# Regio- and Stereospecificity in Cationic Cyclopolymerization of 1,2:5,6-Dianhydro-D-mannitols and Synthesis of Poly[(1→6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol]

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*Received November 28, 1994; Revised Manuscript Received March 13, 1995*®

ABSTRACT: The cyclopolymerizations of 1,2:5,6-dianhydro-D-mannitols were carried out using cationic initiators. For the polymerization of 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol with $BF_3$·$OEt_2$, the *n*-hexane-insoluble polymer consisted mainly of 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol as the cyclic constitutional unit and a large amount of 1,6:2,5-dianhydro-3,4-di-*O*-ethyl-D-glucitol was obtained as the *n*-hexane-soluble reaction product. The degree of polymerization for the *n*-hexane-insoluble polymer was 14−30, and the specific rotation ($[\alpha]^{22}_{546}$) was 42.7−54.3° ($c$ = 1.0 in $CHCl_3$). On the other hand, 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol polymerized with $BF_3$·$OEt_2$- and $SnCl_4$-produced polymers with cyclic and acyclic units due to the restricted free rotation of the bond between the carbons at the 3,4-positions in which the extent of cyclization was about 0.5.

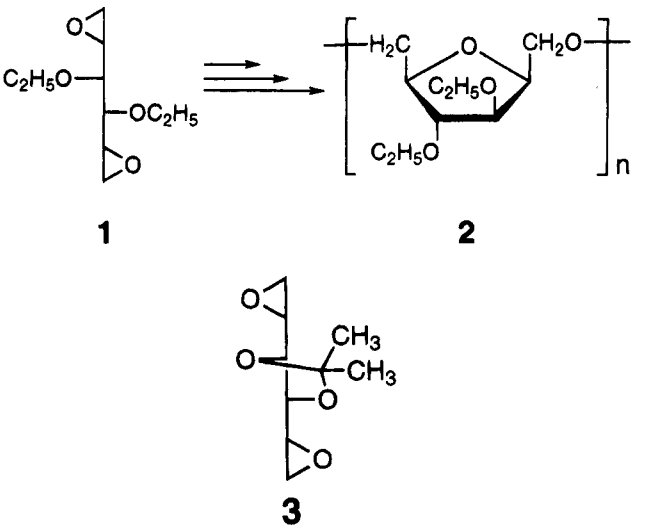
## Introduction

Optically active epoxides are widely used as chiral building blocks for naturally occurring compounds, components of liquid-crystalline molecules, and many other well-stereocontrolled products. For these syntheses, the chiral epoxide needs to react regio- and stereospecifically with the appropriate substrates. Although many studies have reported the stereoselective polymerization of the optically active epoxide and the enantioselective polymerization of the racemic one, the obtained chiral polymers have not found application, such as agents for the optical resolution of racemates.

The cyclization and cyclopolymerization of diepoxides, in particular, the enantiomeric and diastereomeric mixtures of 1,2:5,6-diepoxyhexane, have been an interesting subject in terms of the regiospecificity of the resulting products. Wiggins and Wood reported that 1,2:5,6-diepoxyhexane reacted with water to form the corresponding 2,5-bis(hydromethyl)tetrahydrofuran.[1] Stille et al., Bauer et al., and Aso et al. reported that the diepoxide was polymerized to produce soluble polymers consisting of tetrahydropyran or tetrahydrofuran units as the cyclic constitutional units depending on the catalyst used.[2−4] In a previous study, (2*R*,18*R*)-(−)- and (2*S*,18*S*)-(+)-5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene polymerized regio- and stereospecifically to yield poly[(*R*,*R*)-dibenzo-19-crown-6] and poly[(*S*,*S*)-dibenzo-19-crown-6], respectively, which exhibited a chiral recognition ability toward racemic α-amino acids.[5] Recently, we reported that 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol (**1**) was polymerized with $BF_3$·$OEt_2$ to form polymer **2** consisting of 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol as the cyclic constitutional repeating unit, as shown in Scheme 1.[6] Compound **2** formed complexes with such organic cations as methylene blue and rhodamine 6G along with alkali-metal picrates and also showed a chiral recognition ability for the racemic amino acid derivative.[7]

Wiggins and Wood reported the cyclized compound was obtained by the hydrolysis of 1,2:5,6-diepoxyhexane, but 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (**3**) yielded none of the cyclized compounds.[1] Therefore, for the polymerization of 1,2:5,6-dianhydro-D-mannitols, it is important to elucidate the effect of the monomer structure, i.e., the difference in the substituent at the 3,4-*O*-positions, for the regio- and stereospecificity of the cyclopolymerization.

**Scheme 1**




**1** **2** **3**

In this paper we report the cyclopolymerizations of **1** and **3** with cationic initiators. The cyclopolymerization tendency and the regio- and stereospecificity of **1** and **3**

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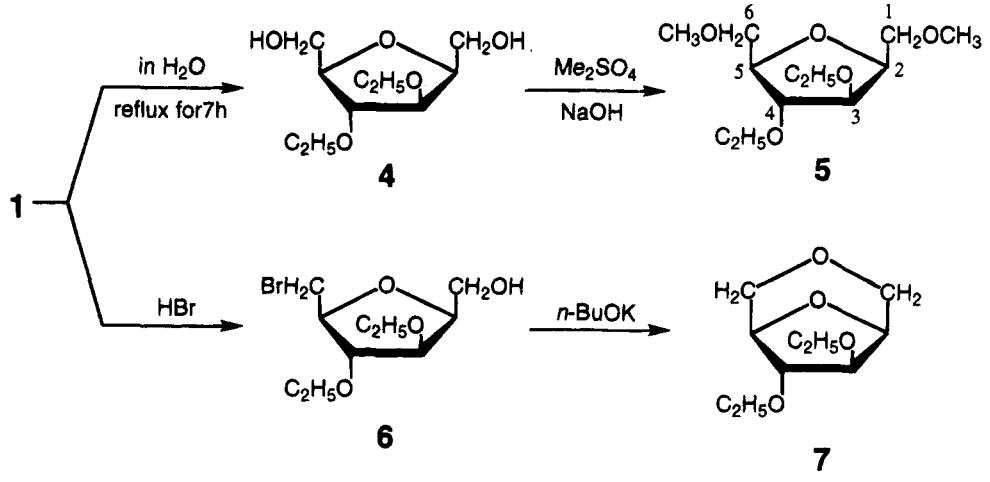
® Abstract published in *Advance ACS Abstracts,* May 1, 1995.

0024-9297/95/2228-4062$09.00/0 

Scheme 2




are discussed by characterizing the resulting polymers. For the cyclopolymerization of **1**, the polymer structure is confirmed by comparing with 2,5-anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (**5**), and 1,6:2,5-dianhydro-3,4-di-*O*-ethyl-D-glucitol (**7**) is obtained as the low molecular weight product in the *n*-hexane-soluble part after separating the *n*-hexane-insoluble polymer (Scheme 2).

## Experimental Section

**Measurement.** $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker MSL 400 instrument. IR spectra were run with a Paragon 1000 FT-IR spectrophotometer. Optical rotations were measured with a Jasco DIP-140 digital polarimeter. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a Waters M45 high-performance liquid chromatograph 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 a polystyrene calibration.

**Materials.** Boron trifluoride etherate ($BF_3{\cdot}OEt_2$) and tin(IV) chloride ($SnCl_4$) were purified by the distillation of commercial products under reduced pressure. Dichloromethane, nitroethane, and toluene were purified by the usual methods and distilled over calcium hydride.

1,2:5,6-Dianhydro-3,4-di-*O*-ethyl-D-mannitol (**1**) and 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (**3**) were prepared from D-mannitol by known methods.[8] **1**: bp 75–76 °C/0.25 mmHg (lit. 67–70 °C/0.1 mmHg); $[\alpha]_D$ −6.0°, $[\alpha]_{577}$ −6.7°, $[\alpha]_{546}$ −8.7°, $[\alpha]_{435}$ −13.5°, and $[\alpha]_{405}$ −15.8° (*c* 1.0 in $CHCl_3$ at 22 °C) (lit. $[\alpha]_D$ −6.2°, *c* 1.0 in $CHCl_3$ at 20 °C); IR (film) 2975, 2930, 2875 (CH), 1092 (COC), 846, 819 $cm^{-1}$ (epoxy); $^1H$ NMR ($CDCl_3$) δ 3.84–3.46 (m, −OCH− and $-OCH_2CH_3$, 6H), 3.31–3.11 and 2.91–2.76 (m, epoxy 6H), 1.20 (t, $CH_2CH_3$, 6H); $^{13}C$ NMR ($CDCl_3$) δ 79.48 (CH), 67.22 ($CH_2CH_3$), 50.45 (epoxy CH), 46.36 (epoxy $CH_2$), 15.50 ($CH_3$). **3**: bp 70–71 °C/0.6 mmHg (lit. 69–71 °C/0.5 mmHg); $[\alpha]_D$ −2.3°, $[\alpha]_{577}$ −2.5°, $[\alpha]_{546}$ −2.9°, $[\alpha]_{435}$ −5.1°, and $[\alpha]_{405}$ −5.9° (*c* 1.0 in $CHCl_3$ at 22 °C) (lit. $[\alpha]_D$ −2.3°, *c* 2.8 in $CHCl_3$ at 20 °C); IR (film) 2990 (ν, CH), 1059 (COC), 860 $cm^{-1}$ (epoxy); $^1H$ NMR ($CDCl_3$) δ 3.84 (dd, *J* = 3.2 and 1.5 Hz, −OCH−, 2H), 3.12–3.14 (m, epoxy CH, 2H), 2.85 (dd, *J* = 4.2 and 4.8 Hz, epoxy $CH_2$, 2H), 2.73 (dd, *J* = 2.6 and 4.8 Hz, 2H), 1.45 (s, $CCH_3$, 6H); $^{13}C$ NMR ($CDCl_3$) δ 110.27 (C), 78.18 (CH), 51.35 (epoxy CH), 45.06 (epoxy $CH_2$), 26.58 ($CH_3$).

**2,5-Anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (5).** The synthetic procedure was reported in a previous paper.[6] Compound **1** was refluxed in water to yield 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol (**4**), and then **4** was treated with dimethyl sulfate to give **5**.

**2,5-Anydro-6-bromo-6-deoxy-3,4-di-*O*-ethyl-D-glucitol (6).** Compounds **6** and **7** were prepared by the procedure similar to that described by Kuszmann.[9] A solution of **1** (2.02 g, 10 mmol) in acetone (5 mL) was added dropwise to an ice-cold, stirred solution of concentrated hydrobromic acid (2 mL) in water (2 mL). The mixture was stirred for 15 min at room temperature and was then made neutral with solid sodium hydrogen carbonate. The precipitated salts were filtered off, and the filtrate was then evaporated. Ethanol was added to, and evaporated from, the residue, which was then filtered with the aid of ethanol. The filtrate was evaporated, and the residue was purified by column chromatography with ethyl acetate/dichloromethane (1/2). Evaporation of the fractions having $R_F$ 0.43 gave 2.40 g (yield 84.8%) of pure **6**: $[\alpha]_{577}$ +3.3°, $[\alpha]_{546}$ +4.6°, $[\alpha]_{435}$ +6.9°, and $[\alpha]_{405}$ +7.7° (*c* 1.0 in $CHCl_3$ at 22 °C); $^1H$ NMR ($CDCl_3$) δ 4.17 (q, *J* = 4.5 Hz, H2 1H), 4.07–4.11 (ddd, *J* = 2.6, 5.5, and 8.0 Hz, H5, 1H), 3.91–3.94 (m, H3 and H4, 2H), 3.81–3.90 (m, H1, 2H), 3.56–3.71 (m, ethyl $CH_2$, 4H), 3.45–3.55 (m, H6, 2H), 2.47 (br, OH, 1H), 1.22 (dt, *J* = 2.4 and 7.0 Hz, ethyl $CH_3$, 6H); $^{13}C$ NMR ($CDCl_3$) δ 84.50, 84.40, 82.47, 81.08, 65.78 (ethyl $CH_2$), 65.26 (ethyl $CH_2$), 61.78 (C1), 32.55 (C6), 15.36 (ethyl $CH_3$). Anal. Calcd for $C_{10}H_{19}O_4Br$: C, 42.40; H, 6.77; Br, 28.23. Found: C, 42.66; H, 6.75; Br, 28.43.

**1,6:2,5-Dianhydro-3,4-di-*O*-ethyl-D-glucitol (7).** A solution of **6** (2.40 g, 8.5 mmol) in 0.5 M 1-butanolic potassium 1-butoxide (19.5 mL) was heated at 100 °C for 1 h. The cooled solution was made neutral with diluted hydrochloric acid and then evaporated. The residue was dissolved in chloroform, and the solution was washed with water, dried, and evaporated. The residue was purified by column chromatography with ethyl acetate/*n*-hexane (2/3). Evaporation of the fractions having $R_F$ 0.43 gave 0.96 g (yield 56.0%) of pure **7**: $[\alpha]_D$ −28.8°, $[\alpha]_{577}$ −33.3°, $[\alpha]_{546}$ −37.7°, $[\alpha]_{435}$ −64.9°, and $[\alpha]_{405}$ −78.2° (*c* 1.0 in $CHCl_3$ at 22 °C); $^1H$ NMR ($CDCl_3$) δ 4.21 (br d, *J* = 6.3 Hz, H2, 1H), 4.10 (d, *J* = 2.4 Hz, H4, 1H), 4.03 (ddd, *J* = 0.9, 2.4, and 6.3 Hz, H3, 1H), 3.98 (br s, H5, 1H), 3.83 (dd, *J* = 1.6 and 11.4 Hz, H6, 1H), 3.79 (d, *J* = 1.4 Hz, H1, 2H), 3.49–3.73 (m, H6 and ethyl $CH_2$, 5H), 1.26 (dt, *J* = 2.9 and 6.9 Hz, ethyl $CH_3$, 6H); $^{13}C$ NMR ($CDCl_3$) δ 86.35 (C3), 86.25 (C4), 79.52 (C5), 76.56 (C2), 69.24 (C6), 66.46 (ethyl $CH_2$), 65.57 (C1), 64.82 (ethyl $CH_2$), 15.41 (ethyl $CH_3$), 15.27 (ethyl $CH_3$); FI-MS (relative intensity) *m/z* 202 ($M^+$ − 100), 203 ($MH^+$ − 13.5), 204 (2.5). Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.62; H, 9.61.

**2,5-Anhydro-3,4-di-*O*-ethyl-6-*O*-methyl-D-glucitol (8).** To a stirred solution of **1** (0.5 g) in methanol (100 mL) was added 2 drops of concentrated hydrochloric acid. The mixture was kept for 24 h at room temperture and then evaporated to give a syrup. The residue was purified by column chromatography using ethyl acetate for elution. The fractions having $R_F$ 0.4 gave **8**: $[\alpha]_D$ +37.8°, $[\alpha]_{577}$ +40.7°, $[\alpha]_{546}$ +45.2°, $[\alpha]_{435}$ +73.9°, and $[\alpha]_{405}$ +88.4° (*c* 1.0 in $CHCl_3$ at 22 °C); $^1H$ NMR ($CDCl_3$) δ 4.09 (q, H2, 1H), 3.96 (dd, *J* = 3.1 and 5.4 Hz, H3, 1H), 3.92 (q, *J* = 5.1 Hz, H5, 1H), 3.80–3.85 (m, H1 and H3, 3H), 3.44–3.70 (m, ethyl $CH_2$, 4H), 3.56 (d, *J* = 5.3 Hz, H6,

**Table 1. Cationic Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-di-*O*-ethyl-D-mannitol (1)[a]**

| catalyst | solvent | yield[b] (%) | $M_n$[c] | $M_w/M_n$[c] | $f_c$[d] (%) | $[\alpha]^{22}_{546}$[e] |
|---|---|---|---|---|---|---|
| $BF_3$·$OEt_2$ | $C_6H_5CH_3$ | 34.3[f] | 4900 | 1.90 | 100 | +49.8 |
| $BF_3$·$OEt_2$ | $CH_2Cl_2$ | 20.7 | 6140 | 1.66 | 100 | +42.7 |
| $BF_3$·$OEt_2$ | $C_2H_5NO_2$ | 22.3 | 2780 | 1.52 | 100 | +54.3 |
| $SnCl_4$ | $C_6H_5CH_3$ | trace | | | | |
| $SnCl_4$ | $CH_2Cl_2$ | trace | | | | |
| $SnCl_4$ | $C_2H_5NO_2$ | trace | | | | |

[a] [1] = 0.5 mol·L$^{-1}$; [1]/[Catalyst] = 100; time, 24 h; temp, 0 °C. [b] Yields of $CHCl_3$-soluble polymer. [c] Measured in THF by GPC using PSt as the standard. [d] Mole fraction of the cyclic structure units in the polymer. [e] *c* 1.0 in chloroform. [f] Organic solvent-insoluble polymer was 8.2%.

2H), 3.41 (s, $-OCH_3$, 3H), 1.22 (dt, $J$ = 2.4 and 6.9 Hz, ethyl $CH_3$, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 84.85 (C3), 83.62 (C4), 81.28 (C5), 79.86 (C2), 73.04 (C6), 65.72, 65.54 (ethyl $CH_2$), 61.79 (C1), 59.24 ($-OCH_3$), 15.39 (ethyl $CH_3$); FI-MS (relative intensity) *m/z* 234 ($M^+$ − 59.1), 235 ($MH^+$ − 100), 236 (14.3), 469 ($(2M + H)^+$ − 23.1). Anal. Calcd for $C_{11}H_{22}O_5$: C, 56.39; H, 9.46. Found: C, 56.42; H, 9.43.

**Polymerization.** All the polymerizations were carried out in side-armed ampules, and $BF_3$·$OEt_2$ and $SnCl_4$ were used as a solution in dichloromethane. At the end of the polymerization, the reaction was mixture poured into a large amount of methanol. The resulting polymers were purified by reprecipitation from chloroform/*n*-hexane.

A typical polymerization procedure is as follows. Monomer **1** (502 mg, 2.48 mmol) was dissolved in dry $CH_2Cl_2$ (5 mL), and then $BF_3$·$OEt_2$ (3.1 μL, 0.02 mmol) was added using a microsyringe. After 24 h at 0 °C, the solution was poured into methanol containing a drop of aqueous ammonia. The solvent was evaporated, and then the residue was washed with *n*-hexane and dried under vacuum to give 104 mg (yield 20.7%) of the *n*-hexane-insoluble polymer: $M_n$ and $M_w/M_n$ were 6140 and 1.66, respectively.

The isolation of the *n*-hexane-soluble products is as follows: The *n*-hexane was evaporated, and the residue was purified by thin layer chromatography with ethyl acetate/*n*-hexane (2/3). Evaporation of the fractions having $R_F$ 0.43 gave 327 mg (yield 65.3%) of the compound whose $^1$H and $^{13}$C NMR spectra and physical properties were identical with those of **7**.

## Results and Discussion

**Cationic Polymerization.** The cationic polymerization of 1,2:5,6-dianhydro-D-mannitols **1** and **3** were carried out with $BF_3$·$OEt_2$ and $SnCl_4$ in dichloromethane, nitroethane, and toluene. Table 1 lists the polymerization results of 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol (**1**). $SnCl_4$ did not produce the polymerization of **1**, and most of the monomer was recovered after 24 h of polymerization. On the other hand, the polymerizations with $BF_3$·$OEt_2$ proceeded homogeneously and all the monomer was consumed, but the *n*-hexane-insoluble polymer yield (20−35%) was relatively low and an appropriate amount of *n*-hexane-soluble low molecular weight products was obtained. The polymers were sticky semisolids and soluble in chloroform, methanol, tetrahydrofuran, and water; the polymer obtained in toluene contained a small portion of the organic solvent-insoluble part. The number-average molecular weight ($M_n$), which was estimated on the basis of polystyrene standards by means of GPC, was 4900 for toluene, 6140 for dichloromethane, and 2780 for nitroethane, corresponding to the degree of polymerization in the range of 14−30. The specific rotations ($[\alpha]^{22}_{546}$) of the polymers obtained were 42.7−54.3° (*c* = 1.0 in $CHCl_3$).

Table 2 lists the results of the polymerization of 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (**3**). The polymerization of **3** proceeded with $BF_3$·$OEt_2$ and $SnCl_4$ to form powdery polymers which were soluble in chloroform, tetrahydrofuran, and methanol but insoluble in *n*-hexane; the polymer obtained with $BF_3$·$OEt_2$ in toluene contained a small portion of the organic solvent-insoluble part. The yields with $BF_3$·$OEt_2$ were higher than those with $SnCl_4$, while the $M_n$s with $BF_3$·$OEt_2$ were smaller than those with $SnCl_4$. The values of specific rotations ($[\alpha]^{22}_{546}$) varied from +7.6° to +14.5° (*c* = 1.0 in $CHCl_3$).

**Table 2. Cationic Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-*O*-isopropylidene-D-mannitol (3)[a]**

| catalyst | solvent | yield[b] (%) | $M_n$[c] | $M_w/M_n$[c] | $f_c$[d] | $[\alpha]^{22}_{546}$[e] |
|---|---|---|---|---|---|---|
| $BF_3$·$OEt_2$ | $C_6H_5CH_3$ | 20.4[f] | 2510 | 2.21 | 0.58 | +14.5 |
| $BF_3$·$OEt_2$ | $CH_2Cl_2$ | 39.5 | 2000 | 1.63 | 0.56 | +7.6 |
| $BF_3$·$OEt_2$ | $C_2H_5NO_2$ | 20.6 | 1090 | 1.25 | 0.45 | +8.8 |
| $SnCl_4$ | $C_6H_5CH_3$ | 12.6 | 3830 | 2.30 | 0.46 | +11.8 |
| $SnCl_4$ | $CH_2Cl_2$ | 13.3 | 3040 | 1.71 | 0.53 | +9.9 |
| $SnCl_4$ | $C_2H_5NO_2$ | 9.6 | 1750 | 1.77 | 0.57 | +11.1 |

[a] [3] = 0.5 mol·L$^{-1}$; [3]/[Catalyst] = 100; time, 24 h; temp, 0 °C. [b] Yields of $CHCl_3$-soluble polymer. [c] Measured in THF by GPC using PSt as the standard. [d] Mole fraction of the cyclic structure units in the polymer. [e] *c* 1.0 in chloroform. [f] Organic solvent-insoluble polymer was 12.4%.

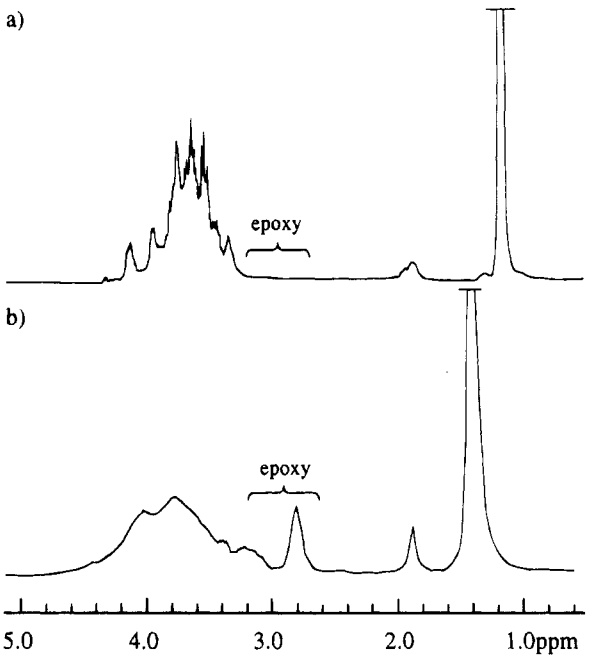
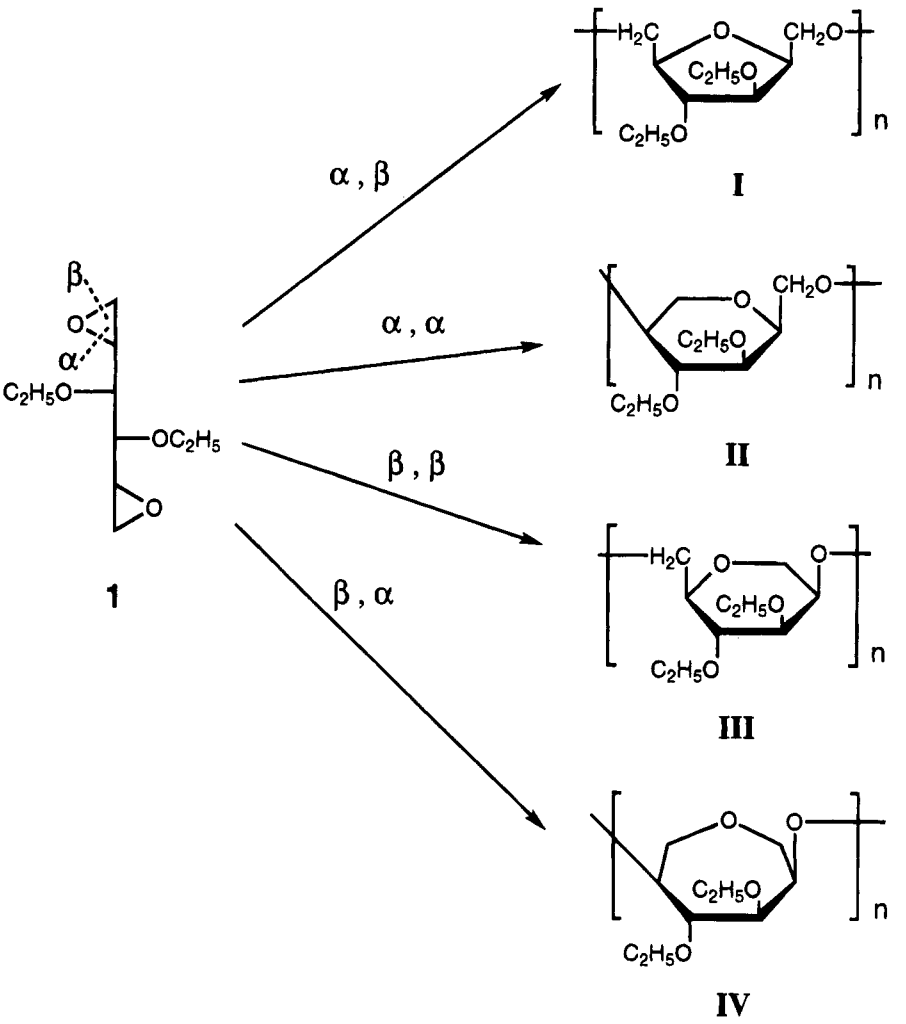



**Figure 1.** $^1$H NMR spectra of (a) the polymer from 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol (**1**) and (b) the polymer from 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (**2**): [Monomer] = 0.5 mol·L$^{-1}$; [Monomer]/[$BF_3$·$OEt_2$] = 100; time, 24 h; temp, 0 °C.

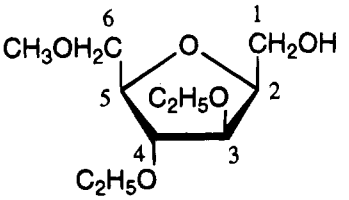
The yields and molecular weights of the obtained polymers varied with the combination of the monomers and catalysts. The molecular weights of the polymers from **1** were higher than those from **3** using $BF_3$·$OEt_2$, which was opposite using $SnCl_4$.

**Polymer Structure.** Since the $^1$H NMR spectrum of the polymer obtained from **1** indicated the absence of the epoxy group as shown in Figure 1a, the polymerization proceeded according to a cyclopolymerization mechanism leading to the polymers with cyclic constitutional repeating units; i.e., the mole fraction of the cyclic structural units ($f_c$) was 1.0. On the other hand, the $^1$H NMR spectrum of the polymer from **3** showed the characteristic resonance at 2.6−3.2 ppm due to the methylene and the methine protons of the epoxide, respectively (Figure 1b). The $f_c$ was 0.45−0.58, which was determined from the relative peak areas of the protons in the $^1$H NMR spectra.

**Scheme 3**




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 retained by opening at the $CH_2$−O bond (β-scission). For the polymerization of **1**, the intramolecular cyclization and the intermolecular reaction through α,α- and β,β-scissions of the two epoxides in a monomer molecule formed the six-membered rings **II** and **III**, respectively, whereas α,β- and β,α-scissions led to the formation of five- and seven-membered rings **I** and **IV**, respectively, as shown in Scheme 3. One of the four possible cyclic units is obtained by the procedure similar to that described by Wiggins;[1] the product obtained from the hydrolysis of **1** is 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol (**4**), and then **4** is treated with dimethyl sulfate to yield 2,5-anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (**5**) (Scheme 2). Figure 2 shows the $^{13}C$ NMR spectra of the polymer from **1** and **5**. The signals at 83.44, 84.32, 83.13, and 79.84 ppm for the polymer are very close to those at 82.30, 84.32, 83.16, and 79.74 ppm assigned to the carbons of C2, C3, C4, and C5, respectively, for **5**. This result indicates that the structure of the polymer from **1** is 1→6 bonded 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol as the five-membered constitutional unit of **I**, i.e., polymer **2**. The signals at 61.86 ($CH_2$), 81.74 (CH), and 84.95 ppm (CH) should be attributed to the polymer chain-end unit, because these chemical shifts are very close to those of the C1, C2, and C3 carbons for 3,4-di-*O*-ethyl-6-*O*-methyl-D-glucitol (**8**). However, many small signals were observed in the $^{13}C$ NMR spectrum of polymer **2**. This result suggests that the polymer should contain cyclic repeating units other than 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol, and this must be discussed after obtaining other possible cyclic units of **II**–**IV**.



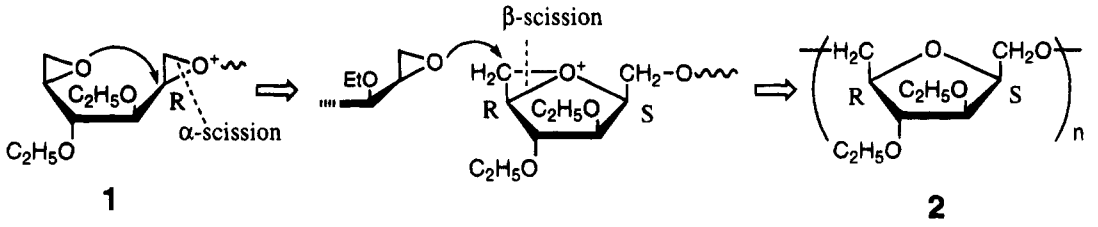
**8**

Wiggins reported that the hydrolysis of **3** formed none of the cyclic compounds under the same conditions in which **1** was refluxed in water to yield the cyclic unimer **4**. The lower cyclization tendency of **3** should be caused by the prohibition of the free rotation around the C3 and C4 substituted with the isopropyridene group, which decreases the regio- and stereospecificity during the cyclopolymerization. The structure of the cyclic unit in the polymer from **3** has not been confirmed in this study and must be further investigated.

## Cyclopolymerization Mechanism

Since polymer **2** consists of (1→6) bonded 2,5-anhydro-D-glucitol recurring units, the polymerization of **1** proceeds through α,β-scission. The proposed mechanism of the cationic cyclopolymerization of **1** is presented

**Scheme 4**



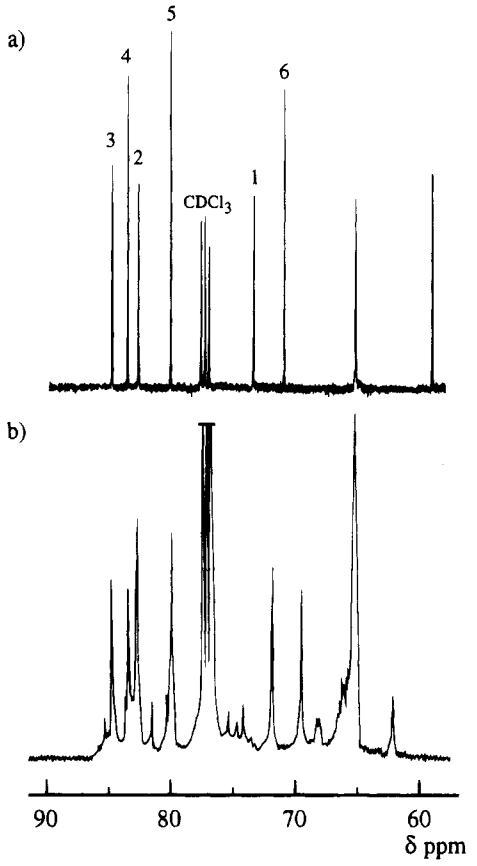




**Figure 2.** $^{13}C$ NMR spectra of (a) 2,5-anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (**5**) and (b) the polymer **2** from 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol (**1**).

in Scheme 4. The intramolecular cyclization occurs via the ring opening of the first epoxide with inversion (R → S) of the configuration by an $S_N2$ attack of the second epoxide function on the α-carbon of the former oxonium ion (α-scission). The ring opening of the second epoxide takes place at the β-carbon with retention (R → R) of the configuration on the asymmetric carbon atoms, the carbon at which the attack is sterically favorable during the intermolecular propagation (β-scission). Therefore, poly[(1→6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol], polymer **2**, is produced by the cyclopolymerization of **1** with a cationic initiator through the regio- and stereospecific mechanism.

For the polymerization of **1**, the *n*-hexane-soluble products were obtained in higher yield rather than the *n*-hexane-insoluble polymers. After purification by preparative thin layer chromatography, a compound with *m*/*z* 202 and $[\alpha]^{22}_{546}$ −37.5° (*c* = 1.0, $CDCl_3$) was isolated in 65.3% yield for the polymerization with $BF_3{\cdot}OEt_2$ in $CH_2Cl_2$. The isolated product was 1,6:2,5-dianhydro-3,4-di-*O*-ethyl-D-glucitol (**7**) because the $^1H$ and $^{13}C$ NMR spectra and the chiroptical properties of both compounds were the same. The formation of **7** should be caused by the unimolecular bicyclic reaction of **1** with cationic species and/or the back-biting of the growing chain end through oxonium cation exchange. With the mechanism of forming **7** becoming clarified, a suitable polymerization condition for producing more regio- and stereospecific polymer with higher molecular weight in higher yield should be realized.

## Conclusions

The cyclopolymerization of 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol with $BF_3{\cdot}OEt_2$ produced the *n*-hexane-insoluble polymer consisting mainly of 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol as a cyclic constitutional unit and a large amount of 1,6:2,5-dianhydro-3,4-di-*O*-ethyl-D-glucitol as the *n*-hexane-soluble reaction product. On the other hand, 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol polymerized with $BF_3{\cdot}OEt_2$ and $SnCl_4$ to yield polymers with cyclic and acyclic units by the restricted free rotation of bonds between the carbons at the 3,4-positions in which the extent of cyclization was about 0.5.

## References and Notes

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MA946203N