Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Cation-Binding Properties of (1→6)-2,5-Anhydro-D-glucitol with 3,4-Di-*O*-Pentyl and Decyl Groups by Cyclopolymerization of 1,2:5,6-Dianhydro-D-mannitols

Toyoji Kakuchi[a]; Toshifumi Satoh[b]; Junji Mata[b]; Satoshi Umeda[b]; Hisaho Hashimoto[bc]; Kazuaki Yokota[b]
[a] Division of Bioscience Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, Japan [b] Division of Molecular Chemistry Graduate School of Engineering, Hokkaido University, Sapporo, Japan [c] Department of Industrial Chemistry, Tomakomai National College of Technology, Tomakomai, Japan

To cite this Article Kakuchi, Toyoji , Satoh, Toshifumi , Mata, Junji , Umeda, Satoshi , Hashimoto, Hisaho and Yokota, Kazuaki(1996) 'Synthesis and Cation-Binding Properties of (1→6)-2,5-Anhydro-D-glucitol with 3,4-Di-*O*-Pentyl and Decyl Groups by Cyclopolymerization of 1,2:5,6-Dianhydro-D-mannitols', Journal of Macromolecular Science, Part A, 33: 3, 325 — 336
To link to this Article: DOI: 10.1080/10601329608014323
URL: http://dx.doi.org/10.1080/10601329608014323

J.M.S.—PURE APPL. CHEM., A33(3), pp. 325–336 (1996)

SYNTHESIS AND CATION-BINDING PROPERTIES OF (1→6)-2,5-ANHYDRO-D-GLUCITOL WITH 3,4-DI-*O*-PENTYL AND DECYL GROUPS BY CYCLOPOLYMERIZATION OF 1,2:5,6-DIANHYDRO-D-MANNITOLS

TOYOJI KAKUCHI*

Division of Bioscience
Graduate School of Environmental Earth Science

TOSHIFUMI SATOH,† JUNJI MATA, SATOSHI UMEDA,
HISAHO HASHIMOTO,‡ and KAZUAKI YOKOTA*

Division of Molecular Chemistry
Graduate School of Engineering

Hokkaido University
Sapporo 060, Japan

ABSTRACT

The cyclopolymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-pentyl-D-mannitol (**1b**) and 1,2:5,6-dianhydro-3,4-di-*O*-decyl-D-mannitol (**1c**) were carried out using $BF_3 \cdot OEt_2$ and *t*-BuOK. All the resulting polymers consisted of cyclic constitutional units, i.e., the extent of cyclization was 100%. The polymer structures for the polymerization with *t*-BuOK were

*To whom all correspondence should be addressed. Telephone: international code + 011-706-2290. FAX: international code + 011-706-7882. E-mail: kakuchi@e5.hines.hokudai.ac.jp

†Research Fellow of the Japan Society for the Promotion of Science.

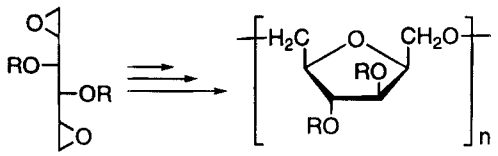
‡Present address: Department of Industrial Chemistry, Tomakomai National College of Technology, Nishikioka 443, Tomakomai 059-12, Japan.

(1→6)-2,5-anhydro-3,4-di-*O*-pentyl-D-glucitol (**2b**) and (1→6)-2,5-anhydro-3,4-di-*O*-decyl-D-glucitol (**2c**), whereas those with $BF_3 \cdot OEt_2$ comprised 2,5-anhydro-D-glucitols as major units along with other cyclic ones. These polymers were soluble in *n*-hexane, $CHCl_3$, and THF, but insoluble in water, which differs from the amphiphilic solubility of (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**2a**). The cation-binding properties of **2b** and **2c** were examined using alkali-metal picrates in order to compare them with those of **2a**. The extraction yields for each cation decreased in the order of **2c** < **2b** < **2a**. Every polymer exhibited a similar cation-binding selectivity in the order $Cs^+ > Rb^+ > K^+ \gg Na^+ > Li^+$. The ratio of K^+ and Na^+, K^+/Na^+, was 4.6 for **2a**, 5.1 for **2b**, and 7.1 for **2c** in the increasing order **2a** < **2b** < **2c**.

INTRODUCTION

For the cyclopolymerization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**1a**), the structure of cyclic repeating units in the resulting polymer depended on the nature of the catalysts used. The polymer using *t*-BuOK was (1→6)-bonded 2,5-anhydro-D-glucitol, i.e., (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**2a**) [1], whereas that consisting of mainly 2,5-anhydro-D-glucitol as the cyclic constitutional units was obtained using $BF_3 \cdot OEt_2$ [2, 3]. The structural characteristic of **2a** is a lack of the anomeric linkage which is found in the naturally occurring polysaccharides, and hence **2a** is a new type of polycarbohydrate. (See Scheme 1.)

Polymer **2a** acted as a host in the host–guest complexation, thereby exhibiting cation-binding selectivity in the order $Cs^+ > Rb^+ > K^+ \gg Na^+ > Li^+$ and the chiral discrimination property toward racemic amino acids [2, 4, 5]. A part of our research interests is the utilization of **2a** as an agent for a specific separation of substrates. The recovery of **2a**, however, was difficult because of its amphiphilic solubility, i.e., **2a** is soluble in $CHCl_3$, THF, and CH_3OH, and also in H_2O. A similar problem was found with crown ether; for example, the hydrophilic property of 18-crown-6 was decreased by introducing a long alkyl chain into the ring [6, 7]. This strategy seems to be useful for improving the solubility property of **2a**. There are two synthetic routes for **2a** with alkyl chain groups: 1) the synthesis and cyclopolymerization of 3,4-di-*O*-alkyl-1,2:5,6-dianhydro-D-mannitol, and 2) the substitu-



1 **2**

1a, 2a: R=CH_3; 1b, 2b: R=*n*-C_5H_{11}; 1c, 2c: R=*n*-$C_{10}H_{21}$; 1d, 2d: R=H

SCHEME 1

tion of alkyl groups at 3,4-di-*O*-positions of (1→6)-2,5-anhydro-D-glucitol (**2d**) [8]. The aim of this study is the synthesis of 3,4-di-*O*-alkyl substituted (1→6)-2,5-anhydro-D-glucitol by the former method.

In this paper we report the cyclopolymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-pentyl- and 3,4-di-*O*-decyl-D-mannitol (**1b** and **1c**) using $BF_3 \cdot OEt_2$ and *t*-BuOK. The polymer structures are confirmed by comparing the ^{13}C-NMR spectra with that of (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**2a**). In addition, the binding properties of **2b** and **2c** toward alkali-metal picrates are examined using the liquid-liquid extraction method.

EXPERIMENTAL

Measurement

^1H- and ^{13}C-NMR spectra were recorded with a Jeol JNM-EX270 instrument. UV spectra were run with a Jasco 660 UV/VIS spectrophotometer. Optical rotation was determined 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 Jasco HPLC system equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight (M_n) was calculated on the basis of polystyrene calibration.

Materials

Boron trifluoride etherate ($BF_3 \cdot OEt_2$) was purified by distillation of a commercial product under reduced pressure. Potassium *tert*-butoxide (*t*-BuOK) was purified by sublimation under vacuum before use. All solvents were purified by the usual methods, and dichloromethane, nitroethane, and toluene were distilled over calcium hydride and 1,4-dioxane and THF from sodium benzophenone.

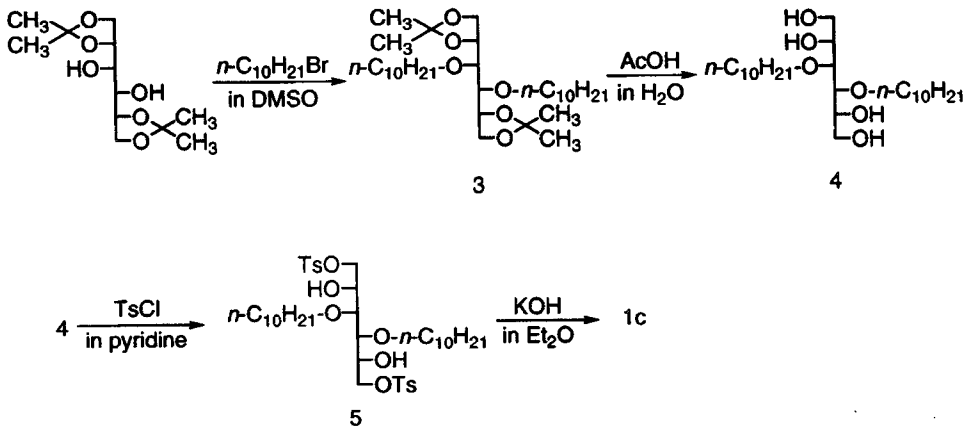
Monomers

1,2:5,6-Dianhydro-3,4-di-*O*-pentyl-D-mannitol (**1b**) was prepared by the procedure of Kuszmann [9], bp 105°C/0.1 torr. $[\alpha]_D$ + 9.3° (*c* = 1.0 in $CHCl_3$ at 22°C); ^1H NMR ($CDCl_3$) δ 0.89 (*t*, $^3J_{vic}$ = 7.1 Hz, 6H, pentyl-CH_3), 1.28–1.36 (b, 8H, pentyl-CH_2), 1.55–1.61 (m, 4H, $OCH_2CH_2-C_3H_7$), 2.79 (dd, J_{gem} = 5.3 Hz, $^3J_{trans}$ = 2.6 Hz, C1-, C6-*trans*-CH_2), 2.85 (dd, J_{gem} = 5.4 Hz, $^3J_{cis}$ = 3.8 Hz, C1-, C6-*cis*-CH_2), 3.12–3.16 (m, 2H, C2-, C5-CH), 3.26–3.30 (m, 2H, C3-, C4-CH), 3.47–3.66 (m, 4H, $-OCH_2-$, C_4H_9, CH); ^{13}C NMR ($CDCl_3$): δ 14.00 (CH_3), 22.45, 28.10, 29.59 (CH_2), 46.13 (C1, C6), 50.54 (C2, C5), 72.01 (OCH_2), 79.56 (C3, C4).

1,2:5,6-Dianhydro-3,4-di-*O*-decyl-D-mannitol (**1c**) was synthesized using the procedure similar to that for **1b**, as shown in Scheme 2.

3,4-Di-*O*-decyl-1,2:5,6-di-*O*-isopropyridene-D-mannitol (3)

To a mixture of 36 g (0.9 mol) of sodium hydride (60% mineral oil suspension) in 300 mL of dry THF was added a solution of 104.8 g (0.4 mol) of 1.2:5,6-di-*O*-isopropyridene-D-mannitol in 300 mL of dry THF. After stirring for 12



SCHEME 2

hours, a solution of 176.9 g (0.8 mol) of 1-bromodecane in 160 mL of dry DMSO was added, and then the mixture was stirred at 50°C for 4 hours. The reaction mixture was chilled, diluted with water, and extracted with chloroform. The extract was washed with water, dried with Na_2SO_4, and evaporated under reduced pressure. The residue was distilled to give 94 g (yield, 43.4%) of **3**, bp 170°C/6 × 10^{-5} torr. $[\alpha]_D$ + 14.4° (*c* = 1.0 in $CHCl_3$ at 22°C); R_f 0.29 (ethyl acetate/*n*-hexane, 1/10); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $^3J_{vic}$ = 6.8 Hz, 6H, CH_3), 1.27 (s, 28H, CH_2), 1.38 (s, 12H, $C(CH_3)_2$), 1.54–1.57 (m, 4H, $-OCH_2CH_2-C_8H_{17}$), 3.52 (d, $^3J_{vic}$ = 6.1 Hz, 2H, C3-, C4-CH), 3.56–3.62 (m, 4H, $-OCH_2-C_9H_{19}$), 3.92 (dd, J_{gem} = 8.2 Hz, $^3J_{cis}$ = 6.6 Hz, C1-, C6-*cis*-CH_2), 4.08 (dd, J_{gem} = 8.2 Hz, $^3J_{trans}$ = 6.2 Hz, C1-, C6-*trans*-CH_2), 4.19 (q, *J* = 6.25 Hz, 2H, C2-, C5-CH); ^{13}C NMR ($CDCl_3$) δ 14.11 (CH_3), 22.68, 26.08 ($C(CH_3)_2$), 25.43, 26.72, 29.32, 29.52, 29.59, 31.89 (CH_2), 30.31 ($-OCH_2CH_2-C_8H_{17}$), 66.81 (C1, C6), 73.42 ($-OCH_2-C_9H_{19}$), 75.81 (C2, C5), 80.40 (C3, C4), 108.45 ($C(CH_3)_2$).

Analysis. Calculated for $C_{32}H_{62}O_6$ (542.84): C, 70.80; H, 11.51. Found: C, 70.79; H, 11.69.

3,4-Di-*O*-decyl-D-mannitol (4)

A solution of 23.2 g (43 mmol) of **3** in 116 mL of acetic acid and 58 mL of water was refluxed for 30 minutes. After cooling, the mixture was evaporated under reduced pressure. This procedure was repeated until the odor of acetic acid disappeared. The residue was recrystallized from ethyl acetate to give 13.7 g (yield, 69.5%) of **4**, mp 93°C. R_f 0.57 (methanol/chloroform, 1/5); $[\alpha]_D$ + 26.7° (*c* = 1.0 in CH_3OH at 22°C); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, $^3J_{vic}$ = 6.9 Hz, 6H, CH_3), 1.25–1.40 (b, 28H, CH_2), 1.53–1.59 (m, 4H, $-OCH_2CH_2-C_8H_{17}$), 3.30–3.37 (m, 4H, $-OCH_2-C_9H_{19}$), 3.56–3.75 (m, 10H, C1-, C6-CH_2, C2-, C3-, C4-, C5-CH), 3.80 (dd, 2H, *J* = 11.1 Hz, *J* = 2.7 Hz, C1-, C6-CH_2); ^{13}C NMR ($CDCl_3$) δ 14.77 (CH_3), 24.03, 27.59, 30.77, 31.01, 32.67 (CH_2), 31.70 ($-OCH_2CH_2-C_8H_{17}$), 65.00 (C1, C6), 74.20 ($-OCH_2-C_9H_{19}$), 72.70 (C2, C5), 80.36 (C3, C4).

Analysis. Calculated for $C_{26}H_{54}O_6$ (462.71): C, 67.49; H, 11.76. Found: C, 66.90; H, 11.93.

3,4-Di-*O*-decyl-1,6-di-*O*-*p*-toluenesulfonyl-D-mannitol (5)

To a solution of 12.7 g (27 mmol) of **4** in 60 mL of pyridine was added 11.3 g (59 mmol) of *p*-toluenesulfonyl chloride at 0°C. After stirring at 0°C for 0.5 hour and then at room temperature for 0.5 hour, water was added, and the mixture was extracted with chloroform. The extracts were washed with dilute hydrochloric acid, dried under Na_2SO_2, and evaporated under reduced pressure. The residue was chromatographed on silica gel with ethyl acetate/*n*-hexane (1/7) to give 17.8 g (yield, 80.2%) of **5**. R_f 0.30; $[\alpha]_D$ + 16.3 (c = 1.0 in $CHCl_3$ at 22°C); ^1H NMR ($CDCl_3$) δ 0.89 (t, 6H, CH_3), 1.26 (s, 28H, CH_2), 1.43–1.48 (m, 4H, $-OCH_2CH_2-C_8H_{17}$), 2.45 (s, 6H, $ArCH_3$), 3.40–3.62 (m, 6H, $-OCH_2-C_9H_{19}$, CH), 3.96–4.01 (m, 2H, CH), 4.17–4.19 (m, 4H, C1-, C6-CH_2), 7.34–7.37 (m, 4H, Ar), 7.79–7.82 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.10 (CH_3), 22.66 ($ArCH_3$), 25.90, 29.30, 29.56, 31.88 (CH_2), 31.70 ($-OCH_2CH_2-C_8H_{17}$), 69.46, 76.60 (CH), 71.11 (C1, C6), 72.95 ($-OCH_2-C_9H_{19}$), 128.03, 129.90 (Ar).

Analysis. Calculated for $C_{40}H_{66}O_{10}S_2$ (771.09): C, 62.31; H, 8.63; S, 8.32. Found: C, 61.46; H, 8.71; S, 8.00.

1,2:5,6-Dianhydro-3,4-di-*O*-decyl-D-mannitol (1c)

A mixture of 18.8 g (24 mmol) of **5** and 3.2 g of ground KOH in 100 mL of ether was vigorously stirred under reflux for 1 hour. After the mixture cooled, the precipitates were removed by filtering the mixture through a pad of Celite, and then the filtrate was evaporated under reduced pressure. The residue was distilled under reduced pressure to give 2.2 g (yield, 22.1%) of **1c** as a colorless liquid, bp 120°C/6 $\times 10^{-5}$ torr. R_f 0.3 (ethyl acetate/*n*-hexane, 1/7); $[\alpha]_D$ + 6.8° (c = 1.0 in $CHCl_3$ at 22°C); ^1H NMR ($CDCl_3$) δ 0.88 (t, $^3J_{vic}$ = 6.9 Hz, 6H, decyl-CH_3), 1.21–1.31 (b, 28H, decyl-CH_2), 1.54–1.62 (m, 4H, $-OCH_2CH_2-C_8H_{17}$), 2.79 (dd, J_{gem} = 5.4 Hz, $^3J_{trans}$ = 2.7 Hz, C6-CH_2), 2.85 (dd, J_{gem} = 5.4 Hz, $^3J_{cis}$ = 3.9 Hz, C6-CH_2), 3.13–3.16 (m, 2H, C2, C5-CH_2), 3.26–3.28 (m, 2H, C3-, C4-CH), 3.46 (dd, 2H, J_{gem} = 9.3 Hz, $^3J_{vic}$ = 6.9 Hz, $-OCH_2-C_9H_{19}$), 3.67 (dd, 2H, J_{gem} = 9.3 Hz, $^3J_{vic}$ = 6.6 Hz, $-OCH_2-C_9H_{19}$); ^{13}C NMR ($CDCl_3$) δ 14.08 (CH_3), 22.64, 25.96, 29.29, 29.41, 29.54, 29.57, 31.88 (CH_2), 29.92 ($-OCH_2CH_2-C_8H_{17}$), 46.11 (C1, C6), 50.54 (C2, C5), 72.03 ($OCH_{21-C9}H_{19}$), 79.56 (C3, C4).

Analysis. Calculated for $C_{26}H_{50}O_4$ (426.69): C, 73.18; H, 11.82. Found: C, 73.01; H, 11.83.

Polymerization Using $BF_3 \cdot OEt_2$

A typical polymerization procedure is as follows: Monomer **1b** (500 mg, 1.75 mmol) was dissolved in dry CH_2Cl_2 (3.50 mL), and a solution of $BF \cdot OEt_t$ in CH_2Cl_2 (24.8 μL in 0.70 mol·L^{-1}, 0.0175 mmol) was added using a microsyringe at 0°C. After 24 hours the reaction mixture was poured into a large amount of methanol containing a drop of aqueous ammonia, and the entire solution was evaporated under reduced pressure. The residue was extracted using *n*-hexane/MeOH, and the

MeOH layer was evaporated under reduced pressure. This procedure was repeated several times until the monomer in the product obtained from the MeOH phase disappeared in the GPC trace (158 mg, 31.6%). The M_n and M_w/M_n were 6200 and 1.98, respectively. $[\alpha]_D$ + 19.7° (C = 1.0 in $CHCl_3$ at 22°C); ^{13}C NMR ($CDCl_3$) δ 14.02 (CH_3), 22.46, 22.50 ($-CH_2CH_3$), 28.33, 28.37 ($-OC_2H_4-CH_2-C_2H_5$), 29.48, 29.54 ($-OCH_2CH_2-C_3H_2$), 69.39 (C6) 69.77, 69.89 ($-OCH_2$), 71.96 (C1), 79.97 (C5), 82.44 (C2), 83.26 (C4), and 84.38 ppm (C3).

Polymerization Using *t*-BuOK

A typical polymerization procedure is as follows: The polymerization was carried out in a H-shaped glass ampule. *t*-BuOK (4.2 mg, 0.035 mmol) and dry THF (0.72 mL) were added to one side of the ampule, and **1c** (309 mg, 0.72 mmol) was added to the other side of the ampule under a nitrogen atmosphere. After sealing under vacuum, the monomer and the catalyst solution were mixed at 60°C. After 48 hours the reaction mixture was poured into a large amount of methanol containing a drop of 0.1 N hydrochloric acid, and the entire solution was evaporated under reduced pressure. The residue was purified by reprecipitation from *n*-hexane/MeOH to give the polymer (170 mg, 53.4%). The M_n and M_w/M_n were 7600 and 1.25, respectively. $[\alpha]_D$ + 23.7° (c = 1.0 in $CHCl_3$ at 22°C); ^{13}C NMR ($CDCl_3$) δ 14.11 (CH_3), 22.68 ($-CH_2CH_3$), 26.19, 26.24 (CH_2), 29.36 (CH_2), 29.54 (CH_2), 29.63, 29.66 (CH_2), 29.84 (CH_2), 29.92 (CH_2), 31.91 (CH_2), 69.30 (C6) 69.80, 69.98 ($-OCH_2$), 72.00 (C1), 79.92 (C5), 82.38 (C2), 83.25 (C4), and 84.45 ppm (C3).

Cation-Binding Property

The extraction of alkali metal picrates was carried out using a procedure similar to the one developed by Pedersen [10]. A solution of polymer in dichloromethane ([2,5-anhydro-D-glucitol units in polymer] = 4.5×10^{-4} mol·L^{-1}) was vigorously shaken in a culture tube with a solution of alkali hydroxide and picric acid in water ([metal hydroxide] = 0.1 mol·L^{-1} and [picric acid] = 7×10^{-5} mol·L^{-1}). After separating into two phases, the alkali picrate extracted into dichloromethane was determined by measuring the absorbance of picrate remaining in the aqueous phase at 357 nm on a UV spectrophotometer.

RESULTS AND DISCUSSION

Cyclopolymerization of 1,2:5,6-Dianhydro-D-mannitol

Table 1 lists the results of the polymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-pentyl-D-mannitol (**1b**) and 1,2:5,6-dianhydro-3,4-di-*O*-decyl-D-mannitol (**1c**) using $BF_3 \cdot {}_3OEt_2$ and *t*-BuOK. All the polymerizations using $BF_3 \cdot OEt_2$ proceeded homogeneously. After 24 hours at 0°C the reaction mixture was poured into methanol containing a drop of aqueous ammonia and the solution was evaporated to yield an oil residue consisting of the monomer and polymer. Monomer **1b** could not be removed from the mixture by the same solvent, such as *n*-hexane, $CHCl_3$, THF, and

TABLE 1. Cyclopolymerization of 1,2:5,6-Dianhydro-3,4-di-*O*-R-D-mannitol (**1**) with $BF_3 \cdot OEt_2$ and *t*-BuOK

Monomer	Catalyst	Solvent	Yield, %	M_n (M_w/M_n)[c]	$[\alpha]_D^{22}$[d]
1b (R = *n*-C_5H_{11})	$BF_3 \cdot OEt_2$[a]	$C_6H_5CH_3$	–	2700 (1.22)	–
		CH_2Cl_2	31.6	6200 (1.34)	+25.8
		$C_2H_5NO_2$	–	2600 (1.61)	–
	t-BuOK[b]	1,4-Dioxane	38.9	6700 (1.27)	+38.9
		THF	39.8	7600 (1.32)	+32.8
1c (R = *n*-$C_{10}H_{21}$)	$BF_3 \cdot OEt_2$[a]	$C_6H_5CH_3$	44.5	4200 (1.20)	+15.6
		CH_2Cl_2	46.2	3900 (1.41)	+16.0
		$C_2H_5NO_2$	48.9	4600 (1.29)	+14.4
	t-BuOK[b]	$C_6H_5CH_3$	74.7	8400 (1.33)	+22.1
		THF	53.4	7600 (1.25)	+23.7

[a][M] = 0.5 mol·L^{-1}; [$BF_3 \cdot OEt_2$] = 5 mmol·L^{-1}; 0°C; 24 hours.
[b][M] = 1.0 mol·L^{-1}; [M]/[*t*-BuOK] = 20; 60°C; 48 hours.
[c]Estimated by GPC using polystyrene as standard.
[d]*c* 1.0 in $CHCl_3$.

MeOH, as the resulting polymer. The mixture was extracted using *n*-hexane/MeOH, and the MeOH layer was evaporated under reduced pressure. This procedure was repeated until the absence of the monomer in the product obtained from MeOH phase was confirmed using GPC measurement. For the polymerization in CH_2Cl_2, the yield was 31.6% and the number-average molecular weight (M_n) was 6200, which corresponded to a degree of polymerization (DP) of 21.6. However, the purification of the raw products obtained in $C_6H_5CH_3$ and $C_2H_5NO_2$ was incomplete because of their lower M_ns. The values of 2700 and 2600 listed in Table 1 were estimated from the GPC traces of the mixtures. On the other hand, the polymers from **1c** were soluble in *n*-hexane, $CHCl_3$, and THF but insoluble in MeOH, so they were purified by reprecipitation from *n*-hexane/MeOH. The polymer yields were 44.5–48.9% and the M_n was 3900–4600 (DP = 9.1–10.8). The specific rotation ($[\alpha]_D$) was +25.8 for the polymer from **1b** and +14.4 to +16.0 for those from **1c** (*c* = 1.0 in $CHCl_3$ at 22°C).

For the polymerization using *t*-BuOK, the catalyst gradually dissolved into the reaction system during a few hours. The solubility properties of the resulting polymers in organic solvents were similar to those using $BF_3 \cdot OEt_2$. The yield and M_n of the polymers were higher than those using $BF_3 \cdot OEt_2$. The highest value of M_n was 7600 (DP = 26.5) for the polymer from **1b** in THF and 8400 (DP = 19.7) for that from **1c** in $C_6H_5CH_3$. The specific rotations ($[\alpha]_D$) were +38.9 and +32.8 for the polymers from **1b** and +22.1 and +23.7 for those from **1c** (*c* = 1.0 in $CHCl_3$ at 22°C).

The polymers synthesized from **1b** and **1c** were soluble in common organic solvents but insoluble in water, which differed from polymer **2a** because of its amphiphilic solubility. This means that these polymers are expected to be easily recovered after using complex agents in the host–guest system.

Polymer Structure

Figure 1 shows the ^{1}H-NMR spectra of the polymers obtained from the polymerizations of **1b** and **1c** in CH_2Cl_2 using $BF_3 \cdot OEt_2$. Because the characteristic absorption at 2.7–3.2 ppm due to the epoxy groups completely disappeared, the polymerization proceeded according to a cyclopolymerization mechanism, leading to polymers consisting of cyclic constitutional repeating units. For the polymers using *t*-BuOK, the absorption due to the epoxy protons also disappeared in the ^{1}H-NMR spectra, i.e., the extent of cyclization was 100% as well as for the polymers using $BF_3 \cdot OEt_2$.

The ^{13}C-NMR spectra of the polymers from **1b** and **1c** using $BF \cdot OEt_2$ are shown in Fig. 2. For the polymer from **1b**, the signals at 79.97, 82.44, 83.26, and 84.38 ppm were the methine carbons and those at 69.39 and 71.96 ppm were the methylene ones. For the polymer from **1c**, those at 79.92, 82.38, 83.25, and 85.45 ppm were the methine carbons and those at 69.30 and 72.00 ppm were the methylene ones. Both of the four signals due to the methine carbons are very close to those at 79.83, 82.23, 84.69, and 85.43 ppm assigned to the carbons of C5, C2, C4, and C3 for 2a, respectively [1–3]. This result indicates that the structure of the polymers from both **1b** and **1c** was 1→6 bonded 2,5-anhydro-D-mannitol as the 5-membered

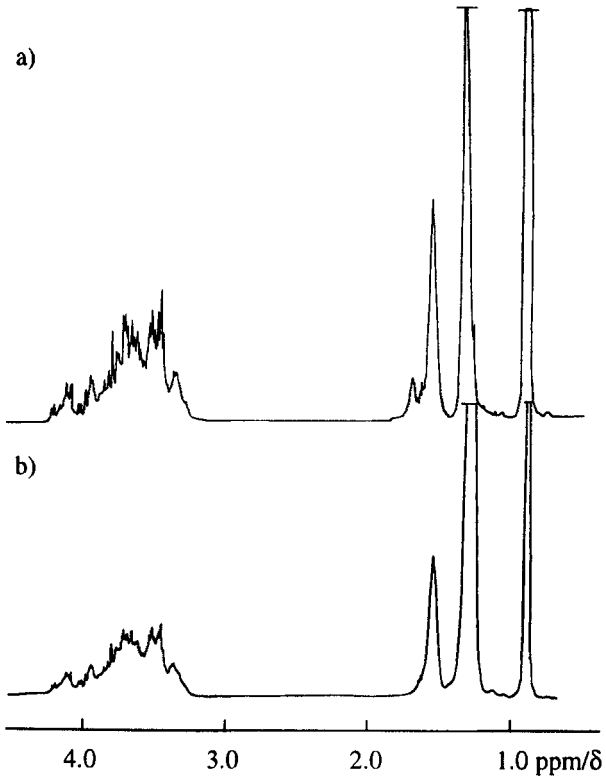


FIG. 1. ^{13}H-NMR (270 MHz, $CDCl_3$) spectra of the polymers **2b** (a) and **2c** (b) obtained with $BF_3 \cdot OEt_2$.

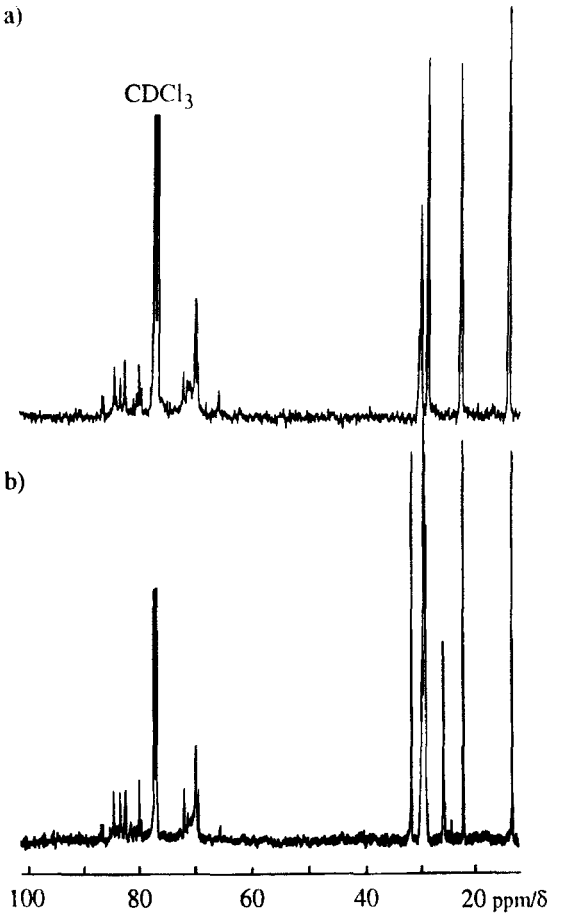


FIG. 2. ^{13}C-NMR (67.5 MHz, $CDCl_3$) spectra of the polymers **2b** (a) and **2c** (b) obtained with $BF_3 \cdot OEt_2$.

constitutional unit. However, many small signals were observed, so that the polymer should contain a slight amount of other cyclic repeating units except for 2,5-anydro-D-mannitol. Their mole fraction could not be determined by ^{13}C-NMR spectra. These results were very similar to the polymer structure from **1a** [3].

On the other hand, sharp signals were observed in the ^{13}C-NMR spectra of the polymers using *t*-BuOK (Fig. 3), which apparently differs from observatons for the polymers using $BF_3 \cdot OEt_2$. This result means that the polymerization using *t*-BuOK was more highly regio- and stereoselective than that using $BF_3 \cdot OEt_2$. The polymer structures from **1b** and **1c** using *t*-BuOK were (1→6)-2,5-anhydro-3,4-di-*O*-pentyl-D-glucitol (**2b**) and (1→6)-2,5-anhydro-3,4-di-*O*-decyl-D-glucitol (**2c**), respectively.

For the cyclopolymerization of **1**, there was a little difference in the cyclic structural units between the polymers using cationic and anionic catalysts, which can be explained by the general rules for ring closure on the basis of the stereoelectronic effect [11]. In general, the cyclization of 1,2:5,6-diepoxyhexane is supposed

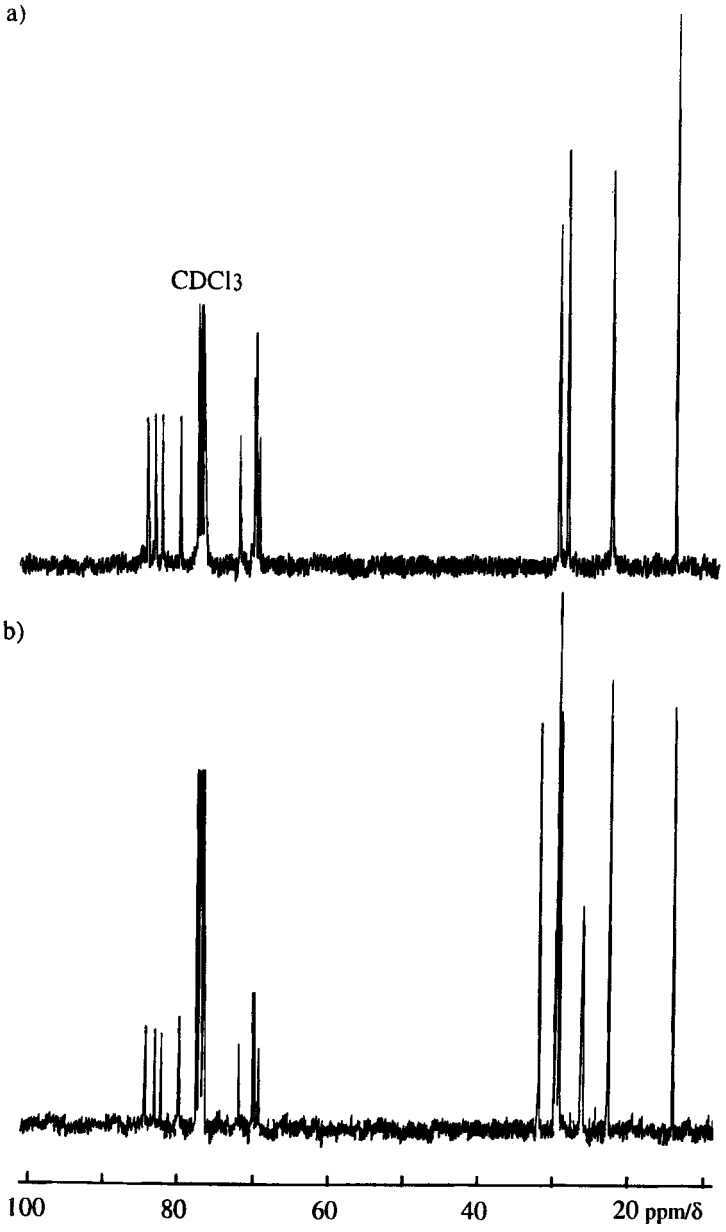


FIG. 3. ^{13}C-NMR (67.5 MHz, $CDCl_3$) spectra of the polymers **2b** (a) and **2c** (b) obtained with *t*-BuOK.

TABLE 2. Extraction Yield of Alkali-Metal Picrates by (1→6)-2,5-Anhydro-3,4-di-*O*-R-D-glucitol (**2**)[a]

Polymer	% Picrate extracted				
	Li^+	Na^+	K^+	Rb^+	Cs^+
2a (R = CH_3)[b]	8.2	13.3	61.3	69.9	76.9
2b (R = n-C_5H_{11})[c]	3.5	9.6	49.4	61.1	66.5
2c (R = n-$C_{10}H_{21}$)[d]	3.7	6.1	43.5	57.1	60.8

[a][2,5-Anhydro-D-glucitol units in polymer] = 4.5×10^{-4} mol·L^{-1} in CH_2Cl_2; [picric acid] = 7×10^{-5} mol·L^{-1} and [alkali hydroxide] = 0.1 mol·L^{-1} in H_2O; 23°C.

[b]M_n = 3000 (DP = 17.2).

[c]M_n = 6700 (DP = 23.4).

[d]M_n = 8400 (DP = 19.7).

to form a 5-membered cyclic product under anionic conditions [12, 13], whereas 5- and 6-membered ones form under cationic conditions. This regioselectivity caused the stereoregularity in the polymer which depended on the catalyst used; nevertheless, the D-mannitol structure in monomer **1** primarily changed to the D-glucitol one in polymer **2**. Therefore **2** should be produced through the regio- and stereospecific cyclopolymerization mechanism. For the intermolecular reaction, the first epoxide cleaved at the β-bond (CH_2—O), resulting in retention of the *R* configuration of the α-carbon. On the other hand, the intramolecular cyclization proceeded through cleavage at the α-bond (CH—O) of the second epoxide to form a 5-membered ring, and the configuration of the α-carbon was inverted from the *R* to the *S* [1, 3, 5, 14].

For 1,2:5,6-dianhydro-D-mannitol (**1**), the 3,4-di-*O*-alkyl substituted monomer were regio- and stereoselectively cyclopolymerized to yield (1→6)-3,4-di-*O*-alkyl-2,5-anhydro-D-glucitol (**2**) except for the monomer with a 3,4-di-*O*-isopropylidene group [14].

Cation-Binding Property

The cation-binding properties of (1→6)-2,5-anhydro-3,4-di-*O*-pentyl-D-glucitol (**2b**) and (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**2a**). For this purpose the specimens used were the polymers with similar degrees of polymerization (DP); **2a** with M_n = 3000 (DP = 17.2), **2b** with M_n = 6700 (DP = 23.4), and **2c** with M_n = 8400 (DP = 19.7). Table 2 lists the results of a one-extraction experiment using picrates of Li^+, Na^+, K^+, Rb^+, and Cs^+. The extraction yields for each cation decreased in the order **2a** > **2b** > **2c**. Every polymer was similar in cation-binding selectivities in the order $Cs^+ > Rb^+ > K^+ \gg Na^+ > Li^+$. However, there is a small difference in the selectivity between K^+ and Na^+. The ratio of K^+ and Na^+, K^+/Na^+, was 4.6 for **2a**, 5.1 for **2b**, and 7.1 for **2c**, resulting in an increase in the order **2a** < **2b** < **2c**. This indicates that the 3,4-di-*O*-alkyl groups of (1→6)-2,5-anhydro-D-glucitol (**2**) slightly affect the cation-binding property, and the oxygens at the 3,4-position act as donor atoms in the host-guest complexation.

CONCLUSIONS

The cyclopolymerizations of 3,4-di-*O*-pentyl- and 3,4-di-*O*-decyl-1,2:5,6-dianhydro-D-mannitol were carried out using $BF3 \cdot OEt_2$ and *t*-BuOK. The polymers obtained using *t*-BuOK, (1→6)-2,5-anhydro-3,4-di-*O*-pentyl-D-glucitol (**2b**) and (1→6)-2,5-anhydro-3,4-di-*O*-decyl-D-glucitol (**2c**), were more highly regio- and stereoselective than those using $BF_3 \cdot OEt_2$. Therefore, this highly selective cyclopolymerization of 1,2:5,6-dianhydrohexitol by using an anionic cataylst is a new method for producing an artificial polycarbohydrate which differs from the ring-opening polymerization of the anhydro sugar. Polymers **2b** and **2c** were soluble in *n*-hexane, $CHCl_3$, and THF but insoluble in water, which differs from the amphiphilic solubility of (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**2a**). For the binding ability toward alkali-metal picrates, the extraction yields for each cation decreased in the order **2c** < **2b** < **2a**. Every polymer exhibited similar cation-binding selectivities in the order $Cs^+ > Rb^+ > K^+ \gg Na^+ > Li^+$, though there was a small difference in the selectivity between K^+ and Na^+.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid Scientific Research from the Ministry of Education, Science, and Culture, Japan.

REFERENCES

[1] T. Satoh, K. Yokota, and T. Kakuchi, *Macromolecules, 28*, 4762 (1955).
[2] T. Kakuchi, Y. Harada, T. Satoh, and K. Yokota, *Polymer, 35*, 204 (1994).
[3] T. Kakuchi, T. Satoh, S. Umeda, H. Hashimoto, and K. Yokota, *Macromolecules, 28*, 5643 (1995).
[4] T. Kakuchi, T. Satoh, S. Umeda, J. Mata, and K. Yokota, *Chirality, 7*, 136 (1995).
[5] H. Hashimoto, T. Kakuchi, and K. Yokota, *J. Org. Chem., 56*, 6471 (1991).
[6] M. Cinquini and P. Tundo, *Synthesis*, p. 516 (1976).
[7] F. Montanari and P. Tundo, *Tetrahedron. Lett., 52*, 5055 (1979).
[8] T. Kakuchi, S. Umeda, T. Satoh, H. Hashimoto, and K. Yokota, *Macromol. Rep., A32*(7), 1007 (1995).
[9] J. Kuszmann, *Carbohydr. Res., 71*, 123 (1979).
[10] C. J. Pedersen, *Fed. Am. Soc. Exp. Biol., 27*, 1305 (1968).
[11] J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, p. 734 (1976).
[12] J. K. Stille and B. M. Culbertson, *J. Polym. Sci., Part A, 2*, 405 (1964).
[13] R. S. Bauer, *J. Polym. Sci., Part A-1, 5*, 2192 (1967).
[14] T. Kakuchi, T. Satoh, S. Umeda, H. Hashimoto, and K. Yokota, *Macromolecules, 28*, 4062 (1995).

Received May 25, 1995
Revision received July 19, 1995