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Preparation of Poly(1,1-dimethyl silabutane) by Anionic Polymerization and Its Crystallization

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ABSTRACT: 1,1-Dimethyl-1-silacyclobutane was polymerized anionically with *sec*-butyllithium as an initiator in various solutions. In *n*-hexane solution with *N*,*N*,*N′*,*N′*-tetramethyl ethylenediamine, high molecular weight poly(1,1-dimethyl silabutane) was prepared without precipitation during propagation. After completion of the polymerization, the chain length of the polymer was extended stoichiometrically by successive additions of the monomer or *tert*-butoxy styrene to the polymer solution. The regularity of the head-to-tail configuration for the polymer was analyzed by ^{1}H NMR, ^{13}C NMR, and two-dimensional ^{1}H−^{13}C correlation measurements. Differential scanning calorimetry and X-ray diffraction measurement demonstrated that poly(1,1-dimethyl silabutane) is a crystalline polymer.

Introduction

Anionic polymerization may be useful for investigating the effect of terminal groups on the crystallization of homopolymers and block or graft copolymers. For instance, the terminal groups will be chemically modified through coupling reactions with a number of functional groups, and block or graft copolymers are prepared by successive addition of dissimilar monomeric species into the polymer. In this regard, several polymers and copolymers that are crystalline have been prepared and studied in previous works.[1−8] However, the polymers are difficult to prepare due to the low boiling temperature of monomers,[5] and the crystallization is difficult to investigate due to both high melting temperature and less stereo regularity of the resulting polymers.[5,9,10]

Poly(1,1-dimethyl silabutane) (PDMSB) prepared by ring-opening anionic polymerization of 1,1-dimethyl-1-silacyclobutane as a monomer is worth noting, because a boiling temperature of 1,1-dimethyl-1-silacyclobutane is high enough to treat it at ambient temperature and a stereo regularity must be ensured by ring opening of the monomer to cleave its Si−C linkage. Furthermore, it may be possible to regard PDMSB as an alternative copolymer composed of three methylene units and a $-\mathrm{Si(CH_3)_2}-$ unit, so that melting temperature, T_m, and glass transition temperature, T_g, should be lower compared to those of polymethylene, i.e., polyethylene.

Recently, the 1,1-dimethyl silabutane (DMSB) oligomer was prepared with alkyllithium as an initiator, and its anionic polymerization was proved to proceed in a living manner.[11,12] However, during the anionic polymerization of 1,1-dimethyl-1-silacyclobutane in THF at room temperature, the DMSB oligomer deposited at its degree of polymerization of about 50, resulting in a cessation of the propagation. This deposit may be expected to be a solution-grown crystal of the DMSB oligomer. Thus, it may be possible to prepare a novel crystalline polymer from 1,1-dimethyl-1-silacyclobutane in terms of living anionic polymerization, if one finds the best condition to increase the degree of polymerization.

To prepare a high molecular weight PDMSB, two factors are concerned in the present study, that is, the ability of 1,1-dimethyl-1-silacyclobutane to polymerize and the solubility of the polymer, both of which depend on the solvent. According to the previous work,[11] PDMSB may be soluble in nonpolar solvents, but not in polar solvents, i.e., THF at low temperature. In contrast, the living anionic polymerization of 1,1-dimethyl-1-silacyclobutane may proceed in the polar solvents but not in nonpolar solvents. In the present study, thus, to polymerize 1,1-dimethyl-1-silacyclobutane in nonpolar solvents, *N*,*N*,*N′*,*N′*-tetramethyl ethylenediamine (TMEDA) as a complexing agent was used with *sec*-butyllithium as an initiator. The anionic polymerization of 1,1-dimethyl-1-silacyclobutane in *n*-hexane solution was investigated by subsequent monomer addition to the polymer solution. The resulting polymer was characterized by NMR spectroscopy, size-exclusion chromatography, differential scanning calorimetry, and X-ray diffraction technique.

Experimental Section

Materials. 1,1-Dimethyl-1-silacyclobutane (Shinetsu Silicone Chemicals Co. Ltd., 99%) was dried over calcium hydride under reduced pressure, purified by distillation with the addition of 1,1-diphenylhexyllithium, and diluted with about 5 excess amounts of solvents used for the polymerization. The solvents used in the present study were *n*-hexane (Nacalai tesque Inc., 96%), THF (Nacalai tesque Inc., 99.5%), benzene (Kishida Reagents Chemicals Co. Ltd., 99%), cyclohexane (Nacalai tesque Inc., 99.5%), toluene (Nacalai tesque Inc., 99.5%), and diethyl ether (Nacalai tesque Inc., 99.5%). *n*-Hexane and cyclohexane were dried over calcium hydride under reduced pressure and purified by distillation with the addition of *n*-butyllithium. THF and ethyl ether were dried with sodium metal and distilled from a mixture of α-methylstyrene tetramer−sodium dianion. Benzene and toluene were dried over calcium hydride under reduced pressure and purified by distillation with the addition of 1,1-diphenylhexyllithium. The initiator, *sec*-butyllithium (Asia lithium Co. 99%), was diluted with *n*-hexane under reduced pressure. The concentration of the initiator was determined by titration with

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Table 1. Condition of Anionic Polymerization

no.	solvent	$T_{\text{int}}{}^{a}$/K	$T_{\text{polym}}{}^{b}$/K	t^{c}/h	$[M_0]/[I_0]$	[TMEDA] /$[I_0]$	$M_{\text{k}}{}^{d}$ X10^{-4}	$M_{\text{n}}{}^{e}$ $\times10^{-4}$	$M_{\text{w}}/M_{\text{n}}$
P1	*n*-hexane	195	300	2	611		6.11	0.47	1.41
P2	THF	195	195	2	950		9.50	1.08	1.74
P3	ethyl ether	195	273	2	853		8.53	1.05	2.55
P4	*n*-hexane/THF	195	195	2	612		6.12	0.45	1.15
P5	*n*-hexane/TMEDA	195	273	2	1200	3	12.0	9.65	1.22
P6	Cyclohexane/TMEDA	273	273	2	850	3	8.50	9.52	1.25
P7	Toluene/TMEDA	195	273	2	883	3	8.83	6.4	2.17
P8	Benzene/TMEDA	273	300	2	865	3	8.65	6.87	1.37

[a] T_{int}: Temperature of intiation. The initiation temperature was kept for 2min. [b] T_{polym}: Temperature of polymerization. [c] t: reaction time. [d] Estimated from a molar ratio of $[M_0]/[I_0]$. [e] Estimated with a calibration curve prepared for polystylene as a standard.

standard HCl solution. TMEDA was dried over calcium hydride under reduced pressure and purified by distillation with the addition of *n*-butyllithium. *tert*-Butoxystyrene (Hokko Chemical Industry Co. Ltd., 99%) was dried over calcium hydride under reduced pressure and purified by distillation with octylbenzophenone-sodium.

Preparation of Poly(1,1-dimethyl silabutane). The living anionic ring-opening polymerization was carried out with *sec*-butyllithium as an initiator under various conditions summarized in Table 1. All of the operations were carried out in a sealed glass apparatus with break-seals under a pressure of 1×10^{-3} Pa or lower. One example for the synthesis of poly(1,1-dimethyl silabutane) was as follows. First, the anionic polymerization of 1,1-dimethyl-1-silacyclobutane (15 g, 0.15mol) was initiated with 12.5 mL of a *n*-hexane solution of *sec*-butyllithium (0.012 mol/L) in *n*-hexane (500 mL) at 195 K for 2 min. Second, 7.5 mL of a *n*-hexane solution of TMEDA (0.32mol/L) to the initiator was introduced to the solution at 273 K and polymerized at 273 K for 2 h to give the products in more than 95% yield. The products were purified by reprecipitation of *n*-hexane solution into methanol three times and dried under reduced pressure at 323 K for more than 3 days.

Subsequent Monomer Addition. After completion of the polymerization, subsequent additions of monomer or *tert*-butoxy styrene were made to the living polymer solution and polymerized at 273 K for 2 h. One example of the subsequent monomer addition was as follows. First, the anionic polymerization of 1,1-dimethyl-1-silacyclobutane (2 g, 0.02 mol) was initiated with 3.4 mL of a *n*-hexane solution of *sec*-butyllithium (0.012 mol/L) in *n*-hexane (300 mL) at 195 K for 2 min. Second, 0.4 mL of a *n*-hexane solution of TMEDA (0.32 mol/L) to the initiator was introduced to the solution at 273 K and polymerized at 273 K for 2 h. Third, subsequently, 2 g of the monomer was added to the living polymer solution and polymerized at 273 K for 2 h each. The products were purified by reprecipitation of *n*-hexane solution into methanol three times and dried under reduced pressure at 323 K for more than 3 days. In the case of subsequent addition of *tert*-butoxy styrene, a 5 M amount of the monomer to the initiator was added to the living polymer solution and polymerized at 273 K for 2 h.

Molecular Characterization. Apparent molecular weights and molecular weight distribution, $M_{\text{w}}/M_{\text{n}}$, of the polymers were determined by GPC system of Tosoh Ltd., with a CCPD pump, a RI-8012 differential refractive index detector, a UV-8011 ultraviolet spectroscopic detector, and a series of three G4000HXL columns (bead size is 5μm, pore size is 10^4 angstrom) with 300 mm length and 7.8 mm i.d. each. THF was used as an eluent, and the flow rate was 0.5 mL/min, at room temperature. Standard polystyrenes were used for a calibration.

NMR measurements were carried out using a JEOL EX-400 NMR spectrometer operating at 399.65 and 100.4 MHz for ^{1}H and ^{13}C, respectively. The polymer was dissolved into chloroform-*d* without TMS. Chemical shifts were referred to chloroform in chloroform-*d*. ^{1}H and ^{13}C NMR measurements were carried out at 323 K at pulse repetition times of 7 and 5 s, respectively. A two-dimensional ^{1}H$-$^{13}C correlation measurement was made to collect two-dimensional hyper complex data. After weighting with a shifted sine-bell function, the data was Fourier transformed in the absolute value mode.

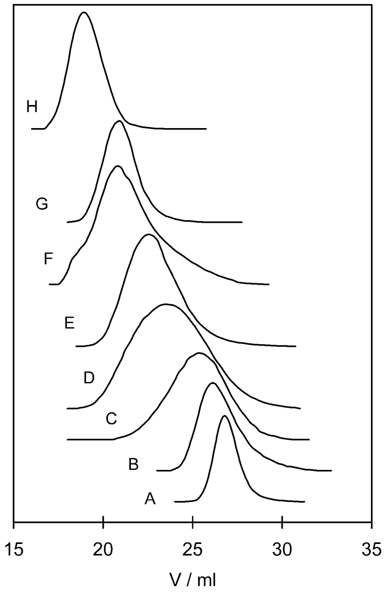

Figure 1. Size exclusion chromatograms of products prepared by anionic polymerization of 1,1-dimethyl-1-silacyclobutane in various solutions: A, *n*-hexane/THF; B, *n*-hexane; C, THF; D, ethyl ether; E, *n*-hexane/TMEDA; F, cyclohexane/TMEDA; G, benzene/TMEDA; H, toluene/TMEDA. The other conditions of the preparation were tabulated in Table 1.

Crystallization and melting of poly(1,1-dimethyl silabutane) prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$ were assessed with a Seiko Instruments DSC 220, which was calibrated with standard indium and linoleic acid before the measurement. The polymer packed into an aluminum pan was heated at 353 K to melt the preexisting crystal before crystallization proceeded. The melted polymer was cooled to the crystallization temperature as soon as possible with liquid nitrogen and was crystallized. After crystallization, the DSC measurement was made from 153 to 373 K at a heating rate of 10 K/min. The melting temperature was determined as a peak top of the melting endotherm, and the glass transition temperature was defined as the point of intersection between the baseline and the tangent line at the inflection point of the DSC thermogram.

Measurement of X-ray diffraction was made with a MAC Science M03X-HF for the film specimen crystallized at 298 K after melting at 353 K.

Results and Discussion

Characterization. Figure 1 shows size exclusion chromatograms for products prepared by anionic polymerization of 1,1-dimethyl-1-silacyclobutane in various solutions, i.e., *n*-hexane/THF, *n*-hexane, THF, ethyl ether, *n*-hexane with TMEDA, cyclohexane with TMEDA, benzene with TMEDA, and toluene with TMEDA. The estimated values of apparent number average

Table 2. Molecular Weight and Molecular Weight Distribution of PDMSB Prepared in *n*-Hexane with TMEDA

[TMEDA]/[Li]	$T_{\mathrm{int}}{}^{a}$/K	$T_{\mathrm{polym}}{}^{b}$/K	t/h^{c}	$[M_0]/[I_0]$	$M_k{}^{d}$ X10^{-5}	$M_n{}^{e}/10^{-5}$	M_w/M_n
0.5	195	273	2	1250	1.25	1.01	1.34
1	195	273	2	1250	1.25	1.03	1.33
2	195	273	2	1220	1.22	1.05	1.26
3	195	273	2	1200	1.20	0.96	1.22
10	195	273	2	1050	1.05	1.15	1.37

[a] T_{int}: Temperature of initiation. The initiation temperature was kept for 2min. [b] T_{polym}: Temperature of polymerization. [c] t: reaction time. [d] Estimated from a molar ratio of $[M_0]/[I_0]$. [e] Estimated with a calibration curve prepared for polystyrene as a standard.

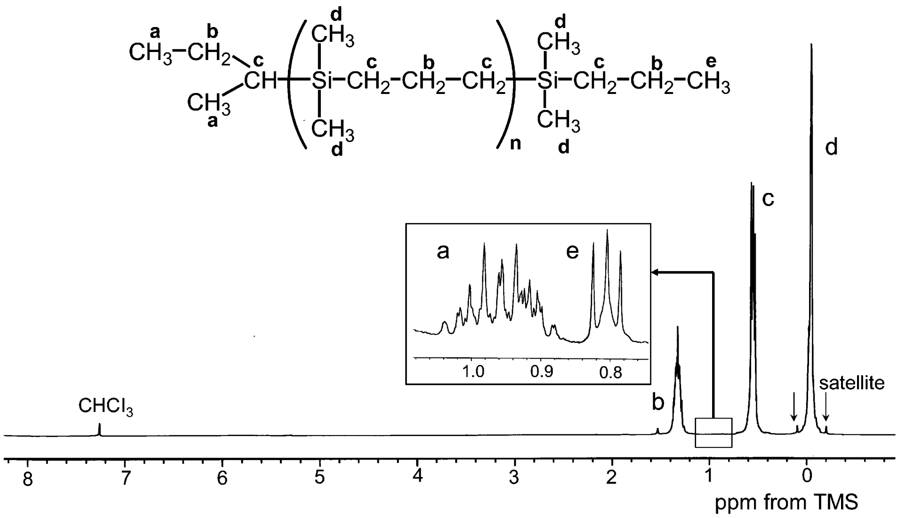

Figure 2. ^{1}H NMR spectrum of PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$. The other conditions of the preparation were tabulated in Table 2.

molecular weight, M_n, apparent weight average molecular weight, M_w, and molecular weight distribution, M_w/M_n, are tabulated in Table 1. These were roughly classified into three categories, that is, low molecular weight, middle molecular weight with a broad distribution, and high molecular weight with a narrow distribution. Among the polymers, the low molecular weight product prepared in THF solution was attributed to deposition during the polymerization as in the case of the previous work.[12] In contrast, the highest M_n of about 10^5 and the narrowest distribution of 1.22 were attained for poly(1,1-dimethyl silabutane) (PDMSB) prepared with *sec*-butyllithium/TMEDA in *n*-hexane solution. This may be due not only to the good solubility of PDMSB in *n*-hexane but also to the complexing effect of TMEDA that is attractive with Li^+.

To clarify the effect of TMEDA in the polymerization of 1,1-dimethyl-1-silacyclobutane in *n*-hexane solution, variations in M_n, M_w, and M_w/M_n of PDMSB on a ratio of [TMEDA]/[Li] at definite [Li] are shown in Table 2. The values of M_n and M_w depended a little on the ratio of [TMEDA]/[Li], whereas the value of M_w/M_n depended significantly upon the ratio of [TMEDA]/[Li], being the smallest at [TMEDA]/[Li] = 3. This may be attributed to a smaller complexing effect and the side reactions because of smaller and larger amounts of TMEDA, respectively. Leading and tailing in the chromatograms were confirmed for the PDMSBs prepared at [TMEDA]/[Li] = 10 and 1, respectively. The best ratio of [TMEDA]/[Li] is 3 for the anionic polymerization of 1,1-dimethyl-1-silacyclobutane in *n*-hexane solution.

A typical ^{1}H NMR spectrum of PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$ is shown in Figure 2. The three major signals that appeared in the aliphatic region were assigned in turn to methyl and methylene groups linking to the Si atom and the methylene group between the methylene groups linking to Si atom, according to the assignment reported in the previous work.[12] Two small triplet signals and a quintet signal were assigned to terminal methyl groups of *sec*-butyl group and 1,1-dimethyl-1-silabutyl group, respectively. An intensity ratio of the

Table 3. Chemical Shift of ^{1}H Signals for PDMSB

	δ/ppm	
^{1}H	Matsumoto et al.	this work
a	0.9[a]	0.86−1.05[b]
b	1.20−1.38	1.37
c	0.52−0.59	0.57
d	−0.07	−0.05
e	0.87	0.77−0.84

[a] *n*-Butyllithium. [b] *sec*-Butyllithium.

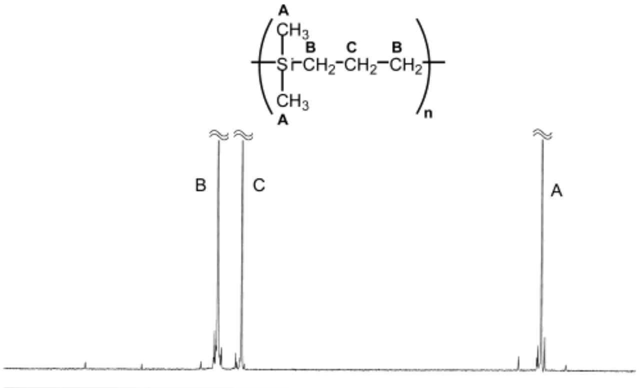

Figure 3. ^{13}C NMR spectrum of PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$. The other conditions of the preparation were tabulated in Table 2.

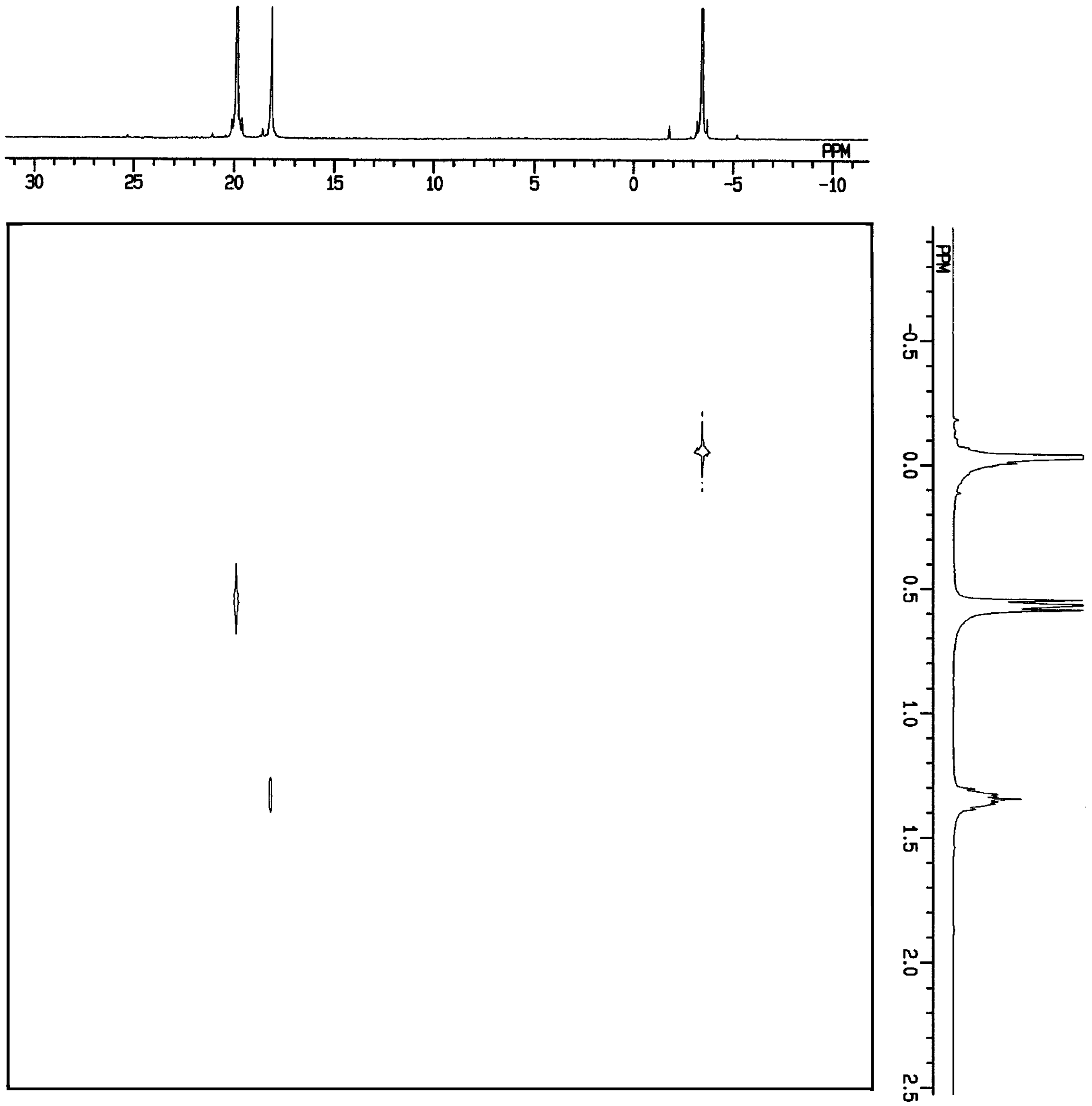

Figure 4. Two-dimensional $^1H-^{13}C$ correlation spectrum of PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$. The other conditions of the preparation were tabulated in Table 2.

sec-butyl group and 1,1-dimethyl-1-silabutyl group was about 2:1, being the same as the stoichiometric ratio. The chemical shifts of these signals are tabulated in Table 3.

Figure 3 shows the ^{13}C NMR spectrum of PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$. Three major signals appeared in the spectrum, as in the case of the ^1H NMR spectrum. To assign the signals, a correlation between ^1H and ^{13}C was analyzed through the two-dimensional $^1H-^{13}C$ correlation measurement. The two-dimensional spectrum for PDMSB is shown in Figure 4, in which the cross-peaks appeared due to the spin coupling between ^1H and ^{13}C. Thus, the ^{13}C signals were correlated to the well-assigned ^1H signals. According to the assignments for the ^1H signals, the signal at −3.1 ppm was assigned to the methyl group linking to the Si atom, and the signal at 20.1 ppm was assigned to the methylene group linking to the Si atom. The signal at 18.5 ppm was assigned to the methylene group between the methylene groups linking to the Si atom, which are more shielded rather than the methylene group linking to the Si atom.[13] The assignments for the major signals are marked in Figure 3. Because the three ^{13}C signals are only shown for DMSB repeating units of PDMSB except for the terminal units, as shown in Figure 3, the DMSB units are suggested to link to each other in a manner of head-to-tail configuration.

Subsequent Monomer Addition. Subsequent monomer addition was made by adding the monomer of $[M_0]/[I_0] = 1.24 \times 10^3$ into the *n*-hexane solution of PDMSB having an active anionic end where [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.8 \times 10^2$. Typical size exclusion chromatograms for PDMSB and subsequently monomer-added PDMSB are shown in Figure 5. The peak is unimodal and symmetrical. The distribution for PDMSB was somewhat broader than that for subsequently monomer-added PDMSB. The fact that the higher the molecular weight is the narrower the distribution is agrees well with the conclusion derived by Flory,[14] who assumed that an initiator produced a polymer without any termination and chain transformation.

Figure 6 shows a plot of number average molecular weight, $M_{n,NMR}$, versus a ratio of [monomer]/[Li] for both

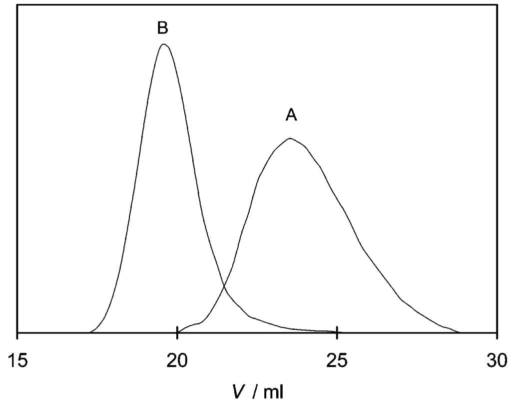

Figure 5. Size exclusion chromatograms for (A) PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.8 \times 10^2$ and (B) PDMSB prepared by subsequent addition of monomer of $[M_0]/[I_0] = 1.24 \times 10^3$ to the solution of (A) having an active anionic end.

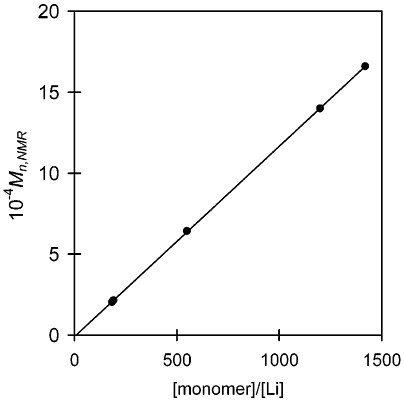

Figure 6. Plot of M_n versus [monomer]/[Li] for PDMSB and subsequently monomer-added PDMSB.

PDMSB and subsequently monomer-added PDMSB, where $M_{n,NMR}$ was estimated from an intensity ratio of methyl group of DMSB unit to methyl group of *sec*-butyl group. The $M_{n,NMR}$ increased linearly as the ratio of [monomer]/[Li] increased. This demonstrates that the anionic polymerization of 1,1-dimethyl-1-silacyclobutane proceeds without chain transfer.[15]

To ensure little chain transfer in the anionic polymerization, *tert*-butoxy styrene was added to the *n*-hexane solution of PDMSB having an active anionic end, where [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.8 \times 10^2$. The ^{1}H NMR spectrum for PDMSB linking to *tert*-butoxy styrene (PDMSB−BOS) is shown in Figure 7. The signals assigned to the DMSB unit were clearly shown in the spectrum for PDMSB−BOS. In contrast, the signal at about 0.8 ppm, assigned to the methyl group of 1,1-dimethyl-1-silabutyl group disappeared, whereas signals raging from 6.8 to 7.1 ppm appeared, which were assigned to the phenyl group as marked in Figure 7. From the intensity ratio of the phenyl group to the *sec*-butyl group, the number of *tert*-butoxy styrene groups linking up to PDMSB was estimated to be about one, suggesting that the active anionic end of PDMSB was end-capped with *tert*-butoxy styrene. This may be supporting evidence that most of the active anionic ends that generate with the initiator are used for polymerization of 1,1-dimethyl-1-silacyclobutane and they react with *tert*-butoxy styrene without chain transfer. Consequently, we conclude that PDMSB was prepared by anionic polymerization of 1,1-dimethyl-1-silacyclobutane without chain transfer in *n*-hexane solution at [TMEDA]/[Li] = 3.

Crystallization and Melting. A typical DSC thermogram for PDMSB, crystallized at 298 K after heating to 353 K, is shown in Figure 8, in which PDMSB was prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$. An endothermic peak was shown in the thermogram at 310 K. This may be expected to be a melting of the resulting crystal as the temperature rises, because a wide-angle X-ray diffraction pattern of the crystallized PDMSB was composed of sharp peaks and a halo as shown in Figure 9. Figure 10 shows a plot of T_m versus crystallization temperatures, T_c.[16] The T_m of PDMSB was linearly proportional to T_c. Thus, an equilibrium melting temperature, T_m^0, was estimated to be 322 K from a point of intersection between the line and a line of $T_m = T_c$.[16] On the other hand, a glass transition temperature was determined to be 218 K.

An exothermic peak due to the crystallization of PDMSB at 283 K is shown in Figure 11. The half-life of the crystallization, $t_{1/2}$, was defined to be the time at

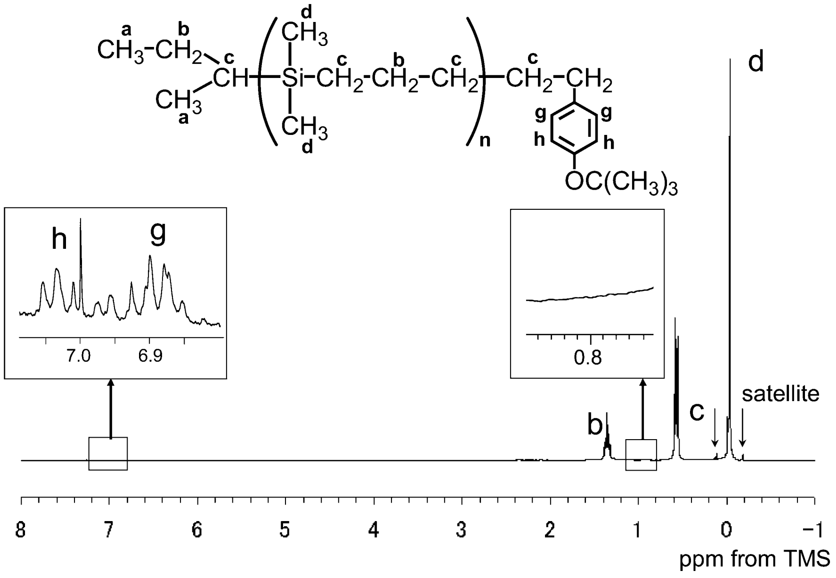

Figure 7. ^{1}H NMR spectrum of PDMSB linking to *tert*-butoxy styrene.

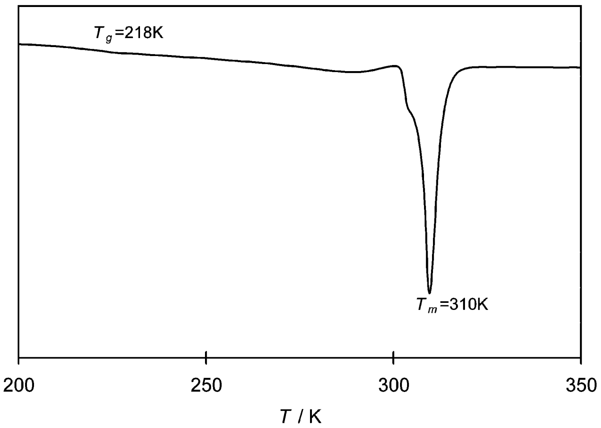

Figure 8. DSC thermogram for PDMSB crystallized at 298 K after heating at 353 K. The PDMSB was prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$.

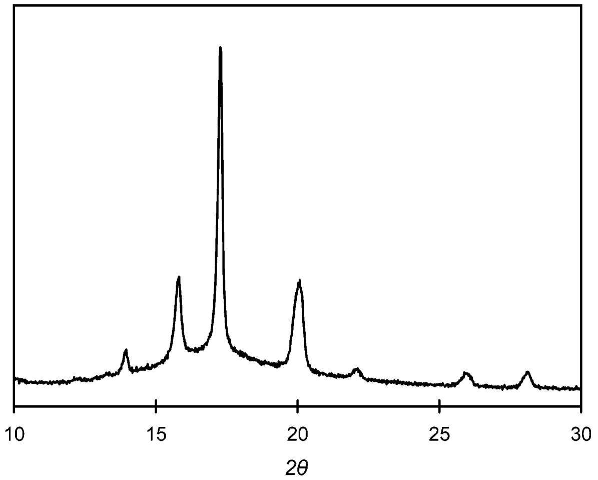

Figure 9. Wide-angle X-ray diffraction pattern of the PDMSB crystallized at 298 K after annealing at 353 K. PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$.

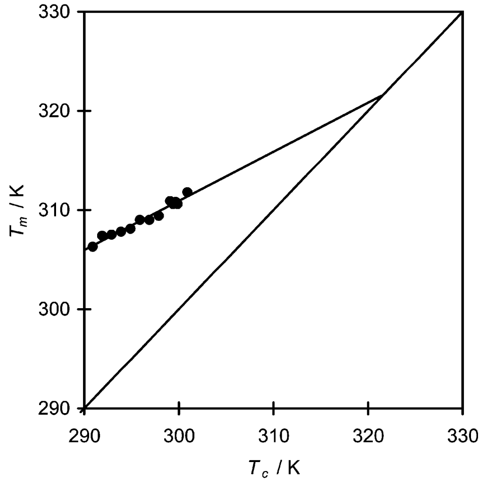

Figure 10. Plot of T_m versus crystallization temperature, T_c, for PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$.

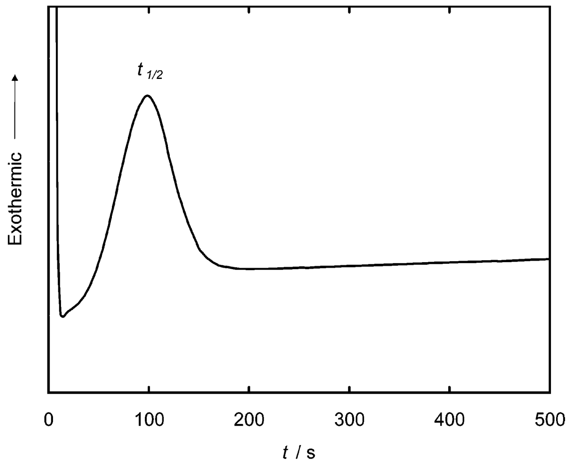

Figure 11. Exothermic peak due to the crystallization at 283 K for PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$.

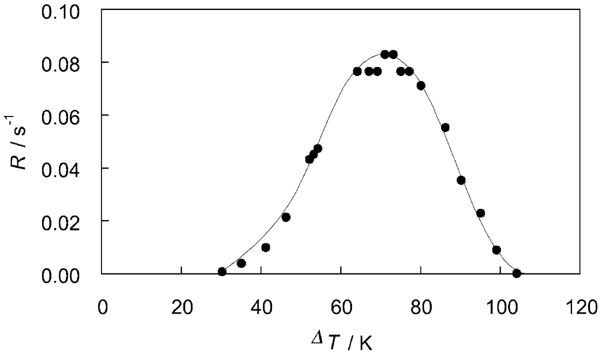

Figure 12. Overall crystallization rate of PDMSB prepared in *n*-hexane solution at [TMEDA]/[Li] = 3 and $[M_0]/[I_0] = 1.2 \times 10^3$.

which the exothermic reached a maximum. Thus, an overall rate of crystallization,[17] R, was estimated from $t_{1/2}$; $R = t_{1/2}^{-1}$. The estimated values of R are plotted against supercooling, $\Delta T = T_m^0 - T_c$, in Figure 12. A locus of R versus ΔT drew a bell-shaped curve between T_g and T_m^0, characteristic of the crystalline polymer. As a result, PDMSB was shown to be the crystalline polymer.

Conclusion

The high molecular weight PDMSB, whose $M_n > 10^5$, was prepared by living anionic polymerization of 1,1-dimethyl-1-silacyclobutane in *n*-hexane solution at [TMEDA]/[Li] = 3. The PDMSB consisted of 1,1-dimethyl silabutane units linking to each other just in a regular head-to-tail configuration and well-defined terminal units. The T_m^0 and T_g of PDMSB were 322 and 218 K, respectively. The overall rate of crystallization depended on supercooling between T_m^0 and T_g, characteristic of the crystalline polymer.

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