7: IR ($CHCl_3$) 1790, 1610, 1470, 1380, 1325, 1160, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.1 (d, J = 12 Hz, 2 H), 8.85 (s, 1 H), 8.3 (d, J = 8 Hz, 1 H), 7.90 (d, J = 8 Hz, 2 H), 7.5–7.15 (m, 3 H), 2.45 (s, 3 H); ^{13}C (75 MHz, $CDCl_3$) δ 167.9, 155.4, 153.3, 137.1, 130.1, 128.5, 124.3, 21.5; MS calcd for $C_{13}H_{12}N_2O_2S$ 260.0620, found 260.0617. Anal. Calcd for $C_{13}H_{12}N_2O_2S$-0.5H_2O: C, 57.97; H, 4.86; N, 10.40. Found: C, 57.71; H, 4.69; N, 10.38.

9: IR ($CHCl_3$) 1632, 1317, 1168, 1090, 1014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.6 (s, 1 H), 7.7 (d, J = 10 Hz, 2 H), 7.3 (d, J = 10 Hz, 2 H), 2.4 (s, 3 H), 1.1 (s, 9 H); ^{13}C (100 MHz) δ 183.8, 144.5, 129.6 (2 C), 129.4 (2 C), 127.8, 37.7, 25.6, 21.5; MS calcd for $C_{12}H_{17}NO_2S$ 239.0980, found 239.0999.

10: IR ($CHCl_3$) 1635, 1325, 1160, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.4 (s, 1 H), 7.8 (d, J = 12 Hz, 2 H), 7.35 (d, J = 12 Hz, 2 H), 5.75–5.5 (m, 1 H), 5.02 (d, J = 14 Hz, 1 H), 5.0 (d, J = 19 Hz, 1 H), 2.45 (s, 3 H), 2.20 (d, J = 12 Hz, 2 H), 1.10 (s, 6 H); ^{13}C (75 MHz, $CDCl_3$) δ 184.0, 132.9, 129.9 (2 C), 128.2 (2 C), 119.0, 43.7, 23.4 (2 C), 2.15; MS calcd for $C_{13}H_{16}NO_2S$ ($M^+ - CH_3$) 250.0902, found 250.0888.

11: IR ($CHCl_3$) 1635, 1320, 1160, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 7.8 (d, J = 8 Hz, 2 H), 7.35 (d, J = 8 Hz, 2 H), 2.45 (s, 3 H), 2.15 (t, J = 7 Hz, 2 H), 1.61–1.58 (m, 2 H), 1.41–1.37 (m, 2 H), 1.10 (s, 6 H), 0.18 (s, 9 H); ^{13}C (100 MHz, $CDCl_3$) δ 183.7, 129.8 (2 C), 128.0 (2 C), 106.4, 40.8, 38.6, 23.6, 23.5 (2 C), 21.7, 20.2, 0.1; MS calcd for $C_{19}H_{29}NO_2SSi$ (M^+) 363.1690, found 363.1688.

12: IR ($CHCl_3$) 1635, 1600, 1350, 1165, 1062 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.5 (s, 1 H), 7.8 (d, J = 10 Hz, 2 H), 7.35 (d, J = 10 Hz, 2 H), 4.25 (d, J = 12 Hz, 1 H), 3.8 (d, J = 12 Hz, 1 H), 2.42 (s, 3 H), 1.41 (s, 6 H), 1.30 (s, 3 H); ^{13}C (75 MHz, $CDCl_3$) δ 178.4, 130.1, 129.7 (2 C), 129.6 (2 C), 128.4, 127.3, 72.2, 26.6, 26.3, 21.6; MS calcd for $C_{13}H_{16}NO_4S$ ($M^+ - CH_3$) 282.0800, found 282.0786.

13: IR ($CDCl_3$) 1630, 1570, 1320, 1160, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.5 (s, 1 H), 7.8 (d, J = 10 Hz, 2 H), 7.3 (d, J = 10 Hz, 2 H), 6.85 (s, 1 H), 4.8 (s, 1 H), 4.70 (s, 1 H), 2.52 (br, 1 H), 2.49 (s, 3 H), 2.31 (br, 1 H), 2.2 (m, 3 H), 1.9 (m, 1 H), 1.8 (s, 3 H), 1.45 (m, 1 H); ^{13}C (50 MHz, $CDCl_3$) δ 172.1, 153.1, 148.3, 144.4, 137.1, 135.8, 129.8 (2 C), 128.0 (2 C), 109.7, 40.1, 32.3, 26.0, 22.79, 21.4, 20.4; MS calcd for $C_{17}H_{21}NO_2S$ 303.1293, found 303.1286. Anal. Calcd for $C_{17}H_{21}NO_2S$-0.45H_2O: C, 65.54; H, 7.09; N, 4.50. Found: C, 65.22; H, 6.70; N, 4.25.

14: IR ($CDCl_3$) 1600, 1330, 1160, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7 Hz, 1 H), 7.80 (d, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 4.90 (d, J = 6 Hz, 1 H), 2.43 (s, 3 H), 1.70–1.50 (m, 7 H), 1.30 (s, 3 H), 1.29–1.18 (m, 1 H), 1.17 (s, 3 H); ^{13}C (75 MHz, $CDCl_3$) δ 179.4, 143.4, 136.9, 129.7 (2 C), 128.1 (2 C), 127.8 (2 C), 119.8, 40.7, 38.0, 33.0, 25.6, 22.6, 22.1, 21.6, 18.5; MS calcd for $C_{17}H_{23}NO_2S$ 305.1449, found 305.1453.

15: 2:1 dr; IR ($CDCl_3$) 1635, 1325, 1160, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8 Hz, 0.33 H), 8.39 (d, J = 8 Hz, 0.67 H), 7.9–7.8 (m, 2 H), 7.7 (d, J = 8 Hz, 2 H), 7.35–7.2 (m, 4 H), 7.17–7.13 (m, 1 H), 5.97–5.90 (m, 1 H), 5.73 (s, 1 H), 2.60–2.20 (m, 8 H), 2.10–0.80 (m, 16 H), 0.71 (s, 1.5 H), 0.61 (s, 1.5 H), 0.49 (s, 1.5 H); ^{13}C (75 MHz, $CDCl_3$) δ 182.1, 130.0, 129.9, 129.8, 128.3, 128.2, 126.9, 124.0, 123.9, 118.6, 56.3, 55.0, 54.9, 54.1, 53.8, 53.4, 42.4, 38.1, 35.7, 35.5, 35.3, 33.7, 32.6, 32.5, 31.7, 31.6, 26.7, 24.1, 23.8, 23.7, 21.3, 20.7, 20.5, 17.1, 17.0, 16.0, 12.7, 12.3; MS calcd for $C_{29}H_{39}NO_3S$ 481.2652, found 481.2646.

18: IR ($CDCl_3$) 3370, 1710, 1420, 1385, 1377, 1350, 1320, 1165, 1012 cm^{-1}; ^1H NMR (300 Mhz, $CDCl_3$) δ 7.71 (d, J = 10 Hz, 2 H), 7.29 (d, J = 10 Hz, 2 H), 6.7 (d, J = 11 Hz, 1 H), 6.05 (d, J = 11 Hz, 1 H0, 5.55 (d, J = 4 Hz, 1 H), 4.55 (dd, J = 12.2 Hz, 1 H), 4.47 (d, J = 7 Hz, 1 H), 4.28 (m, 1 H); ^{13}C (75 MHz, $CDCl_3$) δ 129.9, 126.9, 112.4, 110.3, 109.5, 97.5, 72.5, 70.6, 70.5, 26.0, 25.9, 25.0, 23.9, 21.2; MS calcd for $C_{19}H_{25}NO_7S$ 411.1356, found 411.1348.

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Registry No. 1, 65537-76-0; 2, 51608-60-7; 2 aldehyde, 100-52-7; 3, 135822-87-6; 3 aldehyde, 98-01-1; 4, 135822-88-7; 4 aldehyde, 123-11-5; 5, 135822-89-8; 5 aldehyde, 120-57-0; 6, 135822-90-1; 6 aldehyde, 89-98-5; 7, 135822-91-2; 7 aldehyde, 500-22-1; 8, 73845-02-0; 8 aldehyde, 99-61-6; 9, 135822-92-3; 9 aldehyde, 630-19-3; 10, 135822-93-4; 10 aldehyde, 5497-67-6; 11, 135822-94-5; 11 aldehyde, 135823-01-7; 12, 135822-95-6; 12 aldehyde, 68691-67-8; 13, 135822-96-7; 13 aldehyde, 2111-75-3; 14, 135822-97-8; 14 aldehyde, 20104-05-6; (20*R*)-15, 135823-00-6; (20*S*)-15, 135822-98-9; 15 aldehyde, 3986-89-8; 16, 4933-77-1; 17, 69610-41-9; 18, 135822-99-0; 19, 135823-02-8; Te, 13494-80-9; chloramine T, 127-65-1.

Synthesis of a New Macromolecular Ionophore with 2,5-Anhydro-D-glucitol Units via Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-di-*O*-ethyl-D-mannitol

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Ionophores form a lipophilic complex with cations and transport the cations across the membrane by ion complex–decomplex formation. The naturally occurring ionophores include the polyether antibiotics such as monensin and nigericin consisting of a formally linear array of tetrahydrofuranyl and tetrahydropyranyl rings.

Several poly(cyclooxalkanediyl)s have been reported to act as so-called synthetic polyether ionophores. α,ω-Poly(cyclooxalkanediyl) was prepared through the ring expansion of the oxiranes deriving from the polymers of butadiene or cyclopentene, and the striking ability to bind with various size of cations, for example, Li^+, Ba^{2+}, and methylene blue was shown.[1] Poly(7-oxanorbornene) obtained from the metathesis polymerization was characterized by complexing with various cations containing methylene blue and rhodamine 6G as well.[2] Unlike the crown ethers, these acyclic ionophores are supposed to form helical conformers capable of varying pitch and cavity size to optimize multidentate coordination with a given cation. In this work, we report on the synthesis of a new macromolecular ionophore via stereoselective cyclopolymerization of diepoxide.[3]

Results and Discussion

Monomer **1**, which was synthesized from D-mannitol by the method reported by Kuszmann,[4] was polymerized with BF_3·OEt_2 in CH_2Cl_2. The reaction system was homogeneous, thereby eliminating any tendency to gelation. The product **2** obtained was a sticky semisolid soluble in $CHCl_3$,

(1) Schultz, W. J.; Etter, M. C.; Pocius, A. V.; Smith, S. *J. Am. Chem. Soc.* **1980**, *102*, 7981.
(2) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960.
(3) Several reports have been published on the cyclopolymerization of diepoxy compounds, see: (a) Still, J. K.; Culbertson, B. M. *J. Polym. Sci., Part A: Gen. Pap.* **1964**, *2*, 405. (b) Bauer, R. S. *J. Polym. Sci., Part A-1* **1967**, *5*, 2192. (c) Aso, C.; Aito, Y. *Makromol. Chem.* **1964**, *73*, 141. (d) Still, J. K.; Hillman, J. J. *J. Polym. Sci., Part A-1* **1967**, *5*, 2067. (e) Yokota, K.; Hashimoto, H.; Kakuchi, T.; Takada, Y. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 115. (f) Bartulin, J.; Parra, M.; Pamirez, A.; Zunza, H. *Polym. Bull.* **1989**, *22*, 33. (g) Hashimoto, H.; Kakuchi, T.; Yokota, K. *Polym. Bull.* **1991**, *25*, 153.
(4) Kuszmann, J. *Carbohydr. Res.* **1979**, *71*, 123.

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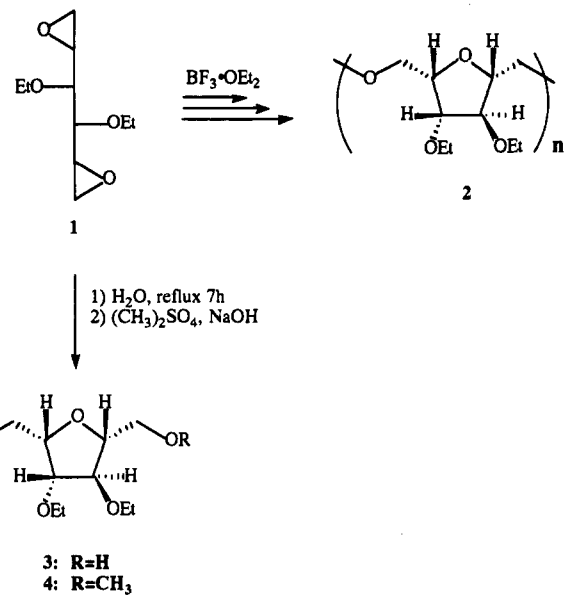
Scheme I



MeOH, and THF and was optically active with a specific rotation $[\alpha]_D$ of +32.7° (*c* 1.14 in $CHCl_3$ at 22 °C). The number-average molecular weight ($\bar{M}_n$) and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were 3550 and 2.3, respectively, which correponds to the degree of polymerization of 18, on the basis of polystyrene standards by means of a gel permeation chromatography. Since the ^1H and ^{13}C NMR spectra of **2** indicated the absence of the epoxy group, the polymerization proceeded according to a cyclopolymerization mechanism leading to the polymer with cyclic constitutional repeating units. Only a trace of polymer was obtained by the polymerizations with $SnCl_4$ or Et_3Al–H_2O–acetylacetone catalyst.[5]

In order to elucidate the cyclic structure of **2**, **1** was hydrolyzed to form a cyclic unimer by the procedure similar to that described by Wiggins for the hydrolysis of 1,2:5,6-dianhydro-3,4-*O*-isopropylidenehexitol,[6] and then its hydrolyzed product was treated with dimethyl sulfate. The identity of the hydrolyzed and the methylated products is confirmed by their ^1H NMR (600-MHz) spectra, in which a 2,5-anhydro-D-glucitol unit is found and thereby both the compounds are recognized as 2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol (**3**) and 2,5-anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (**4**). The good agreement of the ^{13}C NMR spectrum with that of the model compound **4** supports that **2** is composed essentially of the cyclic constitutional unit corresponding to the carbon skeleton of **4**.

Ring opening of a substituted epoxide occurs generally in two ways, that is, by α- or β-scissions.[7] In the polymerization of **1** the intramolecular cyclization with α,α- or β,β-scission of two epoxides in a monomer molecule forms 6-membered rings, whereas α,β- and β,α-scission leads to the formation of 5- and 7-membered rings, respectively. Since **2** consists of (1→6) bonded D-glucitol recurring units, the polymerization proceeds through α,β-scission. The mechanism of the polymerization is shown in Scheme II. The intramolecular cyclization introduces the ring opening of the first epoxide with inversion[8] of the configuration via

Scheme II

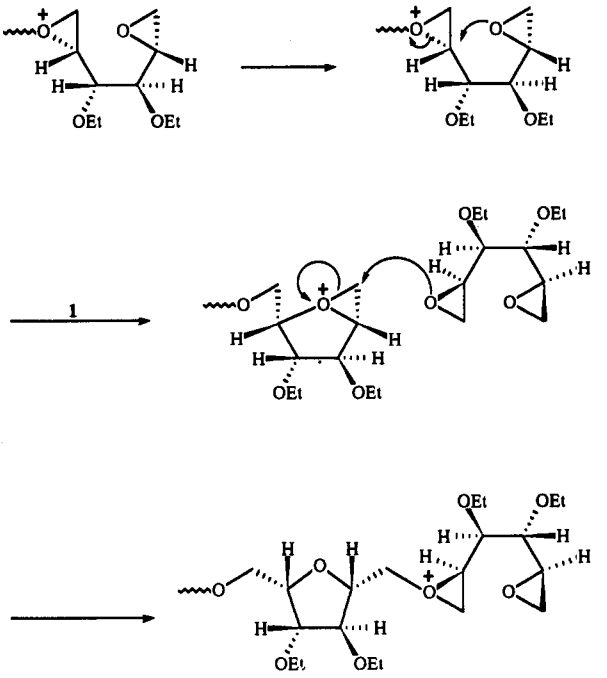


Table I. Extraction of Picrate Salts and Dyes by 2[a]

complexing agent	% picrate extracted					% dye extracted	
	Li^+	Na^+	K^+	Rb^+	Cs^+	M.B.[b]	Rh.6G[c]
2[d]	16.6	38.8	70.8	72.2	71.9	77.0	>99.9
DB-18-C-6[e]	3.7	18.3	93.5	84.9	81.6	0.0[d]	0.0

[a] [Picric acid] = 7×10^{-5} M; [metal hydroxide] = 0.1 M; temperature, 23 °C. [b] [Methylene blue] = 2.24×10^{-5} M. [c] [Rhodamine 6G] = 2.00×10^{-5} M. [d] [**2**] = 1 g·L^{-1}. [e] [Dibenzo-18-crown-6] = 1.26 g·L^{-1} (3.5×10^{-3} M).

Table II. Absorption Maxima of Picrate Salts in the Presence of the Complexing Agent[a]

complexing agent	λ_{max} (nm)				
	Li^+	Na^+	K^+	Rb^+	Cs^+
2	377.2	377.2	377.2	377.2	377.2
DB-18-C-6[b]		368.0	366.8	368.0	374.8

[a] Solvent, CH_2Cl_2. [b] Dibenzo-18-crown-6.

an S_N2 attack of the second epoxide function on the α-carbon of the former oxonium ion. The ring opening of the second epoxide takes place at the β-carbon with retention of the configuration at which carbon the attack is sterically favorable in the intermolecular propagation. In this manner poly[(1→6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol] is yielded by the cyclopolymerization of **1**.

Table I compares **2** with dibenzo-18-crown-6 in the cation-binding ability.[9] The most striking result is that **2** strongly complexes with such larger organic cations as rhodamine 6G and methylene blue in addition to alkali metal ions,[10] unlike the crown ether. The characteristics are very similar to those of poly(2,5-tetrahydrofurandiyl)[1] and poly(7-oxanorbornene),[2] which are supposed to form the helical conformers with the flexible binding cavities.

Every complex of **2** with alkali-metal picrates revealed a pronounced bathochromic shift in comparison with the crown complexes as shown in Table II. Because the absorption maxima of the picrates show the bathochromic

(5) Vandenberg, E. J. *J. Polym. Sci., Part A-1* **1969**, *7*, 525.
(6) (a) Wiggins, L. F.; Wood, D. J. C. *J. Chem. Soc.* **1950**, 1566. (b) Vargha, L.; Kasztreiner, E. *Chem. Ber.* **1959**, *92*, 2506.
(7) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 758.
(8) The α-scission with inversion of the configuration converted D-mannitol unit in the monomer to D-glucitol unit in the polymer.
(9) Pedersen, C. J. *Fed. Am. Soc. Exp. Biol.* **1968**, *27*, 1305.
(10) Wong, K. H.; Yagi, K.; Smid, J. *J. Membr. Biol.* **1974**, *18*, 379.

shift with increasing interionic ion pair distance,[10] the complexes of **2** have the characteristic feature of loose ion pair. The complex with KSCN caused the specific rotation to change,[11] thereby indicating the conformational change in the polymer structure. These observations, therefore, suggest the formation of helical conformer capable of varying in cavity dimensions according to size of such cations as metal ions and dyes.

In conclusion, the cyclopolymerization of diepoxide, namely, 1,2:5,6-dianhydro-3,4-di-*O*-ethyl-D-mannitol, gave poly[(1→6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol], which would effectively bind various sizes of cations in the helical cavity. Further work in this area is in progress.

Experimental Section

General Procedures. NMR spectra were recorded on a Hitachi R90H, a Bruker MSL-400, or a Bruker AMX-600 spectrometer. DEPT, COSY, HMQC, HMBC, DQF-COSY, and NOESY techniques were utilized for assignment of NMR spectra of model compounds and polymers. IR spectra were measured on a JASCO A-102 spectrometer. Specific rotations were measured with JASCO DIP-140 digital polarimeter. UV spectra were recorded on a JASCO UVIDEC-660 spectrometer. Gel permeation chromatography (GPC) in tetrahydrofuran was performed on a WATERS M45 high-performance liquid chromatograph equipped with three columns (Shodex KF-804F).

Solvents for monomer synthesis and polymerizations were dried by general methods: dichloromethane, 1,2-dichloroethane, and nitroethane were dried over CaH_2, and toluene was distilled from sodium–benzophenone. Dibenzo-18-crown-6 was prepared by the method of Pedersen.[12] Methylene blue, rhodamine 6G, and potassium thiocyanate used commercial reagents. 1,2:5,6-Dianhydro-3,4-di-*O*-ethyl-D-mannitol (**1**) was prepared from D-mannitol by the known method.[4] The specific rotation of **1** in $CHCl_3$ (*c* 1.30) at 22 °C: $[\alpha]_D$ −5.2°, $[\alpha]_{577}$ −4.7°, $[\alpha]_{546}$ −5.2°, $[\alpha]_{435}$ −7.2°, and $[\alpha]_{405}$ −7.8° (ref.[4] $[\alpha]_D$ −6.2° (*c* 1.00 in $CHCl_3$)).

Poly[(1→6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol] (2). A typical polymerization procedure is presented here. Monomer **1** (0.50 g, 2.5 mmol) was dissolved in dry CH_2Cl_2 (5 mL), and $BF_3{\cdot}OEt_2$ (3.1 μL, 0.02 mmol) was added by use of a microsyringe. After 24 h at −30 °C, the solution was poured into a large amount of methanol containing a drop of aqueous ammonia, and the resulting solution was replaced by *n*-hexane. The precipitate was isolated and dried under vacuum to yield **2** (190.9 mg, 38%). The specific rotation of **2** in $CHCl_3$ (*c* 1.14) at 22 °C: $[\alpha]_D$ +32.7°, $[\alpha]_{577}$ +33.3°, $[\alpha]_{546}$ +37.3°, $[\alpha]_{435}$ +60.4°, and $[\alpha]_{405}$ +71.4°; IR (film) 2960, 2920, 2890, 2860 (ν, CH), and 1100 cm^{-1} (ν_{as}, COC); ^1H NMR (400 MHz, $CDCl_3$) δ 4.10, 3.93, 3.80–3.33, and 1.19; ^{13}C NMR ($CDCl_3$) δ 84.34 (C-3), 83.15 (C-4), 82.56 and 82.43 (C-2), 79.84 (C-5), 72.06 and 71.87 (C-1), 69.40 (C-6), 65.20 (CH_3CH_2–), and 15.34 (CH_3CH_2–).

2,5-Anhydro-3,4-di-*O*-ethyl-D-glucitol (3). A mixture of 0.52 g (2.6 mmol) of **1** and 10 mL of water was heated under reflux for 7 h, and the solution was then evaporated under reduced pressure. A residual syrup from which the water was removed by azeotropic distillation with benzene and chloroform was purified by column chromatography with chloroform/isopropyl alcohol (8/2, R_f 0.76), give pure **3** (0.35 g, 67%). The specific rotation of **3** in $CHCl_3$ (*c* 1.09) at 20 °C: $[\alpha]_D$ +61.0°, $[\alpha]_{577}$ +64.2°, $[\alpha]_{546}$ +71.9°, $[\alpha]_{435}$ +117.8°, and $[\alpha]_{405}$ +139.4°; IR (film) 3390 (OH), 2960, 2930, 2870 (ν, CH), 1100, 1065, and 1040 cm^{-1} (ν, COC); ^1H NMR (600 MHz, $CDCl_3$) δ 4.10 (H-5), 3.95 (H-4, $^3J_{H\text{-}4,H\text{-}5}$ = 5.2 Hz, $^3J_{H\text{-}3,H\text{-}4}$ = 2.1 Hz), 3.92 (H-2, $^3J_{H\text{-}2,H\text{-}3} \cong$ 6 Hz), 3.89 (H-3), 3.88 (A) and 3.83 (B) (H-6, $^3J_{H\text{-}6A,H\text{-}5}$ = 4.7 Hz, $^3J_{H\text{-}6B,H\text{-}5}$ = 3.9 Hz), 3.84 (A) and 3.69 (B) (H-1, $^3J_{H\text{-}2,H\text{-}1A}$ = 2.6 Hz, $^3J_{H\text{-}2,H\text{-}1B}$ = 3.9 Hz), 3.68 (A) and 3.49 (B) (CH_3CH_2–, $^3J_{gem}$ = 9.0 Hz), 3.60 and 3.55 (CH_3CH_2–), 1.22 (CH_3CH_2–, $^3J_{vic}$ = 6.9 Hz), and 1.21 (CH3CH2–, $^3J_{vic}$ = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 84.86 (C-4), 83.67 (C-2), 83.24 (C-3), 80.26 (C-5), 65.64 (CH_3CH_2–), 62.87 (C-1), 61.81 (C-6), 15.45, and 15.31 (CH_3CH_2–). Anal. Calcd for $C_{10}H_{20}O_5$: C, 54.53; H, 9.15. Found: C, 53.93; H, 9.40.

2,5-Anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (4). To a stirred solution of 0.72 g (3.3 mmol) of **3** in 4.2 mL of dimethyl sulfoxide were simultaneously added a soluton of 0.7 g of sodium hydroxide in 0.7 mL of water and 1.05 g (8.3 mmol) of dimethyl sulfate at the temperature which did not exceed 60 °C. After standing overnight at room temperature, the mixture was poured into water and extracted with chloroform. The extract was dried and evaporated, and the residue was separated by column chromatography with ether. The fractions with R_f 0.69 gave 2,5-anhydro-3,4-di-*O*-ethyl-1,6-di-*O*-methyl-D-glucitol (**4**) (0.66 g, 81%). The specific rotation of **4** in $CHCl_3$ (*c* 1.07) at 22 °C: $[\alpha]_D$ +54.1°, $[\alpha]_{577}$ +56.9°, $[\alpha]_{546}$ +64.2°, $[\alpha]_{435}$ +105.2°, and $[\alpha]_{405}$ +125.3°; IR (film) 2970, 2910, 2875, 2801 (ν, CH), and 1101 cm^{-1} (ν_{as}, COC); ^1H NMR (600 MHz, $CDCl_3$) δ 4.04 (H-5, $^3J_{H\text{-}6A,H\text{-}5}$ = 6.0 Hz, $^3J_{H\text{-}6B,H\text{-}5}$ = 4.7 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 3.9 Hz), 3.85 (H-2, $^3J_{H\text{-}2,H\text{-}1A}$ = 6.0 Hz, $^3J_{H\text{-}2,H\text{-}1B}$ = 6.0 Hz, $^3J_{H\text{-}3,H\text{-}2}$ = 3.4 Hz), 3.70 (H-4, $^3J_{H\text{-}5,H\text{-}4}$ = 3.9 Hz, $^3J_{H\text{-}4,H\text{-}3}$ < 0.5 Hz), 3.64 (H-3, $^3J_{H\text{-}3,H\text{-}2}$ = 3.0 Hz, $^3J_{H\text{-}4,H\text{-}3}$ < 0.5 Hz), 3.51 (A) and 3.55 (B) (H-6, $^3J_{H\text{-}6A,H\text{-}5}$ = 6.9 Hz, $^3J_{H\text{-}6B,H\text{-}5}$ = 4.7 Hz, $^3J_{gem}$ = 9.8 Hz), 3.41 (A) and 3.46 (B) (H-1, $^3J_{H\text{-}2,H\text{-}1A}$ = 5.6 Hz, $^3J_{gem}$ = 9.9 Hz), 3.38 (A) and 3.55 (B) (CH_3CH_2–, $^3J_{vic}$ = 6.9 Hz, $^3J_{gem}$ = 9.0 Hz), 3.45 (A) and 3.50 (B) (CH_3CH_2–), 3.31 (CH_3O–), 1.13 (CH_3CH_2–, $^3J_{vic}$ = 6.9 Hz), and 1.12 (CH_3CH_2–, $^3J_{vic}$ = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 84.3 (C-3), 83.1 (C-4), 82.2 (C-2), 79.7 (C-5), 73.1 (C-1), 70.7 (C-6), 65.0, 64.9 (CH_3CH_2–), 59.0 (CH_3O–), and 15.1 (CH_3CH_2–). Anal. Calcd for $C_{12}H_{24}O_5$: C, 58.04; H, 9.74. Found: C, 58.02; H, 9.76.

Cation Binding Ability. Metal picrate extractions were carried out using a similar procedure as the one developed by Pedersen.[9] Dye extractions were performed by using equal volumes of the dye (0.1 mg in 10 mL of H_2O) and **2** (10 mg in 10 mL of CH_2Cl_2).

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Registry No. **1**, 71223-72-8; **2**, 135822-30-9; **3**, 135822-31-0; **4**, 135822-32-1; methylene blue, 61-73-4; rhodamine 6G, 989-38-8; dibenzo-18-crown-6, 14187-32-7; lithium picrate, 18390-55-1; sodium picrate, 3324-58-1; potassium picrate, 573-83-1; rubidium picrate, 23296-29-9; cerium picrate, 3638-61-7.

Supplementary Material Available: Spectral characterization for **1**–**4** (4 pages). Ordering information is given on any current masthead page.

(11) The complex of **2** with KSCN changed the specific rotation in comparison with that of the original polymer was shown in the Experimental Section: $[\alpha]_D$ +42.7°, $[\alpha]_{577}$ +47.0°, $[\alpha]_{546}$ +52.1°, $[\alpha]_{435}$ +81.9°, and $[\alpha]_{405}$ +93.8° (*c* 1.63 in $CHCl_3$ at 22 °C).

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An MC-SCF Study of the Transition Structures for the Aldol Reaction of Formaldehyde with Acetaldehyde Boron Enolate

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The aldol reaction is one of the most important methods of forming C–C bonds and has become an exceptional tool

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