Polymerization of Monomers Containing Functional Silyl Groups. 10. Anionic Polymerization of 2-Silyl-Substituted 1,3-Butadienes with Mixed Substituents

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ABSTRACT: Anionic polymerizations of three alkyl- and alkoxysilyl-substituted 1,3-butadienes—2-(diisopropoxymethylsilyl)-1,3-butadiene (**2**), 2-(isopropoxydimethylsilyl)-1,3-butadiene (**3**), and 2-(trimethylsilyl)-1,3-butadiene (**4**)—were carried out under various conditions. The stabilities and the reactivities of the active chain end species derived from these monomers and the microstructures of the resulting polymers were found to be affected by the substituents on the silicon atom. In contrast to the previous results in the anionic polymerization of 2-(triisopropoxysilyl)-1,3-butadiene (**1a**), deactivation of chain-end carbanions was observed after the completion of the polymerizations of **2**–**4**. The resulting polymers consisted mainly of 1,4 (70–80%) and 1,2 (20–30%) linkages, whereas 1,4-*E* was the exclusive structure in poly(**1a**) prepared under similar conditions. The relative reactivities of the carbanions at the active chain ends derived from **4**, **3**, **2**, and **1a** were found to decrease in this order by the crossover reactions with isoprene, stryene, and 2-vinylpyridine.

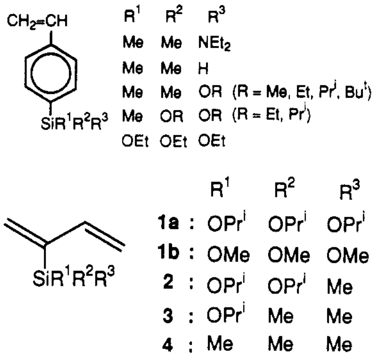
Introduction

Over the past few years, we have been carrying out the anionic polymerization of styrene derivatives containing functional silyl groups such as *p*-[(*N*,*N*-diethylamino)-dimethylsilyl]-,[1] *p*-(dimethylhydrosilyl)-,[2] *p*-(dimethylalkoxysilyl)-,[3] *p*-(dialkoxymethylsilyl)-,[4] and *p*-(trialkoxysilyl)styrenes.[4] Through the study on the anionic polymerizations of these monomers, we have found that stable living polymers were formed under certain conditions. Particularly in the case of monomers having alkoxysilyl groups, steric bulkiness around the silicon atom was the most important factor to prevent the spontaneous termination reaction.

In the previous papers, we have also shown the unique polymerization behaviors in the anionic polymerization of 2-(trialkoxysilyl)-1,3-butadienes (**1a** and **1b**) and 2-(trimethylsilyl)-1,3-butadiene (**4**), where reactive silyl groups were directly attached to the polymerizable moieties.[5,6] During the course of polymerization of these monomers, the substituents on the silicon atom significantly affect the stabilities of the active polymer chain end and the microstructure of the resulting polydienes. For example, a stable living polymer from 2-(triisopropoxysilyl)-1,3-butadiene (**1a**), was formed in THF at −78 °C, resulting in the formation of polymers of predictable molecular weights and of narrow molecular weight distributions (MWD's). Surprisingly, the microstructure of poly(**1a**) thus obtained was exclusively 1,4-*E*, the cis-1,4 linkage of the polymer chain, even though it was prepared in a polar solvent such as THF. In the case of the less hindered trimethoxysilyl-substituted derivative **1b**, partial loss of the chain-end carbanion was observed under identical conditions. Since the molecular weight distribution of poly(**1b**) was narrow, the deactivation of the propagating chain end seemed to have occurred after the complete consumption of the monomer. Although the resulting poly(**1b**) consisted of 100% 1,4 linkage as well as poly(**1a**), 10–30% of the 1,4 linkages were in the *Z* form depending on the counterion used. These results indicate that the stabiity of the living ends and the stereoselectivity are affected by the steric hindrance of the alkoxy groups on the silicon atom.

On the other hand, **4** showed a different polymerization behavior. Broadening of the molecular weight distribution was observed when the polymerization mixture was allowed to stand for a long time, though it shows a narrow MWD just after the completion of polymerization.[6] The microstructures of the resulting polymers were complicated mixtures of 1,4 and 1,2 (or 3,4) linkages. Thus the stability of the active chain end and the mode of polymerization are also affected by the substituent, not only alkoxy but also methyl groups, on the silicon atom.

Chart I



R^1	R^2	R^3
Me	Me	NEt_2
Me	Me	H
Me	Me	OR (R = Me, Et, Pr^i, Bu^t)
Me	OR	OR (R = Et, Pr^i)
OEt	OEt	OEt

	R^1	R^2	R^3
1a :	OPr^i	OPr^i	OPr^i
1b :	OMe	OMe	OMe
2 :	OPr^i	OPr^i	Me
3 :	OPr^i	Me	Me
4 :	Me	Me	Me

As we have mentioned in previous papers, active chain end carbanions derived from styrene derivatives containing alkoxysilyl groups showed similar reactivity to those of styryl- and isoprenyl anions.[3,4] This was confirmed by the crossover reaction with styrene and isoprene. On the other hand, poly(**1a**)yl anion could not react with isoprene because of its low nucleophilicity. The alkoxysilyl groups directly attached to the polymerizable moiety might affect the reactivity of the carbanion.

These results stimulated us to investigate the possibilities of polymerization of silyl butadienes with mixed substituents such as 2-(diisopropoxymethylsilyl)-1,3-butadiene (**2**) and 2-(dimethylisopropoxysilyl)-1,3-butadiene (**3**). In this paper, we discuss the anionic polymerization behavior of four 2-silyl-substituted 1,3-butadienes, **1a**, **2**, **3**, and **4**, where the substituents are changed systematically from isopropoxy to methyl groups.

Experimental Section

Materials. The preparations of 2-(triisopropoxysilyl)-1,3-butadiene (**1a**) and 2-(trimethylsilyl)-1,3-butadiene (**4**) were described elsewhere.[6] 2-(Diisopropoxymethylsilyl)-1,3-butadiene

(2) [bp 48–50 °C/5 mmHg; ^{1}H NMR δ 0.24 (s, 3 H, CH_3Si), 1.16 (d, J = 6.0 Hz, 12 H, $OCHCH_3$), 4.14 (hept, J = 6.0 Hz, 2 H, OCH), 5.08, 5.47 (2 d, J = 10.8, 16.5 Hz, 2 H, $CH_2{=}CH$), 5.69 (s, 1 H, $CH_2{=}C$), 5.80 (s, 1 H, $CH_2{=}C$), 6.43 (dd, J = 10.8, 16.5 Hz, $CH_2{=}CH$); ^{13}C NMR δ −2.76 (CH_3Si), 25.7 (CH_3CHO), 65.3 (CHO), 116.7 ($CH_2{=}CH$), 131.0 ($CH_2{=}C$), 140.9 ($CH_2{=}CH$), 146.3 ($CH_2{=}C$); ^{29}Si NMR δ −21.6] and 2-(dimethylisopropoxysilyl)-1,3-butadiene (3) [bp 59–61 °C/25 mmHg; ^{1}H NMR δ 0.21 (s, 6 H, CH_3Si), 1.14 (d, J = 6.0 Hz, 6 H, $OCHCH_3$), 3.97 (hept, J = 6.0 Hz, 1 H, OCH), 5.10, 5.42 (2 d, J = 10.8, 16.5 Hz, 2 H, $CH_2{=}CH$), 5.53 (s, 1 H, $CH_2{=}C$), 5.77 (s, 1 H, $CH_2{=}C$), 6.44 (dd, J = 10.8, 16.5 Hz, $CH_2{=}CH$); ^{13}C NMR δ −0.76 (CH_3Si), 25.7 (CH_3CHO), 65.4 (CHO), 116.4 ($CH_2{=}CH$), 129.3 ($CH_2{=}C$), 141.1 ($CH_2{=}CH$), 148.7 ($CH_2{=}C$); ^{29}Si NMR δ 4.77], were prepared in a similar manner[6] starting from 1,4-dichloro-2-(dichloromethylsilyl)-2-butene or 1,4-dichloro-2-(dimethylchlorosilyl)-2-butene, which were obtained by the hydrosilylation of 1,4-dichloro-2-butyne with the corresponding hydrosilanes catalyzed with chloroplatinic acid. Alcoholysis and dechlorination procedures are described elsewhere.[6]

The authentic 1,4 and 1,2 model compounds of which the ^{1}H NMR chemical shifts are summarized in Table III were prepared as follows. The preparations of (*E*)-4-(triisopropoxysilyl)-4-octene (**5a**) and (*Z*)-4-(triisopropoxysilyl)-4-octene (**5b**) were described previously.[6] Other 1,4-*E* models—(*E*)-4-(diisopropoxymethylsilyl)-4-octene (**6a**), (*E*)-4-(dimethylisopropoxysilyl)-4-octene (**7a**), and (*E*)-4-(trimethylsilyl)-4-octene (**8a**)—were prepared by the hydrosilylation of 4-octyne with the corresponding chlorosilanes followed by alcoholysis or methylation with methylmagnesium iodide. The 1,4-*Z* models—(*Z*)-4-(diisopropoxymethylsilyl)-4-octene (**6b**), (*Z*)-4-(dimethylisopropoxysilyl)-4-octene (**7b**), and (*Z*)-4-(trimethylsilyl)-4-octene (**8b**)—were obtained by photoisomerization of the corresponding *E* isomer in the presence of thiophenol. The 1,2-model compounds—(3-(3-butyl-1-octen)yl)triisopropoxysilane (**5c**), (3-(3-butyl-1-octen)yl)diisopropoxymethylsilane (**6c**), (3-(3-butyl-1-octen)yl)dimethylisopropoxysilane (**7c**), and (3-(3-butyl-1-octen)yl)trimethylsilane (**8c**)—were prepared by the 1:1:1 addition reaction of BuLi, silyl butadiene, and 1-bromobutane. The products were carefully separated by preparative gas chromatography and analyzed by GC–MS and NMR spectroscopy.

Polymerizations. Anionic polymerization was carried out under high-vacuum conditions (~10^{-6} mmHg) according to the previously reported procedure.[2,3] The isolation and purification of polymers were described elsewhere.[6]

Measurement. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in $CDCl_3$ with either a JEOL GSX-500 or FX-90Q spectrometer. $CHCl_3$ (δ 7.24), $CDCl_3$ (δ 77.1), and $(CH_3)_3SiOSi(CH_3)_3$ (δ 6.8) were used respectively as internal references. The DEPT pulse sequence was employed for ^{29}Si NMR measurement.[7] The molecular weight distributions were measured by gel permeation chromatography (GPC) using a TOSOH HLC-8020 instrument at 40 °C with a differential refractive index detector, THF being the elution solvent at a flow rate of 0.8 mL/min. The number-average molecular weight was measured by vapor pressure osmometry (VPO) using a Corona 117 instrument at 40 °C in benzene solution.

Results and Discussion

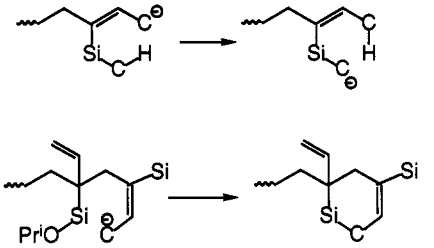
Anionic Polymerization of 2, 3, and 4. As reported previously,[5,6] the polymerization rates of **1a** and **1b** were extremely slow. When oligo(α-methylstyryl)potassium was used as an initiator in THF at −78 °C, it took 90–160 h for the polymerization to be completed, while 3–4 h was sufficient for the quantitative polymerization of conventional dienes such as 1,3-butadiene and isoprene under similar conditions. Similarly, the polymerizations of **2** and **3** were observed to be slow. This was presumably due to the stabilization of the propagating chain end carbanion by the silicon atom through pπ–dπ interactions.[8] The results of the anionic polymerizations of **2** and **3** are summarized in Table I.

Table I
Anionic Polymerization of 2 and 3 in THF at −78 °C[a]

monomer	counterion	time, h	yield, %	M_n (calcd)[b]	M_n (obsd)[c]	M_w/M_n[c]
2	Li^+	72	73	12 000	16 600	1.31
2	Na^+	70	84	13 800	12 600	1.19
2	K^+	88	87	14 700	12 600	1.16
3	Li^+	90	100	13 900	23 800	1.35
3	Na^+	91	100	16 600	17 100	1.20
3	K^+	89	100	17 400	16 200	1.19

[a] Oligo(α-methylstyryl) dianion was used as an initiator. [b] Based on the monomer to initiator ratio. [c] Measured by VPO and GPC.

Scheme I



With the use of oligo(α-methylstyryl)dilithium as an initiator, polymers of relatively broad MWD's were obtained from both **2** and **3**. The gel permeation chromatograms (GPC) of these polymers showed relatively sharp main peaks always accompanied by low molecular weight tails. The observed molecular weights measured by VPO and GPC were larger than the calculated ones based on the monomer to initiator ratio. These results indicate that the deactivation of propagating chain ends occurred to some extent during the course of polymerization. On the other hand, oligo(α-methylstyryl)disodium and/or -dipotassium afforded poly(**2**) and poly(**3**) of narrow MWD's. The observed molecular weights of the polymers and the calculates ones agreed well within experimental error. However, the results of the postpolymerizations of **2** and **3** indicated that most of the propagating carbanions derived from **2** and **3** were deactivated in 90 h at −78 °C even with potassium as a counterion. These results are in sharp contrast to the previously reported living nature of **1a** under identical conditions. The deactivation of the carbanion seemed to occur after the complete consumption of the monomers, since poly(**2**) and poly(**3**) had nearly predictable molecular weights and narrow MWD's. Although the reaction mechanism is not clear yet, a likely explanation would be a proton abstraction from the silylmethyl group at the terminal unit and/or nucleophilic substitution on the silicon atom to form a cyclic structure at the polymer end as illustrated in Scheme I. The difference of reactivities among these carbanions will be discussed in a later section. Table II summarizes the results of the anionic polymerization of 2-(trimethylsilyl)-1,3-butadiene (**4**), where no alkoxy group is substituted. In this case, the polymerization of **4** proceeded faster than those of the alkoxy-substituted monomers in THF at −78 °C. The polymerization was generally completed within 24 h, and the resulting polymers had predictable molecular weights and narrow MWD's. The result of the crossover reaction with 2-vinylpyridine, which will be described in a later section, indicated that the poly(**4**)yl anion was sufficiently stable to afford living polymer. Next, the polymerization was carried out with *sec*-BuLi as an initiator in hexane in the absence and presence of tetramethylethylenediamine (TMEDA). In either case, the calculated molecular weights were larger than the observed ones, and the molecular weight distributions were broad (M_w/M_n ~ 1.3). The GPC traces of both polymers are shown in Figure 1. The polymer obtained without TMEDA had shoulder peaks at the higher molecular

Table II
Anionic Polymerization of 4 under Various Conditions

initiator	solvent	temp, °C	time, h	yield, %	M_n(calcd)[a]	M_n(obsd)[b]	M_w/M_n[b]
Li/α-MeSt	THF	−78	7	50	7 000	8 400	1.13
Na/α-MeSt	THF	−78	2	95	14 900	16 300	1.19
K/α-MeSt	THF	−78	5	63	11 400	12 200	1.16
K/α-MeSt	THF	−78	24	100	7 100	8 700	1.15
sec-BuLi	hexane	20	24	100	5 700	11 000	1.30
sec-BuLi	hexane/TMEDA	−20	48	trace			
sec-BuLi	hexane/TMEDA	20	48	59	2 800	4 000	1.32
sec-BuLi	hexane/TMEDA	20	200	100	5 900	8 300	1.29

[a] Based on the monomer to initiator ratio. [b] Measured by VPO and GPC.

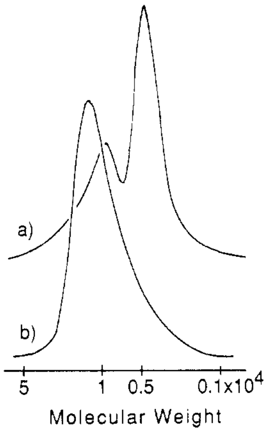


Figure 1. GPC curves of poly(**4**) prepared in different solvents: (a) polymerized in hexane; (b) polymerized in hexane/TMEDA mixture.

weight side whereas a low molecular weight tail was observed in the polymer with the amine modifier. These results indicate that various kinds of side reactions including chain termination occurred in these polymerization conditions.

Microstructures of Poly(1,3-diene)s Containing Silyl Groups. Regulation of the microstructure of the resulting polymer is of considerable interest since the physical properties of polydienes strongly depend on the structure of the repeating units. For each of the polymers obtained here, the mode of polymerization (1,4, 1,2, and 3,4) and geometry of the monomer units (*E* and *Z*) were determined by ^{1}H and ^{13}C NMR spectroscopy. The results and the previously reported result for poly(**1a**) are summarized in Tables III and IV. Figure 2 shows typical ^{1}H NMR spectra of poly(**2**), poly(**3**), and poly(**4**) recorded at 50 °C in $CDCl_3$. For each case, broad signals attributable to both terminal olefinic protons and inner ones were observed at 4.5–6.2 ppm, indicating that these polymers contain 1,2 or 3,4 structures in addition to 1,4 structures. This was also supported by the fact that three signals were clearly observed around 0 ppm due to methyl protons attached to the silicon atom. The assignment of these signals was carried out by comparing their chemical shifts with those of the well-characterized low molecular weight compounds, **5**–**8**. The results are summarized in Table III. The compositions of the microstructures in these polymers were calculated based on these chemical shift data. In the case of poly(**4**) prepared in THF, the chemical shifts of three silylmethyl signals were very close to those of the 1,4-*E*, 1,4-*Z*, and 1,2 models, and no signal attributable to the 3,4 linkage was observed.[9] The signal intensity ratio of olefinic protons in poly(**4**) corresponds well with the values calculated from the area ratio of the three silylmethyl proton signals, which was determined by the curve-fitting program run on an NEC PC-9801VM personal computer. The ^{29}Si NMR spectrum of poly(**4**) showed only three signals, whose chemical shifts were nearly identical to those of the 1,4-*E*, 1,4-*Z*, and 1,2 model compounds employed here. Considering these facts, it can be concluded that poly(**4**) consists of 1,4 and 1,2 linkages.

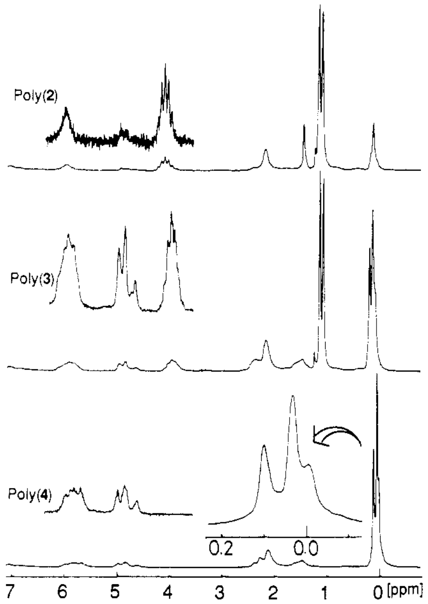


Figure 2. 90-MHz ^{1}H NMR spectra of poly(**2**), poly(**3**), and poly(**4**) recorded at 50 °C in $CDCl_3$.

The microstructures of the resulting polymers were analyzed accordingly, and the results are summarized in Table IV. As can be seen, the 1,4-*E*, cis-1,4 structure of the polymer chain was the main component in each polymer although it was prepared in THF. This was quite different from the case of polyisoprene prepared under identical conditions. The proportions of the 1,4-structure in these silylated polymers decreased and those of the 1,2 structure increased drastically with the increase in the number of methyl groups in their silyl substituents. It is worth noticing here that poly(**1a**) and poly(**1b**) contained no 1,2 structure regardless of the polymerization conditions. The geometry of the monomer units in these polymers was affected by the steric bulkiness of the alkoxy groups on the silicon atom and was exclusively 1,4-*E* for poly(**1a**) and a mixture of 1,4-*E* and 1,4-*Z* for poly(**1b**). Considering these results, it can be concluded that the mode of polymerization such as 1,4 and 1,2 is affected by the electron density of the butadienyl skeleton rather than by steric hindrance. In other words, the group electronegativity[10] of the silyl substituent affects the structure of the repeating units in these polymers. This can also be suggested by the reactivity of the monomers and the corresponding carbanions, which will be discussed in a later section.

When anionic polymerization of **4** was carried out in hexane with *sec*-BuLi as an initiator, polymers of high

Table III
^{1}H NMR Chemical Shifts of Poly(1) to Poly(4) and the Model Compounds

SiR^{1}R^{2}R^3				model compounds			polymer		
R^1	R^2	R^3		1,4-*E*[a]	1,4-*Z*[b]	1,2[c]	1,4-*E*	1,4-*Z*	1,2
OPr^i	OPr^i	OPr^i	=CH	6.06 (t)	6.10 (t)	5.90 (dd)	6.05	6.11	
			=CH$_2$			4.81 (d), 4.95 (d)			
			=CCH$_2$	1.9–2.3			1.9–2.4		
			CH$_2$			1.2–1.6			
OPr^i	OPr^i	Me	=CH	5.95 (t)	5.99 (t)	5.85 (dd)		5.8–6.2	
			=CH$_2$			4.79 (d), 4.95 (d)			4.6–5.0
			=CCH$_2$	1.9–2.3			1.9–2.4		
			CH$_2$			1.2–1.7			1.4–1.7
			SiCH$_3$	0.14 (s)	0.17 (s)	0.06 (s)	0.13 (s)	0.18 (s)	0.09 (s)
OPr^i	Me	Me	=CH	5.83 (t)	5.97 (t)	5.78 (dd)		5.7–6.2	
			=CH$_2$			4.76 (d), 4.92 (d)			4.7–5.0
			=CCH$_2$	1.9–2.2			2.0–2.6		
			CH$_2$			1.2–1.5			1.4–1.7
			SiCH$_3$	0.13 (s)	0.19 (s)	0.04 (s)	0.14 (s)	0.19 (s)	0.08 (s)
Me	Me	Me	=CH	5.69 (t)	5.90 (t)	5.78 (dd)		5.6–6.1	
			=CH$_2$			4.69 (d), 4.90 (d)			4.5–5.1
			=CCH$_2$	2.00–2.15			1.9–2.4		
			CH$_2$			1.15–1.40			1.3–1.8
			SiCH$_3$	0.03 (s)	0.11 (s)	−0.05 (s)	0.03 (s)	0.10 (s)	−0.01 (s)

[a] **5a**, **6a**, **7a**, and **8a**. [b] **5b**, **6b**, **7b**, and **8b**. [c] **5c**, **6c**, **7c**, and **8c**.

Table IV
Microstructure of Poly(1) to Poly(4)

	SiR^{1}R^{2}R^3				microstructure, %			
polymer	R^1	R^2	R^3	condition	1,4-*E*	1,4-*Z*	1,2	3,4
poly(**1a**)	OPr^i	OPr^i	OPr^i	Li/THF	100	0	0	0
				Na/THF	100	0	0	0
				K/THF	100	0	0	0
poly(**1b**)	OMe	OMe	OMe	Li/THF	90	10	0	0
				Na/THF	75	25	0	0
				K/THF	73	27	0	0
poly(**2**)	OPr^i	OPr^i	Me	Li/THF	91	3	6	0
				Na/THF	67	17	16	0
				K/THF	62	19	19	0
poly(**3**)	OPr^i	Me	Me	Li/THF	65	15	20	0
				Na/THF	45	30	25	0
				K/THF	47	30	23	0
poly(**4**)	Me	Me	Me	Li/THF	43	23	34	0
				Na/THF	44	27	29	0
				K/THF	44	28	28	0
				Li/hexane	84	4	12	0
				Li/hexane/TMEDA	67	11	13	9

1,4-*E* content were obtained. This agreed well with the results of anionic polymerization of 2-(triethylsilyl)-1,3-butadiene reported by Ding and Weber[11] and those of conventional 1,3-dienes such as isoprene. The microstructure of poly(**4**) prepared in a hexane/TMEDA mixture was slightly different from the others. Although 1,4-*E* was still the main component in the polymer, the ^{1}H NMR spectra of the polymer showed additional signals due to the 3,4 linkage in the olefinic and silylmethyl regions. The effect of TMEDA on the microstructure was not so significant compared with the case of polyisoprene where the 3,4 structure predominates in the presence of this chelating agent.[12]

Reactivity of 2-Silyl-Substituted 1,3-Butadienyl Anions. In previous papers, we found that the polymerization rate of **1a** in THF was extremely low in comparison with those of isoprene and butadiene.[5,6] Furthermore, it was also found that the nucleophilicity of the poly(**1a**)yl anion was too low to initiate the anionic polymerization of isoprene.[6] To estimate the reactivities of the propagating carbanions derived from **1a**, **2**, **3**, and **4**, the crossover reactions of the carbanions with monomers of different e values were performed to characterize the resulting copolymers. According to the Alfrey–Price Q–e theory,[13] the anionic reactivity of a vinyl monomer is estimated by its e value. Isoprene ($Q = 3.33$, $e = -1.22$), styrene ($Q = 1.00$, $e = -0.80$), and 2-vinylpyridine ($Q = 1.30$, $e = -0.50$)[14] were chosen as monomers for crossover reactions since the reactivities of these monomers are expected to be in the critical range toward the weak carbanions derived from silyl-substituted dienes.

The silyl-substituted dienyl anions were prepared by the reaction of **1a**, **2**, **3**, and **4** with oligo(α-methylstyryl)dipotassium in THF at −78 °C. To minimize the effect of side reactions during the polymerization of the silyl-substituted monomers, the monomer to initiator ratio was lowered to about 10. Under these conditions, silylbutadienes were consumed completely within 10 h, and most of the propagating ends were still active. After 10–12 h, isoprene, styrene, or 2-vinylpyridine was added to the reaction mixture, and it was allowed to react for an additional 10–24 h. The polymers thus obtained were characterized by GPC and NMR.

Table V summarizes the results of the crossover reactions. A solid circle indicates that quantitative block copolymerization occurred by the addition of the second monomer. The resulting block copolymers were found to possess predictable molecular weights and narrow MWD's. An open circle indicates that the initiation efficiency of the active chain end to the second monomer was low, resulting in the formation of a mixture of homopolymer and block copolymers of high molecular weights. A triangle

Table V
Summary of Crossover Reactions[a]

carbanion 			second monomer		
			isoprene $Q = 3.33$ $e = -1.22$	styrene $Q = 1.0$ $e = -0.8$	2-vinylpyridine $Q = 1.30$ $e = -0.50$
R^1	R^2	R^3			
OPr^i	OPr^i	OPr^i	×	○	●
OPr^i	OPr^i	Me	△	○	●
OPr^i	Me	Me	△	△	●
Me	Me	Me	○	●	●

[a] (●) Quantitative block copolymerization; (○) initiation with low efficiency; (△) polymerization with termination; (×) no reaction.

indicates that a termination reaction was observed during the course of the second polymerization. In this case, the yield of copolymer was not quantitative, and most of the second monomer was recovered from the polymerization mixture. The ^1H NMR of these copolymers showed that only a few units of the second monomer were included in the copolymer chain. A cross indicates that no reaction took place under these conditions. Quantitative recoveries of the first homopolymer and the second monomers were realized in this case.

As can be seen from the table, isoprene, styrene, and 2-vinylpyridine show different reactivities toward the 2-silyl-substituted butadiene anions. When the above monomers were added to the anions, the efficiency of block copolymerization increased with the increase of the e value of the second monomer. It is generally recognized that living polyisoprene can initiate the polymerization of these monomers quantitatively to give block copolymers of predictable molecular weights. These results clearly indicate that the carbanions derived from silylbutadienes are stabilized so as to have much lower nucleophilicities than those from isoprene.

The effect of the substituent on the reactivity is also obvious. The reactivity of the carbanion as the propagating chain end drastically increases with the decrease of the number of isopropoxy groups on the silicon atom. Thus the reactivities of the carbanions were found in the order of **4** > **3** > **2** > **1a**. According to the group electronegativity theory,[10] the orbital electronegativities of silyl groups decrease with the increase of the number of the methyl groups on the silicon atom. This reflects that the triisopropoxysilyl group shows a larger electron-withdrawing character than the trimethylsilyl group. The above results indicate that the reactivities of the carbanions at the propagating chain ends are influenced by the electronic effect of the silyl substituent.

The reactivities of the carbanions can also be estimated by the ^{13}C NMR chemical shifts of the corresponding monomers. Figure 3 shows the ^{13}C NMR chemical shifts of the butadienyl frame in the monomers. It is obvious that the chemical shifts of the C3 and C4 carbons are almost insensitive to the kind of substituent on the silicon atom. On the other hand, the C1 and C2 carbon atoms show high- and low-field shifts, respectively, with the increase of the number of methyl groups. The difference of the chemical shifts between the C1 and C4 carbon atoms ($\delta(C1) - \delta(C4)$) is larger than that of isoprene, which is reflected in the anionic reaction mode. In the stoichiometric reaction of butyllithium and **1a**, the nucleophilic addition of initiator was found to occur at the C1 position of the monomer molecule.[15] This suggests that the preferred attack of the carbanion takes place at the C1 position in the polymerization of **1a** whereas both the C1 and C4 carbon atoms are susceptible to nucleophilic addition in the polymerization of isoprene.[16] The progressive high-field shift of the C1 carbons with the increase of methyl groups reflects the increase of electron density of carbon–carbon double bonds in the monomer. In other words, the reactivity of monomers toward anionic species was lowered in the order of **1a** > **2** > **3** > **4** by the electron-donating character of the methyl groups on the silicon atom. In general, the lower the reactivity of the monomer is, the higher that of the corresponding carbanion becomes. Therefore the reactivity of carbanion at the propagating chain end would be in the order of **4** > **3** > **2** > **1a**. Our results in the crossover reactions agreed well with this general rule.

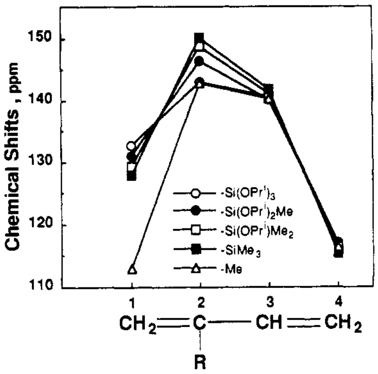
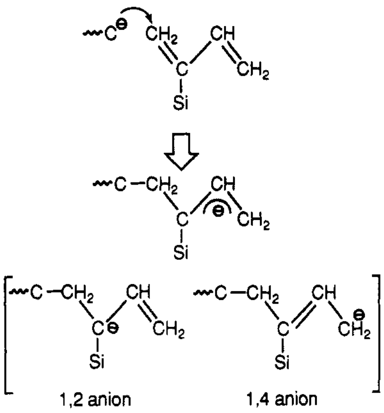


Figure 3. ^{13}C NMR chemical shifts of butadienyl frames of **1a** (R = $Si(OPr^i)_3$ (○), **2** (R = $Si(OPr^i)_2Me$ (●), **3** (R = $Si(OPr^i)Me_2$ (□), **4** (R = $SiMe_3$ (■), and isoprene (R = Me (△).

Scheme II



As mentioned in the previous section, chain-end carbanions derived from **2**, **3**, and **4** could be deactivated after completion of the polymerization whereas that derived from **1a** was sufficiently stable to afford living polymer under identical conditions. These differences could be related with the reactivity of the propagating carbanions, steric hindrance around the silicon atom, and the microstructure of the resulting polymers. Carbanions having higher nucleophilicity derived from monomers having lower electrophilicity might have reacted with the silylmethy group and/or the silicon atom. This kind of nucleophilic substitution on the silicon atom is likely to occur when silyl groups and carbanions are located at an appropriate position. As a matter of fact, the *tert*-butyldimethylsilyl ether of *o*-vinylphenol cannot be polymerized by an anionic initiator whereas the para isomer gives a stable living polymer under the same conditions.[17]

In addition, the reactivity of the carbanion at the chain end would be related with the microstructure of the resulting polymers. The formation of 1,2 structures in poly(**2**), poly(**3**), and poly(**4**) can be explained by the reactivity of active chain end carbanions. As was mentioned in the above section, the nucleophilic attack of the initiator occurs at the C1 position of the monomer to form π-allyl type carbanions, which can be considered to be a resonance hybrid of the 1,2 and 1,4 anions. Since the silicon atom can stabilize the carbanion at the α position,[8] the former carbanion would be less nucleophilic than the latter one. During the anionic polymerization of **1a** and **1b**, the 1,2 anion was too weak to attack the monomer molecules because of the electron-withdrawing character of the three alkosy groups on the silicon atom, resulting in the formation of poly(**1a**) and poly(**1b**) having 100% 1,4 structure. With the increase of the number of methyl groups on the silicon atom, the 1,2 anion became more reactive, resulting in the formation of poly(**2**), poly(**3**), and poly(**4**) containing considerable amounts of 1,2 structures.

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Registry No. **1a**, 104955-51-3; **1a** (homopolymer), 104955-52-4; **1b** (homopolymer), 104955-47-7; **2**, 126726-57-6; **2** (homopolymer), 126726-58-7; **3**, 113177-18-7; **3** (homopolymer), 113177-19-8; **4**, 18301-64-9; **4** (homopolymer), 116767-56-7; **5a**, 117861-52-6; **5b**, 117861-53-7; **5c**, 136892-96-1; **6a**, 136892-97-2; **6b**, 136892-98-3; **6c**, 136892-99-4; **7a**, 136893-00-0; **7b**, 136893-01-1; **7c**, 136893-02-2; **8a**, 64997-08-6; **8b**, 83511-19-7; **8c**, 136893-03-3; THF, 109-99-9; TMEDA, 110-18-9; Li/α-MeSt, 57486-18-5; Na/α-MeSt, 37244-89-6; K/α-MeSt, 52219-57-5; *sec*-BuLi, 598-30-1; $H_3C(CH_2)_4CH_3$, 110-54-3.