Anionic Polymerization of *p*-Pentamethyldisilyl-, *p*-Heptamethyltrisilyl-, and *p*-nonamethyltetrasilylstyrenes¹

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ABSTRACT: The anionic polymerizations of *p*-pentamethyldisilylstyrene (**1**), *p*-heptamethyltrisilylstyrene (**2**), and *p*-nonamethyltetrasilylstyrene (**3**) were carried out under various conditions. The polymerizations of **1** and **2** proceeded in a living manner in THF at -78 °C to quantitatively afford polymers with predictable molecular weights and narrow molecular weight distributions. Suitable initiators for these living anionic polymerizations were *sec*-BuLi, lithium, sodium, and potassium naphthalenides, cumylpotassium, and living oligomers of α -methylstyrene lithium, sodium, and potassium salts. Well-defined diblock copolymers, poly(1)-*block*-polystyrene, poly(2)-*block*-polystyrene, polystyrene-*block*-poly(1), and polystyrene-*block*-poly(2) were successfully synthesized under similar conditions by a two-step sequential monomer addition, namely, styrene followed by **1** or **2**, or vice versa. In contrast, the polymerization of **3** was problematic. No polymer was obtained in the polymerization of **3** in either THF at -78 °C or benzene at 40 °C with *sec*-BuLi and oligo(α -methylstyryl)lithium. Using oligo(α -methylstyryl)potassium as an initiator, **3** was polymerized quantitatively in THF at -78 °C for 0.5 h. Unfortunately, the side reaction, presumably attack of the Si-Si-Si bond by the growing chain-end anion, could not be completely suppressed during the polymerization, which resulted in the formation of high molecular weight polymers by coupling between polymer chains.

Introduction

Silicon–silicon (Si–Si) bonds, unlike their C–C counterparts, exhibit unique and unusual electronic, photochemical, and photophysical properties.² Their chemistry is also unique. For example, Si–Si bonds are cleaved with several electrophiles as well as nucleophiles.³ They are readily oxidized to Si–O–Si bonds because of a strong affinity for oxygen.⁴ These reactivities make polymers containing Si–Si bonds attractive as functional polymers, since their Si–Si bonds can participate in a variety of useful and interesting reactions. However, such reactivities are not favorable in radical and ionic polymerization of monomers with Si–Si bonds.

Despite the reactivity of Si-Si bonds, Saigo and Watanabe demonstrated that *p*-(2-allyl-1,1,2,2-tetramethyl)disilyl- α -methylstyrene could be quantitatively polymerized with *n*-BuLi in THF at -78 °C without difficulty.⁵ In the meantime, we have found for the first time that *p*-pentamethyldisilylstyrene (1) and *p*-heptamethyltrisilylstyrene (2) successfully undergo living anionic polymerization with sec-BuLi and oligo(α-methylstyryl)lithium in THF at -78 °C.¹ The success of the living polymerization clearly demonstrates that the Si-Si and even Si-Si-Si bonds are sufficiently stable toward highly reactive anionic initiators and growing chain-end carbanions derived from 1 and 2. This is in sharp contrast to the fact that Si-Si linkages are readily cleaved by nucleophiles under similar conditions. For example, the Si-Si bond cleavage of disilanes by lithium and sodium-potassium alloy has been known for a long time as one of the most convenient methods for the preparation of R_3SiM (M = Li, K).^{3,6} It has been observed that alkyllithiums and trialkylsilyllithiums are also useful in the cleavage of disilanes.^{3,7} Furthermore,

Matyjaszewski and co-workers reported that poly(methylphenylsilylene) and poly(dihexylsilylene) were degraded by alkali metals and their naphthalenides to exclusively afford cyclic oligomers via the cleavage of their Si–Si bonds.⁸ Saegusa et al. also suggested that the same cleavage was occurring during the anionic ring-opening polymerization of phenylnonamethylcyclopentasilane.⁹ We therefore studied the anionic polymerization of monomers possessing Si–Si and Si–Si– Si bonds in further detail.

Herein, we present full details of the anionic polymerization of **1**, **2**, and *p*-nonamethyltetrasilylstyrene (**3**), a related new styrene derivative possessing a Si–Si– Si–Si bond as shown below:



The overall objective of this study is to explore the generality and limitation of living anionic polymerization of the substituted styrenes with permethylated oligosilane moieties, as part of our program to study the anionic polymerization of monomers containing functional silyl groups.¹⁰

Experimental Section

Materials. Reagents were purchased from Tokyo Kasei, Tokyo, Japan (reagent grade), unless otherwise stated. Both styrene and α -methylstyrene were washed with 10% NaOH and water successively and dried over CaCl₂. After filtration, they were distilled twice from CaH₂ under reduced pressure and then distilled from dibutylmagnesium (ca. 5 mol %) on a vacuum line into ampules with break seals that were pre-

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washed with 1,1-diphenylhexyllithium in heptane. Both benzene and heptane were washed successively with H₂SO₄ and water and dried over CaCl₂. After filtration, they were distilled from P₂O₅ under nitrogen and then distilled from sec-BuLi (ca. 5 mol %) on a vacuum line into ampules with break seals that were prewashed with 1,1-diphenylhexyllithium in heptane. THF was refluxed over sodium wire for 5 h and, after filtration, distilled from LiAlH₄ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a vacuum line. Alkali metal naphthalenides were prepared in sealed reactors with break seals under high vacuum conditions by reactions of the corresponding alkali metals with a 1.1-fold excess of naphthalene in THF for a few hours at 25 °C. After filtration, their concentrations were determined by colorimetric titration using absolute 1-octanol in THF in sealed reactors under high vacuum conditions. Living oligomers of α -methylstyrene were prepared from sec-BuLi or alkali-metal naphthalenides and ca. a 3-fold excess of α-methylstyrene in THF at 25 °C for 1 min and at -78 °C for 1 h. 4-Chlorostyrene (99%, Hokko Chemical Industry Co., Ltd) was distilled over CaH₂ two times under reduced pressures. Pentamethyldisilyl chloride (98%) was purchased from Shinnetsu Chemical. Co., Ltd. Both heptamethyltrisilyl chloride and nonamethyltetrasilyl chloride were prepared according to the procedures previously reported.11

Measurements. Both ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were measured in CDCl3 using a Bruker DPX spectrometer. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ¹H NMR and to CDCl₃ (δ 77.1) for ¹³C NMR. Size-exclusion chromatography (SEC) was performed on a TOSOH HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three polystyrene gel columns (TSKgel G4000HXL, G3000HXL, G2000H_{XL} or TSK_{gel} G5000H_{XL}, G4000H_{XL}, G3000H_{XL}) were used. Measurable molecular weight ranges are 10^3 to 5×10^4 and 10^4 to 5×10^5 , respectively. A calibration curve was made to determine M_n and M_w/M_n values with standard polystyrenes. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple and with equipment of very exact temperature control. Therefore, molecular weight can be measured up to 100 \pm 5 kg/mol.

p-Pentamethyldisilylstyrene (1). The title styrene, 1, was synthesized by the reaction of pentamethyldisilyl chloride with the Grignard reagent of p-chlorostyrene. The Grignard reagent, prepared from p-chlorostyrene (14.7 g, 106 mmol) and magnesium (3.01 g, 111 mmol) in THF (100 mL) was added dropwise to a dry THF solution (50 mL) containing pentamethyldisilyl chloride (15.4 g, 92 mmol). The resulting mixture was stirred at reflux for 5 h. It was acidified with 1 N HCl, extracted with ether, and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using hexanes as eluents. The eluted portions showing one spot were collected and the solvent was evaporated to afford a colorless oil. It was distilled from CaH₂ under reduced pressure at 63-65 °C (0.15 Torr) to yield 1 (9.34 g, 40 mmol, 44%) as a colorless liquid: ¹H NMR (CDCl₃) & 7.30-7.20 (m, 4H, HAr), 6.53 (dd, 1H, =CH), 5.65, 5.05 (2d, 2H, $-C=CH_2$, J = 11.0, 17.7 Hz), 0.18 (s, 6H, Si(CH₃)₂), 0.09 (s, 9H, Si(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.5 (C4, Ar), 137.7 (C1, Ar), 137.1 (CH₂ = CH), 134.1 (C3, Ar), 125.7 (C2, Ar), 113.8 (CH2=CH), -2.13 ((CH3)3-Si(CH₃)₂Si), -3.88 ((CH₃)₃Si(CH₃)₂Si); IR (neat, cm⁻¹) 781 (Si-C stretch), 802 (Si-C stretch), 1246 (Si-CH₃ deformation), 2952 (Si-C stretch).

p-Heptamethytrisilylstyrene (2). The title styrene, **2**, was synthesized by the reaction of heptamethyltrisilyl chloride (20.1 g, 90 mmol) with the Grignard reagent of *p*-chlorostyrene, prepared from *p*-chlorostyrene (13.2 g, 95 mmol) and magnesium (2.71 g, 100 mmol), similar to the synthetic procedure employed for **1**. Styrene, **2**, was isolated by column chromatography on silica gel using hexanes as eluents and dried by fractional distillation from CaH₂ under reduced pressure at 96 – 101 °C (0.16 Torr) to yield **2** (4.99 g, 17 mmol, 19%) as a

colorless liquid: ¹H NMR (CDCl₃) δ 7.30–7.20 (m, 4H, HAr), 6.47 (dd, 1H, =CH), 5.70, 5.10 (2d, 2H, -C=CH₂, *J* = 10.8, 18.0 Hz), 0.26 (s, 6H, (CH₃)₃Si(CH₃)₂Si(*CH*₃)₂Si), 0.03 (s, 6H, (CH₃)₃Si(*CH*₃)₂Si(CH₃)₂Si), -0.11 (s, 9H, Si(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.7 (C4, Ar), 137.2 (CH₂ = *C*H), 134.8 (C1, Ar), 134.0 (C3, Ar), 125.7 (C2, Ar), 113.8 (*C*H₂=CH), -1.34 ((CH₃)₃Si(CH₃)₂Si(*C*H₃)₂Si), -2.95 ((CH₃)₃Si(*C*H₃)₂Si(CH₃)₂Si), -6.66 ((*C*H₃)₃Si(CH₃)₂Si(CH₃)₂Si); IR (neat, cm⁻¹) 779 (Si–C stretch), 813 (Si–C stretch), 1245 (Si–CH₃ deformation), 2952 (Si–C stretch).

p-Nonamethytetrasilylstyrene (3). The title styrene, 3, was synthesized by the reaction of nonamethyltetrasilyl chloride (18.6 g, 65 mmol) with the Grignard reagent of p-chlorostyrene, prepared from p-chlorostyrene (8.82 g, 64 mmol) and magnesium (1.81 g, 67 mmol), similar to the synthetic procedure employed for 1. Styrene, 3, was isolated by column chromatography on silica gel using hexanes as eluents and dried by fractional distillation from CaH₂ under reduced pressure at 110 - 120 °C (0.16 Torr) to yield 3 (4.03 g, 12 mmol, 18%) as a colorless liquid: ¹H NMR (CDCl₃) δ 7.33-7.17 (m, 4H, HAr), 6.62 (dd, 1H, =CH), 5.60, 5.05 (2d, 2H, $-C=CH_2$, J = 11.0, 17.6 Hz), 0.26 (s, 6H, $(CH_3)_3Si(CH_3)_2$ -Si(CH₃)₂Si(CH₃)₂Si), 0.03 (s, 21H, (CH₃)₃Si(CH₃)₂Si(CH₃)₂Si-(CH₃)₂Si); ¹³C NMR (75 MHz, CDCl₃) δ 140.2 (C4, Ar), 137.7(C1, Ar), 137.1(CH₂ = CH), 134.0 (C3, Ar), 125.6(C2, Ar), 113.7 (C H_2 =CH), 0.49 ((CH₃)₃Si(CH₃)₂Si(CH₃)₂Si(CH₃)₂Si), -1.20 ((CH₃)₃Si(CH₃)₂Si(CH₃)₂Si(CH₃)₂Si), -2.81((CH₃)₃Si- $(CH_3)_2Si(CH_3)_2Si(CH_3)_2Si), -5.44 ((CH_3)_3Si(CH_3)_2Si(CH_3)_2Si-2Si(CH_3)_2Si)$ (CH₃)₂Si); IR (neat, cm⁻¹) 777 (Si-C stretch), 812 (Si-C stretch), 1245 (Si-CH₃ deformation), 2947(Si-C stretch).

The styrene derivatives, 1-3, thus synthesized were finally purified by distillation from dibutylmagnesium (ca. 5 mol %) under high vacuum conditions. They were diluted with THF or benzene to about 1 M solutions and stored at -30 °C.

Anionic Polymerization of 1-3. The anionic polymerization was carried out under a high-vacuum condition (10^{-6}) Torr) in sealed glass reactors with break seals. The reactors were always prewashed with the initiator solutions after being sealed off from the vacuum line. A typical polymerization experiment was as follows. A THF (2.44 mL, 0.888 M) solution of $\mathbf{\hat{1}}$ (0.508 g, 2.17 mmol) kept at -78 °C was added to a THF (3.67 mL, 0.0244 M) solution of potassium naphthalenide (0.0895 mmol) through the break-seal with vigorous stirring at -78 °C. The reaction mixture was allowed to stand for an additional 0.5 h at $-78\ ^\circ C$ and quenched with degassed methanol. The polymer was precipitated in methanol, reprecipitated twice from THF into methanol, and freeze-dried from its benzene solution for 24 h. A polymer yield was quantitative. The SEC showed a sharp monomodal distribution: $M_n = 12$ kg/mol, $M_w/M_n = 1.05$. The M_n value determined by VPO was 15 kg/mol and closed to that predicted ($M_n = 13$ kg/mol). ¹H NMR (CDCl₃): δ 7.3–6.2 (m, 4H, HAr), 2.0–1.0 (m, 3H, CH₂– CH), 0.29 (s, 6H, Si(CH₃)₂), 0.01 (s, 9H, Si(CH₃)₃). Similarly, the anionic polymerizations of 1-3 were carried out in either THF at -78° °C or in benzene at 40 °C.

Block Copolymerization. The synthesis of an AB diblock copolymer of **1** and styrene was carried out by the sequential addition of 1 followed by styrene in a manner similar to the homopolymerization. The first stage polymerization was carried out by mixing a THF (0.808 M, 8.25 mL) solution of 1 (1.56 g, 6.67 mmol) with $oligo(\alpha$ -methylstyryl)lithium (0.181 mmol) in THF (6.25 mL) at -78 °C. The reaction mixture was allowed to stir for an additional 0.5 h at -78 °C. A small portion (4.35 mL) was sampled to determine the molecular weight and molecular weight distribution. The second block was prepared by adding a THF (0.938 M, 19.5 mL) solution of styrene (1.90 g, 18.3 mmol) to the living polymer solution produced in the first-stage polymerization. After 0.5 h, the reaction mixture was quenched with degassed methanol, and the polymer (2.95 g, 99% yield) was precipitated in methanol. It was purified by reprecipitation twice and freeze-dried. SEC profiles of the polymers obtained at the first- and second-stage polymerizations showed sharp monomodal distributions. Their $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ values were 8.6 and 19 kg/mol and 1.05 and 1.09, respectively. The observed composition of [1] to [styrene]



Figure 1. ¹H NMR spectra of **1** (A) and the resulting polymer (B).

by ¹H NMR was 26/74 close to the calculated value of 20/80. The anionic block copolymerization of **1**, **2**, or **3** with styrene was carried out in a similar way.

Results and Discussion

Anionic Polymerization of *p*-Pentamethyldisilylstyrene (1). The anionic polymerization of 1 was first carried out in THF at -78 °C for 0.5 h with various anionic initiators such as sec-BuLi, cumylpotassium, and lithium, sodium, and potassium naphthalenides. In addition, living oligomers of α -methylstyrene prepared from sec-BuLi, lithium, sodium, or potassium naphthalenides, and α -methylstyrene were used. There was an instantaneous change in the color of the solution to either orange red (in the case of Li⁺ as a countercation) or dark red (in the cases of Na⁺ and K⁺ as countercations) where the monomer solution was added to each of the initiators. The intense colors remained unchanged at -78 °C even after 24 h, but disappeared immediately by quenching with degassed methanol. Yields of polymers were quantitative in all cases. Figure 1 shows ¹H NMR spectra of 1 and the resulting polymer. A s can be seen, the resonances corresponding to the vinyl protons of 1 disappear completely. The results are summarized in Table 1. Like most styrene monomers, no polymerization occurred with Grignard reagents such as benzylmagnesium chloride and dibutylmagnesium, LiAlH₄, and potassium *tert*-butoxide.

As previously reported,¹ both *sec*-BuLi and oligo(α methylstyryl)lithium were effective initiators to quantitatively afford the polymers with predictable molecular weights and narrow molecular weight distributions; their M_w/M_n values were less than 1.04. Although the estimated M_n values by SEC relative to polystyrene were always somewhat smaller than those calculated from [monomer] to [initiator] ratios, the observed $M_{\rm n}$ values by VPO agreed well with those calculated. As can be seen in Table 1, sodium and potassium naphthalenides, cumylpotassium, and living oligomers of α -methylstyrene sodium and potassium salts are also effective initiators, giving the polymers with $M_{\rm n}$ values close to the calculated ones and narrow molecular weight distributions in 100% yield. Differences among counterions of such initiators were not observed in yields

Table 1. Anionic Polymerization of 1 in THF at -78 °C for 0.5 h^a

	[1]₀/	$M_{ m n} imes 10^{-3}$			
initiator	[initiator] ₀	calcd	SEC^b	VPO	$M_{\rm w}/M_{\rm n}{}^b$
sec-BuLi/aMS ^c	64.1	15	12	16	1.03
<i>sec</i> -BuLi/αMS	124	31	29	38	1.03
<i>sec</i> -BuLi/αMS	323	76	60	81	1.03
sec-BuLi	34.2	8.3	6.1	8.2	1.04
$Li-Nap^d$	39.4	14	12	16	1.06
Na-Nap ^e	28.0	14	10	13	1.11
Na-Nap/αMS	32.8	17	15	19	1.13
Cumyl-K ^f	36.0	12	7.5	10	1.08
K–Nap ^g	22.0	11	7.6	10	1.03
K–Nap	24.2	13	12	15	1.05
K–Kap/αMS	66.0	33	27	36	1.05

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} Both M_n and M_w/M_n values were estimated by SEC using a standard polystyrene calibration curve. ^{*c*} α -Methylstyrene. ^{*d*} Lithium naphthalenide. ^{*e*} Sodium naphthalenide. ^{*f*} Cumylpotassium. ^{*g*} Potassium naphthalenide.

Table 2. Block Copolymerization of Either 1, 2, or 3 and Styrene with Oligo(α -methylstyryl)lithium in THF at $-78 \ ^\circ C^a$

first	second	[M1]0/	[M2]0/	$M_{ m n}$ ×	$M_{ m n} imes 10^{-3}$	
monomer	monomer	[I] ₀	[I] ₀	calcd	\mathbf{obsd}^b	$M_{\rm w}/M_{\rm n}$
styrene	1	65.4	68.3	6.8-16	6.4-13	1.06
1	styrene	36.7	144	8.6-15	8.6-19	1.09
styrene	2	80.5	68.3	8.3-20	8.8-19	1.06
2	styrene	24.0	192	7.0 - 20	6.2 - 19	1.05
3	styrene	14.0	115	4.9 - 12	5.2 - 12	1.09

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} Molecular weights of block copolymers were determined by M_n values of homopolymers by VPO and compositions of block copolymers determined by ¹H NMR. Compositions calculated and observed of block copolymers (first/second) are as follows: 49/51 and 52/48, 20/80 and 26/74, 54/46 and 59/41, 11/89 and 11/89, and 11/89 and 12/88. ^{*c*} M_w/M_n values were estimated by SEC using polystyrene calibration curve.

of polymers (quantitative in all cases), although molecular weight distributions of the polymers obtained with the initiators with Na⁺ were relatively broader than those of the polymers obtained with initiators with Li⁺ and K⁺. These results and the characteristic coloration in the polymerization systems strongly indicate that the anionic polymerization of **1** is living. Thus, the Si–Si bond was sufficiently stable toward the highly reactive anionic initiators and the growing chain-end anions derived from **1** in THF at -78 °C.

The block copolymerization of 1 and styrene was carried out in THF at -78 °C with oligo(α -methylstyryl)lithium by a two-step sequential monomer addition, 1 followed by styrene or vice versa. The first and second polymerization times were 0.5 and 0.5 h, respectively. Yields of polymers were quantitative in all cases. The results are summarized in Table 2.

Figure 2 shows SEC chromatograms of the resulting polymer and its prepolymer of **1**. The SEC peak moves toward higher molecular weight after the addition of styrene, whereas the molecular weight distribution remains narrow. The peak corresponding to the prepolymer of **1** completely disappeared. All of the analytical results by VPO and ¹H NMR indicate that the block copolymerization proceeds to afford the expected AB diblock copolymer of poly(**1**)-*block*-polystyrene. The success of the block copolymerization further confirms the living character of the polymerization of **1**. Similarly, a well-defined BA diblock copolymer, polystyrene-*block*poly(**1**), could be successfully synthesized by reversing



Figure 2. SEC profiles of poly(1)-*block*-polystyrene (A) and poly(1) (B) at the first-stage polymerization: peak A, $M_n = 19$ kg/mol, $M_w/M_n = 1.06$; peak B, $M_n = 5.0$ kg/mol, $M_w/M_n = 1.04$.

Table 3. Anionic Polymerization of 1 with sec-BuLi inBenzene at 40 °C for 1 ha

[1]₀/		$M_{ m n} imes 10^{-3}$			
[sec-BuLi]0	calcd	SEC^b	VPO ^c	$M_{\rm w}/M_{\rm n}{}^b$	
45.9	11	12	16	1.06	
76.7	14	22	29	1.06	
120	29	30	40	1.08	

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} Both M_n and M_w/M_n values were estimated by SEC using a standard polystyrene calibration curve. ^{*c*} In benzene at 40 °C.

the sequence of monomer addition, namely, styrene followed by **1**. Both results indicate that the electrophilicities of styrene and **1** and the nucleophilicities of their living anionic polymers are very similar. This is also supported by the fact that the value (113.8 ppm) of the vinyl β -carbon of **1** is the same as that of styrene (113.8 ppm) in ¹³C NMR chemical shift.

Next, the polymerization of **1** was conducted with *sec*-BuLi in benzene at 40 °C for 1 h. Upon addition of **1** to *sec*-BuLi, an immediate color change from almost colorless to pale yellowish orange occurred and the color remained unchanged for 1 h. Three polymerizations were carried out at different ratios of monomer to initiator. The polymer yields were quantitative in all cases. The results are listed in Table 3.

The resulting polymers showed sharp symmetrical monomodal SEC peaks without shoulders and tailings. However, the observed M_n values by VPO were always higher than those calculated. This is caused by the partial deactivation of *sec*-BuLi prior to the polymerization, possibly due to the Si–Si bond attack by *sec*-BuLi. The similar Si–Si bond attack by organolithium compounds was reported by several research groups.^{3,7} However, the propagation step proceeds without problem, since the molecular weight distributions of the resulting polymers are narrow.

The block copolymerization was carried out under similar conditions by a two-step sequential addition of **1** followed by styrene. The resulting polymer showed a sharp monomodal SEC distribution ($M_w/M_n = 1.06$). No SEC peak corresponding to the prepolymer of **1** was observed. The observed M_n value of the polymer was higher than that calculated (M_n calcd = 33 kg/mol vs. M_n



Figure 3. ¹H NMR spectra of **2** (A) and the resulting polymer (B).

Table 4. Anionic Polymerization of 2 in THF at -78 °C for 0.5 h^a

	[1]₀/	$M_{ m n} imes 10^{-3}$			
initiator	[initiator] ₀	calcd	SEC ^b	VPO	$M_{\rm w}/M_{\rm n}{}^b$
<i>sec</i> -BuLi	29.8	8.7	7.3	10	1.03
sec-BuLi/aMS ^c	23.6	7.6	5.5	8.3	1.08
<i>sec</i> -BuLi/αMS	41.1	12	9.0	12	1.04
<i>sec</i> -BuLi/αMS	89.0	26	21	28	1.03
<i>sec</i> -BuLi/αMS	178	52	39	59	1.04
$Na-Nap^d$	20.0	12	10	12	1.11
Na-Nap/αMS	16.5	11	8.7	12	1.10
K-Nap ^e	22.6	15	11	15	1.05
K–Nap/αMS	17.8	10	7.9	12	1.03
K–Nap/αMS	30.0	18	12	16	1.05
K–Kap/αMS	46.1	27	22	29	1.04

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} Both M_n and M_w/M_n values were estimated by SEC using a standard polystyrene calibration curve. ^{*c*} α -Methylstyrene. ^{*d*} Sodium naphthalenide. ^{*e*} Potassium naphthalenide.

obsd = 43 kg/mol). Accordingly, *sec*-BuLi used as an initiator was partly deactivated, but the growing chain-end anion derived from 1 could initiate quantitatively the polymerization of styrene in benzene at 40 °C.

Anionic Polymerization of *p*-Heptamethyltrisilylstyrene (2). For the anionic polymerization of 2 in THF at -78 °C for 0.5 h, *sec*-BuLi, sodium and potassium naphthalenides, living oligomers of α -methylstyrene prepared from *sec*-BuLi, sodium and potassium naphthalenides and α -methylstyrene were used as initiators. Upon addition of 2 to each initiator, the intense red color appeared and remained unchanged at -78 °C after 24 h. The polymer yields were quantitative in all cases. Figure 3 shows ¹H NMR spectra of 2 and the resulting polymer. The resonances assigned to the vinyl protons of 2 disappeared completely in the polymer. The results are summarized in Table 4.

All initiators were effective, and the resulting polymers showed sharp symmetrical monomodal SEC distributions. The M_n values determined by VPO agreed well with those calculated from [monomer] to [initiator] ratios in all cases. Similar to the polymerization of **1**, the polymers obtained with the initiators with Na⁺ were always slightly broad in molecular weight distribution. Both AB and BA diblock copolymers with well-defined structures were successfully synthesized by the sequential addition of **2** followed by styrene and vice versa in

Table 5. Anionic Polymerization of 2 with sec-BuLi inBenzene at 40 °C for 1 h^a

[1]₀/		$M_{ m n} \ge 10^{-3}$			
[sec-BuLi] ₀	calcd	SEC ^b	VPO ^c	$M_w\!/M_n{}^b$	
19.5	5.7	7.8	13	1.10 ^d	
28.1	8.2	14	21	1.26^{d}	
50.0	15	22	30	${\sim}1.5^{e}$	

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} Both M_n and M_w/M_n values were estimated by SEC using standard polystyrene calibration curve. ^{*c*} In benzene at 40 °C. ^{*d*} Bimodal distribution. ^{*e*} Multimodal distribution.

THF at -78 °C with oligo(α -methylstyryl)lithium. The results are also listed in Table 2. The SEC, VPO, and ¹H NMR analyses confirmed their expected structures. The results of both homopolymerization and block copolymerization indicate that the anionic polymerization of **2** could proceed by a living mechanism. Thus, the Si–Si–Si bond of **2** was also sufficiently stable and did not interfere with the anionic polymerization of **2** under the conditions in THF at -78 °C.

However, the polymerization of **2** with *sec*-BuLi in benzene at 40 °C was problematic. The polymerization mixture exhibited a pale yellowish orange color, which was similar to the color observed in the polymerization of **1** under the same conditions. Three polymerizations were carried out at different ratios of monomer to initiator. The yields of polymers were quantitative in all cases. The results are listed in Table 5.

The polymer obtained at the ratio of [M] to [I] of 20 showed a sharp monomodal SEC peak with a high molecular weight shoulder whose $M_{\rm n}$ value was doubly increased (ca. 10% relative to the main sharp peak). The extent of the high molecular weight shoulder became more significant (ca. 20%) at the ratio of 28. Moreover, several high molecular weight peaks were observed in the polymer obtained at the ratio of 50 as shown in Figure 4. In every case, the M_n value of the polymer determined by VPO was always higher than that calculated. This is possibly due to initiator loss by the reaction of sec-BuLi with the Si-Si-Si bond at the initiation step, similar to the polymerization of 1 as mentioned above. Furthermore, in the polymerization of 2, the growing chain-end anion may attack on the Si-Si-Si bond of another polymer side chain during and after the polymerization, resulting in the formation of high molecular weight polymer as shown in Scheme 1. Although we have not any direct evidence for this, the mechanism shown above seems reasonable based



Figure 4. SEC profile of poly(**3**) obtained at [M]/[I] of 60.4 in THF at -78 °C for 0.5 h with cumylpotassium capped with DPE: $M_n = 27$ kg/mol; $M_w/M_n = 1.24$.

on the Si–Si cleavage of disilanes and polysilanes with anionic species previously reported.^{3,6,7} Therefore, the Si–Si–Si bond is not stable toward *sec*-BuLi and/or the growing chain-anion derived from **2** in benzene at 40 °C.

The formation of high molecular weight polymer could not be suppressed even at the early stage of the polymerization of **3** ([M]/[I] = 50, conversion = 20%), indicating that the side reaction occurs competitively at the early stage of the polymerization. Moreover, the formation was not suppressed in the polymerization of **2** carried out in benzene at 10 °C.

Anionic Polymerization of *p*-Nonamethyltetrasilylstyrene (3). In contrast to the successful polymerizations of 1 and 2, 3 did not polymerize with *sec*-BuLi or oligo(α -methylstyryl)lithium in THF at -78 °C. The characteristic red color of oligo(α -methylstyryl)lithium disappeared immediately on mixing with 3, and no polymer was obtained. Although the polymerization of **3** proceeded to a small extent with oligo(styryl)lithium, the SEC of the resulting product exhibited a multimodal distribution. The ¹H NMR spectrum of the product corresponded to a few units of **3** attached to the oligostyrene. Obviously, the anionic initiators used and the growing chain-end anion, even if produced, reacted with the Si–Si–Si–Si bond of **3** at either the initial or early stage of the polymerization under such conditions.

Monomer, **3**, polymerized using oligo(α -methylstyryl)potassium as an initiator in THF at -78 °C. The polymers were obtained quantitatively after 0.5 h at the ratios of [**3**] to [initiator] in the range of 11–60. The results are summarized in Table 6. Polymers possessing M_n values of less than 10 kg/mol showed sharp mono-



Table 6. Anionic Polymerization of 3 in THF at -78 °C for 0.5 h^a

	[1]。/	1	$M_{\rm n} \ge 10^{-1}$	3	
initiator	[initiator] ₀	calcd	SEC^b	VPO	$M_{\rm w}/M_{\rm n}{}^b$
sec-BuLi	15.0	5.3			
sec-BuLi/aMS ^c	16.7	5.8			
sec-BuLi/aMS	20.1	7.0			
<i>sec</i> -BuLi/αMS	40.0	14			
Cumyl-Kd/aMS	11.0	4.9	5.2	5.8	1.04
Cumyl-K/aMS	26.0	9.1	9.3	10	1.10
Cumyl-K/αMS	34.1	12	10	14	1.18^{e}
Cumyl-K/αMS	42.5	15	14	18	1.19^{e}
Cumyl-K/αMS	60.4	22	15	27	1.24^{e}

^{*a*} Yields of polymers were quantitative with oligo(α -methyl-styryl)potassium (Cumyl-K/ α MS). ^{*b*} Both M_n and M_w/M_n values were estimated by SEC using standard polystyrene calibration curve. ^{*c*} α -Methylstyrene. ^{*d*} Cumylpotassium. ^{*e*} Multimodal ditribution.

modal SEC distributions, M_w/M_n values being less than 1.1. Their M_n values by VPO were close to those calculated. However, additional high molecular weight polymers were always formed when the molecular weight of the polymer exceeded over ca. 12 kg/mol. The extent of the formation became more significant with increasing molecular weight and the shoulder tended to be multimodal. Similar to the case in the polymerization of 2 in benzene as mentioned above, the formation of the high molecular weight polymers may be due to the growing chain-end anion attack on the Si-Si-Si-Si bond of another polymer chain probably after the conclusion of polymerization. In the case where the $M_{\rm n}$ value of poly(3) segment is limited to less than 10 kg/ mol, it is feasible to synthesize a well-defined diblock copolymer, poly(3)-block-polystyrene, by the sequence of monomer addition, 3 followed by styrene. The resulting polymer exhibited a sharp monomodal SEC distribution (see Table 2). As expected, the formation of high molecular weight polymers was always observed in the block copolymers whose poly(3) segments were 12 kg/ mol or more in molecular weight.

In practice, the polymerization of **3** could be controlled under limited conditions with use of the initiators possessing K⁺. On the other hand, no polymerization occurred with the initiators with Li⁺. The effect of countercation is critical in the polymerization of **3**. However, the Si–Si–Si–Si bond was not stable, and the above-mentioned side reaction could not be completely suppressed even in THF at -78 °C. Thus, there is a crucial difference between Si–Si–Si and Si–Si–Si–Si bonds in stability under the condition of living anionic polymerization.

Conclusions

We have investigated the anionic polymerizations of three para-substituted styrene derivatives possessing Si-Si, Si-Si-Si, and Si-Si-Si-Si bonds, **1**-**3**, under various conditions. Both **1** and **2** were successful in undergoing living anionic polymerization in THF at -78 °C. Well-defined diblock copolymers, poly(**1**)-*block*polystyrene, poly(**2**)-*block*-polystyrene, poly(**1**)-*block*poly(**1**), and polystyrene-*block*-poly(**2**) were synthesized under similar conditions by a two-step sequential monomer addition, namely, styrene followed by **1** or **2** or vice versa. The finding that the Si-Si and Si-Si-Si bonds are sufficiently stable under the conditions of living anionic polymerization is of particular interest and significance in the fields of anionic polymerization as well as carbanion chemistry, since it had been believed that these bonds are readily cleaved by reactive anionic species. Thus, the range of functionalized styrenes amenable to living anionic polymerization is broadened. However, the anionic polymerization of **3** had only a limited success, since the Si–Si–Si–Si bond was not completely stable even in THF at -78 °C.

The difference between 1, 2, and 3 is thus critical in the anionic polymerization behavior, although the reason has not been understood at the present time. We tentatively consider that the number of Si–Si linkages (one, two, and three for 1, 2, and 3) and stability of the leaving group produced by the attack of anionic species such as Si⁻, Si–Si⁻, or Si–Si–Si⁻ may possibly be key factors for occurring the side reactions leading to high molecular weight polymer formation and loss of initiator.

References and Notes

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(12) We carried out the model reaction of *sec*-BuLi with 1,1,2,2,2-tetramethyldisilylbenzene in benzene at 40 °C for 1 h in order to examine and minimize the effect the side reaction that seemed to be occurring at the early stage of the polymerization of 1. Unexpectedly, no reaction occurred at all, and 1,1,2,2,2-tetramethyldisilylbenzene was quantitatively recovered under such conditions. No direct evidence for the cleavage of Si-Si bond of 1 by *sec*-BuLi was obtained by this

reaction. However, we still consider that the cleavage of 1 by *sec*-BuLi seems to be occurring, since the Si–Si bond of 1 is more reactive than that of 1,1,2,2,2-tetramethyldisilylben-zene. In the polymerization of 1 with *sec*-BuLi at 1:1 ratio, only oligomers of 1 were produced. The product by the cleavage of 1 by *sec*-BuLi was not obtained.

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