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Anionic Ring-Opening Polymerization of Silacyclopropanes

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ABSTRACT: Synthesis and anionic polymerization of silacyclopropane derivatives, 2-*n*-butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane (1*s*1*t*2*n*-BuSP) and 2-*n*-butyl-1-*tert*-butyl-1-isobutylsilacyclopropane (1*i*1*t*2*n*-BuSP), were investigated. These monomers were prepared by treatment of *sec*-butyl-*tert*-butyldichlorosilane or *tert*-butylisobutyldichlorosilane with lithium in the presence of 1-hexene. Monomers 1*s*1*t*2*n*-BuSP and 1*i*1*t*2*n*-BuSP could be polymerized with a butyllithium initiator in THF at −78 °C in the presence of hexamethylphosphoramide (HMPA). After precipitation in methanol, poly(2-*n*-butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane) (poly(1*s*1*t*2*n*-BuSP)) ($M_n = 2100$, $M_w/M_n = 1.53$, relative to a polystyrene standard) and poly(2-*n*-butyl-1-*tert*-butyl-1-isobutylsilacyclopropane) (poly(1*i*1*t*2*n*-BuSP)) ($M_n = 1800$, $M_w/M_n = 1.60$) were obtained. Contact angles of water with poly(1*s*1*t*2*n*-BuSP) and poly(1*i*1*t*2*n*-BuSP) were determined as 103 and 102°, respectively. This significantly high hydrophobicity is probably due to the unusually large number of methyl groups in the repeating unit.

Introduction

Polycarbosilanes are of growing interest because of their unique characteristics such as high chemical and thermal stability, high hydrophobicity and flexibility, electrical and optical properties, gas permeability, and so on.[1−3] Ring-opening polymerization (ROP) of cyclic carbosilanes[4] is one of the most promising techniques for synthesizing well-defined polycarbosilanes. For instance, ROPs of four-membered ring compounds, 1,3-disilacyclobutanes[5−9] and monosilacyclobutanes,[10−17] have been widely investigated in the last half century. Anionic ROPs of a five-membered ring compound, a silacyclopent-3-ene derivative, have also been studied.[18−23] Although one can expect that the polymerization of three-membered ring compounds, silacyclopropane (silirane) derivatives, may easily proceed due to the large ring strain, little is known about ROP of silacyclopropanes so far. This is due to the difficulty in preparing and isolating the monomer. Despite the thermal instability of the SiC_2 ring due to the excessive ring strain induced by a silicon atom,[24] introduction of organic groups on the three-membered ring can significantly enhance its kinetic stability. In 1975, Seyferth and Annarelli reported the synthesis of a highly substituted silacyclopropane, hexamethylsilacyclopropane.[25,26] They suggested that hexamethylsilacyclopropane could be anionically oligomerized,[25] but the compound was thermally not stable enough (half-life at 37 °C was 81 h) for a detailed investigation. On the other hand, Boudjouk and co-workers recently reported more facile synthesis of silacyclopropane derivatives, or 1,1-di-*tert*-butylsilacyclopropanes.[27] These compounds have very bulky groups on the silicon atoms and are thermally quite stable. They can be isolated by distillation and stored under an inert atmosphere. They have moderate reactivity for undergoing various reactions with aldehydes and ketones, as Woerpel and co-workers reported recently.[28−30] We have chosen this series of compounds as key monomers, and started investigating their polymerization. We have found that silacyclopropanes having moderately bulky substituents on the silicon atom, 2-*n*-butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane (1*s*1*t*2*n*-BuSP) and 2-*n*-butyl-1-*tert*-butyl-1-isobutylsilacyclopropane (1*i*1*t*2*n*-BuSP), can be anionically polymerized in THF in the presence of hexamethylphosphoramide (HMPA).

Experimental Section

Materials. *tert*-Butyltrichlorosilane was purchased from Aldrich (Milwaukee, WI), *sec*-butyllithium (1.0 M, *c*-hexane solution), *tert*-butyllithium (1.5 M, pentane solution), and lithium (ca. 30 wt % dispersion in oil) from Kanto Chemical Co Inc. (Tokyo, Japan), *n*-butyllithium (1.6 M, hexane solution), 1-hexene from Wako Pure Chemical Industries (Osaka, Japan), trichloroisobutylsilane, and 12-crown-4-ether from Tokyo Chemical Industry (Tokyo, Japan). These were used as delivered. Hexamethylphosphoramide (HMPA) purchased from Aldrich and 1,1,4,4-tetramethylethylenediamine (TMEDA) from Wako Pure Industries were distilled twice over CaH_2 under reduced pressure and stored over activated molecular sieves 4A under an argon atmosphere. Tetrahydrofuran (THF) and hexane were freshly distilled over sodium benzophenone ketyl in an argon atmosphere before use. Lithium methoxide (2 M methanol solution) was prepared by treatment of lithium metal (700 mg, 100 mmol) in dry methanol (50 mL) in an argon atmosphere.

Synthesis of *sec*-Butyl-*tert*-butyldichlorosilane. *sec*-Butyllithium (1.0 M cyclohexane solution, 200 mL, 200 mmol) was added to a solution of *tert*-butyltrichlorosilane (38 g, 200 mmol) in hexane (100 mL) at room temperature in an argon atmosphere. After being stirred for 40 h at 70 °C, the solution was filtered through a glass filter and precipitated lithium chloride was removed. The filtrate was concentrated by rotary evaporator, and the residual oil was distilled under reduced pressure to give the title compound (26 g, 120 mmol) in 61% yield. Bp: 58−62 °C (8.0×10^2 Pa). IR (neat): 2937, 2866, 1464, 1366, 1091, 1007, 849, 822 cm^{-1}. ^1H NMR, δ ($CDCl_3$): 0.90−1.10 (m, 1H), 1.01 (t, $J = 7.0$ Hz, 3H), 1.11 (s, 9H), 1.19 (d, $J = 7.5$ Hz, 3H), 1.26−1.92 (m, 1H). ^{13}C NMR, δ ($CDCl_3$): 12.75, 13.31, 23.48, 24.06, 24.47, 25.92. Anal. Calcd for $C_8H_{18}Cl_2Si$: C, 45.60; H, 8.53. Found: C, 44.90; H, 8.49.

Synthesis of 2-*n*-Butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane (1*s*1*t*2*n*-BuSP). A dispersion of lithium (30 wt % in mineral oil, 4.5 g, 190 mmol) was washed three times with THF (10 mL) in an argon atmosphere to remove the mineral oil. Tetrahydrofuran (30 mL) and 1-hexene (7.5 mL, 60 mmol) was added and the mixture was sonicated with ultrasonic waves using ultrasonic cleaner BRANSONIC (Freq

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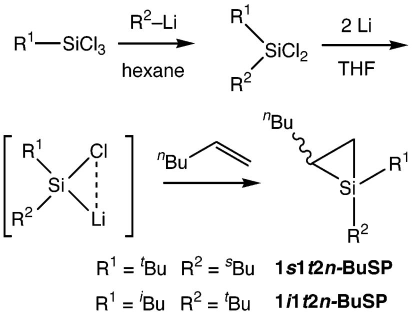
47 kHz, EMERSON-Japan, Tokyo). *sec*-Butyl-*tert*-butyldichlorosilane (6.4 g, 30 mmol) was slowly added to the mixture with the sonication over a period of 2 h at room temperature. The sonication was continued for 2 h more after completing the addition. Then THF was removed by evaporation and replaced by hexane. The hexane soluble fraction was separated from lithium and lithium chloride by filtration. After evaporation of hexane, the residual oil was distilled under reduced pressure to give a four-diastereomeric mixture of the title compound (1.33 g, 5.9 mmol) in 20% yield. Bp: 64−67 °C (1.1×10^2 Pa). ^{1}H NMR, δ ($CDCl_3$): −0.22 to −0.10 (m, a part of 1H), −0.02 to +0.13 (m, a part of 1H), 0.51−0.85 (m, 2H), 0.89 (t, $J = 7.1$ Hz, 3H), 0.92−1.05 (m, 3H), 0.98 (s, a part of 9H), 1.08 (s, a part of 9H), 1.17 (d, $J = 7.1$ Hz, a part of 3H), 1.22 (d, $J = 7.1$ Hz, a part of 3H), 1.25−1.55 (m, 8H), 1.55−1.79 (m, 1H). ^{13}C NMR, δ ($CDCl_3$): 2.49, 3.06, 3.24, 3.31, 11.79, 12.24, 13.49, 13.67, 13.79, 13.85, 14.18, 14.31, 14.43, 15.98, 16.12, 16.85, 16.96, 17.06, 17.25, 17.39, 17.73, 18.10, 18.15, 18.31, 18.44, 18.79, 18.95, 22.73, 26.98, 27.37, 27.73, 28.18, 28.24, 28.37, 28.92, 29.10, 29.72, 31.92, 31.99, 32.06, 32.14, 33.88, 34.06, 34.63, 34.73.

Synthesis of *tert*-Butylisobutyldichlorosilane. *tert*-Butyllithium (1.5 M pentane solution, 33 mL, 50 mmol) was added to a solution of isobutyltrichlorosilane (8.3 mL, 50 mmol) in hexane (50 mL) at room temperature under an argon atmosphere. After being stirred for 40 h at 50 °C, the solution was filtered through a glass filter, and the precipitated lithium chloride was discarded. The filtrate was concentrated by rotary evaporator, and the residual oil was distilled under reduced pressure to provide the title compound (9.0 g, 42 mmol) in 84% yield. Bp: 64−68 °C (1.9×10^3 Pa). IR (neat): 2937, 2866, 1464, 1394, 1367, 1335, 1223, 1165, 1094, 1040, 1009, 941, 833, 820 cm^{-1}. ^{1}H NMR, δ ($CDCl_3$): 0.92−1.10 (m, 2H), 1.04 (d, $J = 7.0$ Hz, 6H), 1.06 (s, 9H), 2.06 (qqt, $J = 7.0, 7.0, 7.0$ Hz, 1H). ^{13}C NMR, δ ($CDCl_3$): 24.23, 24.98, 25.74, 26.08. Anal. Calcd for $C_8H_{18}Cl_2Si$: C, 45.06; H, 8.53. Found: C, 44.89; H, 8.50.

Synthesis of 2-*n*-Butyl-1-*tert*-butyl-1-isobutylsilacyclopropane (1*i*1*t*2*n*-BuSP). A dispersion of lithium (30 wt % in mineral oil, 2.4 g, 100 mmol) was washed three times with THF (10 mL) in an argon atmosphere to remove the mineral oil. Tetrahydrofuran (20 mL) and 1-hexene (5.0 mL, 40 mmol) was added and the mixture was sonicated with ultrasonic waves. *tert*-Butyl-isobutyldichlorosilane (4.1 g, 19 mmol) was slowly added to the mixture with irradiation over a period of 2 h at room temperature. The sonication was continued for two more hours after completing the addition. Then THF was removed by evaporation and replaced by hexane. The hexane-soluble fraction was separated from lithium and lithium chloride by filtration. After evaporation of hexane, the residual oil was distilled to give a two-diastereomeric mixture of the title compound (0.64 g, 2.8 mmol) in 15% yield. Bp: 56−58 °C (8.4×10 Pa). ^{1}H NMR, δ ($CDCl_3$): −0.23−0.14 (m, 1H), 0.50−0.85 (m, 4H), 0.85−1.08 (m, 18H), 1.18−1.43 (m, 6H), 1.55−1.90 (m, 1H). ^{13}C NMR, δ ($CDCl_3$): 3.52, 10.88, 14.75, 16.49, 17.59, 23.02, 23.28, 24.16, 25.02, 25.69, 26.16, 26.42, 26.75, 27.59, 28.96, 29.79, 31.59, 32.03, 32.35, 32.55, 34.22, 35.07.

Polymerization of Silacyclopropanes. Polymerization procedure of monomer 1*s*1*t*2*n*-BuSP was representative. Into a 50 mL round-bottomed flask, equipped with a Teflon-covered magnetic stirring bar, rubber balloon, and rubber septum were placed the monomer (1*s*1*t*2*n*-BuSP, 630 mg, 2.8 mmol), THF (1.4 mL), and HMPA (0.28 mL) in an argon atmosphere. The mixture was cooled to −78 °C, and a hexane solution of butyllithium (1.1 M in hexane, 0.14 mmol, 0.13 mml) was added via a syringe. The mixture was stirred at −78 °C for 1 h, and lithium methoxide (2 M, in methanol) was added. After being stirred for 5 min, the resulting mixture was poured into water and extracted with toluene (50 mL). The organic layer was dried over anhydrous sodium sulfate. A portion of the crude product was taken and analyzed by ^{1}H NMR. The remaining product was dissolved in toluene and poured into excess methanol to precipitate the polymer, which was dried under vacuum to give poly(2-*n*-butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane) (poly(1*s*1*t*2*n*-BuSP)) (170 mg). IR (neat): 2856, 2777, 2708, 1454, 1393, 1362, 1331, 1217, 1186, 1130, 1099, 1030, 1009, 965, 933, 850, 819 (cm^{-1}). ^{1}H NMR, δ ($CDCl_3$): 0.50−0.75 (m, 2nH), 0.75−1.08 (m, 18H), 1.08−1.58 (m, 6H), 1.58−1.95 (m, 4H). ^{13}C NMR, δ ($CDCl_3$): 14.2, 15.0−16.3 (broad), 18.8−21.2 (broad), 21.2−22.2 (broad), 22.8, 23.9, 25.8, 26.3, 27.1, 27.6, 28.5, 28.9, 29.7, 30.1, 31.5, 32.0−34.8 (broad).

Scheme 1



Poly(2-*n*-butyl-1-*tert*-butyl-1-isobutylsilacyclopropane) (poly(1*i*1*t*2*n*-BuSP)). IR (neat): 2852, 2775, 2710, 1450, 1379, 1362, 1319, 1261, 1221, 1161, 1132, 1097, 1041, 1007, 933, 819 cm^{-1}. ^{1}H NMR, δ ($CDCl_3$): 0.55−0.85 (m, 4nH), 0.85−1.15 (m, 16nH), 1.15−1.70 (m, 8nH) 1.70−2.05 (m, 2nH). ^{13}C NMR, δ ($CDCl_3$): 11.5−13.3 (broad), 13.8, 14.2, 17.8−22.4 (broad), 22.7, 23.3, 24.8, 25.0, 26.9, 27.2, 27.5, 28.1, 28.5, 28.9, 29.2, 29.4, 30.4, 31.5, 31.8−35.6 (broad).

Measurements. Gel-permeation chromatography was carried out in chloroform on a JASCO 880-PU chromatograph equipped with four polystyrene gel columns (Shodex K-802, K-803, K-804, and K-805; exclusion limit in molecular weight of polystyrene = 5×10^3, 7×10^4, 4×10^5, and 4×10^6, respectively) and a JASCO 830-RI refractive index detector. Proton NMR spectra were recorded on a JEOL GSX 270 spectrometer in $CDCl_3$, using tetramethylsilane as an internal standard. IR spectra were measured on a Shimadzu FTIR-8400 spectrometer. The contact angle of water on the thin polymer film was measured as follows. A chloroform solution of polysilacyclopropane (1 wt %) was spin-cast on a glass slide. A water droplet was put on the thin polymer film with a microsyringe. A magnified photograph of the droplet was taken, and the angle between the polymer film and the droplet was observed.

Results and Discussion

Monomers. 2-*n*-Butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane (1*s*1*t*2*n*-BuSP) and 2-*n*-butyl-1-*tert*-butyl-1-isobutylsilacyclopropane (1*i*1*t*2*n*-BuSP) were synthesized as shown in Scheme 1. Although the yields of the desired silacyclopropanes were not so high because oligomeric silane byproducts were formed, spectroscopically pure compounds were obtained by distillation under reduced pressure. Proton NMR spectra of 1*s*1*t*2*n*-BuSP and 1*i*1*t*2*n*-BuSP are given in Figures 1 and 2. Signals of three protons from −0.3 to +0.2 ppm and from 0.5 to 0.8 ppm can be assigned to the three-membered ring protons of 1*s*1*t*2*n*-BuSP, and 1*i*1*t*2*n*-BuSP, respectively, in both figures. The obtained silacyclopropanes were cis/trans isomeric mixtures of the substitutents on the three-membered rings. The isomeric ratios were 45/55 for 1*s*1*t*2*n*-BuSP and 28/72 for 1*i*1*t*2*n*-BuSP, which were estimated from the integral ratios of signals at −0.15 and +0.05 ppm in Figure 1 and those at −0.18 and +0.05 ppm in Figure 2. Two bulky substituents, one *tert*-butyl group and an *sec*-butyl or isobutyl group, are indispensable on the silicon atom for synthesizing silacyclopropanes by this method. Without these bulky substituents, a silyllthium inter-

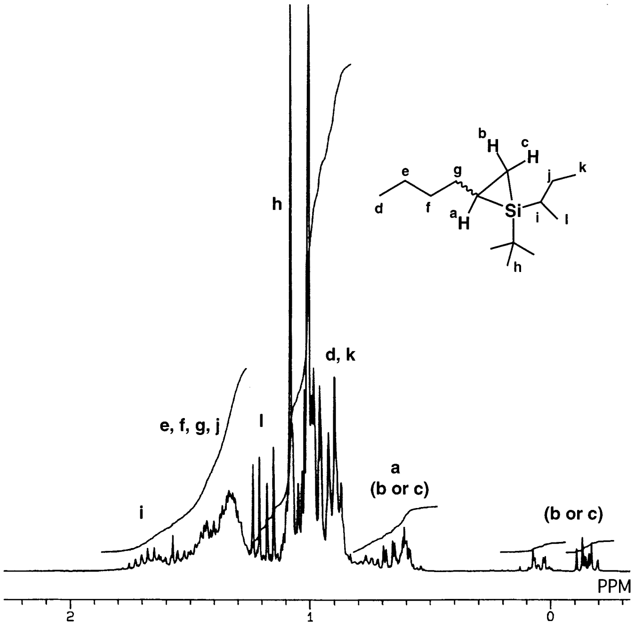


Figure 1. ^{1}H NMR spectrum of 1*s*1*t*2*n*-BuSP.

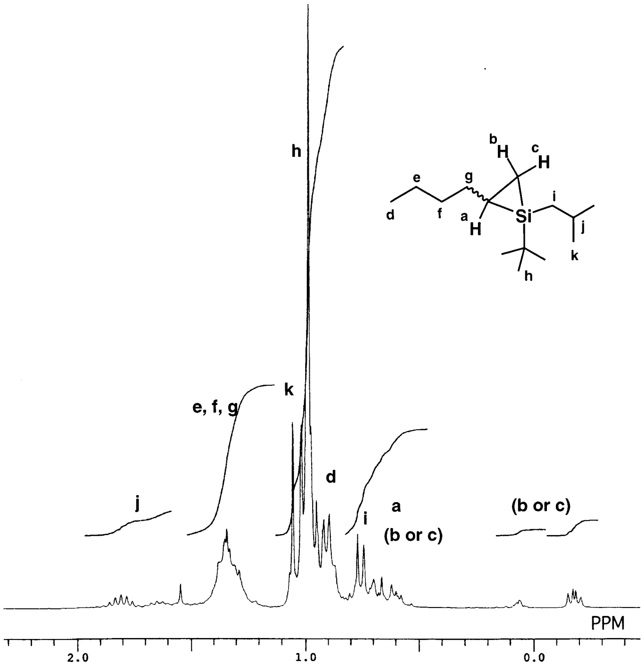
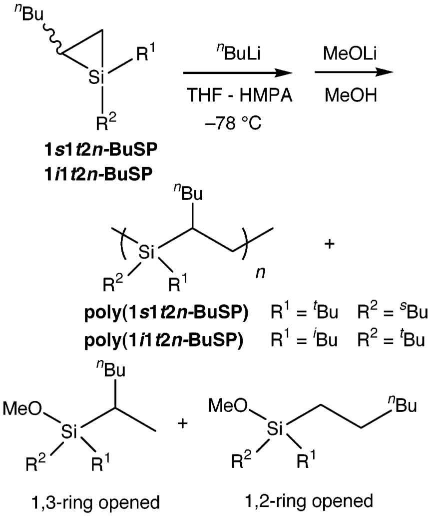


Figure 2. ^{1}H NMR spectrum of 1*i*1*t*2*n*-BuSP.

mediate generated from dichlorosilane and lithium could readily react with other chlorosilanes to give only oligosilanes or cyclosilanes.[31] Attempts to prepare 1,1,2-tri-*n*-butylsilacyclopropane, 1,1-diethyl-2-*n*-butylsilacyclopropane, or 1,1-diisopropyl-2-*n*-butylsilacyclopropane were not successful for the above reason. The alkyl substituent on the 2-position carbon atom is also required for the practical synthesis, since gaseous olefin like ethylene is not available for the normal glass apparatus.[32] Monomers, 1*s*1*t*2*n*-BuSP and 1*i*1*t*2*n*-BuSP, thus synthesized were thermally stable and could be stored in an argon atmosphere. However, they were quite susceptible to air and moisture so they were always handled in an inert atmosphere analogously to those of 1,1-di-*tert*-butyl-2,3-dimethylsilacyclopropanes reported by Boudjouk.[27] Upon exposure to air, the oxidation of the compounds took place and they were transformed into polymeric peroxides.[33]

Scheme 2



Polymerization. Ring-opening polymerization of monomer 1*s*1*t*2*n*-BuSP was examined using butyllithium as an initiator under various conditions (Scheme 2). A methanol solution of lithium methoxide was employed as a terminator, because the remaining monomer could be transformed into the methoxylated ring-opened monomeric compounds with this reagent. Termination with water gave polymeric subproducts by hydrolysis of the monomers and the subsequent polycondensation, which may complicate the analysis of the products. Monomer conversions were determined by ^{1}H NMR analysis of the crude mixture of the polymeric compound and methoxylated monomer. The polymerization results are summarized in Table 1. When the monomer was treated in THF at −78 °C (run 1), no polymerization took place and only methoxylated compounds were obtained. The methoxylated product was an isomeric mixture of 1,2- and 1,3-ring-opened monomers. The ratio of 1,2- and 1,3-ring-opened products was 20:80, which was because the primary anion generated by the 1,3-cleavage was more stable. In contrast to the above result, when the monomer was treated with $^1/_{10}$ equiv of butyllithium in the presence of HMPA, polymeric compounds were obtained along with methoxylated compounds (run 2). The monomer conversion in run 2, which was determined by ^{1}H NMR, was 85%. Figure 3 shows the GPC curve for the crude products. Number-averaged molecular weight (M_n) of the products (except methoxylated monomer) relative to polystyrene was 890. The number-averaged polymerization degree (P_n) estimated from the M_n value relative to standard polystyrenes was 3.9, but the true M_n (P_n) must be larger. Judging from the peak top of the GPC chart in Figure 3, the P_n should be about 8. When $^1/_{20}$ equiv of butyllithium was introduced to the monomer, higher molecular weight products (M_n = 1200) were obtained, but the monomer conversion decreased to 60% (run 3). Polymerization for a prolonged reaction time (3 h) provided a result similar to the polymerization for 1 h, which indicated that the propagating species was gradually deactivated and the polymerization was terminated. We have not understood the termination mechanisms yet, but we suppose that the termination may be caused by a proton abstraction from methylene groups adjacent to the silicon atoms in the monomer or polymer as well as a reaction with trace amount of impurities in the system. The proton NMR spectrum of the polymer after

Table 1. Polymerization Results of Silacyclopropanes Using Butyllithium Initiator[a]

					crude		purified	
run	monomer	additive	$[I]_0/[M]_0$	convn (%)	M_n	M_w	M_n	M_w
1	1*s*1*t*2*n*-BuSP	none	1/10	no polym				
2	1*s*1*t*2*n*-BuSP	HMPA	1/10	85	890	1300	1400	1800
3	1*s*1*t*2*n*-BuSP	HMPA	1/20	60	1200	2300	2100	3200
4	1*s*1*t*2*n*-BuSP	TMEDA	1/10	no polym				
5	1*s*1*t*2*n*-BuSP	crown ether	1/10	no polym				
6	1*i*1*t*2*n*-BuSP	HMPA	1/10	84	940	1400	1600	2700
7	1*i*1*t*2*n*-BuSP	HMPA	1/20	56	1200	2200	1800	2900

[a] Key: $[I]_0$, initial concentration of the initiator; $[M]_0$, initial concentration of the monomer; M_n and M_w, determined by GPC relative to polystyrene standards after reprecipitation.

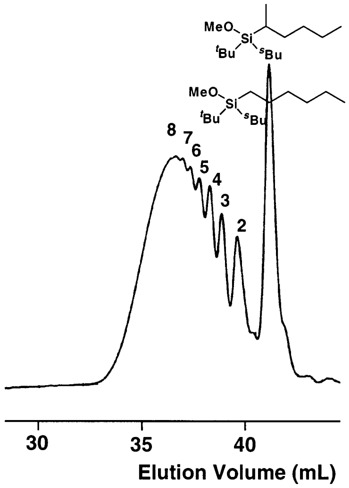


Figure 3. GPC chart for the crude products in the polymerization of 1*s*1*t*2*n*-BuSP (run 2 in Table 1).

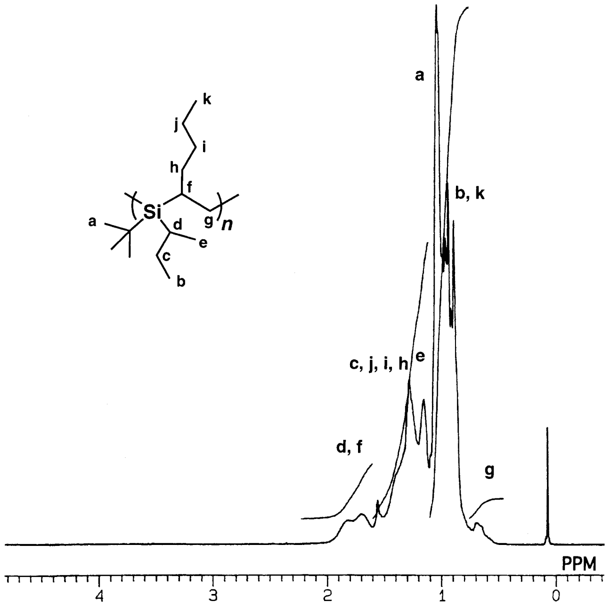


Figure 4. ^{1}H NMR spectrum of poly(1*s*1*t*2*n*-BuSP).

purification by precipitation in methanol is shown in Figure 4. All signals could be assigned to the chemical structure of a ring-opened product shown in the figure. In addition, neither methylene proton nor methyne proton signals adjacent to oxygen due to oxidation or hydrolysis of the Si−C bond in silacyclopropane were observed. From these analyses, the obtained polymer was identified as poly(1*s*1*t*2*n*-BuSP). Although the ratio of 1,2- and 1,3-ring-opened sequences could not be determined from the spectrum, it was supposed that the polymerization mainly proceeded with cleaving the 1,3-bond of the silacylopropane ring, judging from the ratio of 1,2- and 1,3-ring-opened compounds in the methoxylated products. Hexamethylphosphoramide, which solvated the counter lithium cation and activated the carbanion, was necessary for the polymerization. When the monomer was treated with butyllithium in the presence of TMEDA or 12-crown-4 instead of HMPA, no polymerization took place (runs 4 and 5).

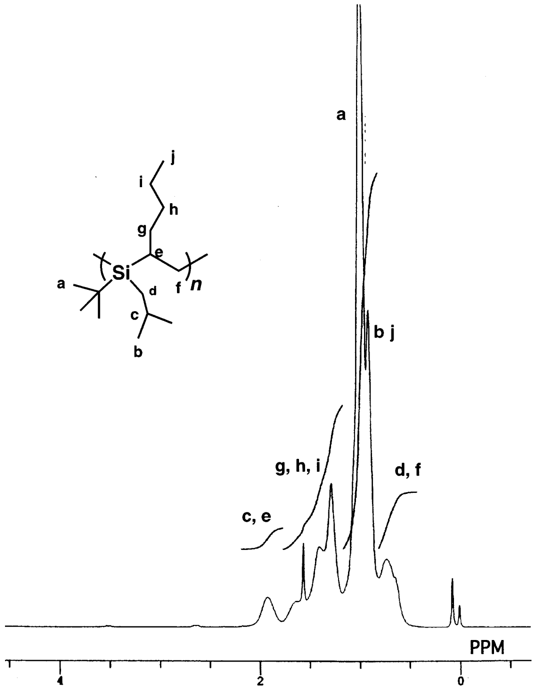


Figure 5. ^{1}H NMR spectrum of poly(1*i*1*t*2*n*-BuSP).

Polymerization of monomer 1*i*1*t*2*n*-BuSP induced by butyllithium was also examined (Scheme 2). The polymerization also proceeded in the presence of HMPA (run 6). The monomer conversion was 84%, and the M_n of the crude products relative to polystyrene was 940 when $^1/_{10}$ equiv of butyllithium was added to the monomer. The proton NMR spectrum of the polymer obtained after precipitation in methanol is shown in Figure 5. We also examined the polymerization of 2-*n*-butyl-1,1-di-*tert*-butylsilacyclobutane under the same reaction conditions, but it could not be polymerized even in the presence of HMPA. Only monomeric, dimeric, and trimeric ring-opened products were produced along with the methoxylated monomer in this case. Two *tert*-butyl groups on the silicon atom are too bulky for the propagation. This means that one of the substituents on the silicon atom must be less bulky than the *tert*-butyl group to successfully polymerize silacyclopropane.

Other polymerization methods were also examined. Bulk 1*s*1*t*2*n*-BuSP was radically polymerized at 120 °C

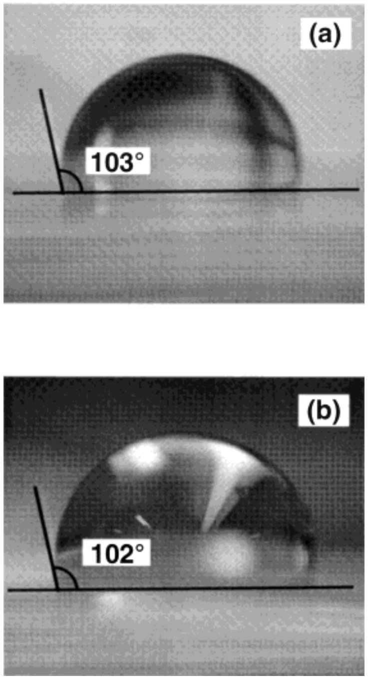


Figure 6. Photographs of a water droplet on the thin films of (a) poly(1*s*1*t*2*n*-BuSP) and (b) poly(1*i*1*t*2*n*-BuSP).

by using benzoyl peroxide as an initiator, and poly(1*s*1*t*2*n*-BuSP) ($M_n = 910$, $M_w/M_n = 1.95$) was obtained. On the other hand, transition-metal-catalyzed polymerization, which is well-known for polysilacyclobutanes,[19] did not proceed in the cases of these monomers. For instance, treatment of 1*s*1*t*2*n*-BuSP with catalytic amount of $H_2PtCl_6 \cdot nH_2O$ at 60 °C gave monomeric ring-opened compounds having a 1-hexenyl or a 1-methylenepentyl substituent, which was produced by β-hydride elimination from the monomer-platinum complex.

Properties of Polysilacyclopropanes

An interesting characteristic of the polysilacyclopropanes is their high hydrophobicity. Thin polymer films were prepared by spin-coating the polymer chloroform solutions on a glass plate. The contact angle of a water droplet on the polymer surface was measured and determined as 103° for poly(1*s*1*t*2*n*-BuSP) and 102° for poly(1*i*1*t*2*n*-BuSP), respectively (Figure 6). For comparison, we measured the contact angle of water on poly(1,1-dimethylsilacyclobutane) ($M_n = 6400$, $M_w/M_n = 1.23$) by the same method and determined it at 92°, which was much lower than the values of polysilacyclopropanes. The contact angles of polysilacyclopropanes synthesized here are remarkably high; they are higher than the reported value for polypropylene (95−98°) and almost comparable with that for poly(tetrafluoroethylene) (108−113°). This is presumably because polysilacyclopropanes synthesized here have no polar functionality but have so many methyl groups. A methyl group is much more hydrophobic than a methylene or a methyne group, and both poly(1*s*1*t*2*n*-BuSP) and poly(1*i*1*t*2*n*-BuSP) have six methyl groups in one repeating unit.

Conclusions

Two silacyclopropane derivatives, 2-*n*-butyl-1-*sec*-butyl-1-*tert*-butylsilacyclopropane (1*s*1*t*2*n*-BuSP) and 2-*n*-butyl-1-*tert*-butyl-1-isobutylsilacyclopropane (1*i*1*t*2*n*-BuSP), were newly synthesized, and their anionic ring-opening polymerizations were explored. We could polymerize these monomers in the presence of HMPA. We consider that the ring-opening polymerization of such highly strained molecules was advantageous for preparing highly substituted polymers. The obtained polymers exhibited remarkably high hydrophobicity, which may be due to the many methyl groups along the polymer backbone. Although we have not yet obtained polymers with a high molecular weight, this new polymerization technique may be useful for preparing novel polycarbosilanes. Optimization of the polymerization condition giving higher molecular weight polymers and further investigation on the polymerization mechanisms are currently in progress.

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