

Microstructures of Poly(1-butadienyloxytrimethylsilane)s Prepared by Aldol Condensation-Type Group Transfer Polymerization

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ABSTRACT: Three polymers of 1-butadienyloxytrimethylsilane (BdTMS), 3-methyl-1-butadienyloxytrimethylsilane (MeBdTMS), and 3-phenyl-1-butadienyloxytrimethylsilane (PhBdTMS) were prepared by aldol condensation-type group transfer polymerization. Microstructures of these polymers were determined by ^1H and ^{13}C NMR. Content of *trans*-1,4 unit in poly(BdTMS), poly(MeBdTMS), and poly(PhBdTMS) decreased in that order, reflecting *s*-conformation of monomer. The results suggest that this polymerization proceeds *via* a bicyclic transition state made up of a monomer, propagating chain end, and catalyst. Poly(BdTMS) contained 14% a 3,4 unit, but poly(MeBdTMS) and poly(PhBdTMS) did not. This suggests that formation of the 3,4 unit depends on the structure of propagating chain end.

KEY WORDS Microstructure / Group Transfer Polymerization / Aldol Condensation / 1-Butadienyloxytrimethylsilane / 3-Methyl-1-butadienyloxytrimethylsilane / 3-Phenyl-1-butadienyloxytrimethylsilane / Transition State / Conformation / α,β -Unsaturated Aldehyde /

In 1986, Webster *et al.* reported that aldol condensation reactions of silyl vinyl ethers could be applied to a new living polymerization, which is called aldol condensation-type group transfer polymerization (aldol-GTP).¹ Since aldol-GTP was found to be useful to supply hydrophilic polymer or oligomer with controlled molecular weight and reactive formyl group at its terminal, some investigation has been carried out in the field of synthesis for specially-designed block polymers² and macromonomers.³

In order to develop applicable monomers to aldol-GTP, we examined 1-butadienyloxytrimethylsilane (BdTMS)⁴ and its derivatives.⁵ In a series of studies on aldol-GTP of BdTMS,^{6,7} it was revealed that BdTMS could be polymerized with *p*-anisaldehyde as an initiator in the presence of ZnBr_2 to give its polymer with a relatively narrow molecular

weight distribution ($M_w/M_n = 1.3\text{—}1.5$). Kinetic investigation of aldol-GTP^{7,8} suggested that the rate determining step is the cationization of the formyl group in the propagating chain end by coordination with ZnBr_2 . The cationic site is subject to nucleophilic addition of the monomer. Furthermore, it was found that selective aldol-GTP for *E*-isomers took place.⁵

In this paper, microstructures of polymers prepared by aldol-GTP of BdTMS and its derivatives are investigated in details. On the basis of a comparison of their microstructures, the most reasonable mechanism for aldol-GTP of BdTMS is discussed.

EXPERIMENTAL

Materials

1-Butadienyloxytrimethylsilane (BdTMS), 3-methyl-1-butadienyloxytrimethylsilane

Table I. Aldol-GTP of BdTMS, MeBdTMS and PhBdTMS with *p*-anisaldehyde and ZnBr₂ in toluene

Monomer	[M] ₀ ^a	[I] ₀ ^a × 10 ²	[C] ₀ ^a × 10 ²	Temp	Time	Yield	<i>M_n</i> ^b × 10 ⁻³	<i>M_w</i> ^b
	mol l ⁻¹			°C	h	%		
BdTMS	1.04	0.3	1.0 ^c	-78	96	72	42.3	1.30
MeBdTMS	1.48	1.5	1.7 ^c	0	3	81	10.0	1.25
PhBdTMS	1.05	1.0	3.0 ^d	0	1	50	10.0	1.20

^a M, monomer; I, *p*-anisaldehyde; C, ZnBr₂.

^b Determined by GPC, calibrated with standard polystyrene samples.

^c ZnBr₂ was used as 1.4 mol l⁻¹ solution in diethyl ether.

^d Solid ZnBr₂ was used.

(MeBdTMS), and 3-phenyl-1-butadienyloxy-trimethylsilane (PhBdTMS) were prepared according to procedures described previously.⁵ Their polymers were prepared by aldol-GTP which were carried out by the use of *p*-anisaldehyde and ZnBr₂ as an initiator and catalyst, respectively.^{5,7,8} The polymerization conditions and results are summarized in Table I.

Measurements

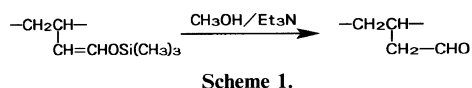
¹H and ¹³C NMR spectra were recorded with a Varian XL-200 spectrometer at room temperature. Sample concentration in deuteriochloroform was 5–10 wt% for ¹H NMR measurement and 10–30 wt% for ¹³C NMR measurement. Chloroform for ¹H and CDCl₃ for ¹³C were used as internal standards.

RESULTS

Microstructure of Poly(BdTMS) Prepared by Aldol-GTP

¹H NMR spectrum of poly(BdTMS) prepared by aldol-GTP is shown in Figure 1a with assignments of signals. The repeating units in the poly(BdTMS) consisted of 1,4 and 3,4 structures. In the resonance region of olefinic protons, signals at 6.1 and 4.7 ppm were assigned to the 3,4 structure and signal at 5.5 ppm to the 1,4 structure. These assignments were supported by comparing with the assignments of poly(1-ethoxybutadiene) prepared by

cationic polymerization.⁹ The assignments of the signals due to 3,4 structure were confirmed by triethylamine-catalyzed methanolysis¹⁰ of poly(BdTMS). When poly(BdTMS) was treated with methanol and triethylamine, the trimethylsilyl enolate moiety in the 3,4 unit rapidly underwent methanolysis as shown in Scheme 1. However, the methanolysis of the trimethylsilyl ether moiety in the 1,4 unit was very slow.



In the ¹H NMR spectrum of the polymer after methanolysis, the signals at 6.1, 4.7, and 0.2 ppm (b', c', and a') in Figure 1a disappeared and a signal due to formyl protons appearing at 9.7 ppm. In the IR spectrum of the polymer, an absorption due to C=C (1660 cm⁻¹) in 3,4 unit disappeared and a new absorption due to formyl C=O (1720 cm⁻¹) appeared. Consequently, the 3,4 unit as well as 1,4 unit existed in the poly(BdTMS). In Figure 1a, no signals due to vinyl group in 1,2 unit were observed. The absence of the 1,2 unit was also confirmed by hydrogenation of poly(BdTMS). If there should be a 1,2 unit in the resulting polymer, any vinyl group would be converted to an ethyl group by hydrogenation with Wilkinson's catalyst.¹¹ However, no signals due to the ethyl group derived from vinyl side chain in 1,2 unit were observed in the ¹³C NMR spectrum of

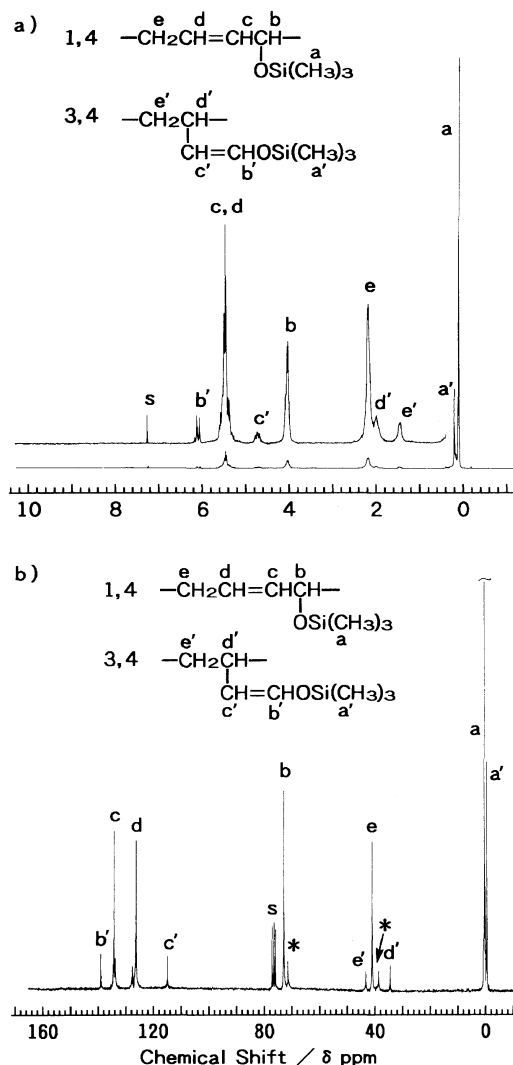
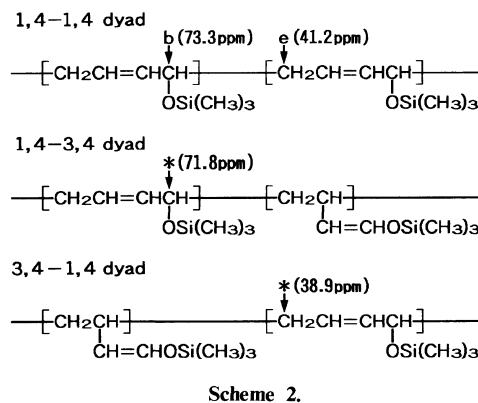


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of poly(BdTMS) in CDCl_3 : s, solvent; *, see the text.

hydrogenated poly(BdTMS). To produce the 1,2 unit by aldol-GTP, BdTMS has to behave as a vinyl substituted vinyloxytrimethylsilane. It has been found that the polymerizability of vinyloxytrimethylsilane was lower than that of BdTMS by aldol group transfer copolymerization of BdTMS and vinyloxytrimethylsilane.¹² Therefore, it can be assumed that the 1,2-addition of BdTMS hardly occurs.

On the basis of the intensities of olefinic ^1H



NMR signals in 1,4 and 3,4 units, poly(BdTMS) consists of about 86% 1,4 and 14% 3,4 units.

The ^{13}C NMR spectrum of the poly(BdTMS) is shown in Figure 1b with assignments of signals. The assignments were made by reference to assignments of polybutadienes¹³ and on the basis of the DEPT spectrum of the poly(BdTMS). The main signals of a–e and a'–e' were assigned to 1,4 and 3,4 units, respectively. Two signals at 38.9 and 71.8 ppm (marked by * in Figure 1b) were assigned to the methylene and methine carbons in the 1,4 unit adjacent to 3,4 unit, respectively, as shown in Scheme 2. The assignments of the two signals can be explained by dyad distribution of 1,4 and 3,4 units. 3,4 Unit content was 14% by ^1H NMR. When the distribution of 3,4 units in the poly(BdTMS) obeys Bernoullian statistics, dyad proportions of 1,4 and 3,4 units are $P_{11}=0.74$, $P_{12}=P_{21}=0.12$, and $P_{22}=0.02$, where the subscripts 1 and 2 express 1,4 and 3,4 units, respectively. Signal intensity ratios were 5.8 ($=I_{73.3}/I_{71.8}$) for siloxymethine carbons (b and * in Figure 1b) and 6.2 ($=I_{41.2}/I_{38.9}$) for methylene carbons (e and * in Figure 1b). These values are in agreement with 6.1 calculated by P_{11}/P_{12} or P_{11}/P_{21} .

The IR spectrum of poly(BdTMS) showed absorption at 960 cm^{-1} characteristic of *trans*-1,4 unit but no absorption at 720 cm^{-1}

characteristic of *cis*-1,4 unit. ^{13}C NMR spectrum of poly(BdTMS) showed no signals due to geometric differences, particularly methylene carbon signal. Therefore, the geometry of 1,4 unit in the poly(BdTMS) is all *trans*.

Microstructure of Poly(MeBdTMS) Prepared by Aldol-GTP

^1H NMR spectrum of poly(MeBdTMS) prepared by aldol-GTP is shown in Figure 2a with assignments of signals. The signals due to only 1,4 structure were observed in the ^1H NMR spectrum. Small signals at 3.77 and 6.8–7.2 ppm were assigned to CH_3O - and $-\text{C}_6\text{H}_4-$ of initiator (*p*-anisaldehyde) residue.

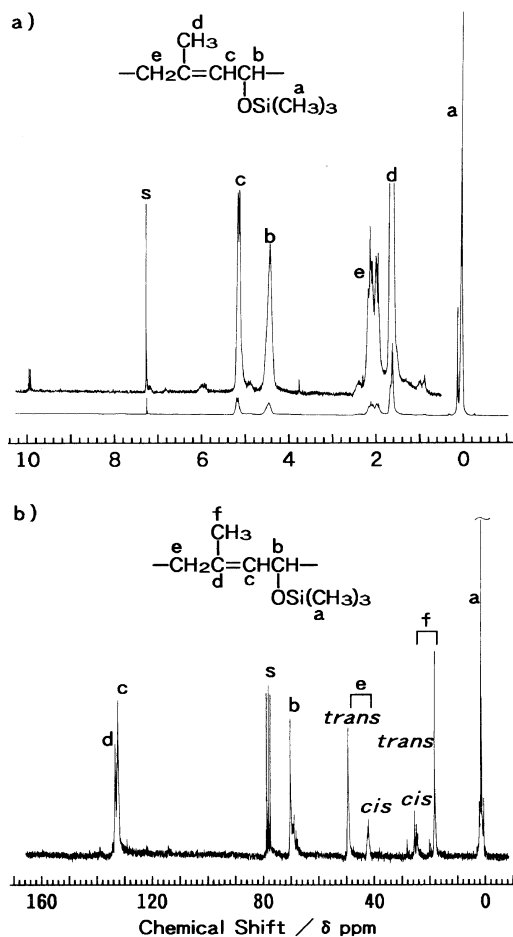


Figure 2. (a) ^1H NMR and (b) ^{13}C NMR spectra of poly(MeBdTMS) in CDCl_3 : s, solvent.

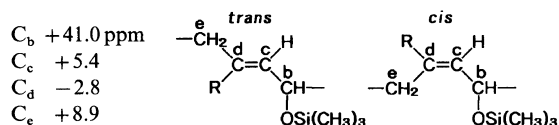
Other small signals at 2.4, 4.9, 5.9, and 9.95 ppm were assigned to the protons in the propagating chain end: $-\text{CHOSi}(\text{CH}_3)_3-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CHO}$. On the basis of their intensities, the initiator residue and the propagating chain end were in the ratio 1 : 1. This correspondence suggests that one molecule of initiator yields one polymer always having an α,β -unsaturated aldehyde moiety at its propagating end.

^{13}C NMR spectrum of the poly(MeBdTMS) is shown in Figure 2b with assignments of signals. The assignments were made by reference to the assignments of polyisoprenes¹³ and on the basis of the DEPT spectrum of the poly(MeBdTMS). The chemical shifts of the methyl and methylene carbons in the poly(MeBdTMS) are lower field than those of the corresponding carbons in the polyisoprene owing to electron-withdrawing character of the trimethylsiloxy group. Both the methyl and methylene carbons in the poly(MeBdTMS) gave two signals due to *cis*-1,4 and *trans*-1,4 structures. The assignments were based on the following facts. The chemical shift difference of 6.9 ppm between two methyl carbon signals of the poly(MeBdTMS) is close to the difference of 7.5 ppm between methyl carbon signal of *trans*-1,4-polyisoprene and that of *cis*-1,4-polyisoprene. Similarly the chemical shift difference of 7.3 ppm between two methylene carbon signals of the poly(MeBdTMS) is close to the difference of 7.4 ppm between methylene carbon signal of *trans*-1,4-polyisoprene and that of *cis*-1,4-polyisoprene. Calculation of ^{13}C chemical shifts of poly(MeBdTMS) was based on the contribution of the trimethylsiloxy group to the ^{13}C chemical shifts. ^{13}C chemical shift differences between polybutadiene and poly(BdTMS) provide a global contribution of the trimethylsiloxy group to the ^{13}C chemical shifts. ^{13}C chemical shift differences between the corresponding carbons of *trans*-1,4-polybutadiene and 1,4 unit of poly(BdTMS) were calculated and are presented in the footnote of Table II. Table II

Table II. ^{13}C chemical shifts of poly(MeBdTMS) and poly(PhBdTMS)

			^{13}C chemical shifts/ppm			
			C_b	C_c	C_d	C_e
Poly(MeBdTMS)	<i>trans</i>	(obsd)	69.5	131.9	132.9	48.7
		(calcd) ^a	67.9	129.8	132.2	48.7
	<i>cis</i>	(obsd)	68.7	131.9	132.9	41.5
		(calcd) ^a	67.8	130.5	132.5	41.2
Poly(PhBdTMS)	<i>trans</i>	(obsd)	68.5	136.0	142.0	48.5
		(calcd) ^a	68.7	138.7	136.8	48.4
	<i>cis</i>	(obsd)	68.5	136.0	142.0	39.0
		(calcd) ^a	68.7	138.7	136.8	38.6

^a Contribution of the trimethylsiloxy group to ^{13}C chemical shifts of diene polymer estimated from *trans*-1,4-polybutadiene and poly(BdTMS).



lists ^{13}C chemical shifts observed for poly-(MeBdTMS) and calculated by application of the contribution of the trimethylsiloxy group to polyisoprene. The calculated chemical shifts were in agreement with the observed ones.

The poly(MeBdTMS) consists of about 69% *trans*-1,4 and 31% *cis*-1,4 units on the basis of the intensities of the two methyl and methylene carbon signals.

Microstructure of Poly(PhBdTMS) Prepared by Aldol-GTP

The ^1H NMR spectrum of poly(PhBdTMS) prepared by aldol-GTP is shown in Figure 3a with assignments of signals. The signals were broad because the main chain can take various conformations and slow segment movement owing to bulky phenyl and trimethylsiloxy substituents. Main signals could be assigned to only the 1,4 structure. Sharp small signals are due to unchanged *Z*-PhBdTMS monomer which did not undergo the aldol-GTP.⁵

The ^{13}C NMR spectrum of the poly-(PhBdTMS) is shown in Figure 3b with assignments of signals. The assignments were made by reference to the assignments of

poly(2-phenylbutadiene)¹⁴ and on the basis of the DEPT spectrum of the poly(PhBdTMS). The methylene carbon in the poly(PhBdTMS) gave two signals due to *cis*-1,4 and *trans*-1,4 structures. The signal at 38–40 ppm was assigned to the methylene carbon in *cis*-1,4 unit, and the other signal at 47–50 ppm was assigned to the methylene carbon in *trans*-1,4 unit, on the basis of the methylene carbon chemical shifts of the *cis*-1,4 and *trans*-1,4-poly(2-phenylbutadiene)s (29.7 and 39.5 ppm, respectively). Table II lists ^{13}C chemical shifts observed for poly(PhBdTMS) and calculated by application of the contribution of the trimethylsiloxy group to poly(2-phenylbutadiene). Both chemical shifts agreed well, except for the olefinic carbons.

The poly(PhBdTMS) consists of about 17% *trans*-1,4 and 83% *cis*-1,4 units on the basis of the intensities of the two methylene carbon signals.

DISCUSSION

Determination of 1,4 Unit Geometry

The microstructure contents of poly-

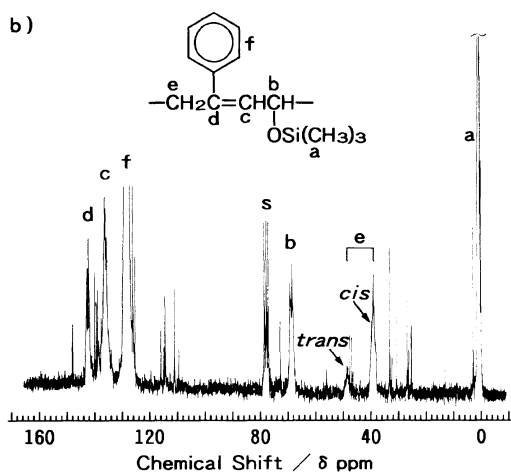
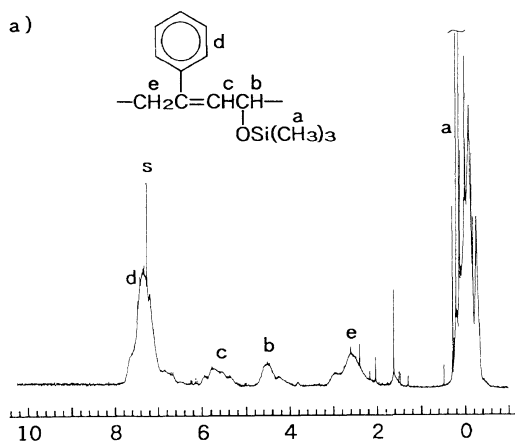
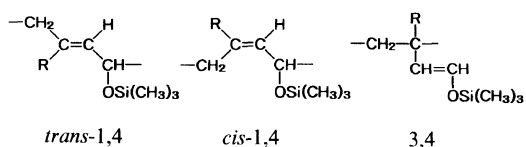


Figure 3. (a) ^1H NMR and (b) ^{13}C NMR spectra of poly(PhBdTMS) in CDCl_3 ; s, solvent.

(BdTMS), poly(MeBdTMS), and poly(PhBdTMS) are summarized in Table III. The content of *trans*-1,4 unit decreased in the order of H-, CH_3 -, and C_6H_5 - substituents of monomers. The results suggest that an olefinic geometry of 1,4 unit reflects a *s*-conformation of butadiene moiety of monomers. It was pointed out that a conformation of the conjugated diene skeleton of incoming monomer must remain unchanged at a transition state of propagation on aldol-GTP. The olefinic geometry of the new propagating end reflects the conformation of an incoming monomer, as shown in Scheme 3. Therefore, the olefinic

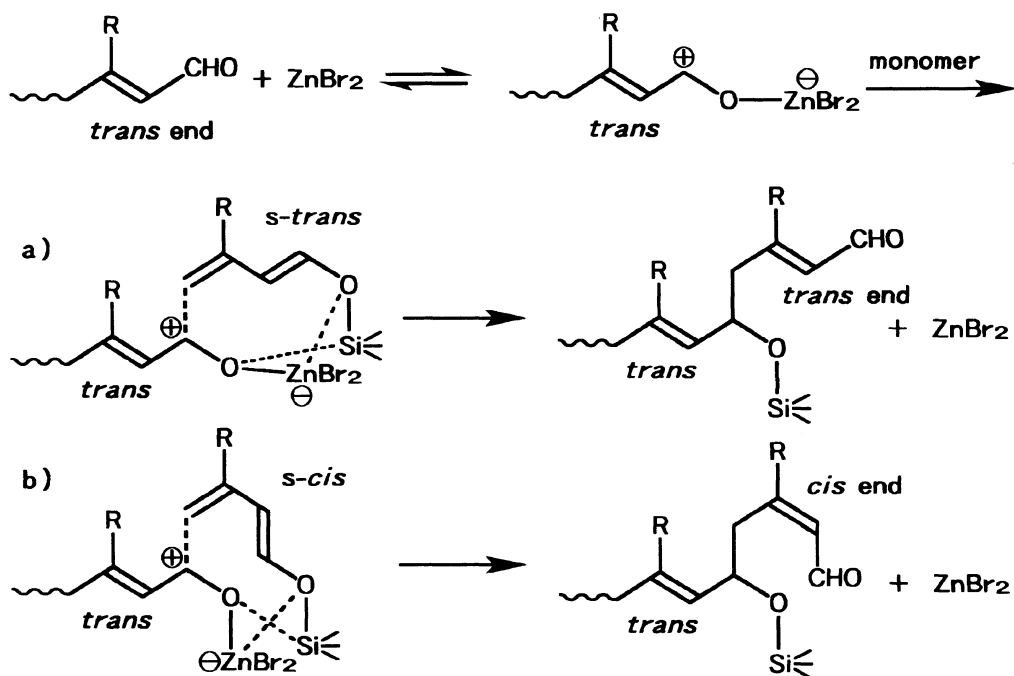
Table III. Microstructures of poly(BdTMS)s prepared by aldol-GTP

Polymer	R	Content of microstructure/%		
		<i>trans</i> -1,4	<i>cis</i> -1,4	3,4
Poly(BdTMS)	H	86	0	14
Poly(MeBdTMS)	CH_3	69	31	0
Poly(PhBdTMS)	C_6H_5	17	83	0

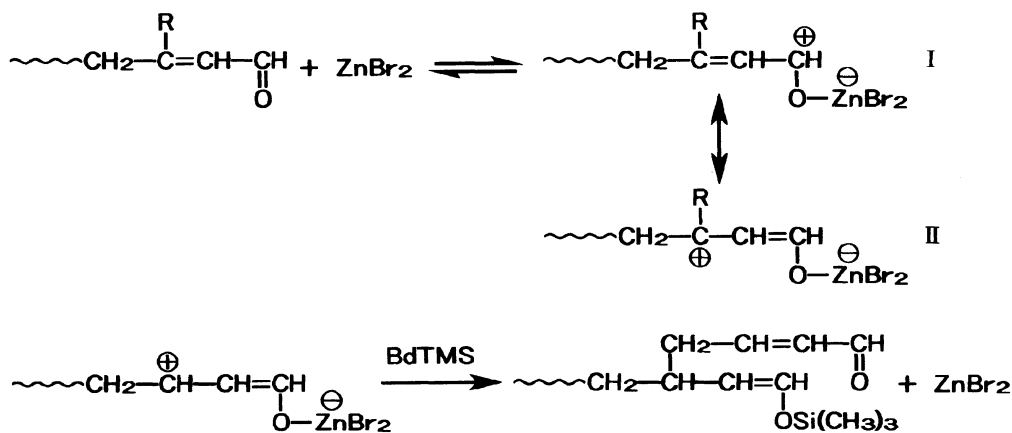


geometry of 1,4 unit depends on whether the incoming monomer takes *s-cis* or *s-trans* conformation. With increasing bulkiness of the 3-position substituent, the 1,3-disubstituted monomer prefers *s-cis* conformation to *s-trans* conformation so as to keep the coplanarity.

UV spectroscopy provides information regarding the *s*-conformation of conjugated diene compounds. Molar absorptivities, ϵ_{max} , of BdTMS, MeBdTMS, and PhBdTMS were 24400 ($\lambda_{\text{max}} = 233$ nm), 21100 ($\lambda_{\text{max}} = 237$ nm), and 11100 ($\lambda_{\text{max}} = 247$ nm), respectively. Large ϵ_{max} of BdTMS indicates that *s-trans* conformation is predominant, while small ϵ_{max} of PhBdTMS indicates that *s-cis* conformation is predominant.¹⁵ The 1,4 unit geometry in poly(BdTMS) was all *trans* because the *s-trans* conformation is favorable to BdTMS. Content of *cis*-1,4 unit in poly(PhBdTMS) was higher than that of *trans*-1,4 unit because the *s-cis* conformation is favorable to PhBdTMS in order to avoid steric crowding between phenyl and trimethylsiloxy group. The methyl substituent of MeBdTMS is not as bulky as phenyl substituent, and thus the *cis/trans* ratio of 1,4 unit geometry in poly(MeBdTMS) is intermediate between that in poly(BdTMS) and that in poly(PhBdTMS).



Scheme 3.



Scheme 4.

Formation of the 3,4 Unit

The 3,4 unit existed only in poly(BdTMS). The structure of propagating chain end of three polymers prepared by aldol-GTP is α,β -unsaturated aldehyde. Carbocation generated by coordination of the end formyl group with ZnBr_2 is in a resonance hybrid of I and II in Scheme 4. Carbocations II as well as I can

undergo nucleophilic addition of monomer. However, carbocation II of the poly(MeBdTMS) end or poly(PhBdTMS) end is presumably less reactive than that of poly(BdTMS) end owing to stabilization by a methyl or phenyl substituent, and furthermore is difficult to undergo nucleophilic monomer addition owing to steric hindrance of the substituent. On

aldol-GTP of BdTMS, monomer reacts with not only carbocation I but also II to yield the 3,4 unit, as shown in Scheme 4. The reaction proceeds perhaps *via* the mechanism shown in Scheme 3, though the coplanarity of conjugated system is distorted slightly. Extension of the conjugated system by phenyl or methyl substituent may prevent such distortion.

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