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Chemical Synthesis of Polysaccharides VI. Synthesis of (1→6)-α-DL-Glucopyranan (DL-Dextran) by the Ring-Opening Polymerization Method

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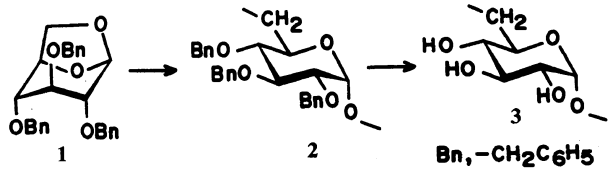
ABSTRACT: A new DL-polysaccharide (1→6)-α-DL-glucopyranan (DL-dextran, **3**) was synthesized by the cationic ring-opening polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-DL-glucopyranose (**1**) followed by debenzylation of the resulting polymer (**2**). The anhydrosugar derivative **1** was prepared from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer, **4**) *via* eight reaction steps. Polymerization of **1** was undertaken using *o*-fluorotoluene, dichloromethane, and 1-nitropropane as solvents and phosphorus pentafluoride, antimony pentachloride, and tantalum pentachloride as initiators at different temperatures ranging from −78 to −45°C. The diad tacticities of **2** and **3** were evaluated from their ^{13}C NMR spectra. The isotactic diad content varied from 55 to 72% depending upon the reaction conditions, being higher for the polymers prepared in a less polar solvent at lower temperature. DL-Dextran **3** having a number average molecular weight up to 3.6×10^4 was soluble in dimethyl sulfoxide and water, did not show a melting point and began to decompose at *ca.* 260°C. Water sorption and enzymatic hydrolysis of **3** were measured and compared with those of natural dextran.

KEY WORDS Synthetic Polysaccharide / Ring-Opening Polymerization / Anhydrosugar / Dextran / Tacticity / Water Sorption / Enzymatic Hydrolysis /

Dextran is a class of polysaccharides containing a backbone of predominantly (1→6)-α-linked D-glucose units.[1] It is produced in nature by bacteria growing on a sucrose substrate. Since dextran first came under close examination more than one hundred years ago, abundant studies have been reported on the chemical structures and biological properties of dextran as well as its enzymatic synthesis.[1,2] In the meantime, dextran has been proposed for use in industrial and medical applications, particularly in the latter field. Thus, partially hydrolyzed dextran with a molecular weight in a range of 5×10^4 to 10×10^4 has been used as a substituent for blood plasma in the treatment of shock,[3,4] and sulfated dextran has been employed as a synthetic analogue of heparin exhibiting anticoagulant activity.[5,6]

Natural dextran has in general branched structures. High molecular weight linear dextran was synthesized by the ring-opening polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose followed by debenzylation,[7,8] and its biological and immunological reactions have been tested in comparison with those for natural dextran.[7] During a series of works on the chemical synthesis of DL-polysaccharides, we synthesized several (1→6)-linked deoxypolysaccharides by the ring-opening polymirization of 1,6-anhydrosugar derivatives obtained from noncarbohydrate sources, and examined their chemical, physical, and physiological properties in

relation to their molecular structures, as model compounds for elucidating sophisticated functions of naturally occurring polysaccharides.[9-17] As a continuation of these works, we describe herein the first chemical synthesis of linear DL-dextran (**3**) by the ring-opening polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-*β*-DL-glucose (IUPAC nomenclature, 2(*a*),3(*a*),4(*a*)-tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane) (**1**), followed by debenzylation of the resultant polymer (**2**), with particular emphasis on the tacticity of the polymer.[18]



RESULTS AND DISCUSSION

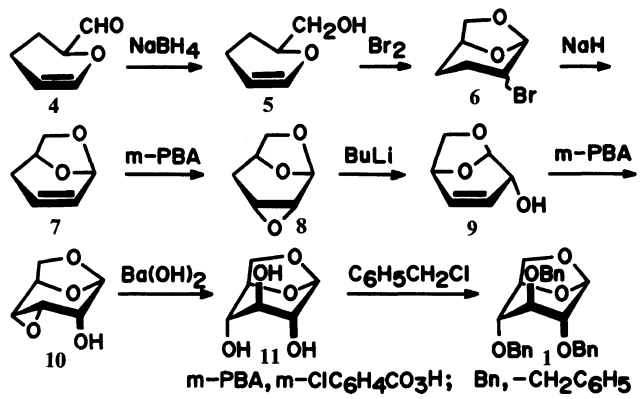
Synthesis of Monomer

1,6-Anhydro-2,3,4-tri-*O*-benzyl-*β*-DL-glucopyranose **1** was synthesized primarily according to the synthetic procedures for DL-glucose described by Brown *et al.*[19-21] with modifications. The synthetic route is illustrated in Scheme I. The preparation of 3,8,9-trioxatricyclo[4.2.1.$0^{2,4}$]nonane (**8**) has been reported in a previous paper.[13] The reaction of **8** with n-butyl lithium in diethyl ether at −5—−10°C gave an unsaturated alcohol (**9**) in moderate yield. Epoxidation of **9** with *m*-chloroperbenzoic acid in dichloromethane took place stereoselectively to yield the corresponding epoxide (**10**). Alkaline hydrolysis of **10** in aqueous dioxane also occurred stereoselectively to produce 1,6-anhydro-*β*-DL-glucopyranose (**11**) as syrup which did not readily crystallize. Subsequent benzylation of **11** with benzyl chloride and sodium hydride in dimethylformamide afforded the tribenzyl derivative **1** which was in turn crystallized from ethanol. The overall yield of **1** from **4** was approximately 5%. The bottleneck step in this synthetic route for **1** is the bromination of **5** in which a nearly equimolar mixture of equatorial and axial stereoisomers is formed and only the axial isomer is subsequently dehydrobrominated to **7**. The new monomer was identified as **1** by elemental analysis and by IR, ^{1}H, and ^{13}C NMR spectroscopies.

Polymerization

Polymerization of optically active 1,6-anhydro-2,3,4-tri-*O*-benzyl-*β*-D-glucopyranose has already been examined in detail by Schuerch *et al.*[22-24] and Uryu *et al.*[25-27] According to their papers, the best conditions for obtaining high molecular weight stereoregular polymers consisting of 1,6-*α*-linked glucosyl residues are as follows: solvent, dichloromethane; initiator, phosphorus pentafluoride; temperature, −60°C. However, as it was one of our chief objects to investigate how the tacticity of polymer **2** derived from racemic monomer **1** varied depending on the reaction conditions, the polymerization of **1** was undertaken under a variety of conditions (solvent, *o*-fluorotoluene, dichloromethane, and 1-nitropropane; initiator, phosphorus pentafluoride, antimony pentachloride, and tantalum pentachloride; temperature, −78—−45°C). The results of the polymerization are listed in Table I.

Polymer **2** was a white solid having a melting point of 42—47°C, which is considerably lower than that (54—58°C) of the corresponding optically active D-polymer derived from 1,6-anhydro-2,3,4-tri-*O*-benzyl-*β*-D-glucopyranose. The solubility of **2** was similar to that of the optically active D-polymer; **2** was



Scheme I. Synthetic route for 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-DL-glucopyranose.

Table I. Polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-DL-glucopyranose (**1**)

Exptl. No.	Monomer	Initiator		Solvent[a]		M/S ratio[b]	Temp	Time	Yield	M_n[c] $\times 10^{-4}$	Iso. diad[d]
	g (mmol)		mol%		ml	g ml^{-1}	°C	h	%		%
T-77	1.08 (2.5)	PF_5	4	DM	1	1.08	−60	0.5	87	4.9	55
T-76	1.08 (2.5)	PF_5	4	DM	2	0.54	−60	0.5	85	5.3	56
T-75[e]	1.08 (2.5)	PF_5	4	DM	2	0.54	−60	0.5	89[f]	10.4	(100)
T-3	0.86 (2.0)	PF_5	5	DM	2	0.43	−60	5	95[g]	2.4	55
T-82	0.86 (2.0)	PF_5	5	DM	6	0.14	−60	96	88	1.8	56
T-72	1.08 (2.5)	PF_5	4	DM	2	0.54	−78	8	80	7.0	55
T-73	1.08 (2.5)	$SbCl_5$	6	DM	2	0.54	−78	20	27	1.6	63
T-78	0.55 (1.3)	PF_5	8	NP	1.5	0.37	−60	2	86	2.4	54
T-79	0.55 (1.3)	$TaCl_5$	*ca.* 8	NP	1.5	0.37	−60	72	10	0.5	57
T-80	0.86 (2.0)	PF_5	5	FTL	6	0.14	−45	96	96	2.8	69
T-81	0.86 (2.0)	PF_5	5	FTL	6	0.14	−60	96	88	3.7	72

[a] DM, dichloromethane; NP, 1-nitropropane; FTL, *o*-fluorotoluene.
[b] Ratio of the weight of monomer to the volume of solvent.
[c] By gel permeation chromatography (polystyrene standard).
[d] By ^{13}C NMR spectroscopy.
[e] Optically active monomer, 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose.
[f] $[\alpha]_D^{25}$ +114.1 (*c*, 0.98, chloroform).
[g] *Anal.* Calcd for $(C_{27}H_{28}O_5)_n$: C, 74.98%; H, 6.25%. Found: C, 74.99%; H, 6.58%.

soluble in a wide variety of organic solvents including benzene, carbon tetrachloride, chloroform, 1,4-dioxane, tetrahydrofuran, ethylacetate, acetone and dimethylformamide.

A typical ^{13}C NMR spectrum of **2** obtained by the polymerization of **1** is presented in Figure 1, together with the assignments of the signals.[28] The appearance of only one signal c at δ 97.32 in the anomeric carbon region indicates that the polymer is exclusively composed of (1→6)-α-linked pyranosyl residues. It is noticeable that the signals i and k appear as a pair of peaks of different intensities, respectively, as clearly demonstrated in the expanded spectrum of the signal i. In view of the fact that the corresponding polymer derived from optically active 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose under similar conditions does not show such splittings, the splittings of the signals i and k are not due to

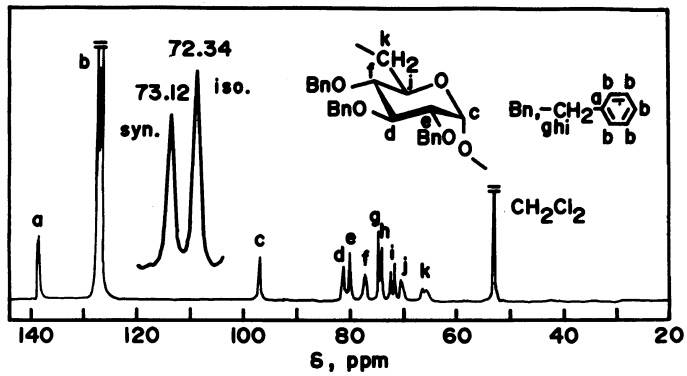


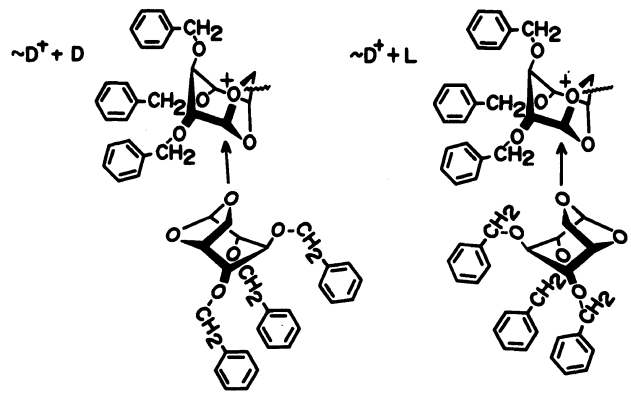
Figure 1. ^{13}C NMR spectrum of 2,3,4-tri-*O*-benzyl-(1→6)-α-DL-glucopyranan prepared in dichloromethane at −60°C with phosphorus pentafluoride as the initiator. Solvent, CH_2Cl_2; temperature, 50°C; 50 MHz; internal reference, tetramethylsilane.

the presence of different structural units but due to the different diad placements of the D- and L-enantiomeric monomeric units in the polymer chain.

On the basis of the comparison of the chemical shifts of the ^{13}C NMR spectrum of **2** with those of the corresponding optically active polymer consisting of the D-enantiomeric units, the peak at δ 72.34 was assigned to the benzyl methylene carbon on O(2) in the DD and LL consecutive units (isotactic diads) and accordingly, the peak at δ 73.12 was assigned to that in the DL and LD crossover units (syndiotactic diads). Such separation of signals due to tacticity is often observed in ^{13}C NMR spectra of polyacetals derived form bicyclic acetals possessing a 6,8-dioxabicyclo[3.2.1]-octane skeleton.[29-31] The well-resolved peaks of the signal i made it possible to determine accurately the diad tacticity of **2** from the relative peak areas. The isotactic diad contents thus determined are given in the last column of Table I.

The diad tacticity of **2** obtained by the polymerization in dichloromethane was not altered with reaction temperature under otherwise identical conditions (T-76 and T-72). When o-fluorotoluene was used as the solvent, the isotactic diad content of **2** increased, although very slightly, at lower temperature (T-80 and T-81). The tacticity of **2** was affected also by the initiators employed; a polymer having a higher isotactic diad content was formed with antimony pentachloride which produces a counter anion of a larger size than that for phosphorus pentafluoride (radius of counter ion, Å:[32] PF_6^-, 2.6; $SbCl_6^-$, 3.0) (T-72 and T-73). The effect of solvents on the tacticity of **2** is more clearly discernible. When less polar *o*-fluorotoluene (ε=4.22) was used as the solvent, **2** having the highest isotactic diad content (72%) was obtained at −60°C (T-81). This value is appreciably higher than that (56%) of **2** prepared in dichloromethane (ε=8.93) under otherwise identical conditions (T-82). However, no significant difference in tacticity was observed between the polymers obtained by the polymerization in dichloromethane and in more polar 1-nitropropane (ε=23.24). The effect of monomer concentration on the tacticity of **2** was negligibly small in the range of the ratio of the weight of monomer to the volume of solvent of 1.08—0.14 for the polymerization in dichloromethane at −60°C with phosphorus pentafluoride as the initiator.

Previously, the authors found, for the first time, that the stereospecific polymerization of a racemic bicyclic acetal, 6,8-dioxabicyclo-[3.2.1]octane, constituting the skeleton of **1**



Scheme II. Possible modes of enantiomer selection at the growing chain end.

was induced by conventional Lewis acid initiators.[29] On the basis of the D,L-copolymerization of enantiomerically unbalanced monomer mixtures, it was confirmed that the stereospecific polymerization giving the polymers which were rich in isotactic diad proceeded by the growing chain end control mechanism,[33] that is, it arose from the enantiomer selection at a growing chain end.[29] The formation of **2** containing isotactic diad ranging from 55 to 72% in the present case also can be accounted for in a similar manner.

According to CPK molecular model inspection, steric and electronic repulsions between a growing chain end and a monomer of the same chirality become minimum, when the monomer approaches the anomeric carbon of the terminal unit by taking a spatial arrangement as illustrated in Scheme II (left). On the other hand, when a growing chain end reacts with a monomer of the opposite chirality, the most preferable approach of the monomer to the anomeric carbon of the terminal unit appears to be that shown in Scheme II (right). In the latter case, however, steric and electronic repulsions between the bulky substituents of the growing chain end and of the incoming monomer seem to be slightly greater than those in the former case; in other words, the former propagation is somewhat energetically favorable. Although omitted in Scheme II for simplification, the penultimate unit of a growing chain end and a counter anion may contribute, more or less, to the enantiomer selection at the chiral growing chain end. It is speculated that, because of the steric requirement of the penultimate and perhaps more remote units, the spatial arrangement of a counter anion of a larger size should be confined to a greater extent than that of a counter anion of a smaller size; that is, the former anion is conceivably forced to lie in such a position as to interfere with the approach of monomer to the growing chain end. Taking the effect of the initiators on the tacticity of **2** into consideration, it would appear that a larger counter anion interferes more greatly with the approach of the monomer whose chirality is opposite to that of the growing chain end. As the tightness of an ion pair generally increases with decreasing polarity of solvents, the influence of the counter ion becomes more significant in solvents of low polarity. Furthermore, the dipole moment of monomer having polar substituents is more susceptible to the orientation effect by a dipole–dipole interaction between a growing chain end and an incoming monomer in less polar solvents, so that the direction of the approach of the monomer to the anomeric carbon of the terminal unit is more intensely restricted than in polar sol-

Table II. Debenzylation of 2,3,4-tri-*O*-benzyl-(1→6)-α-DL-glucopyranan (**2**)

2[a]	NH_3	Toluene	DME[b]	Yield	M_n[c] $\times 10^{-4}$	Iso. diad[d]
g	ml	ml	ml	%		%
0.608 (T-3)	50	13.5	4.5	96[e]	1.5	55
0.718 (T-72)	70	20	8	97	3.6	56
0.221 (T-73)	30	6	2	90	1.1	(63)[f]
0.685 (T-81)	70	20	8	97	2.9	72

[a] Sample numbers correspond to the experimental numbers in Table I.
[b] 1,2-Dimethoxyethane.
[c] By gel permeation chromatography (pullulan standard).
[d] By ^{13}C NMR spectroscopy.
[e] *Anal.* Calcd for $(C_6H_{10}O_5)_n$: C, 44.44%; H, 6.22%. Found: C, 44.45%; H, 6.35%.
[f] Before debenzylation.

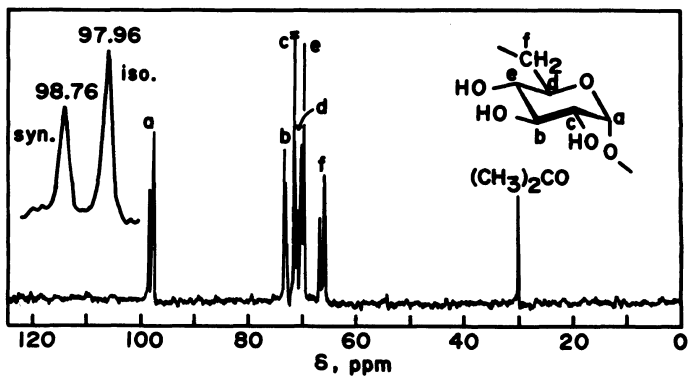


Figure 2. ^{13}C NMR spectrum of (1→6)-α-DL-glucopyranan. Solvent, D_2O; temperature, 50°C; 50 MHz; internal reference, acetone. Polymerization conditions: solvent, CH_2Cl_2; initiator, PF_5; temperature, −60°C.

vents. Consequently, the isotactic propagation between a growing chain end and a monomer of the same chirality becomes more favorable than the syndiotactic propagation between a growing chain end and a monomer of the opposite chirality in less polar solvents. However, in view of the relatively low stereospecificity in the polymerization of **1**, the free energy difference between the two propagations ($\sim D^+ + D$ and $\sim D^+ + L$) must be considerably small, even in less polar solvents.

Conversion to (1→6)-α-DL-Glucopyranan (DL-Dextran)

Polymer **2** was readily debenzylated by the conventional method using metallic sodium in ammonia. Table II presents some of the results of the debenzylation. (1→6)-α-DL-Glucopyranan (DL-dextran) **3** thus prepared was soluble in dimethyl sulfoxide and water, and insoluble in other common organic solvents. In this respect, there was no difference between **3** and (1→6)-α-D-glucopyranan (clinical dextran). However, the former began to decompose at lower temperature (~260°C) than the latter (~295°C) (DSC).

Figure 2 shows the ^{13}C NMR spectrum of **3** derived from **2** prepared by the polymerization in dichloromethane at −60°C with phosphorus pentafluoride as the initiator. The signals were assigned as indicated in Figure 2 by comparison with the ^{13}C NMR data of

(1→6)-α-D-glucopyranan.[28] In Figure 2, each of signals a, b, d, and f appears as a pair of peaks of different intensities, as exemplified by the expanded spectrum of the anomeric carbon signal a. A linear (1→6)-α-D-linked dextran shows six sharp signals unambiguously assigned by selective proton-irradiation, following identification of proton signals by homonuclear irradiation.[28] Therefore, the splittings of the signals of DL-dextran undoubtedly arise from the different diad placements of D- and L-glucose units in the polymer chain. On the basis of the chemical shifts, the peak of a stronger intensity for each of these signal pairs is assignable to the respective carbons in isotactic diads and the peak of a weaker intensity to the corresponding carbons in syndiotactic diads. The diad tacticity of **3** was evaluated from the relative peak areas of the best resolved signal pair f. It was in good agreement with the tacticity determined for **2** before debenzylation.

Water Sorption

Water sorption of synthetic dextran **3** having a number average molecular weight of 1.6×10^4 was measured at relative humidities ranging from 10 to 97% at 25°C, and compared with that of clinical dextran having a comparable molecular weight. Figure 3 represents water sorption isotherms for the two dextrans. Although no significant difference was found between the two dextrans at lower relative humidities, the synthetic DL-dextran showed higher water sorption than the clinical dextran at higher relative humidities. In view of the fact that the water sorption of natural dextran was reduced by an increase in the crystallinity of the samples,[34,35] the difference in water sorption between the two dextrans arises primarily from the lower structural regularity of synthetic DL-dextran; the synthetic DL-dextran used for the measurement was composed of both D- and L-glucose units distributed considerably randomly along the polymer chain (isotactic diad content, 55%). Consequently, the synthetic DL-dextran may form intermolecular hydrogen bonding less effectively than the clinical dextran, thus exhibiting higher water sorption.

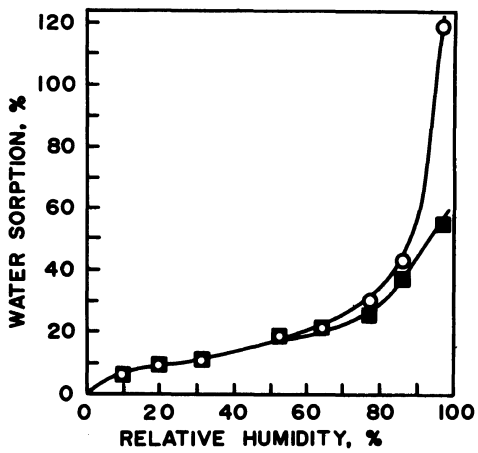


Figure 3. Water sorption of (1→6)-α-glucopyranans at 25°C. ○, synthetic DL-dextran, $M_n = 1.5 \times 10^4$; ■, clinical dextran, $M_n = 1.6 \times 10^4$.

Enzymatic Hydrolysis of DL-Dextran

The hydrolysis of DL-dextran **3** by an endodextranase from a Penicillium species was examined at 37°C in an acetate buffer solution at pH 5.3. The hydrolysis was monitored by calorimetric determination of the reducing end units of the saccharides produced during the reaction. The final degree of hydrolysis of DL-dextran having a number average molecular weight of 3.6×10^4 and an isotactic diad content of 56% was 10.9% based on the total glucose units, whereas that of clinical dextran having a number average molecular weight of 2.8×10^4 was 51.9% under the identical conditions. The remarkable difference between the two dextrans clearly reflects the substrate selectivity in the enzymatic hydrolysis. Detailed analysis of the hydrolysis of DL-dextran in relation to the microstructure will be reported elsewhere.

EXPERIMENTAL

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-DL-glucopyranose (**1**) was synthesized from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (**4**) via eight reaction steps as illustrated in Scheme I. The precursor of monomer **1** was prepared primarily according to the procedure described by Brown *et al.*[19-21] with some modifications.

Preparation of 4(a)-Hydroxy-6,8-dioxabicyclo[3.2.1]oct-2-ene (**9**)[36]

A solution of *n*-butyl lithium in *n*-hexane (46 ml, 72 mmol) was diluted with dry ethyl ether (100 ml). The solution was slowly added to a solution of 3,8,9-trioxatricyclo-[4.2.1.$0^{2,4}$]nonane (**8**, 6.87 g, 54 mmol) in dry diethyl ether (100 ml). The rate of addition was adjusted so as to keep the reaction temperature at −5—−10°C. After the addition of the butyl lithium solution, the reaction mixture was stirred for 1.5 h at −5—−10°C. Diethyl ether (30 ml) saturated with water and then water (70 ml) were cautiously added to the mixture. The organic layer was separated and washed with two 20 ml portions of water. The aqueous layers were combined, salted out, and extracted thoroughly with fifteen 60 ml portions of chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator under reduced pressure. The brown oily residue was purified by column chromatography (column, silica gel; eluent, ethyl acetate : *n*-hexane = 2 : 1, v/v). Yield. 4.67 g (67%); mp, 65—66°C. IR (KBr) cm^{-1}, 3400 ν_{O-H}, 730 δ_{C-H} (*cis* olefin); ^1H NMR ($CDCl_3$), δ 6.20 (dd, J=4.7 Hz J=9.5 Hz, 1H, H-2), 5.82 (ddd, J=1.8 Hz, J=3.8 Hz, J=9.5 Hz, 1H, H-3), 5.52 (m, 1H, H-5), 4.68 (m, 1H, H-1), 3.55—3.70 (m, 3H, H-4 and 2H-7), and 2.20 ppm (d, J=10.8, O–H); ^{13}C NMR ($CDCl_3$), δ 130.44 (C-2), 126.27 (C-3), 102.49 (C-5), 70.41 (C-1), 68.81 (C-7), and 65.61 ppm (C-4).

Preparation of 5(a)-Hydroxy-3,7,9-trioxatricyclo[4.2.1.$0^{2,4}$]nonane (**10**)

m-Chloroperbenzonic acid (purity 80%, 5.1 g, 26 mmol) was added to a solution of **9** (2.5 g, 20 mmol) in dry dichloromethane (100 ml), and the mixture was stirred at room temperature for 20 h. As the reaction proceeded, *m*-chlorobenzoic acid precipitated out of the solution. The precipitate was filtered and washed with cold dichloromethane. The combined filtrates were stirred with anhydrous sodium carbonate to neutralize excess *m*-chloroperbenzoic acid and *m*-chlorobenzoic acid dissolved in the solution. After filtration, the solvent was removed on a rotary evaporator under reduced pressure. The residue was purified by column chromatography (column, silica gel; eluent, ethyl acetate). Yield, 2.5 g (86%); mp, 107—108°C IR (KBr) cm^{-1}, 3440 ν_{O-H}, 1225 ν_{C-O} (epoxide); ^1H NMR ($CDCl_3$), δ 5.22 (d, J= 2.0 Hz, 1H, H-6), 4.70 (m, 1H, H-1), 3.98 (d, J=7.4 Hz, 1H, H-8), 3.79 (dd, J=4.2 Hz, J=7.4 Hz, 1H, H-8), 3.60 (d, J=4.4 Hz, 1H, H-5), 3.35 (m, 1H, H-2), 3.25 (dd, J=1.7 Hz, J=4.4 Hz, H-4), and 2.80 ppm (br, 1H, O-H); ^{13}C NMR ($CDCl_3$), δ 102.33 (C-6), 69.39 (C-8), 65.77 and 65.09 (C-1 and C-5), 50.56 and 49.35 ppm (C-2 and C-4).

Preparation of 1,6-Anhydro-α-DL-glucopyranose (**11**)

A solution of barium hydroxide octahydrate (6.0 g, 19 mmol) in water (40 ml) was added to a solution of **10** (2.20 g, 15 mmol) in 1,4-dioxane (40 ml). The reaction mixture was heated at 100°C for 20 h under a stream of nitrogen. After the reaction mixture was cooled to room temperature and diluted with 1,4-dioxane (75 ml), gaseous carbon dioxide was bubbled into the solution to precipitate barium ion as barium carbonate. The resultant mixture was centrifuged, and the supernatant was separated from the precipitate. A mixture of 1,4-dioxane and water (1 : 1, v/v) was added to the precipitate and

the mixture was again centrifuged. The supernatants were combined and the solvent was removed on a rotary evaporator under reduced pressure to give a yellow syrup. Since attempts to crystallize the crude product were unsuccessful, it was benzylated without further purification.

Preparation of 1,6-Anhydro-2,3,4-tri-O-benzyl-β-DL-glucopyranose (**1**)

To a solution of **11** (2.48 g, 15 mmol) in dimethylformamide (60 ml) there was added in portions sodium hydride (purity 50% in oil dispersion, 3.1 g, 65 mmol) which had been washed twice with *n*-hexane to remove oil. The mixture was stirred for half an hour at room temperature and then heated to 60°C. Benzyl chloride (6.8 g, 54 mmol) was added dropwise to the solution, and the reaction mixture was heated at 60°C for 2 h. It was cooled to room temperature and poured into ice–water (150 ml). The mixture was then extracted with four 50 ml portions of chloroform. The combined chloroform extracts were washed with four 50 ml portions of water and dried over anhydrous magnesium sulfate. The mixture was filtered and the filtrate was freed from the solvent on a rotary evaporator to yield a brown viscous oil. It was chromatographed on silica gel by using a mixed solvent of ethyl acetate and *n*-hexane (1 : 1 v/v) as eluent. The product was repeatedly recrystallized from ethanol. Yield, 2.6 g (37%); mp, 80—81°C; IR (KBr) cm^{-1}, 1500 $\nu_{C=C}$ (phenyl), 1100 ν_{C-O} (ether), 1025 ν_{C-O} (acetal), 750 and 700 δ_{C-H} (monosubstituted phenyl); ^1H NMR ($CDCl_3$), δ 7.20—7.35 (m, 15H, $3C_6H_5$), 5.46 (s, 1H, H-1), 4.58 (s, 2H, $C\underline{H}_2C_6H_5$), 4.54 (s, 2H, $C\underline{H}_2C_6H_5$), 4.43 (s, 2H, $C\underline{H}_2C_6H_5$), 3.89 (d, J=7.0 Hz, 1H, H-6), 3.5—3.7 (m, 3H, H-3, H-5, and H-6), and 3.35 ppm (m, 2H, H-2 and H-4); ^{13}C NMR ($CDCl_3$) δ 137.70 (C_6H_5, *ispso*), 128.18 (C_6H_5, *ortho*), 127.68 and 127.56 (C_6H_5, *meta* and *para*), 100.49 (C-1), 77.02 (C-3), 76.37 (C-2), 76.25 (C-4), 74.33 (C-5), 71.98, 71.65, and 71.08 ppm ($\underline{C}H_2C_6H_5$), 65.37 (C-6) (the numberings are based on the nomenclature in carbohydrate chemistry). *Anal.* Calcd. for $C_{27}H_{28}O_5$: C, 74.98%; H, 6.53%. Found: C, 75.69%; H, 6.49%.

Polymerization Procedures

Monomer **1** was purified by repeated recrystallization from ethanol and finally from a mixed solvent of dichloromethane and *n*-hexane (1 : 2, v/v), and dried in a glass vessel connected to a high vacuum line. Dichloromethane and *o*-fluorotoluene were refluxed over calcium hydride and distilled. Toluene was washed successively with conc. sulfuric acid, water, and aqueous sodium carbonate, refluxed over pieces of sodium metal, and distilled. Antimony pentachloride was distilled under reduced pressure. Phosphorus pentafluoride was generated by heating benzenediazonium hexafluorophosphate. Tantalum pentachloride was used as supplied. A high vacuum technique was employed for polymerization. Polymerization was carried out at different temperatures between −78 to −45°C. After a prescribed period of time, the reaction mixture was poured into a large volume of methanol to precipitate a polymer. It was purified by reprecipitating two or three times from a dichloromethane solution to methanol, followed by freeze-drying from a benzene solution. IR (KBr) cm^{-1}, 3050 ν_{C-H} (arom.), 1090, 1070, and 1020 ν_{C-O} (acetal), 735 and 695 δ_{C-H} (monosubstituted phenyl); ^1H NMR ($CDCl_3$), δ 7.22 (br s, 15H, $3C_6H_5$), 4.3—5.1 (m, 7H, H-1 and $3C\underline{H}_2C_6H_5$), and 3.2—4.1 ppm (m, 6H, H-2, H-3, H-4, H-5 and 2H-6); ^{13}C NMR ($CDCl_3$), δ 138.77, 138.56 and 138.24 (C_6H_5, *ipso*), 128.05, 127.76, and 127.12 (C_6H_5, *ortho*, *meta*, and *para*), 97.32 (C-1), 81.79 and 81.47 (C-3), 80.42 (C-2), 77.53 (C-4), 75.18 ($\underline{C}H_2C_6H_5$), 74.77 ($\underline{C}H_2C_6H_5$), 73.12 and 72.34 ($\underline{C}H_2C_6H_5$), 70.95 and 70.40 (C-5), 66.91 and 65.65 ppm (C-6). *Anal.* Calcd for $(C_{27}H_{28}O_5)_n$: C, 74.98%; H, 6.52%. Found: C, 74.99%; H, 6.58%.

Debenzylation

A solution of polymer **2** (0.6 g) dissolved in a mixed solvent of dimethoxyethane (4.5 ml) and toluene (13.5 ml) was slowly dropped to liquid ammonia (50 ml) on a three-necked flask equipped with a cold finger trap and immersed in a dry ice/methanol bath. After the addition of the solution, the cooling bath was removed, and small pieces of sodium metal (0.7 g) were added in portions to the solution until a dark blue color persisted. After stirring the mixture for 1 h, a small amount of ammonium chloride was cautiously added to decompose the excess sodium, and then water (10 ml) was added dropwise to the mixture. The cold finger trap was removed, and the mixture was stirred until most of the ammonia evaporated. The aqueous and organic layers of the resultant reaction mixture were separated and the organic layer was extracted with two 20 ml portions of water. The water extract combined with the aqueous layer was washed with three 30 ml portions of dichloromethane, and dialyzed in a stream of water for a few days. The aqueous solution was concentrated by a rotary evaporator under reduced pressure and freeze-dried. Yield 0.22 g (96%). IR (KBr) cm^{-1}, 3400 ν_{O-H}, 1150 ν_{C-O} (alcohol), 1100, 1070, and 1020 ν_{C-O} (acetal); ^1H NMR (D_2O), δ 4.84 (d, $J=3.3$ Hz, 1H, H-1), 4.00—3.67 (m, 3H, H-5 and 2H-6), 3.62 (d, $J=10$ Hz, 1H, H-3), 3.46 (dd, $J=3.6$ Hz, $J=11$ Hz, 1H, H-2), 3.38 (t, $J=8.3$ Hz, 1H, H-4); ^{13}C NMR (D_2O), δ 98.76 and 97.96 (C-1), 73.59 and 73.34 (C-3), 71.63 (C-2), 71.16 and 70.40 (C-5), 69.96 (C-4), 66.87, and 66.11 ppm (C-6). *Anal.* Calcd for $(C_6H_{10}O_5)_n$: C, 44.44%; H, 6.22%. Found: C, 44.45%; H, 6.35%.

Characterization

^1H and ^{13}C NMR spectra were recorded on a JEOL FX-200 instrument operating at 200 MHz (^1H) and 50 MHz (^{13}C), respectively, on solutions in deuteriochloroform or deuterium oxide. Tetramethylsilane and acetone were employed as internal references for solutions in deuteriochloroform and deuterium oxide, respectively. IR spectra were measured by a JASCO A-3 spectrometer. Number-average molecular weights of the polymers were estimated by gel permeation chromatography (colum, Shodex A80M, 1 m; eluent, chloroform; polystyrene standard for **2**: column, Shodex OHpak B804 0.5 m plus OHpak B805 0.5 m; eluent, water; pullulan standard for **3**).

Measurement of Water Sorption

Samples were dried to constant weight under reduced pressure at 100°C prior to measurement. A sample (about 0.1 g) was weighed in a phial and placed in a desiccator in which relative humidity was adjusted to a constant value by a saturated aqueous solution of appropriate inorganic salts.[37] The desiccator was kept in a room controlled at 25°C. Water sorption was represented as the percent of weight increase based on the dry sample.

Enzymatic Hydrolysis

Enzymatic hydrolysis of dextrans was carried out by using an endo-dextranase from a Penicillium species (Sigma Chemical Co., Grade I). The progress of the hydrolysis was monitored by colorimetric determination of the reducing end units of the saccharides produced during the hydrolysis.[38] About 30 mg of a sample was weighed in a 25 ml volumetric flask, to which 23 ml of an acetic acid–sodium acetate buffer solution (pH 5.3) was added to dissolve the sample. The flask was immersed in a bath thermostated at 37°C for 15 min, and then an aqueous solution of dextranase (2.4 mg l^{-1}) was added to the mark of the flask. Immediately after mixing, a 1 ml portion of the soltion was pipetted out and mixed with 1 ml of Fehling's solution in a test tube. The test tube was heated for 10 min in a boiling-water bath. After cooling, 1 ml of Nelson's reagent was added to the mixture to dissolve the cuprous oxide completely. The blue solution was then diluted with water to an

appropriate volume in accordance with the quantities of saccharides involved. After specified intervals, 1 ml portions of the solution were taken out and analyzed in a similar manner.

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