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Anionic Ring-Opening Polymerization of Sila- and Germacyclopent-3-enes

Xuehai Zhang, Qingshan Zhou, and William P. Weber*

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Raymond F. Horvath and T. H. Chan*

Department of Chemistry, McGill University, Montreal, Quebec H3A 2K6, Canada

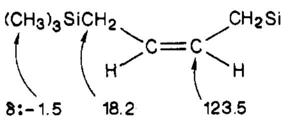
Georges Manuel*

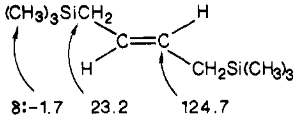
Laboratoire des Organométalliques, UA 477, Université Paul-Sabatier, 31062 Toulouse Cedex, France. *Received August 3, 1987*

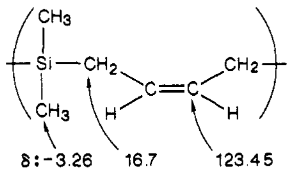
ABSTRACT: 1,1-Dimethyl-1-silacyclopent-3-ene, 1-methyl-1-phenyl-1-silacyclopent-3-ene, 1,1-diphenyl-1-silacyclopent-3-ene, 1,1,3-trimethyl-1-silacyclopent-3-ene, and 1,1-dimethyl-1-germacyclopent-3-ene undergo ring-opening polymerization catalyzed by alkyllithium reagents in the presence of hexamethylphosphoramide or *N,N,N',N'*-tetramethylethylenediamine to yield respectively poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene), poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene), poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene), poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene), and poly(1,1-dimethyl-1-germa-*cis*-pent-3-ene). These polymers have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography. Their thermal stability has been measured by thermogravimetric analysis. The mechanism of this novel ring-opening polymerization is discussed.

Both 1,1-dimethyl-1-silacyclopent-3-ene (I)[1,2] and 1,1-dimethyl-1-germacyclopent-3-ene (II)[3] have been reported to undergo ring-opening metathesis polymerizations to yield low molecular weight materials. Anionic ring opening polymerization of I has been recently reported.[28] We would like to report a general stereospecific anionic polymerization of sila- and germacyclopent-3-enes which in the case of I yields high molecular weight material. Thus treatment of I with a catalytic amount of *n*-butyllithium and either hexamethylphosphoramide (HMPA) or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as cocatalyst in THF gave poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) in 92% yield. The polymer obtained with *n*-butyllithium/TMEDA as initiator has an $\bar{M}_w$ of 158 000 and $\bar{M}_n$ of 69 000. With *n*-butyllithium/HMPA as initiator the polymer has an $\bar{M}_w$ of 120 700 and $\bar{M}_n$ of 30 400. II, 1-methyl-1-phenyl-1-silacyclopent-3-ene (III), and 1,1-diphenyl-1-silacyclopent-3-ene (IV) as well as 1,1,3-trimethyl-1-silacyclopent-3-ene (V) undergo polymerization under similar conditions. The molecular weights of these polymers are lower ($\bar{M}_w$ 10 000–30 000).

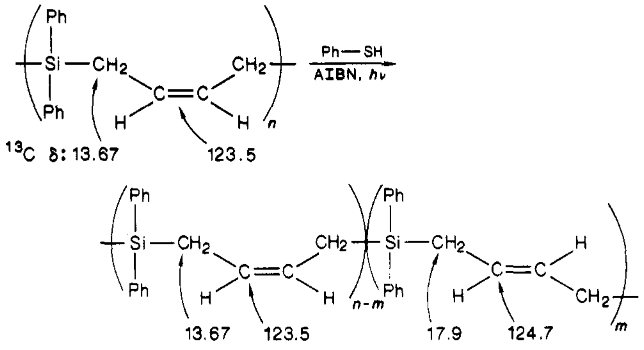
The stereochemistry about the carbon–carbon double bonds of the poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) was assigned by comparison of ^{13}C NMR chemical shifts with those of model compounds.[4] In particular, the significant difference in the ^{13}C chemical shift of allylic carbons adjacent to a cis carbon–carbon double bond compared to that for allylic carbons adjacent to a trans double bond should be noted.







In addition, poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) mp 130–136 °C, was isomerized to a mixture of poly(1,1-diphenyl-1-sila-*cis*(and *trans*)-pent-3-ene), mp 62–70 °C, by reversible addition of photochemically generated phenylthio radicals[5,6] to the stereoregular carbon–carbon double bonds of the starting polymer. This procedure has been utilized to isomerize *cis*-1,4-polybutadiene to a mixture of *cis*- and *trans*-1,4-polybutadiene.[6] NMR spectral data given below support these stereochemical assignments. In particular, it should be noted that the ^{13}C chemical shift for allylic carbons adjacent to a cis carbon carbon double bond come at higher field than those adjacent to a trans carbon–carbon double bond.



This polymerization is unexpected since allyltrimethylsilane undergoes metalation under similar conditions to yield a trimethylsilyl-substituted allyl anion.[7-9] Ring-opening polymerization may result from relief of ring strain. The fact that silacyclobutanes undergo nucleophilic ring opening[10,11] as well as polymerizations catalyzed by various nucleophiles[12-16] is consistent with this hypothesis. However, our attempts to polymerize 1,1-dimethyl-1-silacyclopentane[17] under similar conditions gave only recovered starting material. Alternatively, the geometrical constraints imposed by the silacyclopentene ring may prevent the stabilization of an allylic anion by overlap with empty 3d orbitals of the adjacent silyl center. Further we have found that IV does not undergo ring-opening polymerization catalyzed by *n*-butyllithium with HMPA. However, *n*-butyllithium with TMEDA or methyllithium with either HMPA or TMEDA are effective. This may result from a requirement that the nucleophile attack the silyl

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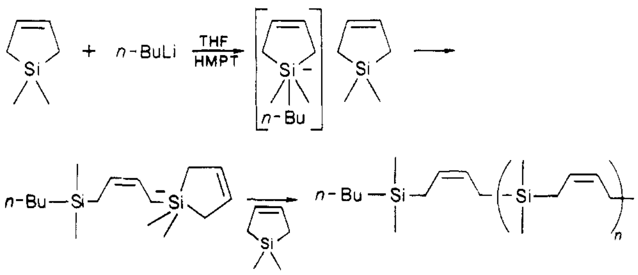
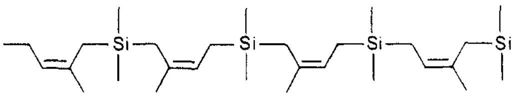
Scheme I



center to yield a reactive pentacoordinate siliconate intermediate. While phenyl groups would be expected to stabilize such a negatively charged silyl center by inductive electron withdrawal, their increased steric bulk might inhibit addition of larger nucleophiles. The fact that the stereochemistry of the double bonds is retained in the polymer strongly suggests that the polymerization does not proceed through a free allyl anion which would be expected to undergo some bond rotation to yield a polymer possessing both cis and trans double bonds along its backbone. These facts lead us to suggest a mechanism in which the polymerization proceeds by reaction of a negatively charged pentacoordinate siliconate anion with a molecule of I to yield a new pentacoordinate siliconate anion as outlined in Scheme I. This would be analogous to the living group-transfer polymerization of methyl methacrylate catalyzed by alkyl trimethylsilyl ketene acetals and fluoride anion.[18-20]

The molecular weights of these polymers are quite high in relation to the ratio of the monomer to alkyllithium initiator utilized, which is generally about 10:1. This suggests that the attack by alkyllithium reagents on the silyl center of the monomer may be slow or reversible while the propagation is rapid. The fact that $\bar{M}_w/\bar{M}_n$ is significantly larger than unity suggests that we may not be dealing with a living polymerization. These questions are under active investigation.

The microstructure of polymer formed by anionic polymerization of V could be analyzed by ^{1}H and ^{13}C NMR spectroscopy. From both ^{1}H and ^{13}C NMR the methyl groups bonded to silicon find themselves in three distinct environments. The ^{13}C NMR of the allylic and vinylic carbons are more complicated. This may result from the fact that the ring-opening polymerization can occur to produce head-to-head, head-to-tail, and tail-to-tail *cis*-1,4-isoprene units joined to dimethylsilyl groups. The regiochemistry of adjacent units appears to affect both allyl and vinyl carbon chemical shifts.



The thermal stability of these polymers was determined by thermogravimetric analysis (TGA) in a nitrogen atmosphere. This family of unsaturated polymers shows three types of behavior in different temperature regions: thermal stability prevails in the first region; slow constant decomposition occurs in the second; fast weight loss is experienced in the third. These polymers leave virtually no residue. For example, poly (1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) is stable to 150 °C. The polymer then loses weight at a rate of 3–5% for every 50 deg increase in temperature between 150 and 350 °C. Rapid weight loss occurs between 350 and 425 °C. By 500 °C 97% weight loss has occurred; see Figure 1. Specific details for other polymers can be found in the Experimental Section.

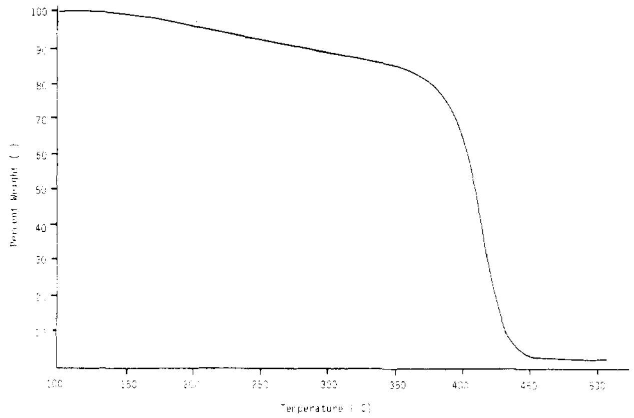


Figure 1. TGA of poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene).

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the Fourier Transform mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were obtained on a Bruker WP-270-SY spectrometer operating in the Fourier transform mode. Ten to fifteen percent solutions in chloroform-*d* or benzene-d_6 were used to obtain ^{29}Si NMR spectra whereas 5% solutions were used for ^{1}H and ^{13}C NMR spectra. Chloroform was utilized as an internal standard for ^{1}H, ^{13}C, and ^{29}Si NMR spectra. All chemical shifts reported are externally referenced to tetramethylsilane. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least one methyl group bonded to them.[21] IR spectra were recorded on a Perkin-Elmer PE 281 spectrometer. These were taken on neat oils between NaCl plates or on chloroform solutions in NaCl cells.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Perkin-Elmer series 10 liquid chromatograph equipped with an LC-25 refractive index detector (maintained at 25 °C), a 3600 data station, and a 660 printer. A 32 cm × 7.7 mm Perkin-Elmer PL 10-μm particle size mixed pore size cross-linked polystyrene gel column was used for the separation. The eluting solvent was HPLC grade THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodispersed polystyrene standards: $\bar{M}_p$ 19400, 87000, 10200, and 2550 whose $\bar{M}_w/\bar{M}_n$ are less than 1.09.

TGA of the polymers was carried out on a Perkin-Elmer TGS-2 at a nitrogen flow rate of 50 cm^3/min. The temperature program for the analysis was 150 °C for 10 min followed by an increase of 5 °C/min to 600 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

1,1-Dimethyl-1-silacyclopent-3-ene (I) was prepared by reaction of dimethyldichlorosilane, 1,3-butadiene, and magnesium in THF following literature procedures.[22,23]

1,1-Dimethyl-1-silacyclopentane was prepared by hydrogenation of I over a Pt on carbon catalyst. It had properties in complete agreement with literature values.[17]

1-Methyl-1-phenyl-1-silacyclopent-3-ene (III) was prepared by reaction of methylphenyldichlorosilane, 1,3-butadiene, and magnesium as above.[22,24,25]

1,1-Dimethyl-1-germacyclopent-3-ene (II) was prepared by reaction of germanium diiodide with 1,3-butadiene which gives 1,1-diiodo-1-germacyclopent-3-ene which was converted to II by reaction with methyl Grignard reagent.[26]

1,1,3-Trimethyl-1-silacyclopent-3-ene (V) was prepared by reaction of dimethyldichlorosilane, isoprene and magnesium as above.[22,23]

1,1-Diphenyl-1-silacyclopent-3-ene (IV) was prepared by reaction of diphenyldichlorosilane, 1,3-butadiene, and magnesium in refluxing THF following literature procedures.[22,27]

Polymerization of I was carried out in flame-dried equipment under an atmosphere of purified nitrogen at −40 °C as follows. In a 25-mL round-bottom flask equipped with a Teflon covered magnetic stirring bar and a rubber septum were placed I (1.2 g, 10.9 mmol), THF (10 mL), and either 5 drops of HMPA or 5 drops of TMEDA. To this mixture was slowly added *n*-butyllithium (0.8 mL, 1.2 M, 0.96 mmol). The mixture quickly became thick. The mixture was stirred for 1 h at −40 °C. The mixture was then warmed to −20 °C and saturated aqueous ammonium chloride was added. The organic layer was separated, washed with brine and water, and dried over molecular sieves (4 Å). After filtration, the solvent was removed by evaporation under vacuum. In this way 1.10 g of polymer, 92% yield, was isolated. The yield of polymer is approximately the same (±2%) and its spectral properties are identical whether HMPA or TMEDA was used as cocatalyst with *n*-butyllithium. With *n*-butyllithium/TMEDA a polymer with $\bar{M}_w/\bar{M}_n$ = 158 000/69 000 was obtained, while with *n*-butyllithium/HMPA a polymer with $\bar{M}_w/\bar{M}_n$ = 120 000/30 400 was isolated. TGA of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene gave the following results. The polymer is thermally stable to 150 °C. Between 150 and 350 °C it loses weight at a rate of 3–5% for every 50 deg increase in temperature. Rapid weight loss occurs between 350 and 425 °C. By 425 °C almost 90% weight loss has occurred.

Attempted polymerization of 1,1-dimethyl-1-silacyclopentane was carried out as above. In a dry 25-mL round-bottom flask equipped with a rubber septum was placed 1.15 g (10 mmol) of 1,1-dimethyl-1-silacyclopentane, 10 mL of THF, and 9 drops of HMPA. The flask was cooled to −40 °C and 1 mL of *n*-butyllithium (1.1 M, 1.1 mmol) was added. The reaction mixture was warmed to −25 °C and stirred for 2 h. After workup only recovered starting material was obtained.

Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) had the following spectral properties: ^{1}H NMR (C_6D_6) δ 0.125 (s, 6 H), 1.58 (d, 4 H, *J* = 7 Hz), 5.485 (t, 2 H, *J* = 7 Hz); ^{1}H NMR ($CDCl_3$) δ −0.022 (s, 6 H), 1.41 (d, 4 H, *J* = 7 Hz), 5.29 (t, 2 H, *J* = 7 Hz); ^{13}C NMR (C_6D_6) δ −3.26 (2 C), 16.72 (2 C), 123.45 (2 C); ^{13}C NMR ($CDCl_3$) δ −3.41 (2 C), 16.47 (2 C), 123.22 (2 C); ^{29}Si NMR δ 2.17; IR ν 1710 (br), 1670 (br), 1630 (C=C), 1345, 1248, 840 cm^{-1}. Anal. Calcd for $C_6H_{12}Si$: C, 64.20; H, 10.78. Found: C, 62.80; H, 10.40.

Poly(1,1-dimethyl-1-germa-*cis*-pent-3-ene) was prepared by polymerization of II as above in 83% yield. *n*-Butyllithium/HMPA was used as cocatalyst. The molecular weight distribution of the polymer was $\bar{M}_w/\bar{M}_n$ = 28 000/5600. Poly(1,1-dimethyl-1-germa-*cis*-pent-3-ene) is only thermally stable to 100 °C. The polymer loses 45% of its initial weight between 150 and 350 °C. Even more rapid weight loss occurs between 350 and 450 °C. By 450 °C almost 95% weight loss has occurred. It had the following spectral properties: ^{1}H NMR (C_6D_6) δ 0.28 (s, 6 H), 1.77 (d, 4 H, *J* = 7 Hz), 5.505 (br t, 2 H, *J* = 7 Hz); ^{13}C NMR δ −3.69 (2 C), 16.62 (2 C), 123.94 (2 C); IR ν 1675 (s), 1630, 820 (s) cm^{-1}. Anal. Calcd for $C_6H_{12}Ge$: C, 45.97; H, 7.66. Found: C, 45.48; H, 7.80.

Poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) was prepared by polymerization of V as above in 84% yield. With *n*-butyllithium/HMPA as cocatalysts a polymer with $\bar{M}_w/\bar{M}_n$ = 23 500/11 400 was obtained while with methyllithium/TMEDA as cocatalysts a polymer with $\bar{M}_w/\bar{M}_n$ = 32 000/15 000 was found. The TGA of poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) is discussed in Results and Discussion. Both of these polymers had identical spectral properties: ^{1}H NMR ($CDCl_3$) δ −0.056 (s), −0.018 (s), 0.030 (s) the intensity ratio of these peaks is approximately 1:3:1 (6 H), 1.30 (d, 2 H, *J* = 8 Hz), 1.455 (d, 2 H, *J* = 1 Hz), 1.655 (d, 3 H, *J* = 1 Hz), 5.01 (t, 1 H, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$) δ −3.34, −2.36, −1.28, 17.30, 18.17, 21.31, 22.18, 26.29, 117.09, 117.25, 130.58, 130.74, 130.96; ^{29}Si NMR δ 1.926; IR ν 1720–1610 br, 1345, 830 cm^{-1}. Anal. Calcd for $C_7H_{14}Si$: C, 66.66; H, 11.17. Found: C, 67.28; H, 11.10.

Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) was prepared by polymerization of III as above in 93% yield by using *n*-butyllithium/HMPA as cocatalysts. The polymer, purified by precipitation from methanol, was a viscous oil. It had the following physical and spectral properties. $\bar{M}_w/\bar{M}_n$ = 23 000/10 000. It is thermally stable to 200 °C. Between 200 and 350 °C the polymer loses weight at a rate of 4–5% for each 50 deg increase in temperature. Rapid weight loss occurs between 350 and 450 °C. By 450 °C almost 85% weight loss has occurred. ^{1}H NMR ($CDCl_3$) δ 0.226 (s, 3 H), 1.61 (d, 4 H, *J* = 6 Hz), 5.30 (t, 2 H, *J* = 6 Hz), 7.5–7.27 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −5.45, 15.30, 123.26, 127.65, 129.01, 133.88, 137.84; ^{29}Si NMR δ −4.33; IR ν 1640, 1435, 1370, 1250, 1120, 830 cm^{-1}. Anal. Calcd for $C_{11}H_{14}Si$: C, 75.86; H, 8.05. Found: C, 73.92; H, 7.47.

Poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) was prepared as above by polymerization of IV. Methyllithium with either HMPA or TMEDA was an effective catalyst. On the other hand, *n*-butyllithium was only effective with TMEDA. The polymer was purified by addition of methanol to a THF solution of the crude reaction product. The polymer which precipitated (89% yield) had the following physical properties; mp 130–136 °C. When *n*-butyllithium/TMEDA was used as cocatalyst the polymer had the following molecular weight distribution: $\bar{M}_w/\bar{M}_n$ = 13 400/7900. When methyllithium/TMEDA was used $\bar{M}_w/\bar{M}_n$ = 12 400/6900 was found. Finally with methyllithium/HMPA $\bar{M}_w/\bar{M}_n$ = 8000/4350. The first two polymers are thermally stable to 250 °C. Between 250 and 300 °C a weight loss of 5% occurs. Rapid weight loss occurs between 300 and 400 °C. Almost 90% of the weight of the starting polymer has been lost by 400 °C. All of these polymers had identical spectral properties. ^{1}H NMR ($CDCl_3$) δ 1.76 (d, 4 H, *J* = 6 Hz), 5.31 (t, 2 H, *J* = 6 Hz), 7.40–7.66 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.67, 123.48, 127.60, 129.22, 134.91, 135.51; ^{29}Si NMR δ −10.54; IR ν 1420, 1360, 1100 cm^{-1}. Anal. Calcd for $C_{16}H_{16}Si$: C, 81.35; H, 7.20. Found: C, 80.34; H, 6.90.

Isomerization of Poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene). One hundred milligrams of the polymer and 15 mg of AIBN were dissolved in 4 mL of dry THF in a quartz tube. The solution was purged with argon gas and sealed with a rubber septum. To this solution was added 10 μL of thiophenol. This solution was irradiated with a 450-W medium-pressure Hanovia Hg lamp for 24 h at 25 °C. The polymer was precipitated from the THF solution by addition of methanol. The polymer was redissolved in THF and reprecipitated by addition of methanol. The polymer had the following properties: mp 62–70 °C; ^{1}H NMR ($CDCl_3$) δ 1.76 (br m, 4 H), 4.70 (br m), 5.3 (br m), 7.3 (br m, 10 H). The ratio of the cis vinyl hydrogen (5.3 ppm) to the trans vinyl hydrogen (4.7 ppm) is 2.2:1. ^{13}C NMR ($CDCl_3$) δ 13.67, 17.90, 123.5, 124.7, 127.6, 129.2, 134.9, 135.5; ^{29}Si NMR δ −10.54, −11.2.

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Registry No. I (homopolymer, 31672-73-8; II (homopolymer), 113569-11-2; III (homopolymer), 113569-12-3; IV (homopolymer), 113569-13-4; V (homopolymer), 34056-65-0.

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Polymerization of Bicyclic Acetals. 15. Propagation Process Accompanied by Oxonium Exchange in the Cationic Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane

Takahito Hirasawa, Masahiko Okada,* and Hiroshi Sumitomo

Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan.
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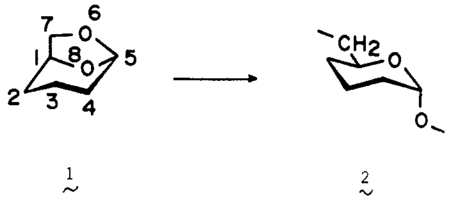
ABSTRACT: A propagation mechanism involving oxonium exchange was proposed for the specific formation of polyacetal exclusively consisting of the *cis*-tetrahydropyran-2,6-diyloxymethylene backbone structure (**4**β) in the cationic ring-opening polymerization of 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**3**). The polymerization of **3** was carried out under various conditions (solvent, dichloromethane and toluene; initiator, phosphorus pentafluoride, antimony pentachloride, and trifluoromethanesulfonic acid; temperature range, −90 to −30 °C). The structures of the polymers were examined by ^{13}C NMR spectroscopy. The polymerization with lower initial monomer concentration at or above −60 °C gave the polymers entirely composed of the cis units, whereas lowering the temperature or increasing the initial monomer concentration favored the formation of the *trans*-tetrahydropyran-2,6-diyloxymethylene unit (**4**α). The polymerization in higher initial monomer concentration at −90 °C gave the polymer completely consisting of the trans units. The formation of the cis unit **4**β in the polymerization of **3** was interpreted in terms of S_N2 type propagation accompanied by oxonium exchange at the penultimate unit of the polymer chain.

Introduction

Cationic ring-opening polymerization of anhydrosugar derivatives having a bicyclic acetal skeleton has been established as one of the most useful methods for the chemical synthesis of polysaccharides with high molecular weights and well-defined structures.[1-3] In relation to the chemical synthesis of stereoregular polysaccharides, some important and interesting information has been obtained on the stereoregulation in the cationic polymerization of bicyclic acetals.[4-9] Thus, the polymerization of the parent compound of 1,6-anhydrosugars, 6,8-dioxabicyclo[3.2.1]octane (**1**), proceeds through an S_N2 type propagation mechanism involving the selective C(5)–O(6) bond cleavage of a growing cyclic trialkyloxonium ion at low temperature to produce a trans-2,6-linked polymer in which the exocyclic acetal oxygen was axially oriented to the tetrahydropyran ring in the repeating unit (**2**, (1→6)-α-pyranosyl residue in the terminology of carbohydrate chemistry).



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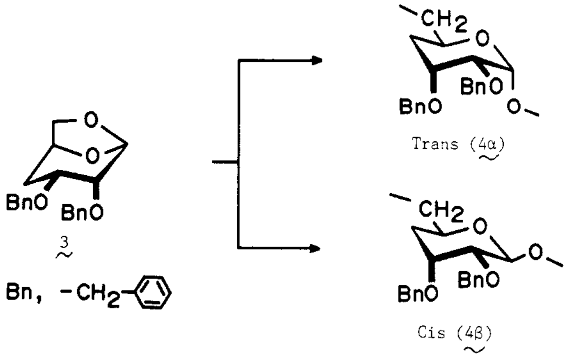
A number of bicyclic acetals and anhydrosugar derivatives having the same skeleton showed similar behaviors in their polymerizations. Therefore, it has been difficult to synthesize structurally regular polymers containing a cis-2,6-linked tetrahydropyran ring in the repeating unit (β-pyranosyl residue) in which the exocyclic acetal oxygen was located equatorially to the tetrahydropyran ring. There have been some reports[4,10,11] referring to the formation of the cis structural units from **1** and related monomers. However, all these papers were based on the recognition that these cis units were produced by side reactions, because in most cases the cis units were formed only as a minor component in the polymerization at higher temperatures.

Among bicyclic acetals having a bicyclo[3.2.1]octane skeleton, 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**3**, 1,6-anhydro-2,3-di-*O*-benzyl-4-deoxy-β-DL-*ribo*-hexopyranose in the nomenclature of carbohydrate chemistry) was recently found to give a polymer entirely composed of cis-2,6-linked tetrahydropyran rings **4**β in the polymerization using phosphorus pentafluoride as an in-



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