Regio- and Stereoselective Cyclopolymerization of 1,2:5,6-Dianhydroallitol and 1,2:5,6-Dianhydrogalactitol Leading to a Novel Carbohydrate Polymer of (2→6)-1,5-Anhydro-DL-galactitol

Masatoshi Kamada, Toshifumi Satoh, and Kazuaki Yokota*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Toyoji Kakuchi*

Division of Bioscience, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan

Received March 29, 1999; Revised Manuscript Received June 16, 1999

ABSTRACT: The cyclopolymerizations of two meso dianhydrohexitols, 1,2:5,6-dianhydro-3,4-di-*O*-methylallitol (**1**) and -galactitol (**3**), were examined to form a polymer with six-membered ring repeating units. Distinct from the cases of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**5**), -L-iditol (**6**), and -D-glucitol (**7**) in which the five-membered ring units were formed with high regio- and stereoselectivity, six-membered ring units were found in polymers **2b**, **4a**, and **4b** obtained by the polymerizations of **1** and **3**. The anionic polymerization of **1** with *t*-BuOK was highly regio- and stereoselective to form polymer **2a** consisting of five-membered ring units, but that of **3** was different in the scission mode of the epoxy groups to form polymer **4a** consisting essentially of six-membered ring units. The cationic polymerization of **1** with BF_3·OEt_2 produced polymer **2b** having a structure consisting of the six-membered ring units as major constituents and five-membered ring units as minor ones. The structure of polymer **4b** from the cationic polymerization of **3** was somewhat complex, comprising unknown units and uncyclized units along with the five- and six-membered ring units. The steric hindrance in the growing ion was an advantage in forming the six-membered ring unit.

Introduction

Monosaccharides, such as D-glucose and D-mannitol, are used as raw materials for monomers in ring-opening polymerization, addition polymerization, and polycondensation.[1−3] Recently, we have developed the cyclopolymerization of 1,2:5,6-dianhydrohexitol as a novel method for producing carbohydrate polymers with regio- and stereoselective structures; e.g., (1→6)-2,5-anhydro-D-glucitol was synthesized from the anionic cyclopolymerizations of 1,2:5,6-dianhydro-D-mannitol and 1,2:5,6-dianhydro-L-iditol and (1→6)-2,5-anhydro-D-mannitol-*co*-2,5-anhydro-L-iditol from 1,2:5,6-dianhydro-D-glucitol.[4−10] These polymers consisted essentially of five-membered cyclic repeating units. The possibility of forming the six-membered unit is of interest in connection with a new development in the synthesis of carbohydrate polymers by cyclopolymerization. Ten hexitols are capable of existence, of which two are meso forms and the other eight are composed of four pairs of optical enantiomers. D-Altritol, *meso*-allitol, and galactitol are three candidates except for D-mannitol, L-iditol, and D-glucitol. Because D-glucitol has a structure combining two halves of D-mannitol and L-iditol, 1,2:5,6-dianhydrohexitol derived from D-glucitol exhibited polymerization behavior intermediate between those of the D-mannitol and L-iditol derivatives. D-Altritol is constructed of two halves of allitol and galactitol derivatives and thus needs to be clarified.

In this paper, we report the cyclopolymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-methylallitol (**1**) and -galactitol (**3**) using anionic and cationic initiators. The structures of the polymers from **1** and **3** are confirmed by comparing their ^{13}C NMR spectra with those of cyclic compounds prepared from the reaction of **1** and **3**. In addition, we discuss the regio- and stereoselectivity of the cyclopolymerization of **1** and **3** along with those of the other 1,2:5,6-dianhydrohexitols.

* To whom all correspondence should be addressed. Tel (Fax) +81-11-706-6602; E-mail yokota@poly.eng.hokudai.ac.jp.

Experimental Section

Measurements. ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-A400 II spectrometer. TLC was carried out on Kieselgel 60 (Merck) unless otherwise noted. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a JASCO GPC-900 system equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were calculated on the basis of polystyrene calibration.

1,2:5,6-Dianhydro-3,4-di-*O*-methylallitol (1). The precursor of monomer **1**, 1,6-di-*O*-benzoyl-2,5-di-*O*-methanesulfonyl-3,4-di-*O*-methylgalactitol, was synthesized from 3,4-di-*O*-methylgalactitol using a procedure similar to that of Kuszmann[11] (Supporting Information). A stirred solution of 1,6-di-*O*-benzoyl-2,5-di-*O*-methanesulfonyl-3,4-di-*O*-methylgalactitol (24.7 g) in chloroform (250 mL) was treated at 0 °C with 4 M methanolic sodium methoxide (20 mL). After 1 h, the mixture was washed with water, dried, and evaporated. The residue gave, on distillation, pure **1** (1.8 g, 24.0%). $R_f = 0.17$ (ethyl acetate); $bp_{0.2} = 67$ °C. ^1H NMR ($CDCl_3$): δ 3.47 (s, OCH_3, 6H), 3.22 (t, C3, C4−CH, 2H), 3.15 (m, C2, C5−CH, 2H), 2.87 (dd, $^2J_{gem} = 5.0$ Hz, $^3J_{cis} = 4.3$ Hz, C1, C6-*cis*-CH_2, 2H), 2.79 (dd, $^2J_{gem} = 5.0$ Hz, $^3J_{trans} = 2.5$ Hz, C1, C6-*trans*-CH_2, 2H). ^{13}C NMR ($CDCl_3$): δ 81.61 (C3, C4), 60.80 (OCH_3), 49.90 (C2, C5), 45.58 (C1, C6). Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.22; H, 8.03.

1,2:5,6-Dianhydro-3,4-di-*O*-methylgalactitol (3). The precursor of monomer **3**, 1,6-di-*O*-*p*-toluenesulfonyl-3,4-di-*O*-me-

10.1021/ma990454k CCC: $18.00 © 1999 American Chemical Society
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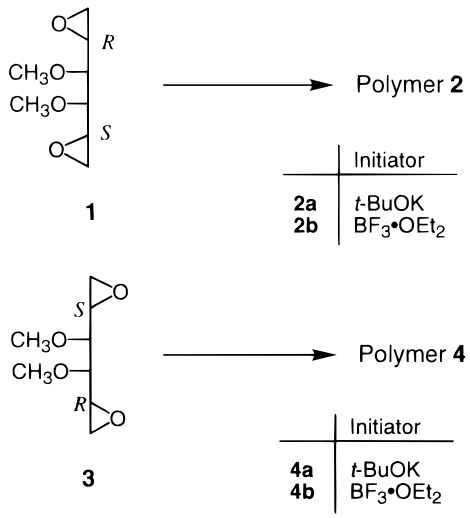
Scheme 1



thylgalactitol, was synthesized from 3,4-di-*O*-methylgalactitol using a procedure similar to that of Kuszmann[11] (Supporting Information). 1,6-Di-*O*-*p*-toluenesulfonyl-3,4-di-*O*-methylgalactitol (7.7 g) was treated with sodium methoxide as described for **1** to give, after column chromatography on silica gel with *n*-hexane/ethyl acetate (2/1) and distillation, pure **3** (2.1 g, 81.3%). $R_f = 0.26$; $bp_{0.4} = 77$ °C. ^{1}H NMR ($CDCl_3$): δ 3.47 (s, OCH_3, 6H), 3.10 (m, C2, C5−CH, 2H), 3.04 (m, C3, C4−CH, 2H), 2.83 (dd, $^2J_{gem} = 5.0$ Hz, $^3J_{cis} = 4.3$ Hz, C1, C6-*cis*-CH_2, 2H), 2.63 (dd, $^2J_{gem} = 5.0$ Hz, $^3J_{trans} = 2.6$ Hz, C1, C6-*trans*-CH_2, 2H). ^{13}C NMR ($CDCl_3$): δ 82.76 (C3, C4), 59.18 (OCH_3), 52.58 (C2, C5), 43.67 (C1, C6). Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.97; H, 8.04.

Cyclopolymerizations. The procedures for polymerizations of **1** and **3** using BF_3•OEt_2 and *t*-BuOK were carried out as described in previous papers.[5,7,10]

Hydration of 1 and 3 with KOH. A solution of **1** (0.5 g) in water (125 mL) was treated at 60 °C with 4 M aqueous potassium hydroxide (3.6 mL). The reaction was continued until the TLC spot of **1** disappeared, and the mixture was then freed of potassium ions using a cation-exchange resin. The solution was evaporated under reduced pressure, and the residue was purified by column chromatography on alumina to give 2,5-anhydro-3,4-di-*O*-methyl-DL-altritol (**9**) (0.50 g, 91%) and 1,5-anhydro-3,4-di-*O*-methyl-DL-allitol (**10**) (0.03 g, 6%). Compounds **9** and **10** were alkylated with dimethyl sulfate to give 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-DL-altritol (**12**) and 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-DL-allitol (**13**), respectively.

3 (0.5 g) was treated with potassium hydroxide by the same procedure as that for **1** to give **9** (0.34 g, 62%) and 1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol (**11**) (0.16 g, 29%). Compound **11** was alkylated with dimethyl sulfate to give 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-DL-galactitol (**14**). The ^{1}H and ^{13}C NMR spectral data and elemental analysis of **12**, **13**, and **14** are given in the Supporting Information.

Results and Discussion

Cyclopolymerization. The anionic polymerizations of monomers **1** and **3** were carried out using *t*-BuOK as an initiator at 60 °C for 48 h. Table 1 summarizes the polymerization results. The polymerization systems were homogeneous for **1** and heterogeneous for **3**. The resulting polymers **2a** and **4a** obtained from **1** and **3**, respectively, were soluble in chloroform and THF. For polymers **2a** and **4a** obtained in toluene, the M_n increased with increasing [M]/[*t*-BuOK] molar ratio. The DP_n was 7.6, 14.4, and 25.1 relative to the values of 5, 10, and 20 calculated from the feed ratio for **2a**. Because this discrepancy is caused by the sparing solubility of *t*-BuOK in toluene, the anionic polymerization of **1** has a living-like nature similar to that of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**5**).[10] On the other hand, the DP_n was 8.8, 12.5, and 14.1 at feed ratios of 5, 10, and 20, respectively, for **4a**. The low value at the ratio of 20 suggests some participation of the chain transfer to the monomer similar to that found in the case of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-L-iditol (**6**) and D-glucitol (**7**).[8,9] The chain transfer, which forms an allyl oxide-initiating moiety through the E2 mechanism (Scheme 2), satisfies the requirement of trans elimination in the configurations of **3**, **6**, and **7**, but not in the configurations of **1** and **5**.[10,12] The anionic polymerization of **1** in THF had the same character as that in toluene. A low yield during the polymerization of **3** in THF, however, suggested the participation of termination, though its nature was obscure.

Table 2 lists the results of the cationic polymerizations of **1** and **3** using BF_3•OEt_2 at 0 °C for 48 h. The polymerizations of **1** and **3** in dichloromethane homogeneously proceeded to give polymers **2b** and **4b**,

Table 1. Anionic Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-di-*O*-methylallitol (1) and 1,2:5,6-Dianhydro-3,4-di-*O*-methylgalactitol (3)[a]

monomer (M)	solvent	[M]/[cat.]	yield, %	M_n (M_w/M_n)[b]	extent of cyclization, f_c[c]
1	toluene	5	89.5	1320 (1.3)	1.0
	toluene	10	95.9	2510 (1.5)	1.0
	toluene	20	94.5	4370 (1.3)	1.0
	THF	20	91.5	4720 (1.5)	1.0
3	toluene	5	80.2	1530 (1.4)	1.0
	toluene	10	78.0	2170 (1.5)	1.0
	toluene	20	91.2	2460 (1.4)	1.0
	THF	20	27.0	1280 (1.4)	1.0

[a] Catalyst, *t*-BuOK; [M] = 1.0 mol L^{-1}; temp, 60 °C; time, 48 h. [b] Measured in THF by GPC using polystyrene as the standard. [c] Determined by ^{1}H NMR spectra.

Scheme 2

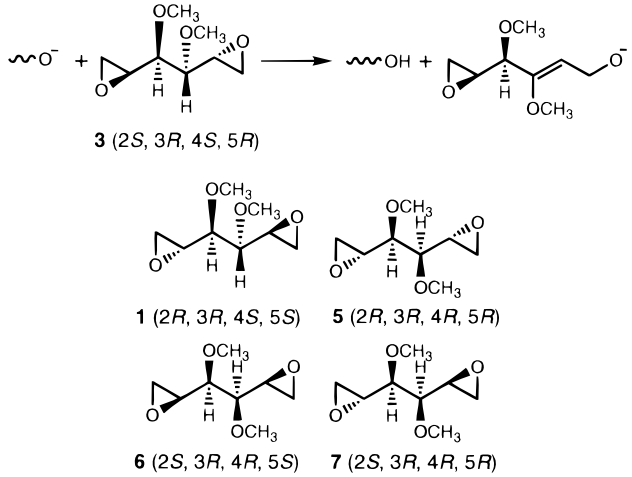


Table 2. Cationic Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-di-*O*-methylallitol (1) and 1,2:5,6-Dianhydro-3,4-di-*O*-methyl-galactitol (3)[a]

monomer (M)	solvent	[M]/[cat.]	yield,[b] %	M_n (M_w/M_n)[c]	extent of cyclization, f_c[d]
1	CH_2Cl_2	100	76.4	2300 (4.8)	1.0
	toluene	100	46.9 (6.0)	1720 (−)	1.0
3	CH_2Cl_2	100	43.4	1050 (1.6)	0.93
	toluene	100	62.1 (12.7)	2650 (−)	0.89

[a] Catalyst, BF_3•OEt_2; [M] = 0.5 mol L^{-1}; temp, 0 °C; time, 48 h. [b] The value in a parentheses was yield of organic solvent-insoluble part. [c] Measured in THF by GPC using polystyrene as the standard. [d] Determined by ^{1}H NMR spectra.

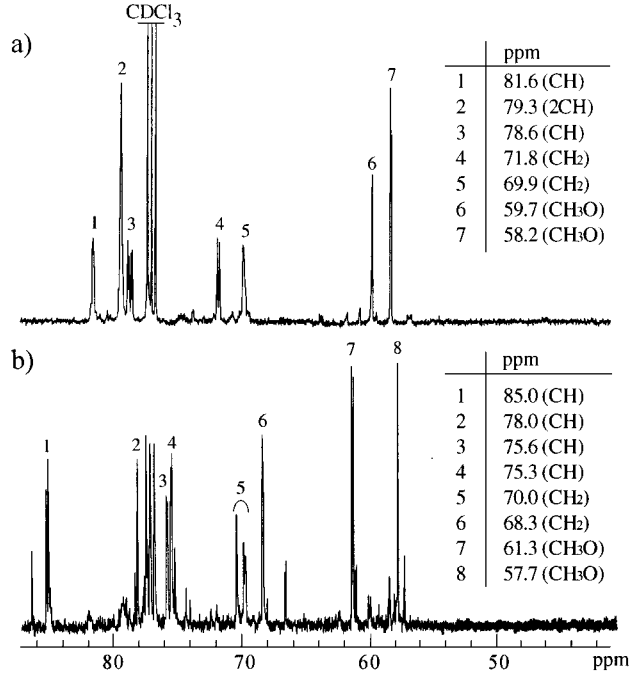


Figure 1. ^{13}C NMR spectra of polymers **2a** (a) and **4a** (b) using *t*-BuOK.

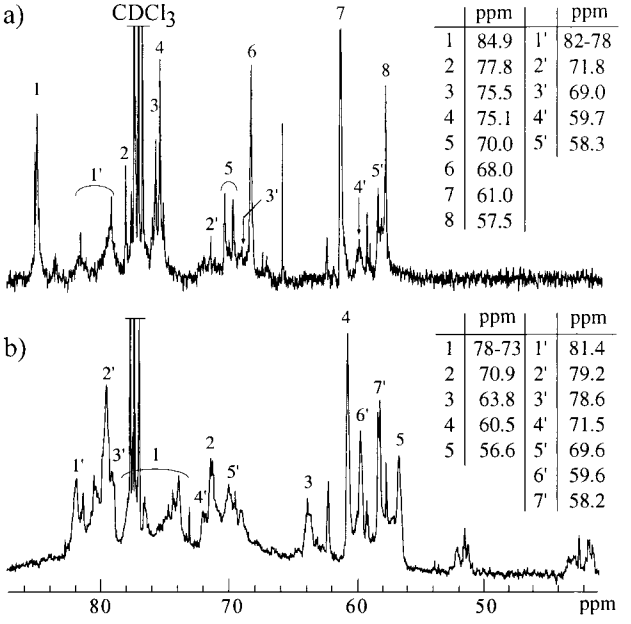


Figure 2. ^{13}C NMR spectra of polymers **2b** (a) and **4b** (b) using $BF_3 \cdot OEt_2$.

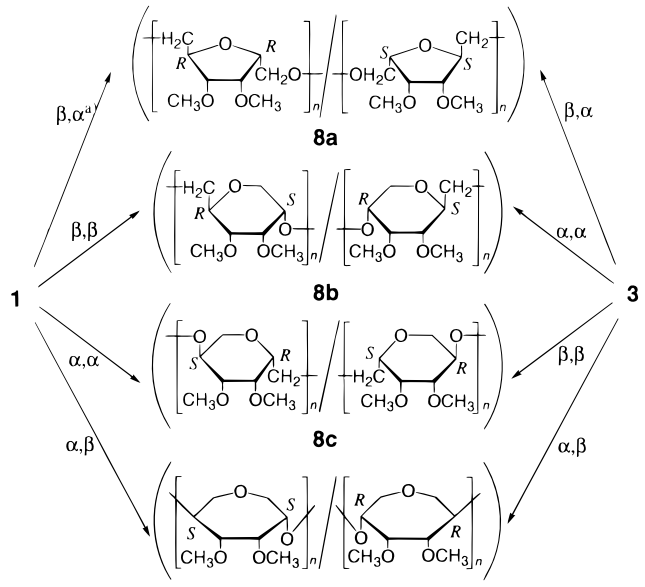
respectively, which were somewhat sticky semisolids and were soluble in common organic solvents. The M_n was 2300 for **2b** and 1050 for **4b**, corresponding to a DP_n of 13.2 and 6.0, respectively. On the other hand, the polymerization system in toluene was heterogeneous, and a considerable amount of insoluble polymer was formed along with the soluble polymer. Cross-links developed during the cationic polymerizations of **1** and **3** in toluene.

Polymer Structure. Figure 1 shows the ^{13}C NMR spectra of polymers **2a** and **4a**. The characteristic absorptions at 43.7 and 52.6 ppm due to the methylene and the methine carbon of the epoxy groups completely disappeared, and the extent of cyclization (f_c) was 1.0 for each of the polymers. The ^{13}C NMR spectrum of polymer **2b** also showed a complete disappearance of the epoxy groups (Figure 2). On the other hand, the ^{13}C NMR spectral analysis indicated that polymer **4b** contained a small amount of residual epoxy groups. A part of the pendant epoxy groups should participate in cross-links to form the insoluble polymer. The f_c's of the soluble polymer were 0.89−0.93, which were estimated from the relative peak areas of the protons in the ^1H NMR spectra.

The cyclopolymerizations of **1** and **3** are composed of the intermolecular reaction and the intramolecular cyclization through α,α-, *β*,*β*-, α,*β*-, and *β*,α-scissions of the two epoxides in a monomer, where α- and *β*-scissions mean the ring opening at the CH−O and the CH_2−O bonds, respectively. Scheme 3 represents the possible cyclic units **8a**−**d**. Meso monomers **1** and **3** form the polymers with a pair of enantiomeric cyclic units.

Model compounds for the constitutional units, therefore, were synthesized by the hydrations of **1** and **3** using KOH to clarify the structure of polymers **2** and **4**. The hydration of **1** yielded 2,5-anhydro-3,4-di-*O*-methyl-DL-altritol (**9**) and 1,5-anhydro-3,4-di-*O*-methyl-DL-allitol (**10**), and that of **3** yielded 1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol (**11**) in addition to **9**. The resulting cyclic compounds **9**, **10**, and **11** were treated with

Scheme 3[a]

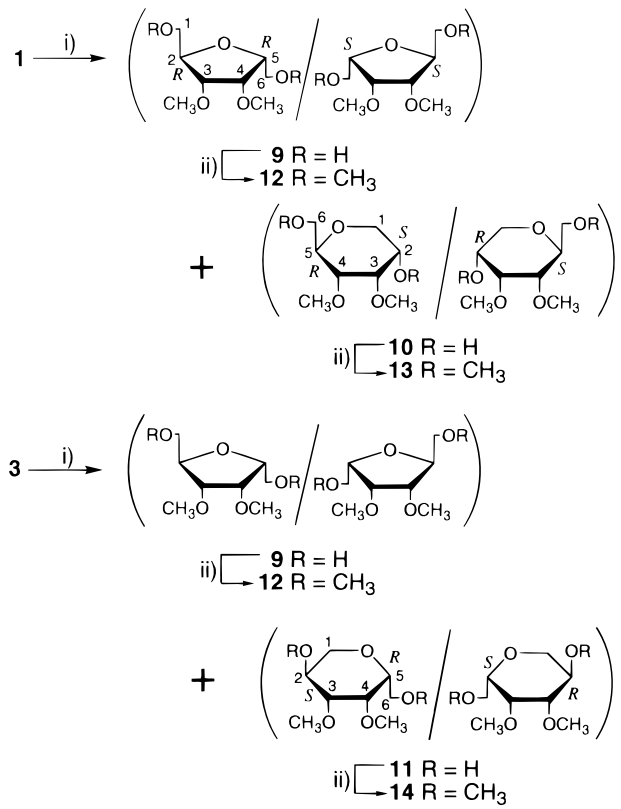


[a] The former and latter symbols (α or *β*) correspond to the intermolecular and intramolecular scissions, respectively.

dimethyl sulfate to convert them into the model compounds, 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-DL-altritol (**12**), 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-DL-allitol (**13**), and 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-DL-galactitol (**14**), as shown in Scheme 4 along with their ^{13}C NMR chemical shifts.

Seven signals for polymer **2a** (Figure 1a) agreed very closely with those assigned to the methine, the methylene, and the 3- and 4-methoxy carbons for **12**, indicating that polymer **2a** consists of five-membered rings, i.e., 2,5-anhydro-3,4-di-*O*-methyl-DL-altritol units (**8a**). The signals observed in Figure 1a were split into two bands, which should be caused by the diversity of sequences of the two enantiomeric units. On the other hand, eight main signals were observed for polymer **4a** (Figure 1b), which were similar to those assigned for **14**. Polymer **4a** consists essentially of 1,5-anhydro-3,4-di-*O*-methyl-

Scheme 4



i) KOH, H_2O, 60°C. ii) $(CH_3)_2SO_4$, NaOH.

^{13}C NMR chemical shifts (ppm)

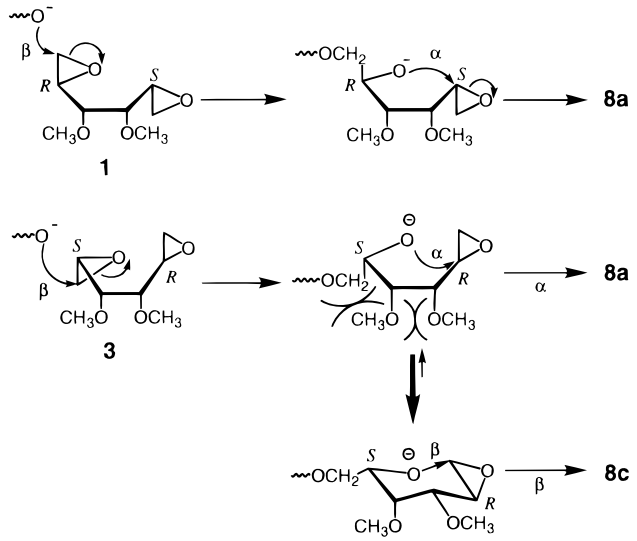
	1	2	3	4	5	6	CH_3O	CH_3O
12	72.91	79.38	81.40	79.60	78.78	71.09	59.80	58.32
13	63.72	77.88	74.42	77.53	73.51	71.74	60.82	57.16
14	67.95	76.14	85.01	75.49	77.59	71.38	61.21	57.79

DL-galactitol units of six-membered rings, corresponding to **8c**. Each of the signals was split into two or more bands by the sequences of the two enantiomeric units also in Figure 1b.

The ^{13}C NMR spectra of polymers **2b** and **4b** were somewhat complex, which suggested that their structures were composed of plural repeating units, as shown in Figure 2. For polymer **2b**, about 14 main signals can be divided into two groups (Figure 2a). The signals of 1−8 agree with those for **14** and those of 1′−5′ for **12**. Thus, polymer **2b** has a structure consisting of **8c** with six-membered rings as the major constitutional unit and **8a** with five-membered rings as the minor unit. Although the signals for polymer **4b** with a small amount of uncyclized units were broad in Figure 2b, two groups, 1−5 and 1′−7′, were observed. The first group of signals is compatible with the carbons for **13**, and the second group is assigned to **12**. Polymer **4b**, therefore, comprises **8a** and **8b** with five- and six-membered rings, respectively. In addition, other unknown units along with an uncyclized unit are present in the polymer.

The formation of six-membered repeating units was found in the cyclopolymerizations of **1** and **3**. The anionic polymerization of **3** produced a polymer consisting essentially of (2→6)-1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol, and the cationic polymerization of **1** led to

Scheme 5



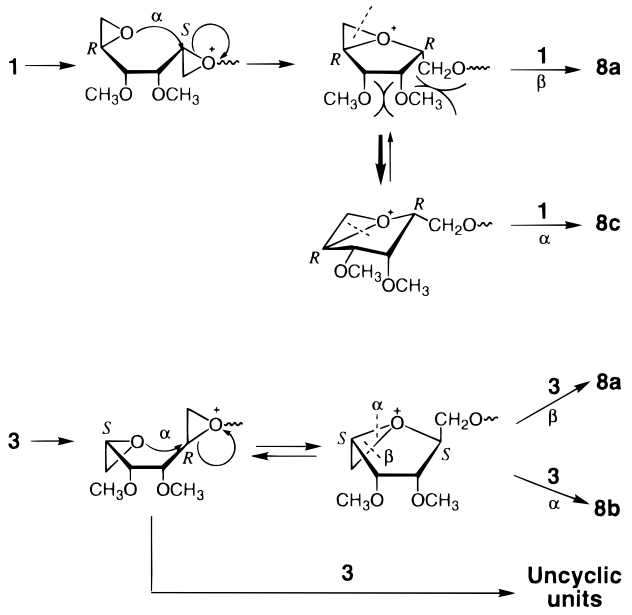
the formation of 1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol units (**8c**) as the major constituent. The cationic cyclopolymerization of **3** gave a polymer containing 1,5-anhydro-3,4-di-*O*-methyl-DL-allitol units (**8b**) as a minor constituent.

Cyclopolymerization Mechanism. For the polymerization of the monosubstituted epoxide through an S_N2-type mechanism, the configuration of the asymmetric carbon atom is inverted by the ring opening at the CH−O bond (α-scission) but retained by that at the CH_2−O bond (*β*-scission). During the anionic cyclopolymerizations of **1**, the repeating unit **8a** was formed by the intermolecular reaction and the intramolecular cyclization through *β*,α-scissions of the two epoxides in the monomer, as shown in Scheme 5. The α-scission of the 1,2-epoxide moiety leads to inversion of the configuration (*S*→*R*), whereas the *β*-scission of the 5,6-epoxide moiety causes retention of the configuration (*R*→*R*). These polymerization steps result in the formation of the (2*R*,5*R*)-configuration. The *β*,α-scissions from the 5,6-epoxide to the 1,2-epoxide form the (2*S*,5*S*)-configuration. A pair of enantiomeric repeating units is thus present in polymer **2a**. This high regio- and stereoselectivity agrees with that for the anionic cyclopolymerization of 1,2:5,6-dianhydrohexitols, such as D-mannitol, L-iditol, and D-glucitol.

On the other hand, the anionic polymerization of **3** mainly proceeded through *β*,*β*-scissions to form **8c** with (2*R*,5*S*)- and (2*S*,5*R*)-configurations. The growing anion in cyclization should avoid unfavorable conformation due to the eclipsed arrangements of three neighboring substituents in the five-membered ring and converts its conformation into the staggered arrangement in the six-membered ring, as shown in Scheme 5. Thus, the steric hindrance in the transition state is an advantage in forming the six-membered ring unit.

During the cationic cyclopolymerization of **1**, the obtained polymer is (2→6)-1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol-*co*-(1→6)-2,5-anhydro-3,4-di-*O*-methyl-DL-altritol in which the former unit, **8c**, and the latter unit, **8a**, are formed through α,α- and *β*,α-scissions, respectively. The formation of the five-membered ring unit was generally found in the cationic polymerization of 1,2:5,6-dianhydrohexitols, such as D-mannitol, L-iditol, and D-glucitol.[5,9] The conformation of the growing oxonium ion in cyclization changes from the five-membered ring

Scheme 6



having eclipsed arrangements of three neighboring substituents to the six-membered ring of favorably staggered arrangements also in this case (Scheme 6). The growing ion in the favorable conformation led to forming the major repeating unit, **8c**, but that in the disadvantaged conformation also participated in propagation to form **8a** as the minor units. The six-membered ring unit through the α,α-scissions in the cationic polymerization of **1** is the same structure as that through the *β*,*β*-scissions in the anionic polymerization of **3**.

On the other hand, the cationic polymerization of **3** was complicated by steric hindrance in the process. The process in which the growing oxonium ion leads to the transition state of cyclization is subject to steric hindrance, in contrast to the cationic polymerization of **1** in which the process from the transition state to the completion of cyclization confronts the problem (Scheme 6). The polymerization of **3**, which is difficult to cyclize, results in the formation of a residual epoxy group, a six-membered ring unit through α,α-scissions, a five-membered ring unit through *β*,α-scissions, and other unknown units.

The formation of the five-membered ring in the polymerization of 1,2:5,6-dianhydrohexitols follows Baldwin's rule, which is applicable to ring closure based on a stereoelectronic effect.[13] The formation of the six-membered ring in the cases of **1** and **3**, therefore, is an interesting example of regioselectivity of an anti-Baldwin type.

Conclusion

Two meso diepoxy monomers, 1,2:5,6-dianhydro-3,4-di-*O*-methylallitol (**1**) and -galactitol (**3**), were polymerized with *t*-BuOK and $BF_3{\cdot}OEt_2$ to desire the possibility of forming the six-membered unit. The anionic polymerization of **1** produced (1→6)-2,5-anhydro-3,4-di-*O*-methyl-DL-altritol through *β*,α-scissions of the two epoxides, which was similar to those of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol, -L-iditol, and -D-glucitol. On the other hand, the anionic polymerization of **3** mainly proceeded through *β*,*β*-scissions to form (2→6)-1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol. For the cationic cyclopolymerization of **1**, (2→6)-1,5-anhydro-3,4-di-*O*-methyl-DL-galactitol-*co*-(1→6)-2,5-anhydro-3,4-di-*O*-methyl-DL-altritol was formed through α,α-scissions, while the structure of the cationic polymer from **3** was complicated.

The anionic and cationic polymerizations of **3** and **1**, respectively, yielded the six-membered rings with the same structure and especially the former polymerization was highly regio- and stereoselective.

Supporting Information Available: Syntheses of the precursors of monomers **15**−**18** and NMR spectral data and elemental analysis of **12**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Schuerch, C. *Acc. Chem. Res.* **1973**, *6*, 184.
(2) Schuerch, C. *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 157.
(3) Strietholt, W. A.; Thiem, J.; Höweler, U. F. B. *Makromol. Chem.* **1991**, *192*, 317.
(4) Kakuchi, T.; Satoh, T.; Umeda, S.; Hashimoto, H.; Yokota, K. *Macromolecules* **1995**, *28*, 4062.
(5) Kakuchi, T.; Satoh, T.; Umeda, S.; Hashimoto, H.; Yokota, K. *Macromolecules* **1995**, *28*, 5643.
(6) Kakuchi, T.; Umeda, S.; Satoh, T.; Hashimoto, H.; Yokota, K. *Macromol. Rep.* **1995**, *A32*, 1007.
(7) Satoh, T.; Hatakeyama, T.; Umeda, S.; Yokota, K.; Kakuchi, T. *Macromolecules* **1996**, *29*, 3447.
(8) Satoh, T.; Hatakeyama, T.; Umeda, S.; Kamada, M.; Yokota, K.; Kakuchi, T. *Macromolecules* **1996**, *29*, 6681.
(9) Satoh, T.; Hatakeyama, T.; Umeda, S.; Yokota, K.; Kakuchi, T. *Polym. J.* **1996**, *28*, 520.
(10) Hatakeyama, T.; Kamada, M.; Satoh, T.; Yokota, K.; Kakuchi, T. *Macromolecules* **1998**, *31*, 2889.
(11) Kuszmann, J. *Carbohydr. Res.* **1979**, *71*, 123.
(12) Hatakeyama, T.; Kamada, M.; Satoh, T.; Yokota, K.; Kakuchi, T. *Koubunshi Ronbunshu* **1997**, *54*, 710.
(13) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

MA990454K