopted in this report. The synthetic scheme for the preparation of allylhydromethylphenylsilane and poly(methylphenylsilylenetrimethylene) is shown in Scheme 1.

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Scheme 1. Synthesis of Monomer and Polymer

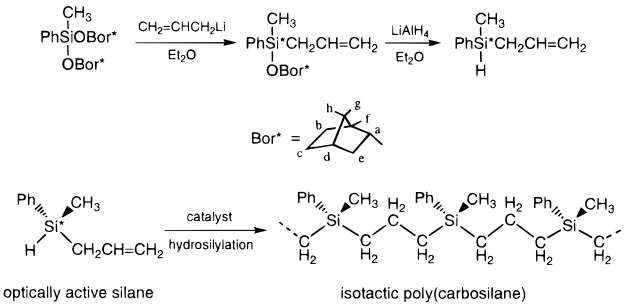

Table 1. Effects of the Reaction Conditions on d.e. of the Alkylated Product at − 40 °C

	dialkoxysilane	alkyllithium	solvent	time (h)	d.e. (%)
1	methylphenyldimenthyloxy	allyllithium	ether	15	20
2	allylmethyldimenthyloxy	phenyllithium	ether−hexane	20	30
3	methylphenyldibornyloxy	allyllithium	ether	24	60
4	allylmethyldibornyloxy	phenyllithium	ether−hexane	24	5

Diastereoisomeric splitting of the ^{1}H NMR signals was seen for SiCH_3 at 0.35 and 0.36 ppm, and for *H*a at 4.00 and 4.06 ppm, for the allylated products allylmethylphenyl[(−)-bornyloxy]silane. The diastereomeric excess (d.e.) estimated from the peak areas at 0.35 and 0.36 ppm was 60.8%. Reduction by lithium aluminum hydride gave allylhydromethylphenylsilane having $[\alpha]_D^{25} = -16.0°$ (*c* 0.50, pentane). The enantiomeric excess (e.e.) of the product could not be estimated. The effects of the alkoxy group (menthyloxy, bornyloxy) and the reaction conditions on the d.e. of the alkylated product are shown in Table 1. Dibornyloxysilane gave higher d.e. than dimenthyloxysilane[13] with allyllithium.

The 300 and 750 MHz ^{1}H, 125.7 MHz ^{13}C, and 79.5 MHz ^{29}Si NMR spectra of the polymer are shown in Figure 1. In the aliphatic region of the 300 MHz ^{1}H spectrum (Figure 1a), three types of signals assignable to SiCH_3 (0.13 ppm), α-CH_2 (0.70 ppm), and *β*-CH_2 (1.29 ppm) were observed. No signal derived from α-addition was observed. The facts that only three kind of singlets and only one singlet were observed in the aliphatic region in ^{13}C (Figure 1d) and ^{29}Si (Figure 1e) spectra, respectively, also support the high *β*-regioselectivity in the hydrosilylation reaction.

In the 300 MHz ^{1}H spectrum, the splitting of the methyl signal resulting from triad tacticity was observed. However, the peak separation is not good enough to quantitatively evaluate the concentration of each triad. Stereoisomeric splitting caused by diad or triad tacticity is not evidently seen in the ^{13}C and ^{29}Si spectra. In the 750 MHz ^{1}H spectrum (Figure 1b), the SiCH_3 signal is split into three singlets at 0.120, 0.125, and 0.131 ppm, and the separation of the methyl signal became good enough to evaluate the concentration of the triad tacticity. Even with the separated signal at hand, it is impossible to assign which signal to which triad. The 750 MHz ^{1}H NMR spectrum of the polymer obtained from the optically active monomer is shown in Figure 1c. Although it is not obvious if the hydrosilylation proceeds with retention or inversion of the Si stereochemistry, it is reasonable to conclude that a polymer rich in isotacticity is obtained from the optically active monomer. In Figure 1c, the signal at 0.120 ppm became relatively stronger and that at 0.131 ppm relatively weaker compared with those of the polymer

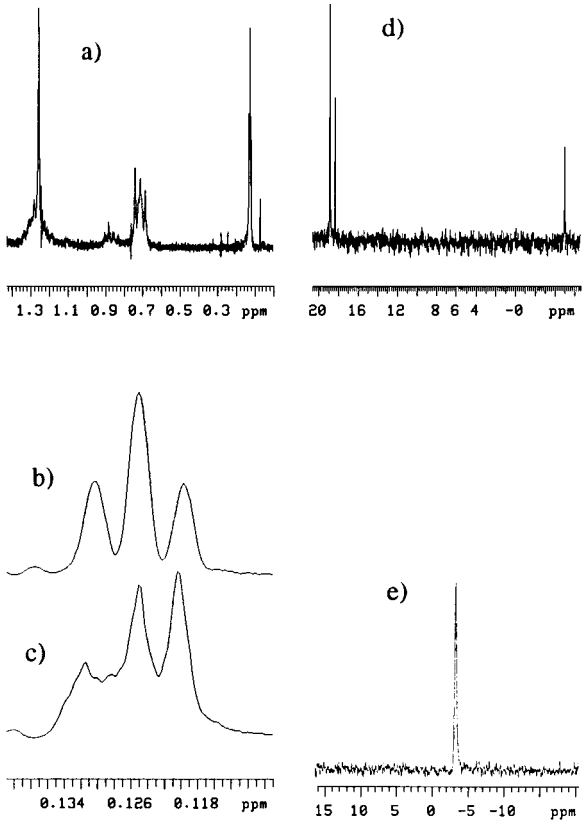

Figure 1. NMR spectra of polymers: (a) 300 MHz ^{1}H, (b) 750 MHz ^{1}H, (d) 125.7 MHz ^{13}C, (e) 79.5 MHz ^{29}Si spectra of polymer from racemic monomer, (c) 750 MHz ^{1}H spectrum from optically active monomer.

Table 2. Stereochemistry in Polymerization

e.e. of the monomer (%)	calculated triad population[a]			inversion[b] (%)
	S	H	I	
60	0.16	0.32	0.52	0
50	0.19	0.37	0.44	8.3
0	0.25	0.50	0.25	50

[a] Calculated assuming Bernoullian statistics. [b] Assuming 60% e.e. of the starting monomer.

from the racemic monomer. On the basis of these facts, the signals at 0.120 and 0.131 ppm were assigned to the isotactic and syndiotactic triad, respectively, and that at 0.125 to the heterotactic triad. The calculated concentration of each triad starting from the optically active monomer with 60.8% e.e., assuming complete retention of Si stereochemistry in the reduction step by lithium aluminum hydride and in the polymerization, is S:H:I = 1.0:2.0:3.3 (0.16:0.32:0.52). The actual concentration of each triad evaluated from Figure 1c was 1.0:2.0:2.3 (0.19:0.37:0.44). This corresponds to 50.0% e.e. of starting monomer without racemization in the polymerization step (Table 2). Since reduction of the alkoxysilane by lithium aluminum hydride proceeds with retention of stereochemistry,[17] such a decrease in tacticity can be caused either by racemization of the monomer itself or in the hydrosilylation step. Nevertheless, a polymer rich in isotacticity was obtained. Further study on the detailed reaction mechanism is now in progress.

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References and Notes

(1) (a) Yajima, S.; Hayashi, J.; Omori, M. *Chem. Lett.* **1975**, 931−934. (b) Yajima, S.; Okamura, K.; Hayashi, J. *Chem. Lett.* **1975**, 1209−1212.

(2) (a) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *J. Organomet. Chem.* **1972**, *44*, 291−297. (b) Liao, C. X.; Weber, W. P. *Polym. Bull.* **1992**, *28*, 281−286. (c) Matsumoto, K.; Yamaoka, H. *Macromolecules* **1995**, *28*, 7029−7031. (d) Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873- 8874.

(3) (a) Rushkin, I. L.; Interrante, L. V. *Macromolecules* **1995**, *28*, 5160−5161. (b) Rushkin, I. L.; Interrante, L. V. *Macromolecules* **1996**, *29*, 3123−3128.

(4) Suzuki, M.; Kaneko, T.; Morishima, Y.; Obayashi, T.; Saegusa, T. *Polym. J.* **1996**, *28*, 16−23.

(5) (a) Curry, J. W. *J. Am. Chem. Soc.* **1956**, *78*, 1686−1689. (b) Boury, B.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A. *Organometallics* **1991**, *10*, 1457−1461. (c) Pang, Y.; I-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671−5675. (d) Dvornic, P. R.; Gerov, V. V.; Govedarica, M. N. *Macromolecules* **1994**, *27*, 7575−7580.

(6) Weber, W. P. *Trends Polym. Sci.* **1993**, *1*, 356−360.

(7) Shintani, K.; Ooi, O.; Mori, A.; Kawakami, Y. *Polym. Bull.* **1996**, *37*, 705−710.

(8) (a) Mori, A.; Hishida, T.; Soga, Y.; Kawakami, Y. *Chem. Lett.* **1995**, 107−108. (b) Mori, A.; Sato, H.; Mizuno, K.; Hiyama, T.; Shintani, K.; Kawakami, Y. *Chem. Lett.* **1996**, 517−518.

(9) (a) Koopmann, F.; Frey, H. *Makromol. Rapid Commun.* **1995**, *16*, 363−372. (b) Koopmann, F.; Frey, H. *Macromolecules* **1996**, *29*, 3701−3706. (c) Sargeant, S. J.; Weber, W. P. *Macromolecules* **1993**, *26*, 2400−2407. (d) Guo, H.; Volke, R.; Weber, W. P.; Ganicz, T.; Pluta, M.; B.-Florjanezyk, E.; Stnczyk, W. J. *Organomet. Chem.* **1993**, *444*, C9−11.

(10) (a) Bacqué, E.; Pilot, J.-P.; Birot, M.; Dunogues, J. *Macromolecules* **1988**, *21*, 1, 30−34. (b) Bacqué, E.; Pilot, J.-P.; Birot, M.; Dunogues, J. *Macromolecules* **1988**, *21*, 34−38.

(11) Chai, M.; Saito, T.; Pi, Z.; Tessier, C.; Rinaldi, P. L. *Macromolecules* **1997**, *30*, 1240−1242.

(12) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; Vol. 7, p 4716.

(13) Richter, W. J. *J. Organomet. Chem.* **1979**, *169*, 9−17.

(14) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191−192.

(15) (a) Sommer, L. H.; Frey, C. L. *J. Am. Chem. Soc.* **1959**, *81*, 1013. (b) Corriu, R. J. P.; Lanneau, G. F.; Leard, M. *J. Organomet. Chem.* **1974**, *64*, 79−91.

(16) Corriu, R. J. P. *J. Organomet. Chem.* **1974**, *64*, C51−54.

(17) Sommer, L. H.; Michael, K. W.; Korte, W. D. *J. Am. Chem. Soc.* **1967**, *89*, 9, 868−875.

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