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Polymerization of Monomers Containing Functional Silyl Groups. 13. Anionic Polymerization of 2-[(*N*,*N*-Dialkylamino)dimethylsilyl]-1,3-butadiene Derivatives

Akira Hirao,* Yashuhiro Hiraishi, and Seiichi Nakahama

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152, Japan

Katsuhiko Takenaka

Department of Materials Science & Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan

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ABSTRACT: Four 2-[(*N*,*N*-dialkylamino)silyl] substituted 1,3-butadiene derivatives, 2-[(*N*,*N*-diethylamino)dimethylsilyl]-1,3-butadiene (**1**), 2-[(*N*,*N*-dibutylamino)dimethylsilyl]-1,3-butadiene (**2**), 2-[(1-pyrrolidinyl)dimethylsilyl]-1,3-butadiene (**3**), and 2-[[*N*-[2′-(*N*′,*N*′-dimethylamino)ethyl]-*N*-methylamino]-dimethylsilyl]-1,3-butadiene (**4**), were newly synthesized and polymerized under various conditions of anionic polymerization. Under the condition of THF at −78 °C, all the monomers, **1**−**4**, underwent living polymerization to afford the polymers of predictable molecular weights and narrow molecular weight distributions. On the other hand, side reactions occurred to some extent in the polymerizations of **1**−**4** carried out in heptane at 40 °C, although yields of polymers were quantitative in all cases within 1 h. The polymers obtained in THF consisted mainly of 1,4 (83−91%) and 1,2 (9−17%) linkages, while all the polymers obtained in heptane were structurally pure 1,4-addition products. There were mixtures of 1,4-*E* (16−32%) and 1,4-*Z* (68−84%) structures in the polymers of **1**−**3**. The polymer of **4** was found to have a structure of exclusively 1,4-*E* unit.

Introduction

Over the past 10 years, we have been investigating a series of anionic polymerizations of styrene,[1−5] 1,3-butadiene,[6−8] and alkyl methacrylate derivatives[9] containing functional silyl groups. The functional silyl groups studied involved Si−O, Si−O−Si, Si−N, Si−H, Si−Si, and Si−Si−Si bonds, with which many reactions characteristic to silicon atoms can be carried out on the polymer chains.[10] However, it is reported in many previous literature reports that most of such groups are capable of being readily displaced by attack with strong bases and nucleophiles often used as anionic initiators.[11] One can therefore speculate that such functional silyl groups may be the sources of undesirable side reactions to prevent the anionic polymerization of the above-mentioned monomers. Under careful conditions, however, these monomers were found to undergo smoothly anionic polymerization to produce stable living polymers. Thus, we have obtained various well-defined homopolymers and block copolymers with predictable molecular weights and narrow molecular weight distributions as well as functional silyl groups. For these features the polymers are regarded as a new class of well-defined functional polymers with a wide variety of applications.

Among the polymerizations studied previously, the anionic polymerization behavior of 2-(tri-2-propoxysilyl)-1,3-butadiene is of particular interest. As mentioned before, a stable living polymer was produced, although this butadiene has Si−O bonds of the 2-(propoxysilyl) group which are susceptible to anion attack. Another interesting feature of this polymerization system was the microstructure of the resulting polymer. Surprisingly, the polymerization in THF was observed to proceed in the 1,4 mode to give a structurally pure 1,4 adduct. More surprisingly, the geometry of the monomer units was exclusively *E* configuration. This is a marked contrast to the microstructures of polybutadiene and polyisoprene under the same condition which are predominantly 1,2- and 3,4-vinyl structures, respectively. Thus, we have found that the polymerization of 2-(tri-2-propoxysilyl)-1,3-butadiene proceeds in a living manner as well as regio- and stereospecific manners.[7,8]

It is evident that the presence of a tri-2-propoxysilyl group substituted at the 2-position plays a very important role in controlling the regio- and stereochemistry of the resulting polymer. Similar polymerization behaviors were also observed in the anionic polymerization of structurally related 2-(alkoxysilyl)-1,3-butadienes. It is therefore interesting to study how another silyl substituent will influence polymerization behavior.

In this paper, we report the results of the anionic polymerization of the 1,3-butadiene derivatives, the 2-positions of which are substituted with (*N*,*N*-dialkylamino)silyl groups. The following four monomers, 2-[(*N*,*N*-diethylamino)dimethylsilyl]-1,3-butadiene (**1**), 2-[(*N*,*N*-dibutylamino)dimethylsilyl]-1,3-butadiene (**2**), 2-[(1-pyrrolidinyl)dimethylsilyl]-1,3-butadiene (**3**), and 2-[[*N*-[2′-(*N*′,*N*′-dimethylamino)ethyl]-*N*-methylamino]-dimethylsilyl]-1,3-butadiene (**4**), are newly synthesized and polymerized anionically:

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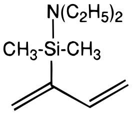

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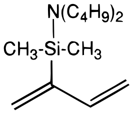

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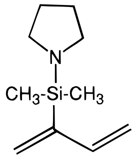

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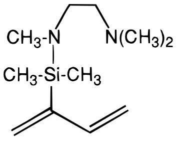

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Their anionic polymerization behaviors will be compared with those of 2-(alkoxysilyl)-1,3-butadiene derivatives.

Experimental Section

Materials. Monomers and solvents were purified according to the general procedures previously reported.[4,7,8]

2-[(*N*,*N*-Diethylamino)dimethylsilyl]-1,3-butadiene (1). All the monomers, **1**−**4**, were synthesized by the reactions of the Grignard reagent of chloroprene with the corresponding (*N*,*N*-dialkylamino)dimethylsilyl chloride. A typical synthetic procedure for **1** is as follows: To a THF solution of 1,3-butadien-2-ylmagnesium chloride[12] (200 mL of a 1.00 M solution in THF, 200 mmol) was added dropwise (*N*,*N*-diethylamino)dimethylsilyl chloride (19.3 g, 117 mmol) in THF (30 mL) at 0 °C under an atmosphere of nitrogen. After the mixture had been heated gradually to reflux overnight, it was cooled and filtered, and the residual white solid was washed with a dry pentane−THF mixture several times under a nitrogen atmosphere. After evaporation, the residual oil was fractionally distilled twice and finally distilled over $LiAlH_4$ at 47−49 °C (13 Torr) to give 8.05 g (44.0 mmol, 40% yield) of **1** as a colorless liquid. A low yield was due to undesirable polymerization, and significant amounts of oligomeric and polymeric materials were produced: ^1H NMR (C_6D_6) δ 6.40 (1H, dd, J = 10.5, 18.4 Hz, CH=), 5.82, 5.63 (2H, 2s, CH_2=C), 5.51 (1H, d, J = 18.4 Hz, CH_2=CH−), 5.16 (1H, d, J = 10.5 Hz, CH_2=CH−), 2.77 (4H, q, J = 7.0 Hz, N−CH_2), 0.97 (6H, t, J = 7.0 Hz, N−C−CH_3), 0.27 (6H, s, Si−CH_3); ^{13}C NMR (C_6D_6) δ 150.3 (C2), 142.5 (C3), 129.9 (C1), 116.4 (C4), 41.0 (N−C), 16.5 (N−C−*C*), −9.3 (Si−C); IR 1593, 1450, 1373, 1174, 992, 828 cm^{-1}.

2-[(*N*,*N*-Dibutylamino)dimethylsilyl]-1,3-butadiene (2). **2** was obtained in 13% yield by the reaction of a 2-fold excess of 1,3-butadiene-2-ylmagnesium chloride with (*N*,*N*-dibutylamino)dimethylsilyl chloride in THF at reflux for 24 h. Fractional distillation over $LiAlH_4$ afforded **2** as a colorless liquid: bp 56−58 °C (2.0 Torr); ^1H NMR (C_6D_6) δ 6.43 (1H, dd, J = 10.1, 15.4 Hz, CH=), 5.81, 5.59 (2H, 2s, CH_2=C), 5.46 (1H, d, J = 15.4 Hz, CH_2=CH−), 5.19 (1H, d, J = 10.1 Hz, CH_2=CH−), 2.82 (4H, q, J = 6.6 Hz, N−CH_2), 1.56−1.06 (8H, m, N−C−CH_2−CH_2−), 0.93 (6H, t, J = 6.6 Hz, N−C−C−C−CH_3), 0.31 (6H, s, Si−CH_3); ^{13}C NMR (C_6D_6) δ 149.8 (C2), 142.0 (C3), 129.5 (C1), 116.0 (C4), 47.0 (N−C), 32.8 (N−C−*C*), 20.7 (N−C−C−*C*), 14.3 (N−C−C−C−*C*), 0.87 (Si−C); IR 1584, 1458, 1367, 1163, 990, 821 cm^{-1}.

2-[(1-Pyrrolidinyl)dimethylsilyl]-1,3-butadiene (3). **3** was obtained in 68% yield by the reaction of a 1.2-fold excess of 1,3-butadiene-2-ylmagnesium chloride with (1-pyrrolidinyl)-dimethylsilyl chloride in THF at reflux for 24 h. Fractional distillation over $LiAlH_4$ afforded **3** as a colorless liquid: bp 52−53 °C (4.0 Torr); ^1H NMR (C_6D_6) δ 6.41 (1H, dd, J = 10.7, 17.6 Hz, CH=), 5.78, 5.54 (2H, 2s, CH_2=C), 5.37 (1H, d, J = 17.6 Hz, CH_2=CH−), 5.14 (1H, d, J = 10.7 Hz, CH_2=CH−), 3.00−2.86 (4H, m, N−CH_2), 1.64−1.49 (4H, m, N−C−CH_2), 0.29 (6H, s, Si−CH_3); ^{13}C NMR (C_6D_6) δ 149.8 (C2), 142.1 (C3), 128.7 (C1), 115.5 (C4), 47.2 (N−C), 27.2 (N−C−*C*), 2.03 (Si−C); IR 1614, 1447, 1369, 1068, 983, 828 cm^{-1}.

2-[[*N*-[2′-(*N*′,*N*′-Dimethylamino)ethyl]-*N*-methylamino]-dimethylsilyl]-1,3-butadiene (4). **4** was obtained in 71% yield by the reaction of a 1.5-fold excess of 1,3-butadiene-2-ylmagnesium chloride with [*N*-[2′-*N*′,*N*′-dimethylamino)ethyl]-*N*-methylamino]dimethylsilyl chloride in THF at reflux for 24 h. Fractional distillation over $LiAlH_4$ afforded **4** as a colorless liquid: bp 58−60 °C (1.0 Torr); ^1H NMR (C_6D_6) δ 6.41 (1H, dd, J = 10.4, 17.4 Hz, CH=), 5.79, 5.59 (2H, 2s, CH_2=C), 5.40 (1H, d, J = 17.4 Hz, CH_2=CH−), 5.18 (1H, d, J = 10.4 Hz, CH_2=CH−), 2.92 (2H, t, J = 6.8 Hz, Si−N−CH_2), 2.49 (3H, s, Si−N−CH_3), 2.31 (2H, t, J = 6.8 Hz, Si−N−C−CH_2−N), 2.13 (6H, s, N(CH_3)$_2$), 0.29 (6H, s, Si−CH_3); ^{13}C NMR (C_6D_6) δ 149.9 (C2), 141.9 (C3), 129.1 (C1), 115.6 (C4), 59.8 (Si−N−C−*C*−N), 49.5 (Si−N−*C*−C−N), 46.0 (Si−N−C−C−N−*C*H_3), 35.3 (Si−N−CH_3), 1.59 (Si−C); IR 1613, 1458, 1367, 1161, 992, 821 cm^{-1}.

Special care is needed for handling these monomers, because they are gradually hydrolyzed with moisture in the air. To remove impurities in the monomers, phenylmagnesium chloride (ca. 5 mol %) was added to the monomers. The mixtures were then degassed and stirred for several hours at room temperature and distilled on a vacuum line into ampules with break-seals that were prewashed with potassium naphthalenide in THF.

Polymerization Procedure. All the polymerizations were carried out under high-vacuum conditions (10^{-6} Torr) in all-glass apparatuses with break-seals in the usual manner. Since the polymers of **1**−**4** were gradually hydrolyzed in air, the polymer solutions were carefully poured into a large excess of absolute methanol under a nitrogen atmosphere. The polymers precipitated in the bottom as viscous liquids were washed with absolute methanol several times and dried in vacuo for 24 h. The resulting polymers thus purified were characterized by IR, ^1H and ^{13}C NMR, and SEC.

Substitution Reaction of a *N*,*N*-Dialkylamino Group with a 2-Propoxy Group in the Polymer Side Chain. Under a nitrogen atmosphere, absolute 2-propanol (10 equiv to the aminosilyl group) and acetic acid (0.1 equiv) were added to a solution of the polymer (1.0 g) in THF (10 mL). The mixture was stirred at 40 °C for 48 h. The polymer was isolated by precipitation in methanol, purified by reprecipitation two more times from THF to methanol, washed with methanol, and dried in vacuo for 24 h.

Measurements. IR spectra were recorded on a Jasco IR-G spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX-270 (270 MHz for ^1H and 67.80 MHz for ^{13}C) in $CDCl_3$ and C_6D_6. Size-exclusion chromatograms (SEC) were recorded on a Toyo Soda HLC-802 instrument at 40 °C with THF as the carrier solvent. Vapor-pressure osmometry (VPO) measurements were made with a Corona 117 instrument in a benzene solution with a highly sensitive thermoelectric couple and equipment of very exact temperature control. Molecular weights to 50 000 could be determined within an analytical error of ±5%.

Results and Discussion

Silylamines and other related compounds with Si−N bonds are reactive under acidic conditions in which Si−N bonds are readily cleaved.[13] On the other hand, they are fairly stable toward highly reactive basic reagents and/or nucleophiles. In practice, there are several examples which indicate that Si−N bonds are inert toward Grignard reagents and organolithium compounds. Even some organolithium compounds containing Si−N bonds can be synthesized.[14,15] We have recently demonstrated that 4-[(*N*,*N*-diethylamino)dimethylsilyl]styrene successfully undergoes anionic living polymerization.[4] These results clearly show that Si−N bonds are stable enough toward highly reactive basic reagents, nucleophiles, and the condition of anionic living polymerization of styrene. Accordingly, the four 2-[(*N*,*N*-dialkylamino)silyl] substituted 1,3-butadienes, **1**−**4**, employed in this study are expected to undergo anionic living polymerization.

Anionic Polymerization of 1. The anionic polymerization of **1** was first attempted under the conditions of THF at −78 °C. The initiators used are cumylpotassium and living oligomers of α-methylstyrene prepared from lithium naphthalenide, *sec*-BuLi, or potassium napthalenide with 2−3-fold excess equiva-

Table 1. Anionic Polymerization of 1 in THF at −78 °C

initiator	time, h	yield, %	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ obsd[a]	M_w/M_n[b]
Li-Nap[c]/α-MS[d]	2.5	54	7.5	7.2	1.07
sec-BuLi/α-MS	4	89	6.9	7.4	1.07
Li-Nap/α-MS	4	90	14	12	1.11
Li-Nap/α-MS	24	100	21	19	1.11
cumyl-K[e]	20	100	7.6	6.0	1.06
K-Nap[f]/α-MS	4	90	9.0	8.9	1.09
K-Nap/α-MS	24	100	15	12	1.09
K-Nap/α-MS	24	100	18	16	1.08

[a] Measured by VPO in benzene. [b] Measured by SEC. [c] Lithium napthalenide. [d] α-Methylstyrene. [e] Cumylpotassium. [f] Potassium napthalenide.

lents of α-methylstyrene. On mixing the first quantity of **1** with each of these initiator solutions, dark red or orange−red color characteristic of the initiators in THF turns instantaneously to brown (Li^+) or reddish−brown (K^+) color, which remains as long as the temperature is kept at −78 °C. The colors disappeared immediately on addition of absolute 2-propanol. The resulting polymers were very sensitive to moisture and often cross-linked to become insoluble during workup in air. Therefore, special care is required for isolation and purification steps. Under an atmosphere of nitrogen, the polymer solution was carefully poured into a large excess of absolute methanol. The polymer was usually precipitated in the bottom as a viscous liquid, washed with absolute methanol several times, and dried. Characterizations of the polymers by IR, NMR, and SEC were carried out as soon as possible. For determination of molecular weight by VPO, the polymers were transformed into the more stable poly[2-(2-propoxy)dimethylsilyl-1,3-butadiene]s by treating with 2-propanol with a catalytic amount of acetic acid.

The results are summarized in Table 1. The polymerization of **1** was relatively fast and was complete within 24 h in THF at −78 °C, compared to the polymerization of 2-(trialkoxysilyl)-1,3-butadienes in which complete conversion usually required more than 100 h.[6−8] The resulting polymers all were observed by SEC analysis to have symmetrical single peaks and were narrow in distribution. Neither shoulder nor tailing was present in each peak. Their number-average molecular weights determined by VPO were closed to those calculated based on monomer to initiator ratios. These results clearly indicate the living character of the polymerization of **1** under the conditions employed here. Thus, the Si−N bond does not interfere with the anionic polymerization of **1**, similar to the case of anionic polymerization of 4-[(*N*,*N*-diethylamino)-dimethylsilyl]styrene previously reported.[4]

We next examined the anionic polymerization of **1** with *sec*-BuLi in heptane at 40 °C. A pale yellow color appeared on mixing of **1** with *sec*-BuLi, suggesting the formation of polydienyl anion derived from **1**. The polymerization was complete within 1 h. The results are listed in Table 3. The polymer obtained at a low monomer to initiator ratio ([M]/[I] = 28) showed a symmetrical SEC distribution composed of a single peak and was narrow in molecular weight. The observed value of M_n was relatively greater than that calculated. On the other hand, a considerable tailing to the low molecular weight side was observed by the SEC trace of the resulting polymer when polymerized at a [M]/[I] ratio of 77. A similar tendency was observed in the anionic polymerization of other monomers of **2**−**4** in heptane. This will be discussed in the next section.

Table 2. Anionic Polymerization of 2−4 in THF at −78 °C

monomer	initiator	time, h	yield, %	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ obsd[a]	M_w/M_n[b]
2	Li-Nap[c]	24	100	12	10	1.13
2	cumyl-K[d]	24	100	9.0	7.6	1.09
3	Li-Nap	120	100	13	13	1.15
3	K-Nap[e]/α-MS[f]	24	100	13	13	1.17
3	cumyl-K	24	100	7.6	8.7	1.11
3	cumyl-K	72	100	9.3	11	1.13
4	Li-Nap	24	27	3.5	3.4	1.09
4	Li-Nap	120	57	6.6	6.0	1.21
4	cumyl-K	24	100	7.5	7.3	1.07
4	cumyl-K	24	100	19	19	1.09
4	cumyl-K	72	100	9.8	11	1.14

[a] Measured by VPO in benzene. [b] Measured by SEC. [c] Lithium napthalenide. [d] Cumylpotassium. [e] Potassium napthalenide. [f] α-Methylstyrene.

The polymers of **1** are soluble in pentane, hexane, heptane, benzene, carbon tetrachloride, diethyl ether, 1,4-dioxane, and THF while insoluble in ethyl acetate, acetone, pyridine, DMF, ethanol, methanol, and H_2O. The glass transition temperatures (T_g) of the resulting polymers obtained in THF and in heptane were −40 and −50 °C, respectively.

Anionic Polymerizations of 2−4. The results of the anionic polymerizations of **2**−**4** in THF at −78 °C are summarized in Table 2. The polymerization of **2** was complete within 24 h with either lithium naphthalenide or cumylpotassium. Both polymers thus obtained showed symmetrical peaks with narrow molecular weight distributions, as were measured by SEC. The M_n values from VPO and as calculated were seen to be almost identical. Based on the results, the anionic polymerization of **2** also proceeds in a living manner.

The anionic polymerizations of **3** and **4** were complete within 24 h with organopotassium initiators such as cumylpotassium and potassium salt of α-methylstyrene living oligomer, while the polymerization proceeded slowly with the use of lithium napthalenide. In the polymerization of **3**, for example, 120 h was needed for complete conversion and only 57% conversion was achieved in the case of **4** even after 120 h. It is considered that the most likely cause for slow polymerization rates of both monomers is due to the steric hindrance around growing chain ends produced by the strong coordination of N atoms to Li^+. A less bulky pyrrolidinyl group and the bidentate nature of the [2-(*N*,*N*-dimethylamino)ethyl]methylamino group may be favorable for such coordination.

As was seen in Table 2, M_n values by VPO were in good agreement with those calculated in the resulting polymers of **3** and **4**. Their SEC traces showed single peaks with narrow molecular weight distributions, with the values of M_w/M_n being around 1.1 in all cases. Similar to the polymerization of **1** and **2**, both the polymerizations of **3** and **4** seem to proceed in a living manner. However, small but detectable amounts (ca. 5%) of high molecular weight shoulders were often observed in these polymers. The shoulders became more significant (ca. 10%) for longer polymerization time to 120 h. On the formation of high molecular weight polymers, we speculate that the silylvinylenes in polymer main chains might be attacked intermolecularly by the anions at growing chain ends. The possible reaction is given in Scheme 1.

Scheme 1 is strongly suggested by the facts that similar addition reactions of vinylsilane derivatives

Scheme 1

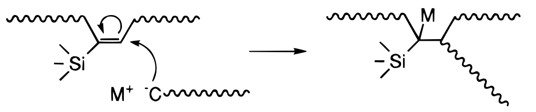


Table 3. Anionic Polymerization of 1−4 with *sec*-BuLi in Heptane at 40 °C[a]

monomer	[monomer]/[BuLi]	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[c]
1	28	5.1	8.9	1.09
1	77	14	14	1.32
2	28	6.7	13	1.09
2	49	12	22	1.38
3[d]	41	7.4	12	1.11
3	83	15	48[e]	1.35[e]
4	28	6.0	7.2	1.12
4	51	11	15	1.43

[a] Yields were quantitative in all cases. [b] Measured by VPO in benzene. [c] Measured by SEC. [d] Polymerization was carried out at 20 °C. [e] Soluble part.

occurred with highly reactive nucleophiles such as EtLi,[16] BuLi,[17] LDA,[18] and $(CH_3)_2PLi$.[18] A further support is provided by the fact that the anionic polymerizations of vinylsilanes proceed readily with organolithium reagents.[19]

Next, the anionic polymerizations of **2**−**4** were carried out at 40 °C in heptane with *sec*-BuLi for 1 h. All the polymerizations were completed under the conditions. The results are summarized in Table 3.

When the polymerizations were carried out at lower [M]/[I] ratios (less than 40), the polymers obtained all showed symmetrical single SEC peaks with narrow distributions. The observed M_n values by VPO were, however, greater than those calculated. On the other hand, the polymers obtained at higher [M]/[I] ratios were observed by their SEC charts to possess shoulders and tailings in addition to main peaks with narrow distributions. Their M_w/M_n values increased to around 1.4. Deviations of the observed M_n values from calculated ones were also observed. In the case of polymerization of **3** at 40 °C, the polymer precipitated with time. It was insoluble in organic solvents, indicating that it was cross-linked. Soluble parts (10−20 wt %) of the polymers were observed to possess much higher M_n values than calculated ones and broad molecular weight distributions. It is thus obvious that side reactions become more significant. In the polymerization of **3** at 20 °C, however, no polymer was precipitated at all. The resulting polymer was soluble and possessed a narrow molecular weight distribution ($M_w/M_n = 1.11$). The M_n observed was 12 000 and was again higher than 7400 of the M_n calculated.

Since CaH_2 was used for the purification of monomers employed in the polymerization in heptane, it may be difficult to remove impurities completely in the monomers. It can therefore be expected that greater M_n values than those calculated are partly caused by the loss of *sec*-BuLi due to impurities. A most probable side reaction leading to broadened molecular weight distribution may possibly be the intermolecular addition of silylvinylenes with anions at growing chain ends, as suggested in the polymerizations of **3** and **4** carried out in THF. This may also be responsible for the insoluble polymer formed in the polymerization of **3**.

Block Copolymerization. The living character of the anionic polymerization of **1** enables us to prepare novel well-defined block copolymers with reactive aminosilyl groups by the sequential addition method of two different monomers. In addition, the reactivity of the living anion derived from **1** can be estimated by the result of sequential block copolymerization. For this purpose, we have chosen three monomers with different reactivities. They are 2-vinylpyridine, styrene, and isoprene. Their reactivities toward anionic species are estimated from their *e*-values (0.84, −0.80, and −1.27 for 2-vinylpyridine, styrene, and isoprene, respectively) and decrease in this order:

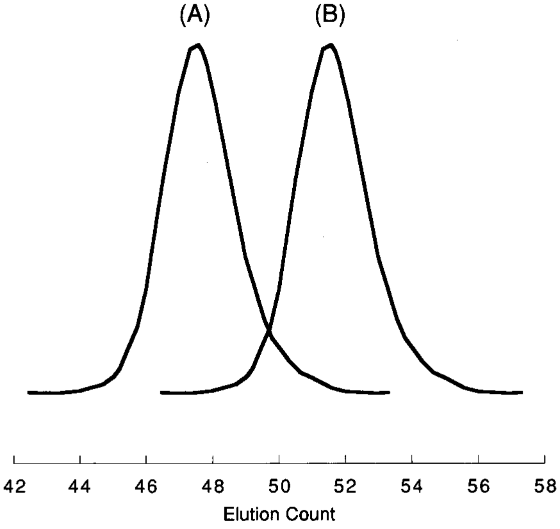


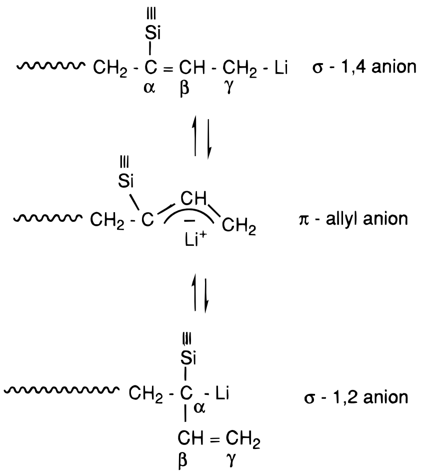
Figure 1. SEC charts of a block copolymer of **1** and 2-vinylpyridine (A) and a homopolymer of **1** (B) obtained at the first step initiated with cumylpotassium in THF at −78 °C: (A) poly(**1**-*b*-2-vinylpyridine), $M_n = 25\,000$, $M_w/M_n = 1.15$; (B) homopolymer of **1**, $M_n = 11\,000$, $M_w/M_n = 1.15$.

The anionic block copolymerization was first attempted by the sequential addition of **1** and 2-vinylpyridine in THF at −78 °C with cumylpotassium. The polymerization times were 24 and 4 h, respectively. The SEC showed that the curve corresponding to a homopolymer of **1** shifted completely to the higher molecular weight side as shown in Figure 1. The resulting polymer was found to possess a narrow molecular weight distribution. Both the homopolymer (M_n (obsd) = 11 000) and the resulting block copolymer and 1.15, respectively (M_n (obsd) = 25 000) possess the value of M_w/M_n of 1.15. Thus, a well-defined block copolymer of poly(**1**-*b*-2-vinylpyridine) was quantitatively obtained. This result also provides direct evidence that the living anion derived from **1** is stable and no deactivation occurs under the condition.

Two glass transition temperatures corresponding to both polymer segments were observed by DSC measurement of the block copolymer, indicating that a microphase separation occurred.

On the other hand, the block copolymerization by the sequential addition of **1** and styrene resulted in the formation of a mixture of a homopolymer of **1** and a block copolymer with a very high molecular weight. It is estimated from their SEC peak areas and their M_n values that only 20% of the living polymer of **1** initiated the polymerization of styrene. In the block copolymerization of **1** and isoprene which was the least reactive monomer employed in this study, no appreciable polymerization of isoprene occurred with the living polymer of **1**. It is rather surprising that the living polymer of **1** could not initiate the polymerization of isoprene at

Scheme 2



all, because both **1** and isoprene are structurally similar 1,3-butadiene derivatives. These results indicate that the reactivity of the living anion derived from **1** is similar to that of the living polymer of 2-vinylpyridine and lower than those of living polymers of styrene and isoprene.

The reactivity of the living anion derived from **1** thus elucidated by the block copolymerization shows similar reactivities of 2-(alkoxysilyl) substituted 1,3-butadienes reported previously.[7,8] As will be mentioned in the next section, it is considered that the anionic polymerization of **1** may proceed in a 1,4-chain end in which σ-type localized 1,2 and 1,4 anions as well as a delocalized π-type anion exist in equilibrium. They are illustrated in Scheme 2.

These anions may be considerably stabilized by the interaction of an empty π-orbital of silicon and an anion α to it as well as allyl anions.

Microstructures of Polymers. For the polymerization of 1,3-dienic monomers such as 1,3-butadiene and isoprene, it is important to prepare the polymers of *cis*-1,4 microstructures similar to that of natural rubber. In the field of anionic polymerization, these polymers are generally obtained by the polymerizations in hydrocarbon solvents with the use of RLi as an initiator. On the other hand, 1,3-butadiene and isoprene polymerized in polar solvents such as THF give the polymers whose microstructures are predominantly 1,2, and 3,4 units.

We have recently demonstrated that the microstructures of the poly[2-(trialkoxysilyl)-1,3-butadiene]s are quite different from those of polyisoprene and poly(1,3-butadiene). For example, the poly[2-(trialkoxysilyl)-1,3-butadiene]s were structurally pure 1,4-addition products, although they were prepared in THF. Neither 1,2 nor 3,4 structure was present in these polymers. More surprisingly, it was observed that the poly[2-(tri-2-propoxysilyl)-1,3-butadiene] exclusively consisted of 1,4-*E* structure. Accordingly, the microstructures of the resulting polymers from **1**−**4** are of particular interest in this regard.

For each polymer obtained here, the mode of polymerization (1,4, 1,2, and 3,4) and geometry of monomer units (*E* and *Z*) were determined by ^{1}H and ^{13}C NMR spectroscopies. In the ^{1}H NMR spectrum (in C_6D_6) of poly(**1**) obtained by polymerization with *sec*-BuLi in heptane at 40 °C, there were two signals at 6.3 and 2.4 ppm which corresponded to olefin and methylene protons. The signals assigned for silylmethyl protons and aminoethyl protons were also observed at 0.35 ppm (singlet), 2.9 ppm (quartet), and 3.1 ppm (triplet) as expected. Any other signals for vinyl groups corresponding to either 1,2- or 3,4-vinyl structure were not observed. Accordingly, the spectrum indicates clearly that the polymer is a structurally pure 1,4-addition product. The integral ratio of these signals also supports the structure of a 1,4 unit.

The ^{13}C NMR spectrum of the same polymer sample in C_6D_6 showed olefinic resonances in the range of 145−138 ppm assigned to =CH and =C−Si carbons. Two peaks corresponding to *E* and *Z* isomers for each carbon were clearly observed in this spectrum. They were observed at 140.6 and 138.7 ppm for =C−Si carbon and 142.2 and 144.3 ppm for =CH carbon, respectively. Furthermore, the signals assigned for silylmethyl carbon consisted of two peaks at −0.85 and 0.85 ppm.

Since we already assigned the structures of 1,4-*E* and *Z* of poly[2-(2-propoxy)dimethylsilyl-1,3-butadiene] in our previous paper, the (diethylamino)silyl group of the polymer was transformed quantitatively into a 2-propoxysilyl group by treating the polymer with 2-propanol in the presence of a catalytic amount of acetic acid, and the resulting polymer was analyzed by NMR. Compared to the original spectrum of poly[2-[(*N*,*N*-diethylamino)dimethylsilyl]-1,3-butadiene] with that of polymer thus transformed, the peaks at 142.2, 140.6, and −0.85 ppm are assigned to the resonances for =CH, =C−Si, and Si−CH_3 carbons of the *E* isomer, while the peaks at 144.3, 138.7, and 0.85 are those for the *Z* isomer. The ratio of *E*:*Z* can be estimated from each peak area to be 16:84. It was again confirmed that the resonance peaks for the structures of 1,2 and 3,4 units were not observed in both spectra.

The microstructure of the polymer obtained in THF at −78 °C was definitely different from that of the polymer in heptane at 40 °C. The ^{1}H NMR in $CDCl_3$ showed two resonance peaks at 4.6−4.9 and 5.6−6.2 ppm which were attributed to olefinic protons of $=CH_2$ and =CH groups, respectively. Compared to the spectrum of the polymer obtained in heptane and the model compounds, the signal at 4.6−4.9 ppm can be assigned as $=CH_2$ protons of 1,2 structure. Both =CH protons of 1,2 and 1,4 structures are included in the peaks observed at 5.6−6.2 ppm. The signal of $=CH_2$ protons of 3,4 structure was not observed in the spectrum. The ratio of 1.4:1.2 was estimated to be 84:16 from these peak areas.

In the ^{13}C NMR spectrum of the same sample in C_6D_6, there were observed three peaks at 0.85, −0.85, and −2.86 ppm in the region corresponding to silylmethyl carbon. As mentioned above, two peaks at 0.85 and −0.85 ppm correspond to the silylmethyl carbons of 1,4-*Z* and 1,4-*E* isomers, respectively. Therefore, the peak at −2.86 ppm may possibly be attributed to the silylmethyl carbon of 1,2 structure. The area ratio of these peaks at 0.85, −0.85, and −2.86 ppm is 25:58:17. Using these values we can determine the ratio of 1,4 and 1,2 to be 83 (25 + 58):17. This agrees well with the ratio of 84:16 determined based on the ^{1}H NMR spectrum. Accordingly, it is concluded that the polymer obtained in THF has a mixed structure of 1,4-*Z*, *E*-1,4, and 1,2 units whose ratio is 25:58:17.

Similarly, the microstructures of polymers of **2**−**4** obtained in heptane as well as in THF were determined from their ^{1}H and ^{13}C NMR spectra and summarized

Table 4. Microstructures of Polymers of 1−4 Obtained under Various Conditions

	conditions		microstructures (%)			
polymer	countercation	solvent	1,4-*E*	1,4-*Z*	1,2	3,4
poly(**1**)	Li^+	THF	57	27	16	0
poly(**1**)	K^+	THF	58	25	17	0
poly(**1**)	Li^+	heptane	16	84	0	0
poly(**2**)	Li^+	THF	51	34	15	0
poly(**2**)	K^+	THF	56	34	10	0
poly(**2**)	Li^+	heptane	30	70	0	0
poly(**3**)	Li^+	THF	58	25	17	0
poly(**3**)	K^+	THF	61	27	12	0
poly(**3**)	Li^+	heptane	32	68	0	0
poly(**4**)	Li^+	THF	66	23	11	0
poly(**4**)	K^+	THF	60	31	9	0
poly(**4**)	Li^+	heptane	100	0	0	0
poly(**5**)[a]	Li^+	THF	65	15	20	0
poly(**5**)	K^+	THF	47	30	23	0

[a] Poly(**5**): poly[2-[(2-propoxy)dimethylsilyl]-1,3-butadiene].

in Table 4. As a reference, the microstructure of poly[2-(2-propoxydimethylsilyl)-1,3-butadiene] obtained in THF is listed in this table. As can be seen, the microstructures of the polymers of **2**−**4** obtained in THF are very similar in all samples and also are similar to that of poly[2-(2-propoxydimethylsilyl)-1,3-butadiene]. In each of all samples, 10−20% of the 1,2 content is included in addition to 1,4 contents. Since 1,2 in-chain units cannot be formed from a 4,1 chain end, it is assumed that the growing chain ends derived from **1**−**4** are the 1,4 chain ends. Presumably there are localized-delocalized equilibriums among 1,4 and 1,2 σ-bonded chain ends and delocalized π-bonded chain ends, as was shown before in Scheme 2.

1,4 Addition results from a reaction between the monomer and the growing chain anion at the γ-carbon, while 1,2 addition occurs when the monomer reacts with the anion at the α-carbon. The results showing the predominant 1,4 structures can reasonably account for higher reactivities of the anions at the γ-carbons than those at the α-carbons, even though the equilibrium shifts considerably to the anions at the α-carbons.

We previously reported that the anionic polymerizations of 2-(alkoxysilyl)-substituted 1,3-butadienes proceeded via the 1,4 chain ends including 1,2 chain ends and π-bonded allyl chain ends but not the 4,1 chain ends. This is supported by the fact that the resulting polymers have mixed structures of 1,4 and 1,2 units with no 3,4 units detectable. Additional support for this comes from model reactions of 2-(alkoxysilyl)-substituted 1,3-butadiene with BuLi in which 1,4 and 1,2 adducts are exclusively produced.

For example, the 1:1:1 addition products of BuLi, 2-(tri-2-propoxysilyl)-1,3-butadiene, and the terminator were obtained by the addition of the diene to a slight excess of BuLi at −78 °C, followed by termination with alcohol or alkyl halide. The resulting addition products were carefully separated by preparative gas chromatography and analyzed by ^1H and ^{13}C NMR. Only 1,2- and 1,4-addition products were always obtained by any combinations of BuLi (*n*- or *tert*-BuLi) and the terminators (2-propanol, methyl iodide, or allyl bromide).

The ^{13}C NMR spectra of 2-silyl-substituted 1,3-butadienes also provide information that growing chain ends would be 1,4. It is observed that their resonance peaks of the C1 carbons (128−132 ppm) are shifted much lower than those of the C4 carbons (116−117 ppm). This suggests that preferred attack of the growing anions may occur at the C1 carbons but not the C4 ones in the polymerizations of 2-(alkoxysilyl)-substituted 1,3-butadienes. In the anionic polymerization of isoprene, on the other hand, it is estimated from the chemical shift values of both carbons that the C4 carbon (116 ppm) rather than the C1 carbon (112.5 ppm) is attacked by the growing anion. In fact, the polymerization of isoprene was reported to proceed via the 4,1 chain end.[20] In the ^{13}C NMR spectra of **1**−**4**, the resonances for the C1 and C4 carbons were observed at 128.7−129.9 ppm and at 115.5−116.4 ppm, respectively. Similar to the cases of 2-(alkoxysilyl)-substituted 1,3-butadienes, the growing anions from **1**−**4** may also attack the C1 carbons of monomers to produce 1,4 chain ends.

All the polymers obtained in heptane contained only 1,4 structures regardless of different (dialkylamino)silyl substituents. The geometry of the monomer units was, however, affected by the substituent. There were mixtures of 1,4-*E* and 1,4-*Z* structures in the polymers obtained from **1**−**3**. The content of the *Z* isomeric form was major in each case. Interestingly, the polymer obtained from **4** was found to have a structure of exclusively 1,4-*E* unit. It is considered that a favorable conformation for leading to 1,4-*E* addition may be formed by the strong intramolecular coordination of a [2-(*N*,*N*-dimethylamino)ethyl]methylamino group to lithium cation at the growing chain end.

Substitution Reactions of *N*,*N*-Dialkylamino Groups with 2-Propoxy Groups in Polymer Side Chains. Silylamines are known to be powerful silylating agents of alcohols.[11] Therefore, the Si−N bonds in the polymers are readily displaced by the much stronger Si−O bonds with alcohols. In fact, complete conversion from the *N*,*N*-dialkylamino groups to 2-propoxy groups was achieved in the polymers of **1**−**4** obtained in heptane by treating the polymers with 2-propanol (10 equiv to the dialkylamino groups) in the presence of 0.1 equiv of acetic acid. The structures of the resulting polymers were all found to be identical with that of poly[2-(2-propoxydimethylsilyl)-1,3-butadiene) by ^1H and ^{13}C NMR spectra. The SEC peaks of the resulting polymers were sharp unimodal peaks eluted in reasonable molecular weight regions, indicating that neither cross-linking nor undesirable side reactions occurred during the reactions. These transformed polymers are particularly useful for determining the stereochemistry (*E* and *Z* configurations) of the polymers.

Curiously, the reactions were not complete in the polymers obtained in THF under the same condition. In all polymer samples, the reactions always finished in 80−86% conversions. No further reactions proceeded even for longer reaction times and at higher reaction temperatures. Instead, insoluble polymers by cross-linking were produced under more severe conditions. It is observed from the ^1H and ^{13}C NMR analyses of the polymers before and after the reactions that the structures of 1,2 units remain unchanged, while complete transformation from the dialkylamino to 2-propoxy group is achieved in the structures of 1,4 units. Thus, the reactions are found to proceed chemoselectively. Although the reason is not understood at the present time, it is convenient to distinguish between the structures of 1,4 and 1,2 units. Further experiments using another catalyst should be needed to elucidate the reaction mechanism.

References and Notes

(1) Hirao, A.; Nagawa, T.; Hatayama, T.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1985**, *18*, 2101.

(2) Hirao, A.; Hatayama, T.; Nagawa, T.; Yamaguchi, M.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1987**, *20*, 242.

(3) Hirao; Hatayama, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 1505.

(4) Hirao, A.; Taki, T.; Nakahama, S. *Macromolecules* **1991**, *24*, 1455.

(5) Hirao, A.; Ando, Y.; Nakahama, S. *Macromol. Symp.* **1995**, *95*, 293.

(6) Takenaka, K.; Hirao, A.; Hattori, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 2034.

(7) Takenaka, K.; Hattori, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 1563.

(8) Takenaka, K.; Hattori, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1992**, *25*, 96.

(9) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1992**, *25*, 96.

(10) Hirao, A.; Nakahama, S. *Prog. Polym. Sci.* **1992**, *17*, 283.

(11) *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds: Sulfur, Selenium, Silicon, Boron, Organo-metallic Compounds;* Jones, N. D., Ed.; Pergamon: New York, 1979; Vol. 3, p 541.

(12) Nunomoto, S.; Yamashita, Y. *J. Org. Chem.* **1979**, *44*, 4788.

(13) Bassindale, A. R.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *25*, 57.

(14) Walton, D. R. M. *J. Chem. Soc. C* **1966**, 1706.

(15) Basha, F. Z.; DeBernardis, J. F. *Tetrahedron Lett.* **1984**, *25*, 5271.

(16) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

(17) Cunico, R. F. *J. Organomet. Chem.* **1973**, *60*, 219.

(18) Groke, J.; Möller, U. *J. Organomet. Chem.* **1969**, *17*, 263.

(19) Asami, R.; Oku, J.; Takeuchi, M.; Nakamura, K.; Takaki, M. *Polym. J.* **1988**, *20*, 699.

(20) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983; p 146.

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