(16) Ito, H.; MacDonald, S. A.; Willson, C. G.; Moore, J. W.; Gharapetian, H. M.; Guillet, J. E. *Macromolecules* **1986**, *19*, 1839.

(17) ^{13}C NMR (12% w/v in $CDCl_3$, 50.1 MHz) −2.58, 28.90, 50.16, 248.63 ppm vs. internal Me_4Si; ^{1}H NMR (1% in $CDCl_3$, 200 MHz) 0.2, 1.35, 1.85, 2.7 ppm (v br). GPC determinations were carried out using THF as a solvent at 30.0 °C. All molecular weights are given vs. polystyrene standards.

(18) Thin (~0.5 μm) films of PVTMSK were spin coated from solutions in chloroform or chlorobenzene on quartz or NaCl plates or on polished silicon wafers. They were exposed in air to deep-UV radiation from a high-pressure Xe–Hg lamp by using an Optical Associates Inc. light source. The 260 ± 20 nm band was isolated by using a pair of dichroic mirrors, and the mid-UV/vis part of the spectrum was isolated by exposing the samples through an optical-quality glass slide (λ > 300 nm). The radiation doses were measured by using silicon detectors and radiochromic films (Far West Technology).

(19) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 454. Review: Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

Antoni S. Gozdz*
Bell Communications Research
Red Bank, New Jersey 07701-7020

Hans J. Reich and Michael D. Bowe
S. M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received April 30, 1987

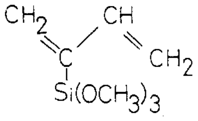
Polymerization of Monomers Containing Functional Silyl Groups. 4. Anionic Polymerization of 2-(Trimethoxysilyl)-1,3-butadiene

Introduction. Anionic living polymerization is one of the most elegant tools for the preparation of polymers having well-defined chain structure.[1] Unfortunately, it is generally considered that the monomers applicable to this method have so far been limited to nonfunctional conjugated hydrocarbon monomers such as styrene and butadiene.

Recently we have found[2,3] that the anionic polymerization of para-substituted styrenes with alkoxysilyl functionality proceeds without chain transfer and termination reactions to afford stable living polymers at −78 °C. As a result, we have obtained well-defined polymers with controlled molecular weight and with narrow molecular weight distributions. In addition, the resulting polymers have an alkoxysilyl group in each monomer unit and therefore may be used for grafting onto inorganic materials as well as for cross-linking between polymer chains by hydrolysis of alkoxysilyl group and subsequent condensation of the silanols formed.

In this paper, we wish to report the anionic polymerization of 2-(trimethoxysilyl)-1,3-butadiene, which has a similar hydrolyzable alkoxysilyl functionality.

Experimental Section. 2-(Trimethoxysilyl)-1,3-butadiene (1) was synthesized by the reaction of 1,4-dichloro-2-(trichlorosilyl)-2-butene with methanol, followed by dechlorination with Zn powder.[4] The resulting colorless liquid was purified by fractional distillation under reduced pressure; bp 70–71 °C at 20 mmHg, yield 67% based on the chlorosilane used. ^{1}H NMR 3.53 (s, 9 H, CH_3O); 5.10, 5.40 (2d, 2 H, J = 10, 17 Hz, $CH_2{=}CH$); 5.73, 5.89 (2s, 2 H, $CH_2{=}C$); 6.44 ppm (dd, 1 H, J = 10, 17 Hz, $CH_2{=}CH$). The anionic polymerization of 1 was carried out under high-vacuum conditions (~10^{-6} mmHg) according to the previously described procedures.[2,3]



1

(*E*)-4-(Trimethoxysilyl)-4-octene and the *E*,*Z* mixture, which imitate the 1,4-structure of monomer unit in the polymer, were synthesized. The *E* isomer was prepared by hydrosilylation of 4-octyne with trimethoxysilane catalyzed by chloroplatimic acid.[5] The *E*,*Z* mixture was obtained by the photoisomerization of the *E* isomer.[6]

^{1}H and ^{13}C NMR spectra were recorded with a JEOL GX-400 instrument in $CDCl_3$. Gel permeation chromatography (GPC) utilized a Toyosoda HLC-802 instrument 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 in benzene solution.

Result and Discussion. Although 2-(trimethoxysilyl)-1,3-butadiene (1) and the related compounds have been recently synthesized by Sato and his co-workers[4] as new silane coupling agents, polymerization of this monomer has not been published up to now. Since we have been carrying out the anionic polymerization of styrenes with functional silyl groups,[2,3] this compound is one of the most attractive diene monomers in the series of our study.

The polymerization of 1 was carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium as initiator. The polymerization appeared to be extremely slow and to be completed after 90–160 h. Sticky polymers were obtained quantitatively by adding the polymerization mixture into a large excess of water. Alkoxysilyl groups on the polymer chain were stable throughout the anionic polymerization and the workup process. This was confirmed by ^{1}H NMR analysis of the polymer.

The results of anionic polymerization of 1 are summarized in Table I. As can be seen, there is fairly good agreement between the predicted molecular weights based on the ratios of monomer to initiator and the observed values measured by VPO. For each polymer, analysis by GPC reveals a unimodal molecular weight distribution of very low polydispersity. These results are consistent with relatively rapid initiation and the absence of chain-transfer and termination reactions during the course of the polymerization of 1.

The microstructure of the resulting polymers is of considerable interest since physical properties of polydienes depend upon the structure of the repeating units. For poly(1) obtained here, we have determined the mode of polymerization (1,4, 1,2, or 3,4) and geometry of the monomer units (*E* or *Z*) by ^{1}H and ^{13}C NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectrum of poly(1), where signals due to methylene protons of the main chain and methoxy protons appeared at 2.2 and 3.5 ppm, respectively. In the olefinic proton region, only two individual peaks centered at 6.14 and 6.21 ppm were observed. The relative integrated intensity of this spectrum showed that the proton ratio was exactly 1 ($=$CH):4 ($-CH_2$):9 ($-OCH_3$). This strongly suggests that poly(1) prepared in this study consists of 1,4-adducts. The appearance of two peaks in the olefinic region in Figure 1 indicates that monomer units are incorporated as a mixture of geometric isomers, *E* and *Z*. These peaks were assigned by comparing their chemical shifts with those of well-defined, low molecular weight model compounds, (*E*)-4-(trimethoxysilyl)-4-octene and the *E*,*Z* mixture. The chemical shifts of olefinic protons in these model compounds are summarized in Table II. As

0024-9297/87/2220-2034$01.50/0

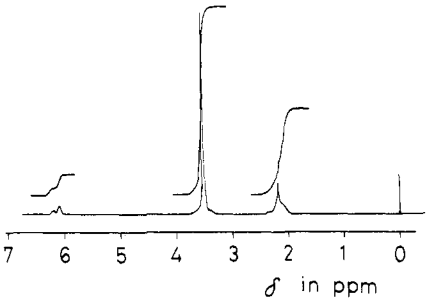


Figure 1. ^1H NMR spectrum of poly(1).

Table I
Anionic Polymerization of 1 in THF at -78 °C

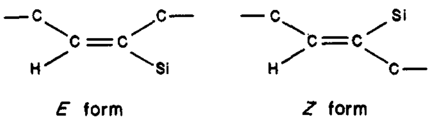
1 mmol	K-Naph, mmol	α-MeSt, mmol	$\bar{M}_n \times 10^{-4}$ calcd^a	$\bar{M}_n \times 10^{-4}$ obsd^b	$\bar{M}_w/\bar{M}_n$
3.95	0.205	0.358	0.71	0.79	1.09
12.10	0.300	0.576	1.4	1.4	1.10
13.00	0.112	0.280	4.1	4.6	1.14

[a] $\bar{M}_n$(calcd): calculated from the monomer to initiator ratio. [b] $\bar{M}_n$(obsd): calculated by vapor pressure osmometry in benzene.

Table II
^1H and ^{13}C Chemical Shifts of Olefinic Proton and Carbons of 4-(Trimethoxysilyl)-4-octene and Poly(1)^a

		model compounds		poly(1)	
		E form	*Z* form	*E* form	*Z* form
^1H	=CH	6.09	6.15	6.14	6.21
^{13}C	=CSi	131.6	127.4	131.1	127.8
	=CH	146.4	148.3	146.4	148.5

[a] Solvent $CDCl_3$; ppm from internal tetramethylsilane.



can be seen, the olefinic proton of the *Z* isomer resonates at lower field than that of the *E* isomer. A similar tendency was also reported for trialkylsilyl-substituted olefins.[7] Accordingly, the olefinic proton signals centered at 6.14 and 6.21 ppm in Figure 1 can be assigned to *E* and *Z* forms of monomer units incorporated in the polymer, respectively. The estimated *E*:*Z* ratio was about 70:30.

Further information about the microstructure of poly(1) was provided by ^{13}C NMR analysis. Figure 2 shows olefinic region of the proton-decoupled ^{13}C NMR spectrum of the resulting polymer, where two pairs of olefinic carbons are observed. Detail assignments of the signals were carried out by comparing the chemical shifts with those of the corresponding model compounds. They are summarized in Table II. Two major peaks at 146.4 and 131.1 ppm in Figure 2 can be assigned to carbons of 1,4-*E* configuration, and the other minor peaks at 148.5 and 127.8 ppm are attributable to those of 1,4-*Z* form. Based on the assumption that nuclear Overhauser enhancement is equally effective to both carbons of isomeric forms, the *E*:*Z* ratio of monomer units in the polymer chain is estimated to be 67:23 from relative intensities of the signals at 146.4 and 148.5 ppm, which agrees with the result of the ^1H NMR study. It should be noted that no other peaks which can be assigned to 1,2- or 3,4-structure were observed within the detection limits of our ^{13}C NMR spectrometer. This is in contrast to the anionic polymerizations of butadiene and isoprene[8,9] where dangling vinyl structures were main components under the conditions employed here. Detail study of polymerization of this monomer and its derivatives will be published in the near future.

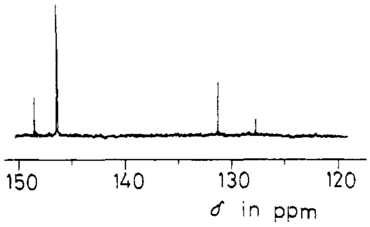


Figure 2. Olefinic region of proton-decoupled ^{13}C NMR spectrum of poly(1).

Registry No. 1, 104955-47-7; $H_3C(CH_2)_2C(Si(OCH_3)_3){=}CH(CH_2)_2CH_3$, 109432-67-9.

References and Notes

(1) Morton, M. *Anionic Polymerization, Principles and Practice*; Academic: New York, 1983.
(2) Hirao, A.; Nagawa, T.; Hatayama, T.; Yamaguchi, K.; Nakahama, N. *Macromolecules* **1985**, *18*, 2101.
(3) Hirao, A.; Hatayama, T.; Nagawa, T.; Yamaguchi, M.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1987**, *20*, 242.
(4) Sato, F.; Uchiyama, H.; Samaddar, A. K. *Chem. Ind.* **1984**, 743.
(5) Fleming, I. In *Comprehensive Organic Chemistry*; Pergamon, 1979, Vol. 3, p 541.
(6) Cunneen, J. I.; Higgins, G. M. C.; Watson, W. F. *J. Polym. Sci.* **1959**, *40*, 1.
(7) Chan, T. H.; Mychajlowskij, W.; Amoroux, R. *Tetrahedron Lett.* 1977, 1605.
(8) Tobolsky, A. V.; Rogers, C. E. *J. Polym. Sci.* **1959**, *40*, 73.
(9) Forman, L. E. In *Polymer Chemistry of Synthetic Elastmers*; Wiley Interscience: New York, 1969; Part II, pp 567–569.

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

Department of Polymer Chemistry
Faculty of Engineering, Tokyo Institute of Technology
Ohokayama, Meguro-ku, Tokyo 152, Japan

Received January 20, 1987

β-Hydrogen Abstraction and Regiospecific Insertion in Syndiotactic Polymerization of Styrene

In this paper are reported some results concerning the mechanism of polymerization of styrene to a highly syndiotactic polymer.[1,2] In particular the insertion of the monomer into the active bonds of the catalytic complexes is investigated, both in the initiation and the chain propagation steps.

In a previous paper[3] it was reported that a sharp methylene resonance at 18.4 ppm is observed in the ^{13}C NMR spectrum of highly syndiotactic polystyrene prepared in the presence of the homogeneous catalytic system tetrabenzyltitanium (TBT)/methylalumoxane (MAO)/triethylaluminum 70% enriched with ^{13}C on the methylene carbon (^{13}TEA). The resonance considered was assigned to the presence of [4-^{13}C]-2-phenylpentyl end groups arising from secondary insertion of styrene on active metal–^{13}C enriched ethyl bonds (chain initiation step) formed either via exchange between the catalytic complexes and ^{13}TEA or via chain transfer with ^{13}TEA:

$$M{-}{}^{13}CH_2CH_3 + C_8H_8 \rightarrow M{-}CH(C_6H_5)CH_2{}^{13}CH_2CH_3$$

where M = metal of the catalytic complex. According to ref 3, in the considered chain initiation step, secondary insertion occurs exclusively since no methylene resonance