Cyclopolymerization of 1,2:5,6-Diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol and -L-iditol Leading to a Novel Thiosugar Polymer

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Introduction

Naturally occurring polysaccharides, such as cellulose and chitin, have received considerable attention in terms of raw materials for optical resolution and biorelated applications. On the other hand, the functional property of artificial polysaccharides is expected to differ from that of natural ones; therefore, there is great interest in a synthetic method leading to a novel type of polysaccharide. Previously, we reported that the cyclopolymerization of 1,2:5,6-dianhydrohexitol proceeded through the regio- and stereoselective mechanism to give a stereoregular polymer such as (1→6)-2,5-anhydrohexitol.[1−17] The structural characteristic of the polymers is the lack of an anomeric linkage, which is quite different from naturally occurring polysaccharides. In addition, (1→6)-2,5-anhydro-D-glucitol derivatives showed a selective binding ability for metal cations, and a chiral discrimination property, and the 3,4-di-*O*-sulfonylated polymer induced lymphocyte activation.[18−25]

To develop the cyclopolymerization method, it is important to expand the scope and limits in terms of applicable monomers leading to polymers consisting of modified sugar units, such as deoxysugar, aminosugar, and thiosugar. For example, diepisulfide, which can be easily obtained from the diepoxide, is a monomer for producing thiosugar polymers that is expected to act as a soft base due to the greatly enhanced nucleophilicity of sulfur compared with oxygen. Previously, we reported the preliminaries for the cyclopolymerization of 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (**1**) leading to the thiosugar polymer with high Ag^+- and Cu^{2+}-binding abilities.[26] The present study aims to clarify the characteristic reactivity for the cyclopolymerization of 1,2:5,6-diepithiohexitol along with the polymer structures.

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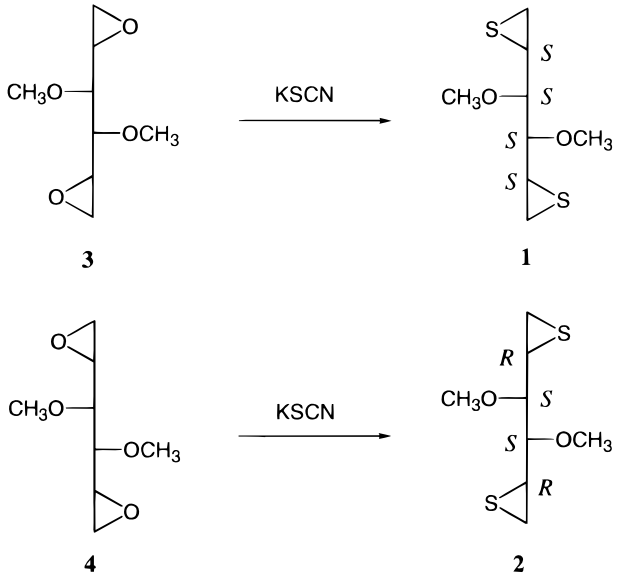
Scheme 1



3 **1** **4** **2**

In this paper, we report the cyclopolymerization of **1** and its diastereoisomer, 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-L-iditol (**2**), using cationic and anionic initiators. The cyclopolymerization mechanisms are discussed on the basis of thiosugar units in the polymers, which were determined by comparison of the ^{13}C NMR spectra between the polymers and the cyclic model compounds.

Experimental Section

Measurements. Quantitative ^{13}C NMR were obtained under the conditions of a 20% (wt/vol) sample in chloroform-*d* ($CDCl_3$) at 25 °C, 45° pulse angle, inverse gated decoupling with a 7.0 s delay, 6000 scans, and tetramethylsilane as the internal reference. The molecular weights of the polymer samples were 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 the molecular weight distribution (M_w/M_n) were calculated on the basis of a polystyrene calibration. Optical rotation was determined with a JASCO DIP-1000 digital polarimeter. FI and FD−MS were obtained with a JEOL JMS−SX102A mass spectrometer.

Materials. Potassium thiocyanate was purified by recrystallization from MeOH. Dichloromethane and nitroethane were purified by the usual methods and distilled from calcium hydride. Toluene, THF, and 1,4-dioxane were purified by the usual methods and distilled from sodium−benzophenone ketyl. Boron trifluoride ($BF_3{\cdot}OEt_2$) and tin(IV) chloride ($SnCl_4$) were purified by the distillation of commercial products under reduced pressure. Potassium *tert*-butoxide (*t*-BuOK) was purified by sublimation of the commercial product under reduced pressure. Florisil (75−150 mesh) was purchased from the Kanto Chemical Co. 1,2:5,6-Dianhydro-3,4-di-*O*-methyl-L-iditol (**3**) and 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**4**) were prepared from D-mannitol according to the method of Kuszmann.[28]

1,2:5,6-Diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (1). A solution of **3** (15.5 g, 89.1 mmol) in tetrahydrofuran (81 mL) was added to a stirred solution of potassium thiocyanate (53.5 g, 552 mmol) in water (65 mL) at 0 °C. After standing overnight at room temperature, the mixture extracted with chloroform. The extract was washed with water and dried with magnesium sulfate, and the solvent was evaporated. The

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Table 1. Cationic Cyclopolymerizations of 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (1) and 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-L-iditol (2)[a]

monomer (**M**)	catalyst	solvent	[**M**]/[cat.]	time, h	yield, %	M_n (M_w/M_n)[b]	$[\alpha]^{22}_{546}$[c]
1	$BF_3{\cdot}OEt_2$	CH_2Cl_2	10	48	27.2	3300 (2.2)	+10.8
		CH_2Cl_2 [d]	10	100	19.1	4600 (1.6)	+11.1
		$C_6H_5CH_3$	10	100	5.8	1900 (1.6)	+18.2
		$C_2H_5NO_2$	10	100	34.2	2400 (1.5)	+15.5
	$SnCl_4$	CH_2Cl_2	10	100	86.9	2200 (1.4)	+25.4
2	$BF_3{\cdot}OEt_2$	CH_2Cl_2	10	100	14.6	1200 (1.6)	−18.6
		CH_2Cl_2	20	100	16.7	1600 (1.9)	−14.5

[a] [Monomer] = 0.5 mol·L^{-1}, temperature 0 °C. [b] Measured in $CHCl_3$ by GPC using PSt as standard. [c] c = 1.0, $CHCl_3$. [d] Temperature: −30 °C.

residue was purified by column chromatography on Florisil with toluene/ethyl acetate (20/1) and distilled under reduced pressure to give pure **1** as a white solid (6.93 g, 37.7%). Bp: 104−108 °C/0.5 mmHg. Mp: 90 °C. R_f: 0.30. $[\alpha]_{546}$ = −37.9° (c 0.88 in $CHCl_3$ at 22 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (s, methoxy, 6H), 3.16 (ddd, ^3J = 8.3 Hz, 6.0 Hz, 5.6 Hz, epithio CH, 2H), 2.83 (d, J = 8.3 Hz, 2H), 2.70 (dd, $^3J_{cis}$ = 6.1 Hz, J_{gem} = 1.2 Hz, epithio methylene, 2H), and 2.44 ppm (dd, $^3J_{trans}$ = 5.5 Hz, J_{gem} = 1.1 Hz, epithio methylene, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.26 (CH), 59.00 (methoxy), 32.91 (CH, epithio), and 25.70 ppm (CH_2, epithio). Anal. Calcd for $C_8H_{14}O_2S_2$ (206.3): C, 46.57; H, 6.84; S, 31.08. Found: C, 46.44; H, 6.73; S, 31.36.

1,2:5,6-Diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-L-iditol (2). Monomer **2** was prepared from **4** (3.0 g, 17.2 mmol). After column chromatography on Florisil, the residue was distilled under reduced pressure to give pure **2** as a colorless liquid (0.89 g, 25.0%). Bp: 150 °C/0.5 mmHg. R_f: 0.30; $[\alpha]_{546}$ = +43.8° (c 0.97 in $CHCl_3$ at 22 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (s, methoxy, 6H), 3.12−3.04 (m, epithio CH, 2H), 3.03−2.98 (m, J = 8.3 Hz, 2H), 2.47 (dd, $^3J_{cis}$ = 6.3 Hz, J_{gem} = 1.5 Hz, epithio methylene, 2H), and 2.24 ppm (dd, $^3J_{trans}$ = 5.6 Hz, J_{gem} = 1.5 Hz, epithio methylene, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 87.13 (CH), 58.96 (methoxy), 33.41 (CH, epithio), and 19.98 ppm (CH_2, epithio). Anal. Calcd for $C_8H_{14}O_2S_2$ (206.3): C, 46.57; H, 6.84; S, 31.08. Found: C, 46.50; H, 6.71; S, 31.12.

2,5-Anhydro-1,5-dithio-3,4,6-tri-*O*-methyl-D-glucitol (5) and 1,5-Anhydro-2,5-dithio-3,4,5-tri-*O*-methyl-D-mannitol (6). A solution of **1** (0.75 g, 3.6 mmol) in methanol (200 mL) containing a drop of hydrochloric acid was stirring at room temperature for 2 weeks. The mixture was neutralized by adding methanolic sodium methoxide, and then the slovent was evaporated in vacuo. Water was added, and the mixture was extracted with chloroform. The extract was dried and the residue was purified by column chromatography with toluene/ethyl acetate (10/1). Evaporation of the fractions having R_f values of 0.32 and 0.22 gave **5** (29%) and **6** (56%), respectively. The structures of the products were assigned on the basis of the results of ^{1}H, ^{13}C, cosy, and CH-cosy NMR measurements. **5**: $[\alpha]_{546}$ +18.7° (c 1.07, $CHCl_3$, 22 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92−3.89 (m, C*H*−OCH_3, 2H), 3.63 (dt, J = 4.39 Hz, 7.56 Hz, C*H*−CH_2SH, 1H), 3.59 (dd, J = 7.56 Hz, 9.03 Hz, C*H*$_2$−OCH_3, 1H), 3.48−3.45 (m, C*H*−CH_2OCH_3, 1H), 3.41−3.39 (m, C*H*$_2$−OCH_3, 1H), 3.44 (s, OCH_3, 3H), 3.43 (s, OCH_3, 3H), 3.37 (s, OCH_3, 3H), 2.89 (ddd, J = 7.56 Hz, 9.50 Hz, 13.4 Hz, C*H*$_2$−SH, 1H), 2.70−2.63 (m, C*H*$_2$−SH, 1H) and 1.67 ppm (dd, J = 7.80 Hz, 9.50 Hz, S*H*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.38 (C3), 85.24 (C4), 74.97 (C6), 58.75, 57.78, 57.63 (OCH_3), 51.96 (C2), 48.76 (C5) and 24.53 ppm (C1). Anal. Calcd for $C_8H_{14}O_2S_2$ (238.36): C, 45.35; H, 7.61; S, 26.9. Found: C, 45.38; H, 7.42; S, 27.02. FI−MS (m/z and relative intensity): 238 (M^+, 100), 239 (MH^+, 11.92), 240 (10.16). **6**: $[\alpha]_{546}$ −17.0° (c 0.96, $CHCl_3$, 22 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77−3.73 (m, C*H*−OCH_3 and C*H*$_2$−OCH_3, 2H), 3.63−3.59 (m, C*H*$_2$−OCH_3, 1H), 3.56−3.51 (m, C*H*−SH, 1H), 3.49 (s, OCH_3, 3H), 3.48 (s, OCH_3, 3H), 3.38 (s, OCH_3, 3H), 3.32 (dd, J = 2.93 Hz, 5.12 Hz, C*H*-OCH_3, 1H), 2.89 (m, C*H*$_2$−S and C*H*−CH_2OCH_3, 2H), 2.66 (dd, J_{gem} = 13.7 Hz, J_{eq-ax} = 2.68 Hz, C*H*$_2$−S, 1H) and 2.20 ppm (d, J = 9.76 Hz, S*H*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.49 (C4), 75.63 (C3), 72.27 (C6), 58.88, 58.64, 58.59 (OCH_3), 41.87 (C5), 39.40 (C2) and 30.46 ppm (C1). Anal. Calcd for $C_8H_{14}O_2S_2$ (238.36): C, 45.35; H, 7.61; S, 26.9. Found: C, 45.15; H, 7.50; S, 26.84. FI−MS (m/z and relative intensity): 238 (M^+, 100), 239 (MH^+, 20.98), 240 (17.99).

Typical Polymerization Procedure. The polymerizations using $BF_3{\cdot}OEt_2$, $SnCl_4$, and t-BuOK were carried out by a procedure similar to that described in a previous paper.[26] For the polymerization of **1** using $BF_3{\cdot}OEt_2$ in CH_2Cl_2, the yield and M_n were 27.2% and 3300. $[\alpha]_{546}$ = +10.8° (c 1.0 in $CHCl_3$ at 22 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15−3.95 (m, methine), 3.90−3.74 (m, methine), 3.54−3.27 (m, methoxy and methine), 3.12−2.81 (m, methylene), and 2.80−2.65 ppm (m, methylene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.51 (CH), 86.42, 86.28, 86.13 (CH), 85.18, 74.86, 59.27, 58.76, 58.66, 57.92 (methoxy), 57.67, 57.38 (methoxy), 57.27, 50.98, 50.94 (CH), 50.54, 50.48, 50.43, 50.40 (CH), 49.45, 46.47, 37.74, 37.60 (CH_2), 36.89, 32.39, 32.03, and 31.97 ppm (CH_2).

Results and Discussion

Cyclopolymerization. During the reactions of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-L-iditol (**3**) and D-mannitol (**4**) to form 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (**1**) and L-iditol (**2**), respectively, the displacement of the oxygen atom by sulfur inverts the configurations of the C2 and C5 carbons, so that these asymmetric characteristics are retained. Monomer **1** is a white solid with the specific rotation ($[\alpha]_{546}^{22}$, c 0.88, $CHCl_3$) of −37.9°, while **2** is a colorless liquid with a $[\alpha]_{546}^{22}$ (c 0.97, $CHCl_3$) of +43.8°.

Lewis acids, such as $BF_3{\cdot}OEt_2$ and $SnCl_4$, were used to initiate the polymerization of the diepisulfides. Table 1 lists the results of the cationic polymerizations of **1** and **2**. The polymerizations proceeded without gelation to give white powdery products, which were soluble in $CHCl_3$, CH_2CH_2, and anisole, sparingly soluble in THF, 1,4-dioxane and pyridine, and insoluble in toluene, DMSO, DMF, and CH_3OH. The number-average molecular weights (M_ns) were relatively low, being 1200−4600, corresponding to the degree of polymerization (DP_n) of 6 to 22. The polymerization reactivity of **1** was higher than that of **2**, which was similar to the results of **3** and **4**. The specific rotations ($[\alpha]^{22}_{546}$) varied from +10.8 to +25.4° for the polymers from **1** and were −14.5 and −18.6° for the polymers from **2**.

Table 2 lists the results of the polymerizations of **1** and **2** using the anionic catalyst t-BuOK. The anionic polymerization system in THF and 1,4-dioxane gradually became a heterogeneous one as the reaction progressed, and the polymer was obtained in high yield. The obtained polymers have characteristics similar to those produced by the cationic polymerization. The M_ns of the resulting polymers increased with the increasing molar ratio of monomer to initiator, such as from 11 800 to 47 700 for **1** and from 9300 to 41 200 for **2**. The yields

Table 2. Anionic Cyclopolymerization of 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (1) and 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-L-iditol (2)[a]

monomer (**M**)	solvent	temp, °C	[**M**]/[cat.]	time, h	yield, %	M_n (M_w/M_n)[b]	$[\alpha]^{22}_{546}$[c]
1	THF	60	10	0.5	91.1	11 800 (1.8)	+24.9
		60	20	0.5	86.2	20 900 (1.9)	+23.4
		60	40	5	86.6	47 700 (2.2)	+22.9
	1,4-dioxane	60	40	5	81.3	58 300 (2.2)	+26.9
	toluene	60	10[d]	5 min	71.5	16 200 (4.2)	+32.3
2	THF	60	10	0.5	72.9	9 300 (1.6)	−29.8
		60	20	0.5	74.4	11 800 (2.6)	−38.4
		60	40	5	55.5	41 200 (1.6)	−38.8

[a] [Monomer] = 0.2 mol·L^{-1}; catalyst, *t*-BuOK. [b] Measured in $CHCl_3$ by GPC using PSt as standard. [c] c = 1.0, $CHCl_3$. [d] [Monomer] = 0.1 mol·L^{-1}.

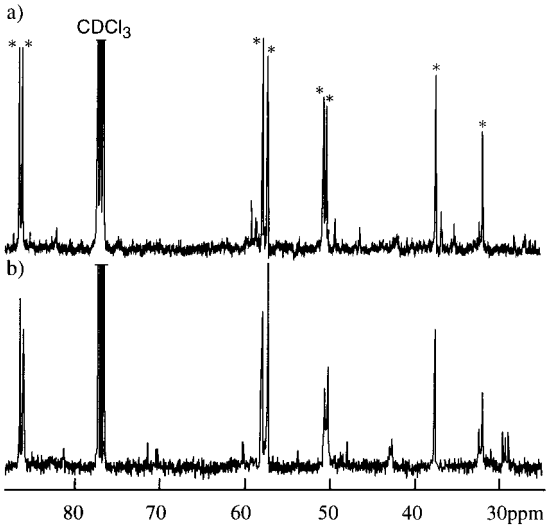


Figure 1. ^{13}C NMR spectra of the polymers obtained by the cationic polymerizations of 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (**1**) (a) and 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-L-iditol (**2**) (b) with BF_3·OEt_2.

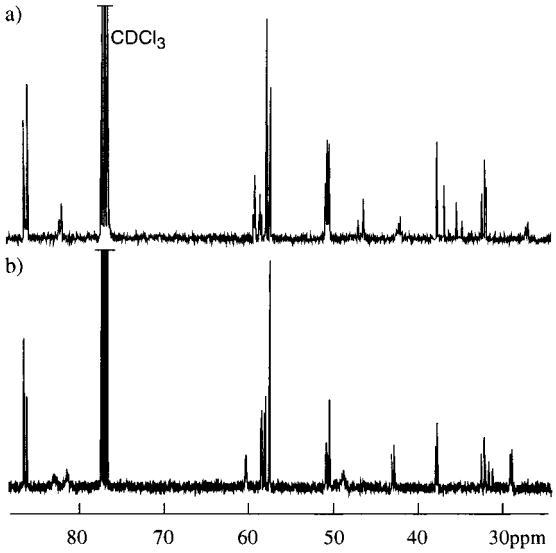


Figure 2. ^{13}C NMR spectra of the polymers obtained by the anionic polymerizations of 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-D-mannitol (**1**) (a) and 1,2:5,6-diepithio-3,4-di-*O*-methyl-1,2,5,6-tetradeoxy-L-iditol (**2**) (b) with *t*-BuOK.

and M_ns of the polymer from **1** were also higher than those of **2**, which were similar to the results of **3** and **4** in the anionic polymerization.[8,9] The polymerization in toluene heterogeneously proceeded to produce a polymer with an M_n of over 10 000. For monomers **1** and **2**, the yields and M_ns of the anionic polymers were higher than those of the cationic polymers. The specific rotations ($[\alpha]^{22}_{546}$) of the polymers obtained from **1** were found in the range of +22.9 to +32.3°, and the polymers from **2** had specific rotations of −29.8 to −38.8°, though there was no obvious relation between the M_ns and the specific rotation.

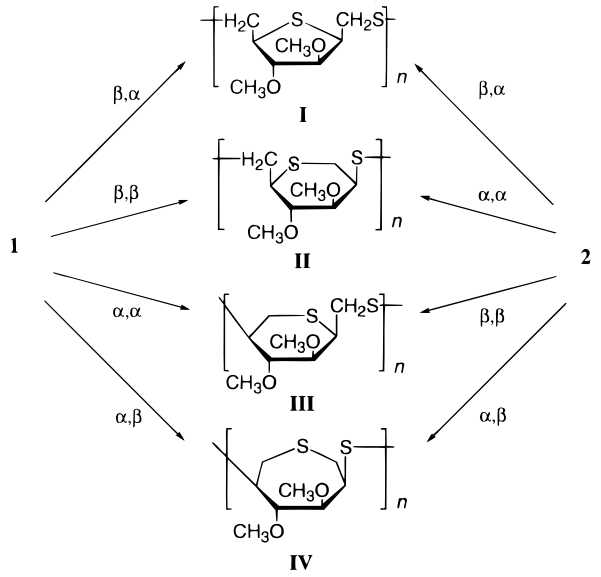
Polymer Structure. In all the polymers, the epithio group was not observed in the ^1H and ^{13}C NMR spectra, indicating that the cationic and anionic polymerizations of **1** and **2** proceeded according to a cyclopolymerization mechanism leading to the polymers with cyclic constitutional repeating units. Figure 1 shows the ^{13}C NMR spectra of the polymers obtained with BF_3·OEt_2. In Figure 1a, the signals at 86.51, 86.13, 50.74, and 50.39 ppm were assigned to the methine carbons, the two signals at 37.60 and 31.97 ppm to the methylene carbons, and the signals at 57.94 and 57.40 ppm to the methoxy carbons. Similar peaks were also found in Figure 1b. These spectral results suggested that the cyclic constitutional repeating units in the polymers were the same for the cationic cyclopolymerizations of **1** and **2**. For all cationic polymers, the content of the major units, which was estimated by ^{13}C NMR using the inverse gated spin decoupling technique, was constant at ca. 80%, though the polymerization conditions were varied. The signals due to the major unit are also found in the polymers obtained by the anionic polymerizations of **1** and **2**, as shown in Figure 2. The content of the major unit in the polymer using *t*-BuOK was below 60%, indicating that the cationic polymer was more stereoregular than the anionic polymer.

For the cationic and anionic cyclopolymerizations of the two diastereomeric diepisulfides **1** and **2**, the produced polymers had the same structure, as well as those of the two diastereomeric diepoxides, **3** and **4**.[5,8,9]

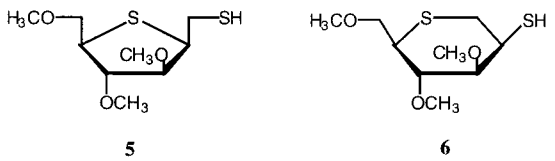
The cationic and anionic cyclopolymerizations of diepisulfides **1** and **2** have the possibility of producing four kinds of recurring units having five-, six-, and seven-membered rings by the ring-opening mode of two epithio groups in a monomer, as shown in Scheme 2. For the cyclopolymerization of **1**, the β,β- and α,α-scissions form six-membered rings (**II** and **III**), whereas the β,α- and α,β-scissions lead to the 5 and seven-membered rings (**I** and **IV**), respectively. On the other hand, for the polymerization of **2**, the β,β- and α,α-scissions form six-membered rings, **III** and **II**, which are opposite of **1**, while the β,α- and α,β-scissions lead to the 5 and seven-membered rings, **I** and **IV**, as well as **1**.

To confirm the structure of the resulting polymer, the cyclization of **1** with a catalytic amount of HCl was carried out in methanol. The ring-opening and ring-forming reaction of **1** produced five- and six-membered compounds, i.e., 2,5-anhydro-1,5-dithio-3,4,6-tri-*O*-methyl-D-glucitol (**5**) and 1,5-anhydro-2,5-dithio-3,4,5-tri-*O*-

Scheme 2[a]



[a] The former and the latter symbols correspond to the intermolecular and intramolecular scissions, respectively.



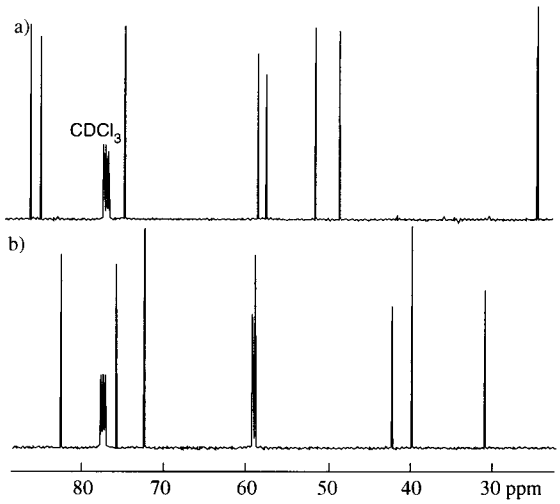
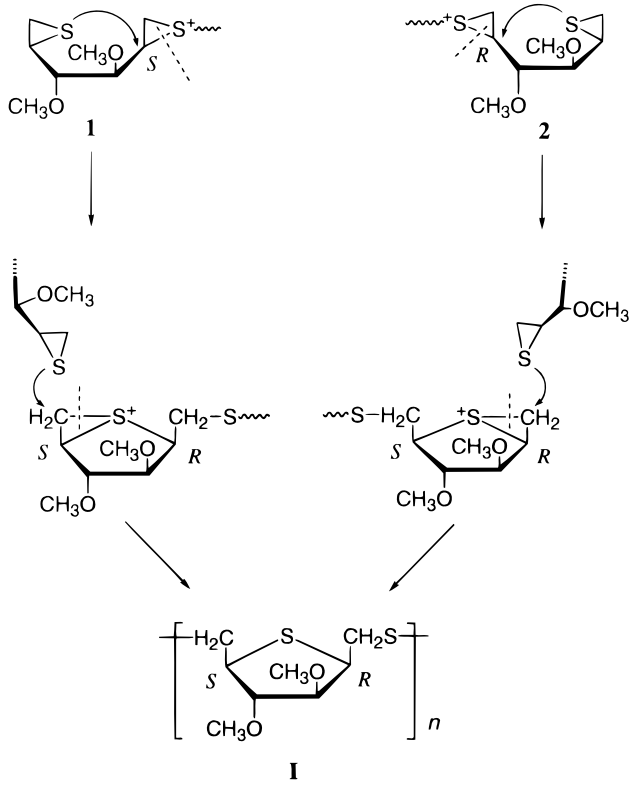


Figure 3. ^{13}C NMR spectra of 2,5-anhydro-1,5-dithio-3,4,6-tri-*O*-methyl-D-glucitol (**5**) (a) and 1,5-anhydro-2,5-dithio-3,4,5-tri-*O*-methyl-D-mannitol (**6**) (b).

methyl-D-mannitol (**6**). Figure 3 shows the ^{13}C NMR spectra of **5** and **6**. The ^{13}C NMR spectrum of **5** consists of three pair of carbons situated in similar surroundings, i.e., 3,4-carbons, 2,5-carbons, and methoxy carbons. On the other hand, for the spectrum of **6**, there is no symmetrical carbon pair except for the methoxy carbons. The three pairs of carbons for **5** closely agreed with the peaks marked with an asterisk in Figure 1, suggesting that the polymers from **1** and **2** mainly consist of the five-membered ring **I**, the 2,5-anhydro-1,5-dithio-3,4-di-*O*-methyl-D-glucitol unit. These signals of the polymer, however, are split into two or more. In addition, there were several small peaks, which should be attributed to the six-membered ring units, i.e., 1,5-anhydro-2,5-dithio-3,4-di-*O*-methyl-D-mannitol units for the polymerization of **1** and 2,6-anhydro-1,6-dithio-3,4-di-*O*-methyl-L-iditol units for that of **2**. Therefore, the split peaks are caused by the difference in sequence between the five- and six-membered ring units.

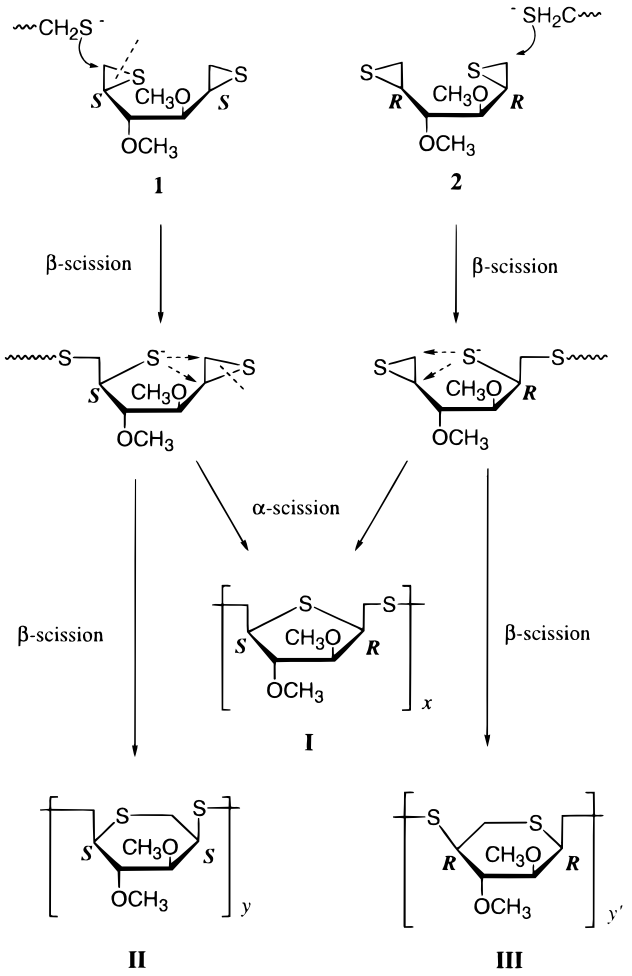
Scheme 3



Cyclopolymerization Mechanism. The cyclopolymerizations of **1** and **2** using BF_3·OEt_2 and *t*-BuOK produced the polymers consisting of mainly five-membered cyclic units **I**, though the cationic cyclopolymerization was more stereoregular than the anionic one. The proposed mechanism of the cationic cyclopolymerization is presented in Scheme 3. The five-membered cyclic unit **I** is formed through an intramolecular cyclization with α-scission of the epithio group and an intermolecular addition with *β*-scission of the epithio group. The intramolecular cyclization with the α-scission occurs with inversion of the configuration at the asymmetric carbon atoms (*S*→*R* for **1** and *R*→*S* for **2**), whereas the intermolecular propagation with the *β*-scission leads retention of the configuration (*S*→*S* for **1** and *R*→*R* for **2**). The attack at the *β*-carbon is sterically favored during the intermolecular addition. The alternating mechanism between the intramolecular cyclization and the intermolecular propagation gave rise to the thiosugar polymer.

The anionic cyclopolymerizations of **1** and **2** proceeded through the intramolecular cyclization with α-scission and the intermolecular reaction with *β*-scission to yield the polymer consisting of the five-membered cyclic unit as the major unit, as shown in Scheme 4. The lower content of the major units in the polymers from **1** and **2** means that the regioselectivity of the intramolecular cyclization was lower than that for the anionic polymerization of **3** and **4**, in which the content of the five-membered units was almost 100%.[8,9] These results indicate that the anionic ring-formation of **1** and **2** did not proceed according to Baldwin's rule because the sulfur atom has a larger size than the oxygen atom.[28]

Scheme 4



The intramolecular cyclization with *β*-scission formed the six-membered rings, **II** and **III**, as the minor units.

Conclusion

The cationic and anionic cyclopolymerizations of 1,2:5,6-diepithio-1,2,5,6-tetradeoxy-3,4-di-*O*-methyl-D-mannitol (**1**) and 1,2:5,6-diepithio-1,2,5,6-tetradeoxy-3,4-di-*O*-methyl-L-iditol (**2**) were a novel method for producing thiosugar polymers. The polymers consisted of the five-membered cyclic unit, i.e., 2,5-anhydro-1,5-dithio-3,4-di-*O*-methyl-D-glucitol, as the major repeating constitutional unit. Although the polymerization reactivity using *t*-BuOK was higher than that using BF_3·OEt_2 and $SnCl_4$, the stereoregularity of the former polymerization was lower than that of the latter polymerization.

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