Polymerization of Monomers Containing Functional Silyl Groups. 6. Anionic Polymerization of 2-(Trialkoxysilyl)-1,3-butadiene

Katsuhiko Takenaka, Takashi Hattori, Akira Hirao, and Seiichi Nakahama*

Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152, Japan. *Received May 23, 1988*

ABSTRACT: Anionic polymerizations of 2-(trimethoxysilyl)-1,3-butadiene (1) and 2-(triisopropoxysilyl)-1,3-butadiene (2) were carried out under various conditions. In the anionic polymerization of 1, polymers of desired molecular weight with narrow molecular weight distributions were obtained when polymerized in THF at −78 °C with potassium or cesium as countercation. In the case of lithium and sodium cations, the partial loss of carbanion was observed even at −78 °C, resulting in polymers of relatively broad molecular weight distributions. In the anionic polymerization of 2, stable living polymer was formed at −78 °C regardless of the countercation used. The nearly monodispersed homopoly(2) and block copolymers containing poly(2) segment were obtained with desired molecular weights. The microstructures of the resulting polymers were analyzed by ^1H and ^{13}C NMR spectroscopy. For both monomers, the polymerization proceeded in the 1,4-mode regardless of the countercation. The geometry of the monomer units in the polymer was affected by the steric hindrance on the silicon atom and the countercation used. Under typical polymerization conditions, 1,4-*E* was the predominant microstructure of the resulting polymers.

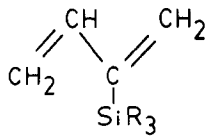
Introduction

In a previous paper, we have reported the living nature of the anionic polymerization of 2-(trimethoxysilyl)-1,3-butadiene (1) and formation of the homopolymer of predictable molecular weight with narrow molecular weight distribution.[1] The microstructure of the polymer was also analyzed to be a mixture of 1,4-*E* and -*Z*, where the *E* configuration predominated. It is worth noticing here that no detectable amount of 1,2- and 3,4-adducts was formed even though the polymerization was carried out in polar solvents, such as THF. Anionic polymerizations of butadiene and isoprene in THF proceed mainly in the 1,2- and 3,4-mode.

Recently, the propagating chain ends of poly(1) have been found to be deactivated in some cases. As was already reported, bulky alkoxy groups attached to the silicon atom play an important role in stabilizing the anionic living polymerization of 4-(dimethylalkoxysilyl)styrenes.[2] Taking account of this fact, anionic polymerization of 2-(triisopropoxysilyl)-1,3-butadiene (2) was expected to give a stable propagating end.

Ding and Weber reported that the anionic polymerization of 2-(triethylsilyl)-1,3-butadiene in hexane and THF containing HMPA proceeded predominantly in the 1,4-mode to give a polymer of predictable molecular weight with rather broad molecular weight distribution, although the stability of the anionic propagating chain end was not clarified.[3]

In this paper, we wish to report the results of the anionic polymerizations of 1 and 2 under various conditions and discuss the activity and stability of the propagating chain ends and mode of polymerizations. In addition, 2-(trimethylsilyl)-1,3-butadiene (3) was polymerized with anionic initiators in THF. The polymerization behavior of 3 is also compared with those of 1 and 2.



1: R = OMe
2: R = OPr^i
3: R = Me

Results and Discussion

Anionic Polymerization of 1. The results of anionic polymerization of 1 under various conditions are shown in Table I. Upon addition of the monomer to THF solutions of lithium and sodium salts of oligo(α-methylstyrene) dianion at −78 °C, the red color of the initiator changed immediately to reddish brown (Li) or brownish orange (Na). The color of the system gradually faded to faint yellow within 24 h and the conversion of the monomer leveled off at less than 50%, indicating that the polymerization was almost terminated. The observed molecular weights of the resulting polymers by vapor pressure osmometry agree fairly well with those calculated from the molar ratio of reacted monomer and initiator as shown in Table I. Relatively broad molecular weight distributions are probably due to competing termination with propagation reaction.

Table I
Anionic Polymerization of 1 in THF with $(\alpha\text{-MeSt})_n^{2-}2M^{+}$ [a]

counterion	temp, °C	time, h	conv, %	$\bar{M}_n$ calcd[b]	$\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
Li^+	−78	43	26	4900	6400	1.20
Na^+	−78	67	50	9100	9300	1.37
K^+	0	24	100	13000	14000	1.22
K^+	−78	90	100	14000	14000	1.11
Cs^+	−78	90	100	13000	15000	1.07

[a] Initiator was prepared from alkaline-metal naphthalenide and an excess amount of α-methylstyrene just prior to use. [b] Calculated from monomer to initiator ratio. [c] Measured by VPO. [d] Measured by GPC.

When potassium and cesium were used as countercations, the brownish orange color of the reaction mixture was maintained at −78 °C even after complete conversion of the monomer. Sticky polymer was quantitatively obtained after the workup. The trimethoxysilyl group on the polymer chain was stable through the anionic polymerization and reprecipitation processes, as confirmed by ^1H NMR analysis of the polymer. As can be seen in Table I, good agreement between the predicted molecular weights and the measured values is obtained. For each polymer, GPC analysis reveals a very narrow molecular weight distribution. These results suggest relatively rapid initiation and virtual absence of chain-transfer and termination reactions during the course of polymerization of 1 with potassium and cesium countercations, while the propagating end with lithium and sodium cations is deactivated before depletion of the monomer. When the monomer was added to the initiator solution at −78 °C and then allowed to stand at 0 °C, the polymerization was completed in 24 h to afford poly(1) with narrow molecular weight distribution, indicating that the polymerization proceeded much faster without side reactions than those at −78 °C.

0024-9297/89/2222-1563$01.50/0

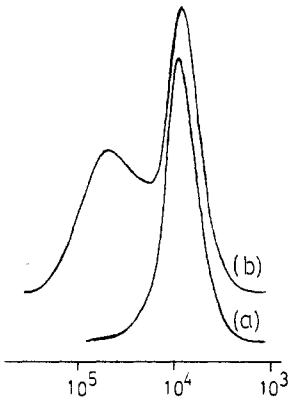


Figure 1. GPC curves of the polymers produced by postpolymerization of 1: prepolymer (a) was prepared with oligo(α-methylstyryl)dipotassium at −78 °C for 86 h; postpolymer (b) was prepared by the reaction of 1 with an aliquot of the prepolymer at −78 °C for 76 h.

Further information on the stability of the propagating chain end derived from 1 is obtained by postpolymerization. First, 1 was polymerized with oligo(α-methylstyryl) dipotassium at −78 °C for 86 h. After depletion of 1, another portion of the monomer was added to the reaction mixture, which was allowed to stand at that temperature for an additional 76 h. Figure 1 shows GPC curves of the resulting polymers obtained at each step. The postpolymer has a significant shoulder at the elution count where the unimodal and sharp distribution curve of the prepolymer has a peak. Obviously a part of the propagating chain end was deactivated. The termination reaction may be important only near or after the completion of polymerization; otherwise, the molecular weight distribution of prepolymer becomes broad and the GPC trace shows a tailing in the low molecular weight side.

Anionic Polymerization of 2. In our previous investigation on the anionic polymerization of styrene derivatives containing alkoxy silyl groups,[2] bulky groups on the silicon atom were found to protect the silicon atom from attack of the active propagating chain ends. A similar steric effect might be also observed in case of the anionic polymerization of 1,3-butadiene derivatives. Accordingly, 2-(triisopropoxysilyl)-1,3-butadiene (**2**) was prepared as a bulky counterpart and polymerized under various conditions.

Upon addition of the monomer to the initiator solution at −78 °C, the red color of oligo(α-methylstyryl) dianion changed immediately to reddish-brown regardless of the countercation used. The characteristic color seemed to be unchanged even after depletion of the monomer for 90–160 h. After quenching the system with a small amount of methanol, sticky polymers were isolated and purified by reprecipitation in quantitative yields. The ^{1}H NMR analysis of the polymer reveals that hydrolysis and alcoholysis of the triisopropoxysilyl group do not occur on the polymer chain during workup. The result of anionic polymerization of **2** is summarized in Table II. Polymers of desired molecular weights were obtained regardless of the countercation used. Although the poly(**2**)s were nearly monodispersed, the values of $\bar{M}_w/\bar{M}_n$'s increased slightly with decreasing diameter of countercation.

The polymerization of **2** was much slower than those of butadiene and isoprene at −78 °C.[4] When initiated at −78 °C and polymerized at 0 °C, the reaction was accelerated to completion in 20 h without broadening of the molecular weight distribution. In order to check the stability of active chain end of poly(**2**), postpolymerization was carried out at two different temperatures. Figure 2(Ia,Ib) shows the

Table II
Anionic Polymerization of 2 in THF with (α-MeSt)$_n^{2-}$2M^{+} [a]

counterion	temp, °C	time, h	conv, %	$\bar{M}_n$ calcd[b]	$\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
Li^+	−78	95	100	11000	12000	1.25
Na^+	−78	95	100	12000	11000	1.12
K^+	0	3	74	12000	10000	1.21
K^+	−20	20	100	11000	11000	1.18
K^+	−78	92	91	12000	11000	1.12
K^+	−78	100	91	21000	19000	1.10
K^+	−78	160	90	36000	31000	1.11
Cs^+	−78	95	86	11000	10000	1.08

[a] Initiator was prepared from alkaline-metal naphthalenide and an excess amount of α-methylstyrene just prior to use. [b] Calculated from monomer to initiator ratio. [c] Measure by VPO. [d] Measured by GPC.

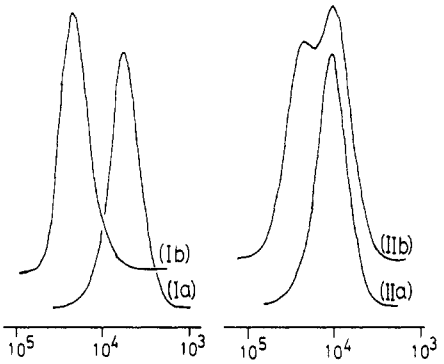


Figure 2. GPC curves of the polymers produced by postpolymerization of **2**; the polymerization was initiated with oligo(α-methylstyryl) dipotassium in THF at −78 °C for 69 h and at 20 °C for 3 h to afford the prepolymers Ia and IIa, respectively; postpolymers Ib and IIb were produced by the reaction of **2** with an aliquot of the prepolymers Ia and IIa, respectively, at −78 °C.

GPC traces of pre- and postpolymers produced at −78 °C. Unlike the case of poly(**1**), both traces are unimodal and very narrow. The elution curve of postpolymer moves toward the high molecular weight side and shows no shoulder at the elution count corresponding to the prepolymer. The result of postpolymerization indicates that the propagating chain end of poly(**2**) is stable at −78 °C for 69 h and is able to initiate additional polymerization of **2**.

When the prepolymer was polymerized at 20 °C for 3 h, however, the GPC curve of the postpolymer shown in Figure 2(IIb) showed a significant shoulder due to prepolymer. This strongly suggests that the propagating chain end of poly(**2**) was partly deactivated at the higher temperature.

Anionic Polymerization of 3. Very recently, Ding and Weber reported[3] the anionic polymerization of 2-(triethylsilyl)-1,3-butadiene. Although the molecular weight distributions of the polymers were relatively broad, the calculated molecular weights of the polymers based on the ratios of reacted monomer to initiator agreed fairly well with the measured ones. 2-(Trimethylsilyl)-1,3-butadiene (**3**) was prepared and polymerized with anionic initiators. Table III summarizes the result of the polymerization of **3**. Upon addition of the monomer to THF solution of α-methylstyryl dipotassium, the red color of the initiator turned to reddish brown. This color seemed unchanged at −78 °C for 24 h. The polymerization of **3** proceeded faster than those of the trialkoxysilyl derivatives and was complete in 24 h to give polymers of desired molecular weight with narrow molecular weight distributions. When allowed to stand for 68 h after the completion of polymerization, however, a significant second peak appears at

Table III
Anionic Polymerization of 3 in THF with $(\alpha\text{-MeSt})_n^{2-}2K^+$ [a]

counterion	temp, °C	time, h	conv, %	$\bar{M}_n$ calcd[b]	$\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
K^+	−78	5	46	9500	15000	1.17
K^+	−78	24	100	7100	8700	1.14
K^+	−78	68	97	7500	40000	1.80

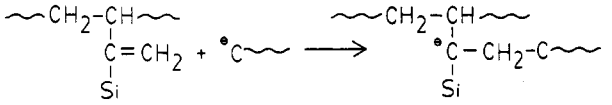
[a] Initiator was prepared from alkaline-metal naphthalenide and an excess amount of α-methylstyrene just prior to use. [b] Calculated from monomer to initiator ratio. [c] Measured by VPO. [d] Measured by GPC.

Table IV
Block Copolymerization of 2 with Isoprene

type	initiator	$\bar{M}_{n\,calcd}$[a]	$\bar{M}_{n\,obsd}$[b]
ABA	$(\alpha\text{-MeSt})_n^{2-}2K^+$	4000–13000–4000	5000–13000–5000
BA	*s*-BuLi	10000–2500	10000–2800

[a] Calculated based on monomer to initiator ratio. [b] Measured by VPO and ^1H NMR.

Scheme I



the high molecular weight side of the gel-permeation chromatogram. Although the exact reason is not clear, one of the most likely explanation is attack of the active chain end on dangling vinyl groups on the polymer chain as outlined in Scheme I.

Block Copolymerization. The synthesis of block copolymers, which leads to heterophase materials, has always stimulated a great deal of interest. As was mentioned above, the termination free character of the anionic polymerization of **2** makes it possible to synthesize block copolymers containing the poly(alkoxysilylbutadiene) segment which may have reactivity toward silanol and metal oxides on the surfaces of inorganic materials.

The ABA and BA type of block copolymers, where A and B represented poly(**2**) and polyisoprene, respectively, were prepared by addition of **2** to living polyisoprene. The results are summarized in Table IV. The predicted molecular weight based on the amount of initiator and fed monomer agrees well with the observed values measured by GPC and NMR.

In order to prepare block copolymer with inverse sequence, isoprene was added to living poly(**2**). However, no further polymerization proceeded. Unambiguously, the living end of poly(**2**) was not destroyed, which was already confirmed by postpolymerization, nor did it initiated polymerization of isoprene. Considering these facts, the living poly(**2**)yl anion is too weak a base to initiate the anionic polymerization of isoprene. When styrene was added in place of isoprene to living poly(**2**), a mixture of homopoly(**2**) and block copolymer containing high molecular weight polystyrene segment was obtained. From ^1H NMR analysis and molecular weight measurement of the block copolymer obtained by fractional precipitation of the mixture, only a few percent of active chain end of poly(**2**) was estimated to initiate the polymerization of styrene. The weak nucleophilicity of poly(**2**)yl anion can be explained by the stabilization of the carbanion through a $p\pi$–$d\pi$ interaction involving silicon atom.[5]

Microstructures of Poly(1,3-dienes) Containing Silyl Groups. The microstructure of the resulting polymer is of considerable interest since physical properties of polydienes depend upon the structure of the repeating units. 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 ^1H and ^{13}C NMR spectroscopy.

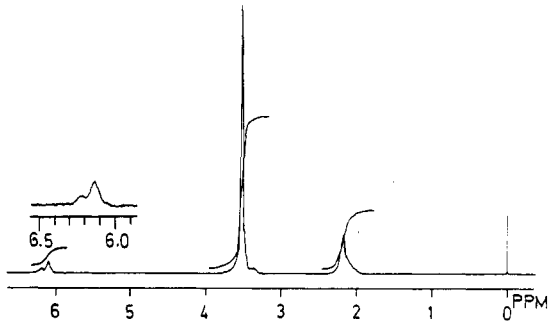


Figure 3. ^1H NMR spectrum of poly(**1**) prepared with potassium countercation.

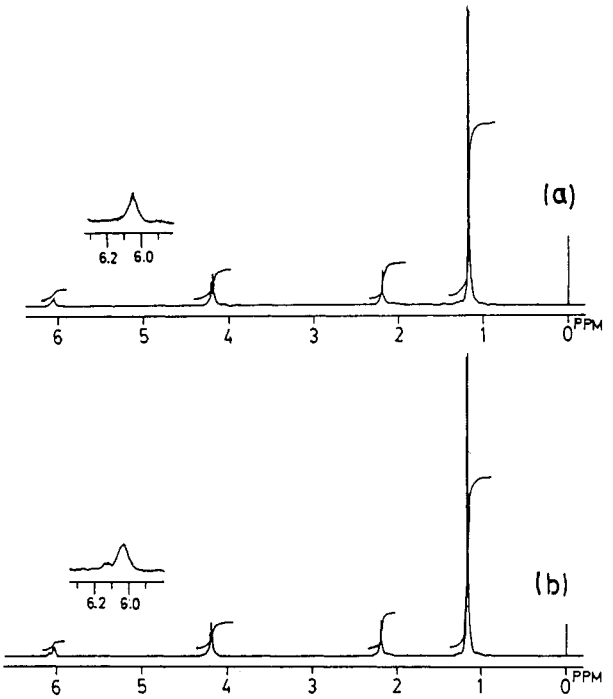


Figure 4. ^1H NMR spectra of poly(**2**) produced with potassium cation (a) and with cesium cation (b).

Table V
Microstructure of Poly(1) and Poly(2)[a]

counterion	poly(1) 1,4- *E*	poly(1) 1,4- *Z*	poly(2) 1,4- *E*	poly(2) 1,4- *Z*
Li^+	90	10	100	0
Na^+	75	25	100	0
K^+	73	27	100	0
Cs^+	59	41	81	19

[a] Prepared at −78 °C in THF.

Figure 3 shows the ^1H NMR spectrum of poly(**1**) prepared with oligo(α-methylstyryl) dipotassium. As was previously reported,[1] the relative integrated intensities of the signals were exactly 1 (=CH) :4 ($-CH_2$) :9 ($-OCH_3$), indicating the predominance of the 1,4-structure in the polymer. An appearance of two individual signals due to olefinic proton at 6.14 and 6.21 ppm corresponds to geometric isomers, *E* and *Z*, respectively, in the polymer chain. The details of the assignment were described elsewhere.[1] The *E*:*Z* ratios of the polymers obtained under various conditions were calculated from relative intensities of the respective signals. The results are summarized in Table

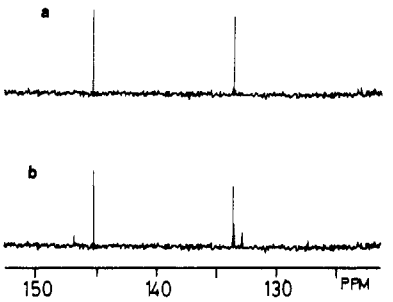


Figure 5. Olefinic region of proton-decoupled ^{13}C NMR spectra of poly(2) produced with potassium cation (a) and with cesium cation (b).

V. The content of the *E* isomeric form is major and gradually decreases with increasing countercation diameter.

Poly(2) was also analyzed in a similar manner. Figure 4 shows the ^1H NMR spectrum of poly(2), in which the signals due to the methyl and methyne protons of isopropoxy group, the methylene proton of main chain, and the olefinic proton appeared at 1.2, 4.3, 2.2, and around 6.1 ppm, respectively. The relative integrated intensities of these signals were exactly 18 (CH_3) :3 (—OCH) :4 ($—CH_2$) :1 (=CH), showing that the monomer unit was linked exclusively in the 1,4-mode. Note the appearance of single olefinic proton signal at 6.05 ppm in poly(2)s prepared with lithium, sodium, and potassium countercation. This suggests that the monomer unit in the poly(2) was incorporated stereoselectively, either 1,4-*E* or 1,4-*Z*. On the other hand, ^1H NMR of poly(2) prepared with cesium countercation gives an additional minor peak at 6.11 ppm as well as the major one at 6.05 ppm, indicating that both of 1,4-*E* and 1,4-*Z* linkages were involved in the polymer chain.

Further information about the microstructure of poly(2) was provided by ^{13}C NMR analysis. Figure 5 shows the olefinic region of proton-decoupled ^{13}C NMR spectra of poly(2)s. Only one pair of signals attributable to olefinic carbons was observed for the polymers produced with lithium, sodium, and potassium countercation. In the case of the poly(2) prepared with oligo(α-methylstyryl) dicesium, two pairs of signals due to olefinic carbons appeared in the spectrum. This result is consistent with that of ^1H NMR analysis mentioned above.

In the previous paper, we determined the geometry of the monomer unit in poly(1) by comparison of the chemical shifts of authentic compounds.[1] Similarly, (*E*)-4-(triisopropoxysilyl)-4-octene, a well-defined model compound for the monomer unit of poly(2), was prepared by hydrosilylation of 4-octyne with triisopropoxysilane catalyzed by chloroplatinic acid. An attempt to obtain the *Z* isomer by photoisomerization of the *E* form was unsuccessful, presumably due to the high stability of the *E* isomer. Alternatively, an *E*,*Z* mixture of 4-(triisopropoxysilyl)-4-octene was prepared by alcoholysis of (*E*,*Z*)-4-(trimethoxysilyl)-4-octene in a large excess of isopropyl alcohol. the ^1H and ^{13}C chemical shifts of the model compounds and poly(2) are summarized in Table VI. As can be seen, the chemical shift of the olefinic proton of the poly(2), prepared with lithium, sodium, and potassium countercation, is very close to that of the *E* model. However, the ^{13}C chemical shifts of olefinic carbons of the poly(2) and those of the *E* model do not agree well with each other. It is obvious that the signals due to methyne and quaternary carbons of the *E* model shift to lower and higher field, respectively, by isomerization from the *E* to the *Z* form.[6] Such low- and high-field shifts of the respective signals are also observed for the poly(2)s produced with lithium and cesium countercations. Considering these results, the pairs of signals at 145.3, 133.7 ppm and 146.8, 132.9 ppm can be assigned to carbons of the *E*-1,4 and *Z*-1,4 monomer unit, respectively. Therefore, the poly(2) prepared with lithium, sodium, and potassium as a countercation exclusively consist of the 1,4-*E* structure, whereas the 1,4-*Z* mode polymerization partly occurs with cesium countercation.

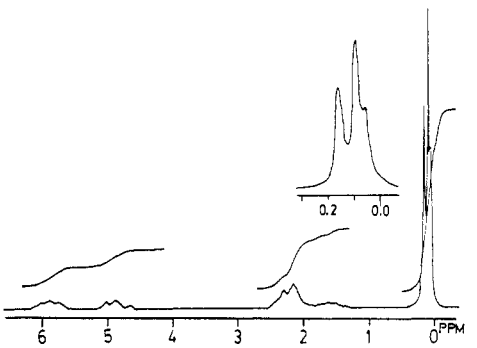


Figure 6. 90-MHz ^1H NMR spectrum of poly(3).

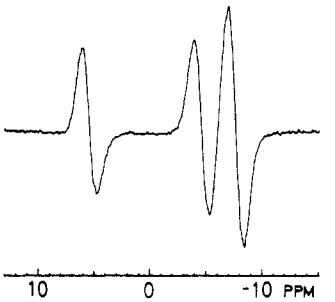


Figure 7. 17.8-MHz proton-coupled ^{29}Si NMR spectrum of poly(3) recorded with INEPT pulse sequence.

Table VI
^1H and ^{13}C Chemical Shifts of Olefinic Proton and Carbons of 4-(Triisopropoxysilyl)-4-octene and Poly(2)[a]

		model compds		poly(2)	
		E form	*Z* form	*E* form	*Z* form
^1H	=CH	6.06	6.10	6.05	6.11[b]
^{13}C	=CSi	134.8	133.9	133.7	132.9[b]
	=CH	144.7	146.6	145.3	146.8[b]

[a] Solvent $CDCl_3$; PPM from internal tetramethylsilane. [b] Observed only with cesium countercation.

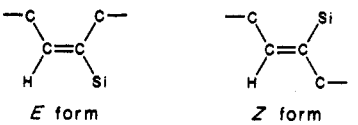


Table VI also lists the ^1H and ^{29}Si NMR spectra of poly(3) are shown in Figure 6 and Figure 7. Three signals at 0.05–0.15 ppm can be assigned to protons of trimethylsilyl groups. The corresponding three resonances of silicon-29 nuclei were observed at 5.4, −4.5, and −7.6 ppm in ^{29}Si NMR spectrum shown in Figure 7. In the olefinic region, proton signals due to terminal and inner olefins are scattered between 4.5 and 6.4 ppm. These results suggest that the microstructure of poly(3) obtained in this study is a complicated mixture of 1,4-, 1,2-, and 3,4-adducts. The similar tendency was also reported in the NMR study of poly(2-(triethylsilyl)-1,3-butadiene) prepared in THF, where eight vinyl carbon resonances were observed.[3]

Significant differences in the microstructures of poly[(trialkoxysilyl)butadienes] and poly[(trialkylsilyl)butadienes] suggest that the substituents on silicon atom have a major effect on the mode of polymerization and the

geometry of the repeating units.

Experimental Section

Materials. 2-(Trimethoxysilyl)-1,3-butadiene (1) was kindly donated by Nissan Chemical Industry. It was distilled under reduced pressure and distilled again from phenylmagnesium chloride under vacuum. Bp 70–71 °C (20 mmHg). ^{1}H NMR δ 3.53 (s, 9 H, CH_3O); 5.10, 5.40 (2 d, 2 H, J = 10,17 Hz, CH_2=CH); 5.73, 5.89 (2 s, 2 H, CH_2=C); 6.44 (dd, 1 H, J = 10, 17 Hz, CH_2=C*H*). ^{13}C NMR δ 50.1 (CH_3O); 117.1 (CH_2=CH); 133.0 (CH_2=C); 139.9 (CH_2=*C*H); 142.5 (=C—Si) ^{29}Si NMR δ −55.1.

2-(Triisopropoxysilyl)-1,3-butadiene (2) was synthesized by the reaction of 1,4-dichloro-2-(trichlorosilyl)-2-butene[7] with isopropyl alcohol followed by dechlorination with Zn powder. To a THF solution of 1,4-dichloro-2-(trichlorosilyl)-2-butene (23.9 g, 92.4 mmol in 100 mL of dry THF), absolute isopropyl alcohol (24.3 g, 400 mmol) and triethylamine (35.5 g, 350 mmol) were added dropwise at 0 °C. After the completion of the addition, the reaction mixture was stirred overnight at 20 °C and finally heated to 60 °C to complete the reaction. The mixture was cooled in an ice bath and diluted with hexane to precipitate the salt. After removal of the salt with "Hyflo-Super-Cel" (Johns-Manville Co.), 17.4 g (55 mmol) of 1,4-dichloro-2-(triisopropoxysilyl)-2-butene was isolated as a colorless liquid by fractional distillation under reduced pressure; bp 91–92 °C (1.7 mmHg), yield 60% based on chlorosilane used.

To a suspension of zinc powder (4.60 g, 70.3 mmol) in THF (20 mL), 1,4-dichloro-2-(triisopropoxysilyl)-2-butene (17.1 g, 52 mmol) in 10 mL of THF was added dropwise at reflux temperature. The reaction mixture was refluxed for 2 h and then cooled in an ice bath and diluted with pentane to precipitate the inorganic salt. After removing salt and solvent by filtration and evaporation, 8.73 g (34 mmol) of 2-(triisopropoxysilyl)-1,3-butadiene (2) was isolated by fractional distillation under reduced pressure. Bp 59–60 °C (3 mmHg). Yield 64%. ^{1}H NMR δ 1.18 (d, 18 H, J = 6 Hz, CH_3); 4.23 (m, 3 H, J = 6 Hz, OCH); 5.06 (2 d, 2 H, J = 10, 17 Hz, CH_2=CH); 5.77 (s, 2 H, CH_2=C); 6.41 (dd, 1 H, J = 10, 17 Hz, CH_2=C*H*). ^{13}C NMR δ 25.5 (CH_3); 65.4 (OCH); 117.1 (CH=CH_2); 132.6 (C=CH_2); 140.7 (*C*H=CH_2); 143.0 (=CSi). ^{29}Si NMR δ −63.0.

2-(Trimethylsilyl)-1,3-butadiene (3) was prepared by the coupling reaction of 1,3-butadien-2-ylmagnesium chloride[8] and trimethylsilyl chloride. To a THF solution of 1,3-butadien-2-ylmagnesium chloride (1 mol/L, 200 mmol) 19.5 g (180 mmol) of trimethylsilyl chloride was added at room temperature and the mixture was refluxed for 3 h. Then the reaction mixture was poured into a large excess of 2 N HCl and extracted three times with pentane. The combined organic layer was washed at least 10 times with water to remove THF and then dried over anhydrous $MgSO_4$. After the solvent was evaporated, 2-(trimethylsilyl)-1,3-butadiene (3) was isolated as a colorless liquid by distillation under reduced pressure. Yield 67% based on the 2-chloro-1,3-butadiene used. Bp 47–51 °C (120 mmHg). ^{1}H NMR δ 0.20 (s, 9 H, $SiCH_3$); 5.05 (d, 1 H, J = 10.6 Hz, CH_2=CH); 5.22 (d, 1 H, J = 17.4 Hz, CH_2=CH); 5.44, 5.74 (2 d, 2 H, J = 3.2 Hz, CH_2=C); 6.45 (dd, 1 H, J = 10.6, 17.4 Hz, CH_2=C*H*). ^{13}C NMR δ −0.90 ($SiCH_3$); 115.4 (CH_2=CH); 128.0 (CH_2=C); 141.8 (=CH); 150.1 (=CSi). ^{29}Si NMR δ −5.7.

(*E*)-4-(Trimethoxysilyl)-4-octene and (*E*)-(triisopropoxysilyl)-4-octene were prepared by hydrosilylation of 4-octyne with the corresponding trialkoxysilanes catalyzed by chloroplatinic acid.[9] An *E,Z* mixture of trimethoxy adduct was obtained by the photoisomerization of the *E* isomer. However, (*E*)-(triisopropoxysilyl)-4-octene was not isomerized to the *Z* form by UV irradiation. Therefore, the *E,Z* mixture was prepared by alcoholysis of the corresponding trimethoxy adduct in large excess of isopropyl alcohol containing a small amount of *p*-toluenesulfonic acid.

The anionic polymerization was carried out under high vacuum conditions ($\sim 10^{-6}$ mmHg) according to the previously described procedures.[2] After the completion of polymerization, the reaction mixture was poured into a large excess of water to precipitate polymers. The aqueous mixture was extracted three times with ether and the combined organic layer was dried over anhydrous $MgSO_4$. The polymer obtained was purified by reprecipitation two additional times from THF/methanol and dried in vacuo.

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a JEOL GX-400 instrument. ^{29}Si NMR spectra were recorded of $CDCl_3$ solutions with a JEOL FX-90Q instrument at 17.8 MHz with using the INEPT pulse sequence ($^3J_{SiOCH}$ = 3.5 Hz, $^2J_{SiCH}$ = 6.8 Hz).[10] Tetramethoxysilane (δ −78.25) or hexamethyldisiloxane (δ 6.80) was used as an internal standard. Gel permeation chromatography (GPC) was measured by using a Toyosoda HLC-802 instrument at 40 °C with differential refractive index detection, THF being the elution solvent. The number-average molecular weight was measured by vapor pressure osmometry (VPO) using a CORONA 117 instrument at 40 °C in benzene solution.

Registry No. 1, 93830-52-5; 1 (homopolymer), 104955-47-7; 2, 104955-51-3; 2 (homopolymer), 104955-52-4; (2)(isoprene) (block copolymer), 117861-50-4; 3, 18301-64-9; 3 (homopolymer), 116767-56-7; (α-Mest)$_n^{2-}$2Li$^+$, 57486-16-5; (α-Mest)$_n^{2-}$2Na$^+$, 37244-89-6; (α-Mest)$_n^{2-}$2K$^+$, 52219-57-5; (α-Mest)$_n^{2-}$2Ce$^+$, 117895-96-2; 1,4-dichloro-2-(trichlorosilyl)-2-butene, 1586-88-5; isopropanol, 67-63-0; 1,4-dichloro-2-(triisopropoxysilyl)-2-butene, 117861-51-5; 1,3-butadien-2-yl magnesium chloride, 126-99-8; trimethylsilyl chloride, 75-77-4; (*E*)-4-(triisopropoxysilyl)-4-octene, 117861-52-6; (*Z*)-4-(triisopropoxysilyl)-4-octene, 117861-53-7.

References and Notes

(1) Tekenaka, K.; Hirao, A.; Hattori, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 2034.
(2) (a) Hirao, A.; Nagawa, T.; Hatayama, T.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1985**, *18*, 2101. (b) Hirao, A.; Hatayama, T.; Nagawa, T.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1987**, *20*, 242.
(3) Ding, Y.-X.; Weber, W. P. *Macromolecules* **1988**, *21*, 530.
(4) Forman, L. E. In *Polymer Chemistry of Synthetic Elastomers Part II*; Wiley Interscience: New York, 1969; pp 559–596 and the references therein.
(5) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 12–13.
(6) A similar tendency was confirmed for olefinic carbons of 4-(trimethoxysilyl)-4-octenes; signals due to the methyne carbon at 146.4 ppm and quaternary carbon at 131.6 ppm of the *E* isomer shifted to 148.3 and 127.4 ppm, respectively, by photoisomerization. See ref 1.
(7) Sato, F.; Uchiyama, H.; Samaddar, A. K. *Chem. Ind.* **1984**, 743.
(8) Nunomoto, S.; Yamashita, Y. *J. Org. Chem.* **1979**, *44*, 4788.
(9) Fleming, I. In *Comprehensive Organic Chemistry*; Pergamon: Elmsford, NY, 1979; Vol. 3, p 541.
(10) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877.