Regio- and Stereoselective Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-di-*O*-methyl-D-glucitol Leading to Polymers with 2,5-Anhydro-3,4-di-*O*-methyl-D-mannitol and/or -L-iditol Units

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ABSTRACT: The cyclopolymerization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol was carried out using cationic and anionic catalysts. The polymerizations proceeded homogeneously up to high conversion and gave linear polymers without formation of gel. For the cationic cyclopolymerizations using $\text{BF}_3 \cdot \text{OEt}_2$ and SnCl_4 , the resulting polymer was confirmed to have the constitutional unit mainly of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol by comparing its ^{13}C NMR spectrum with that of 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol. For anionic cyclopolymerization using *t*-BuOK, the obtained polymer consisted of two cyclic repeating units, 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol and 2,5-anhydro-3,4-di-*O*-methyl-L-iditol. For the regio- and stereoselective polymerizations, intra- and intermolecular reactions introduced α - and β -scissions of the epoxides with inversion and retention of the configuration at the α -carbon, respectively.

KEY WORDS Cationic Polymerization / Anionic Polymerization / Cyclopolymerization / D-Glucitol / D-Mannitol / L-Iditol / Five-membered Ring / Regioselective / Stereoselective / Baldwin Rule /

The synthesis of polysaccharide with the same or mimetic structure as that of the natural product was studied for biochemical, biomedical, and other applications. The ring-opening polymerization of anhydro sugars is established as a strategy for producing highly stereoregular polycarbohydrates.^{1–11} The cyclopolymerization of 1,2:5,6-dianhydrohexitol is also a useful method.^{12–19} Both 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**1**) and -L-iditol (**2**) were cyclopolymerized using boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) to produce a polymer consisting mainly of 2,5-anhydro-3,4-di-*O*-methyl-D-glucitol as the constitutional cyclic unit.¹⁵ The anionic cyclopolymerization of **1** using potassium *tert*-butoxide (*t*-BuOK) was highly regio- and stereoselective and the polymer obtained had a stereospecific structure, *i.e.*, (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**3**).^{16,17} D-Mannitol and L-iditol have C_2 symmetry, and the two epoxy groups in the monomer are equal in reactivity. This symmetric character is responsible for producing a polymer consisting of a single constitutional unit. Therefore, it is interesting to elucidate the character of 1,2:5,6-dianhydrohexitol with C_1 symmetry in cyclopolymerization. There are ten hexitols which contain two meso forms and four pairs of optical enantiomers. Two pairs of D- and L-isomers in mannitol and iditol are C_2 symmetric and the other pairs are asymmetric. D-Glucitol is contained in the latter pairs and therefore 1,2:5,6-dianhydro-D-glucitol possesses two epoxy groups whose reactivities are nonequivalent.

This paper reports the cyclopolymerization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**) using cationic and anionic catalysts. The structures of the polymers (**5**) are discussed by comparing their ^{13}C NMR spectra with those of 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol

(**6**), -L-iditol (**7**) and -D-glucitol (**8**) as model compounds. Polymer **5** prepared using $\text{BF}_3 \cdot \text{OEt}_2$ was composed mainly of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol as the constitutional cyclic unit corresponding to **6**. On the other hand, polymer **5** prepared using *t*-BuOK contained two kind of cyclic units corresponding to **6** and **7**.

EXPERIMENTAL

Measurements

^1H and ^{13}C NMR spectra were recorded with JEOL JNM-EX270 and JNM-A400 II. Optical rotations were determined with a JASCO DIP-140 digital polarimeter. The molecular weight of polymers was measured by gel permeation chromatography (GPC) in tetrahydrofuran on a JASCO HPLC system equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were calculated on the basis of a polystyrene calibration. Thin layer chromatography was performed on silicagel 60 F₂₅₄ (0.25 and 2.0 mm thick, Merck).

Materials

Dichloromethane and nitroethane were distilled over calcium hydride. Toluene, tetrahydrofuran, and 1,4-dioxane were purified by the usual method and distilled from sodium-benzophenone. Borontrifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) and tin(IV) chloride (SnCl_4) were purified by distillation of commercial products under reduced pressure, and used as a solution in dry dichloromethane. Potassium *tert*-butoxide (*t*-BuOK) was purified by sublimation under vacuum before use. 2,5-Anhydro-D-mannitol was purchased from Aldrich. 2,5-Anhydro-

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1,3,4,6-tetra-*O*-methyl-D-glucitol (**8**) was synthesized from **1** by the same procedure in a previous report.¹⁵

1,2:5,6-Dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**)

Monomer **4** was prepared from D-glucitol according to the reported procedure.²⁰ **4** was distilled over CaH₂ under reduced pressure before polymerization run. bp 0.3 = 72–73°C; $[\alpha]_D - 6.3^\circ$, $[\alpha]_{577} - 8.3^\circ$, $[\alpha]_{546} - 9.6^\circ$, $[\alpha]_{435} - 15.6^\circ$, and $[\alpha]_{405} - 18.8^\circ$ (*c* 1.0 in CHCl₃ at 22°C); ¹H NMR (400 MHz, CDCl₃): δ 3.57 (s, CH₃O-, 3H), 3.45 (s, CH₃O-, 3H), 3.10–3.21 (m, 3H), 3.03 (dd, *J* = 7.0 and 3.3 Hz, 1H), 2.89 (dd, *J* = 5.3 and 3.7 Hz, 1H), 2.78–2.81 (m, 2H), and 2.55 ppm (dd, *J* = 4.8 and 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 83.71 and 82.03 (CH), 59.77 and 59.42 (CH₃O-), 53.00 and 50.74 (CH, epoxy), and 46.68 and 43.27 ppm (CH₂, epoxy).

2,5-Anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol (**6**)

To a stirred solution of 2,5-anhydro-D-mannitol (Aldrich, 40 mg, 0.244 mmol) in dimethyl sulfoxide (0.3 mL) was simultaneously added a solution of sodium hydroxide (0.11 g, 2.75 mmol) in water (0.11 mL) and dimethyl sulfate (0.12 mL, 1.27 mmol) at a rate that the temperature of reaction mixture did not exceed 60°C. Stirring was continued at this temperature for 30 min. After standing overnight at room temperature, the mixture was poured into water, and extracted with chloroform. The extract was dried, and the residue purified by thin-layer chromatography with hexane–ethyl acetate (1 : 1, *R_f* 0.47) to give pure **6** as a colorless syrup (31 mg, 57.8%): $[\alpha]_D + 36.3^\circ$, $[\alpha]_{577} + 38.3^\circ$, $[\alpha]_{546} + 44.1^\circ$, $[\alpha]_{435} + 75.0^\circ$, and $[\alpha]_{405} + 89.0^\circ$ (*c* 1.0 in CHCl₃ at 23°C); ¹H NMR (270 MHz, CDCl₃): δ 4.10 (ddd, *J* = 9.1, 5.6, and 1.3 Hz, H-2, 5, 2H), 3.74 (dd, *J* = 3.4 and 1.3 Hz, H-3, 4, 2H), 3.51 (dd, *J* = 5.6 and 1.3 Hz, H-1, 6, 4H), and 3.41 ppm (s, 4MeO, 12H); ¹³C NMR (68 MHz, CDCl₃): δ 86.70 (C-3, 4), 81.30 (C-2, 5), 72.78 (C-1, 6), 59.21 (2MeO), and 57.52 ppm (2MeO). *Anal.* Calcd for C₁₀H₂₀O₅: C, 54.53%; H, 9.15%. Found C, 54.28%; H, 9.10%.

2,5-Anhydro-1,3,4,6-tetra-*O*-methyl-L-iditol (**7**)

2,5-Anhydro-L-iditol (40 mg, 0.244 mmol), prepared according to the method of Bock *et al.*,²¹ in dimethyl sulfoxide (0.3 mL) was treated with a solution of sodium hydroxide (0.11 g, 2.75 mmol) in water (0.11 mL) and dimethyl sulfate (0.12 mL, 1.27 mmol) as described for **5**, to give, after thin-layer chromatography with hexane–ethyl acetate (1 : 1, *R_f* 0.45), pure **7** as a colorless syrup (37.3 mg, 69.6%): $[\alpha]_D + 7.1^\circ$, $[\alpha]_{577} + 7.2^\circ$, $[\alpha]_{546} + 8.6^\circ$, $[\alpha]_{435} + 17.9^\circ$, and $[\alpha]_{405} + 22.6^\circ$ (*c* 1.0 in CHCl₃ at 23°C); ¹H NMR (270 MHz, CDCl₃): δ 4.26–4.20 (m, H-2, 5, 2H), 3.80 (dd, *J* = 5.0 and 1.3 Hz, H-3, 4, 2H), 3.55 (dd, *J* = 6.1 and 4.1 Hz, H-1, 6, 4H), 3.41 (s, 2MeO, 6H), and 3.38 ppm (s, 2MeO, 6H); ¹³C NMR (68 MHz, CDCl₃): δ 83.29 (C-3, 4), 78.53 (C-2, 5), 70.71 (C-1, 6), 59.14 (2MeO), and 58.03 ppm (2MeO). *Anal.* Calcd for C₁₀H₂₀O₅: C, 54.53%; H, 9.15%. Found C, 54.91%; H, 8.77%.

Cationic Polymerization

A typical polymerization procedure is as follows: Monomer **4** (0.5 g, 2.87 mmol) was dissolved in dry

CH₂Cl₂ (5.74 mL), and BF₃·OEt₂ in CH₂Cl₂ (39.1 μ L in 0.73 mol·L⁻¹, 0.0285 mmol) was added by a microsyringe at 0°C. After 24 h, the reaction mixture was poured into a excess methanol containing a drop of aqueous ammonia, and the entire solution was evaporated under reduced pressure. The residue was washed with *n*-hexane several times and dried under vacuum to give the polymer (355 mg, 70.9%). The number-averaged molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*) were 3770 and 3.77, respectively. $[\alpha]_D + 43.9^\circ$, $[\alpha]_{577} + 44.9^\circ$, $[\alpha]_{546} + 50.2^\circ$, $[\alpha]_{435} + 80.3^\circ$, and $[\alpha]_{405} + 93.9^\circ$ (*c* 1.0 in CHCl₃ at 22°C); ¹³C NMR (100 MHz, CDCl₃): δ 86.77 (CH), 81.51 (CH), 71.59 (CH₂), and 57.56 ppm (CH₃).

Anionic Polymerization A typical polymerization procedure is as follows: Polymerization was carried out in an H-shaped glass ampoule. *t*-BuOK (12.2 mg, 0.11 mmol) and dry tetrahydrofuran (THF) (2.0 mL) were added to one side of the ampoule, and **4** (0.355 g, 2.04 mmol) was added to the other side under a nitrogen atmosphere. After sealing under vacuum, the monomer and catalyst solution were mixed at 60°C. After 48 h, the reaction mixture was poured into a excess methanol containing a drop of 0.1 N hydrochloric acid, and the system was evaporated under reduced pressure. The residue was treated as described for the cationic polymerization to give the polymer (0.282 g, 79.5%). The *M_n* and *M_w*/*M_n* were 4960 and 1.71, respectively. $[\alpha]_{577} + 73.4^\circ$, $[\alpha]_{546} + 81.4^\circ$, $[\alpha]_{435} + 133.0^\circ$, and $[\alpha]_{405} + 156.2^\circ$ (*c* 1.0 in CHCl₃ at 22°C); ¹³C NMR (68 MHz, CDCl₃): δ 86.72 (CH), 83.21 (CH), 81.43 (CH), 78.71 (CH), 71.42 (CH₂), 69.35 (CH₂), 58.10 (CH₃), and 57.52 ppm (CH₃).

RESULTS

Cyclopolymerization

The polymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**) using BF₃·OEt₂ and SnCl₄ proceeded homogeneously up to high conversion under the conditions. The result was shown in Table I. The obtained polymers were yellowish-brown semisolids, and soluble in chloroform, methanol, tetrahydrofuran, and water but insoluble in *n*-hexane, except that the po-

Table I. Cationic polymerization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**)^a

Catalyst	Solvent	Yield	<i>M_n</i> ^b	<i>M_w</i> / <i>M_n</i> ^b	$[\alpha]_{546}^{22^\circ}$ ^c
		%			
BF ₃ ·OEt ₂	CH ₂ Cl ₂	70.9	3,770	3.77	+50.2°
	C ₆ H ₅ CH ₃	7.4 ^d	2,010	5.05	+52.6°
	C ₂ H ₅ NO ₂	81.8	3,340	3.68	+62.7°
SnCl ₄	CH ₂ Cl ₂	8.1	1,370	1.55	+40.6°
	C ₆ H ₅ CH ₃	5.2	1,430	1.61	+55.0°
	C ₂ H ₅ NO ₂	12.4	1,090	1.43	+61.9°

^a [4] = 0.5 mol L⁻¹; [4]/[Cat.] = 100; temp, 0°C; time, 24 h. ^b Measured in THF by GPC using poly(styrene) as standard. ^c Measured in CHCl₃ (*c* = 1.0). ^d Yield of the organic solvent-insoluble polymer was 14.5%.

Table II. Polymerization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**) with *t*-BuOK^a

Solvent	Yield %	M_n^b	M_w/M_n^b	$[\alpha]_{546}^{22\text{ }^c}$	y/x^d
1,4-Dioxane	79.4	5,510	1.59	+69.2°	1.5
THF	79.5	4,960	1.71	+81.4°	1.5
C ₆ H ₅ CH ₃	88.0	4,530	1.48	+76.7°	1.3

^a [4] = 1.0 mol l⁻¹; [4]/[*t*-BuOK] = 20; temp, 60°C; time, 48 h.^b Measured in THF by GPC using poly(styrene) as standard. ^c Measured in CHCl₃ (*c* = 1.0). ^d Values determined by ¹³C NMR using inverse gated spin decoupling. The area ratios of C-1, C-2, and C-3 in 2,5-anhydro-3,4-di-*O*-methyl-L-iditol unit to those in -D-mannitol unit were estimated, respectively, and the values were averaged.

lymerization using BF₃·OEt₂ in toluene gave the organic solvent-insoluble polymer in a 14.5% yield together with the soluble polymer in a 7.4% yield. The yields and number-average molecular weights (M_n s) for the polymers obtained in dichloromethane and nitroethane using BF₃·OEt₂ were higher than those for the others. For the polymer in the system of BF₃·OEt₂/CH₂Cl₂, the yield and M_n were 71% and 3770 corresponding to the number-average degree of polymerization (DP) of 22, respectively.

Table II lists the results of the polymerization of **4** using *t*-BuOK. The polymerization systems were homogeneous and gradually turned brown. The resulting polymers were viscous liquids and soluble in organic solvents and water as in the case of those obtained using cationic initiators. M_n s were 4530 to 5510 with an M_w/M_n value of 1.48–1.71. Specific rotations ($[\alpha]_{546}^{22}$) were +40.6° to +62.7° for the polymers using BF₃·OEt₂ and SnCl₄, and +69.2° to +81.4° for those using *t*-BuOK (*c* = 1.0 in CHCl₃). For both polymers, the specific rotation should be affected by the composition of constitutional units and the M_n , but this is an unresolved problem and further study is needed.

Polymer Structure

Figure 1 shows the ¹H NMR spectra of polymer **5** obtained using BF₃·OEt₂ and *t*-BuOK. The characteristic signals in the range of 2.5 to 3.2 ppm due to the epoxy groups completely disappeared; therefore, the extent of cyclization was 100%, *i.e.*, both polymerizations proceeded according to a cyclopolymerization mechanism leading to the polymers with cyclic constitutional repeating units. In both spectra, an apparent difference was observed in the regions of 3.4–4.4 ppm, which suggests differences in stereochemistry between the polymers from the systems of BF₃·OEt₂ and *t*-BuOK.

For the cyclopolymerizations of **1** and **2**, the cyclic constitutional unit in polymer **3** was a five-membered ring, as shown in Scheme 1.¹⁵ In order to confirm the cyclic structural unit in polymer **5**, the ¹³C NMR spectra of the polymers were compared with those of three 2,5-anhydrohexitols, *i.e.*, 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol (**6**), -L-iditol (**7**), and -D-glucitol (**8**). Table III summarizes the ¹³C NMR chemical shifts of these compounds. Although ten peaks were present in the spectrum of **8**, only five peaks were found in each of the spectra, **6** and **7**, which reflects the C₂ symmetry of

Figure 1. ¹H NMR spectra of polymers prepared from 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**) using (a) BF₃·OEt₂ in dichloromethane and (b) *t*-BuOK in toluene. **Scheme 1.**

compounds **6** and **7**.

The ¹³C NMR spectra also were apparently different between the polymers in the systems of BF₃·OEt₂ and

Table III. ^{13}C NMR chemical shifts of 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol (**6**), -L-iditol (**7**), and -D-glucitol (**8**)^a

	C-1	C-2	C-3	C-4	C-5	C-6	3,4- <i>O</i> -CH ₃	1,6- <i>O</i> -CH ₃
	δ/ppm							
6	72.78	81.30	86.70	86.70	81.30	72.78	57.52	59.21
7	70.71	78.53	83.29	83.29	78.53	70.71	58.03	59.14
8	73.15	82.26	85.69	84.75	79.83	70.66	57.35, 57.42	59.19, 59.25

^a All values were measured in CDCl_3 solution using tetramethylsilane as a reference.

Figure 2. ^{13}C NMR spectra of the polymers prepared from 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**4**) using (a) $\text{BF}_3 \cdot \text{OEt}_2$ in dichloromethane and (b) *t*-BuOK in toluene. **Scheme 2.**

t-BuOK, as shown in Figure 2. For the polymer using $\text{BF}_3 \cdot \text{OEt}_2$, four main peaks at 86.77, 81.51, 71.59, and 57.56 ppm were assigned to the methine, methine, methylene, and methoxy carbons, respectively, and thus the polymer resembles **6** very closely in chemical shifts. The structure of polymer **5** using cationic catalysts should thereby be mainly 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol as the five-membered constitutional unit. Several weak absorptions found in the spectrum of the polymer (Figure 2a), however, indicate that there might exist six- and seven-membered rings as minor constitutional units together with the 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol as major unit.

The spectrum of the polymer using *t*-BuOK consists of eight main peaks in which four peaks at 86.72 (methine), 81.43 (methine), 71.58 (methylene), and 57.52 ppm (methoxy) are similar to those assigned to the carbons of C-3,4, C-2,5, C-1,6, and the methoxy groups for **6**, respectively, and the other four peaks at 83.21 (methine), 78.71 (methine), 69.35 (methylene), and 58.10 ppm (methyl) are close to those for **7** in chemical shifts. Therefore, the polymer obtained by anionic polymerization consists of two cyclic repeating units, 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol and -L-iditol, as seen in Scheme 2. The peaks observed in Figure 2b were slightly broad and some split into two bands. This should be caused by the differences in sequences of the two five-membered repeating units, because the cross-peaks corresponding to six- or seven-membered ring units could not be observed in the ^{13}C - ^1H COSY measurement. The ratio of 2,5-anhydro-3,4-di-*O*-methyl-L-iditol units to -D-mannitol units (y/x) in the polymer was estimated by ^{13}C NMR using the inverse gated spin decoupling technique and was indicated in Table II. For the anionic cyclopolymerization in 1,4-dioxane, the ratio y/x was 1.5, which means that the polymerization was favorable for forming 2,5-anhydro-3,4-di-*O*-methyl-L-iditol unit.

DISCUSSION

For both polymers prepared by the cationic and anionic polymerizations of **4**, absorption due to 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-glucitol (**8**) was not observed in the ^{13}C NMR spectra. A absence of **8** units was also confirmed by ^{13}C - ^1H COSY. This indicates that these polymerizations would proceed through the inversion of the configuration at the C-2 or C-5 of **4**, *i.e.*, through the $\text{S}_{\text{N}}2$ reaction.

For the cationic polymerization of monosubstituted epoxides through the S_N2 -type mechanism, the configuration of the asymmetric carbon atom is inverted due to the ring opening at the CH-O bond (α -scission) and retention by the $\text{CH}_2\text{-O}$ bond (β -scission). The anionic polymerization proceeds exclusively through the β -scission. In monomer **4**, epoxides at the 1,2- and 5,6-positions are different in reactivity, because of their different stereochemistry. Therefore, the possible cyclic units in polymer **5** may be considered eight stereoisomers (**5a-h**) formed through the S_N2 -type mechanism, as shown in Scheme 3, where α_{12} and β_{12} , and α_{56} and β_{56} represent α - and β -scissions in the 1,2- and 5,6-epoxides, respectively. In the cyclopolymerization of **4**, the intermolecular reaction and intramolecular cyclization through α_{12}, α_{56} -, α_{56}, α_{12} -, β_{12}, β_{56} -, and β_{56}, β_{12} -scissions of the two epoxides in the molecule form the 6-membered rings **5a**, **5b**, **5g**, and **5h**, respectively; whereas, β_{12}, α_{56} - and β_{56}, α_{12} -scissions lead to the formation of the 5-membered rings **5e** and **5f**, and α_{12}, β_{56} - and α_{56}, β_{12} -scissions to that of the 7-membered rings **5c** and **5d**.

Because the ^{13}C NMR spectrum of polymer **5** obtained using $\text{BF}_3 \cdot \text{OEt}_2$ showed that the cyclic repeating unit consists mainly of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol **5f**, the cationic polymerization of **4** is concluded to involve β_{56}, α_{12} -scission selectively. In intramolecular cyclization, the α -carbon of the 1,2-epoxide moiety having oxonium ion form is attacked by the oxygen atom of the 5,6-epoxide, and the resulting bicyclic oxonium ion is subsequently attacked at the β -carbon by a monomer in the intermolecular reaction as shown in Scheme 4. The α -scission of the 1,2-epoxide moiety leads to inversion of the configuration ($S \rightarrow R$), whereas the β -scission of the 5,6-epoxide moiety causes retention of the configuration ($R \rightarrow R$). Thus, the formation of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol **5f** results from the regio- and stereoselective mechanism. It is worth noting that the ring-opening mode of the epoxide is different for the inter- and intramolecular reactions.

Scheme 3^a.

^a Former and latter symbols correspond to intermolecular and intramolecular scissions, respectively.

Scheme 4.

Scheme 5.

The former reaction takes place preferentially at the 1,2-epoxide moiety as a nucleophile between the two epoxide moieties in the monomer.

The anionic cyclopolymerization of **4** produced a polymer consisting of two cyclic repeating units, 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol **5e** and L-iditol **5f**. In the polymerization, intermolecular reaction through β -scission is established with retention of configuration, but the intramolecular cyclization through α -scission occurred with inversion. In β_{12}, α_{56} -scission, (1) retention at C-2 ($S \rightarrow S$) and inversion at C-5 ($R \rightarrow S$) to form cyclic unit **5e** with *S,S*-configuration, and the β_{56}, α_{12} -scission is the opposite, (2) retention at the C-5 ($R \rightarrow R$) and inversion at the C-2 ($S \rightarrow R$) to form cyclic unit **5f** with *R,R*-configuration, as shown in Scheme 5. The two processes competitively take place to produce a polymer consisting of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol **5f** and -D-mannitol **5e** with a ratio (y/x) of about 1.5. Although involving two processes, the polymerization proceeds through a regio- and stereoselective mechanism in each process. The intermolecular reaction takes place selectively at the 1,2-epoxide moiety rather than the 5,6-epoxide moiety of monomer in the anionic polymerization. The alternating process of β -scission in the intermolecular reaction and α -scission in the intramolecular cyclization is the most striking aspect in the anionic polymerization. The superiority of α -scission in the intramolecular cyclization to form the five-membered rings in both polymerizations can be explained by the Baldwin rule which is generally suited to ring closure on the basis of stereoelectronic effect.^{22,23}

The intramolecular cyclization of **4** was regio- and stereoselective to form five-membered repeating units, though the presence of other cyclized units for the cationic polymerization and the formation of two 2,5-anhydrohexitol units for the anionic polymerization. For intermolecular propagation, the 1,2-epoxy group of **4** predominantly reacted with the growing chain-end, which should be caused by differences in the stereochemistry of the transition state between the 1,2-epoxy and 5,6-epoxy groups. Therefore, to elucidate these phenomena, we are currently calculating the energy of

transition by ab initio and semi-empirical calculations.

CONCLUSIONS

The polymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol were carried out using cationic and anionic catalysts. The polymerizations proceeded through the cyclopolymerization mechanism leading to polymers with cyclic constitutional units. The cationic cyclopolymerization yielded a polymer consisting mainly of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol units. The anionic polymerization involves two processes to yield a polymer consisting of 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol and L-iditol units. The intermolecular reaction exclusively selected the 1,2-epoxide moiety of monomer in the cationic polymerization but slightly favored the 5,6-epoxide moiety in the anionic polymerization. The intra- and intermolecular reactions introduced α - and β -scissions of the epoxides with inversion and retention of the configuration at the α -carbon of epoxide moiety, respectively, in both polymerizations which are regio- and stereoselective.

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