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Ring-Opening Polymerization of 1,4-Anhydro-α-D-glucopyranose Derivatives Having Acyl Groups and Synthesis of (1→5)-β-D-Glucofuranan

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ABSTRACT: The influence of initiator, solvent, monomer concentration, and temperature on the ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-6-*O*-pivaloyl-α-D-glucopyranose (**1**) and 1,4-anhydro-3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-glucopyranose (**2**) was investigated. Polymerization of **1** gave non-stereoregular polymers consisting of mainly (1→5)-α-glucofuranosidic units with an $[\alpha]_D$ value of *ca.* +84°. Polymerization of **2** with phosphorus pentafluoride catalyst produced new stereoregular polysaccharide derivatives, 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranans, with an $[\alpha]_D$ value of *ca.* −66°. Substituted polymers were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, polarimetry, and gel permeation chromatography. Debenzylation and depivaloylation of the substituted polymers afforded unsubstituted (1→5)-β-glucofuranan. The electronic effect on the ring-opening polymerization and the mechanism of the ring-opening polymerization are discussed. This is the first paper to describe the preparation of (1→5)-β-glucofuranan with an $[\alpha]_D$ value of *ca.* −204°.

Introduction

Many efforts have been devoted to the synthesis of cellulose. The condensation of 2,3,6-glucose tricarbanilate with phosphorus pentoxide in a mixture of chloroform/dimethyl sulfoxide has been reported to give a cellulose-like polymer with high stereoregularity, but the molecular weight of the resulting polysaccharide after removing the protective group was low.[1] Recently, Kobayashi *et al.* achieved *in vitro* synthesis of cellulose *via* a non-biosynthetic path by condensation of β-D-cellobiosyl fluoride with cellulase.[2] However, it is impossible to yield regioselectively derivatized cellulose from the nonprotected cellulose obtained by their method. Such cellulose derivatives are important for studying the relationship between structure and properties. These polymers may be obtained only by an organic synthetic method.

On the other hand, the synthetic approach to cellulose *via* ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose, for the first time reported by Micheel *et al.*[3,4] yielded a cellulose-like polymer. Uryu *et al.*[5] also tried the polymerization of the same monomer but obtained an unexpected stereoregular (1→5)-α-D-glucofuranan, with stereochemistry elucidated on the basis of the antiperiplanar theory of Deslongchamps.[6] Since 1,4-anhydro-α-D-glucopyranose, which may also be regarded as 1,5-anhydro-β-D-glucofuranose, has two ring-opening modes, that is, 1,4- or 1,5-ring scission, there are four possible structural units in the polymer obtained, which are caused by the ring-opening modes and anomeric α- and β-configurations. Ring-opening polymerization is affected by reaction conditions, and there is a possibility of achieving the chemical synthesis of cellulose by finding optimum reaction conditions.

We previously reported the substituent effects on the stereoselective glycosylation in the syntheses of cello oligosaccharides.[7,8] The benzyl group at O-3 was indispensable for obtaining β-linked glucosides stereospecifically[7] in high yield, and the pivaloyl group introduced into the O-2 led to β-glycosidic linkage by the β-side attack of the glycosyl acceptor because of the neighboring-group participation.[8]

There is a good possibility of synthesizing the expected β-(1→4)-glucan with both stereo- and regioselectivities by the ring-opening polymerization utilizing such substituent effects. In fact, Ichikawa *et al.*[9] and Kobayashi *et al.*,[10] recently, reported the syntheses of (1→6)-β-D-galacto oligosaccharides by applying the neighboring-group participation of the 2-*O*-acyl group. There are no papers describing such substituent effects in ring-opening polymerization of 1,4-anhydro-α-D-glucopyranose derivatives.

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Table 1. Polymerization of 1,4-Anhydro-2,3-di-*O*-benzyl-6-*O*-pivaloyl-α-D-glucopyranose

exp no.	initiator	concn, mol %	solv	monomer/solv, g/100 mL	temp, °C	time, h	yield, %	10^{-3} M_{GPC}	DP	$[\alpha]_D$, deg	polymer structure, %[a] (1→5)-α-F	(1→5)-β-F	(1→4)-α-P	(1→4)-β-P
1	PF_5	40	CH_2Cl_2	100	−78	189	74	8.1	18.9	+94.9	58	0	42	0
2	PF_5	20	CH_2Cl_2	100	−78	192	56	7.0	16.6	+82.1	44	0	46	10
3	PF_5	5	CH_2Cl_2	100	−78	192	54	9.4	22.1	+90.2	42	0	41	17
4	PF_5	20	CH_2Cl_2	50	−30	252	88	4.0	9.5	+78.4	54	16	22	8
5	PF_5	5	CH_2Cl_2	100	−30	191	83	12.5	29.3	+86.6	72	0	22	6
6	PF_5	20	CH_2Cl_2	50	0	252	80	4.2	9.8	+68.2	37	14	32	17
7	PF_5	5	CH_2Cl_2	100	0	229	62	7.2	16.8	+83.7	*ca.* 100	0	trace	trace
11	PF_5	20	toluene	50	−30	262	64	4.9	11.5	+77.2	62	trace	17	21
12	PF_5	5	toluene	50	−30	233	18	4.9	11.6	+108	91	0	9	trace
14	BF_3·Et_2O	5	CH_2Cl_2	100	−30	238	78	15.0	35.2	+65.7	55	6	24	15
16	$SbCl_5$	5	CH_2Cl_2	100	−30	166	72	5.8	13.6	+56.7	71	16	0	13

[a] Determined from the proportion of anomeric peaks in the ^{13}C-NMR spectrum of poly(1).

Table 2. Polymerization of 1,4-Anhydro-3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-glucopyranose

exp no.	initiator	concn, mol %	solv	monomer/solv, g/100 mL	temp, °C	time, h	yield, %	10^{-3} M_{GPC}	DP	$[\alpha]_D$, deg	polymer structure, %[a] (1→5)-α-F	(1→5)-β-F	(1→4)-α-P	(1→4)-β-P
21	PF_5	15	CH_2Cl_2	50	−30	22	54	3.8	8.9	−57.1	0	*ca.* 100	0	0
22	PF_5	10	CH_2Cl_2	50	−30	21	80	7.3	17.1	−66.2	0	*ca.* 100	0	0
23	PF_5	5	CH_2Cl_2	50	−30	34	87	9.4	22.0	−66.9	0	100	0	0
24	PF_5	5	CH_2Cl_2	33	−30	23	61	6.7	15.8	−65.1	0	100	0	0
25	PF_5	5	CH_2Cl_2	25	−30	27	71	5.3	12.4	−63.7	0	100	0	0
26	PF_5	1	CH_2Cl_2	50	−30	39	13	7.3	17.2	−61.2	0	100	0	0
30	PF_5	5	toluene	100	−30	32	65	12.8	30.1	−69.1	0	100	0	0
31	PF_5	5	toluene	50	−30	25	100	13.0	30.8	−69.3	0	100	0	0
32	PF_5	1	toluene	50	−30	38	60	18.1	42.6	−61.2	0	100	0	0
36	PF_5	5	CH_2ClCH_2Cl	50	−30	41	86	7.3	17.1	−64.6	0	100	0	0
37	PF_5	5	CH_3NO_2	50	−28	27	52	8.0	18.7	−76.0	0	100	0	0
40	BF_3·Et_2O	5	CH_2Cl_2	50	−30	60	78	7.5	17.6	−69.3	0	100	0	0
41	$SbCl_5$	5	CH_2Cl_2	50	−30	20	100	3.4	8.1	−65.6	0	100	0	0

[a] Determined from the proportion of anomeric peaks in the ^{13}C-NMR spectrum of poly(2).

In the previous paper, we reported the synthesis of two novel compounds, 1,4-anhydro-2,3-di-*O*-benzyl-6-*O*-pivaloyl-α-D-glucopyranose (**1**) and 1,4-anhydro-3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-glucopyranose (**2**), for the purpose of the chemical synthesis of cellulose.[11] These compounds may be expected to give regioselective 1,4-pyranan by the electron-withdrawing acyl group at the 6-O position and to induce stereoselective β-glycosidic bond formation by the neighboring-group participation of the 2-*O*-acyl group.

In this study, we investigated the possibility of synthesizing (1→4)-β-D-glucopyranan (cellulose) *via* the ring-opening polymerization of **1** and **2**.

Results and Discussion

Molecular Weights of Poly(1)s and Poly(2)s Synthesized from 1 and 2, Respectively. The influence of reaction conditions on the molecular weight of the polymers was investigated. The results are summarized in Tables 1 and 2. Number-averaged molecular weights of poly(1)s and poly(2)s, determined by gel permeation chromatography (GPC) using polystyrene standards, ranged from 4000 (DP = 9.5) to 12 500 (DP = 29.3) and from 3400 (DP = 8.1) to 18 100 (DP = 42.6), respectively.

Compound **1** polymerized at −78 °C, but compound **2** did not at that temperature because **2** crystallized out at −78 °C. Number-averaged molecular weights of poly(**2**)s obtained using phosphorus pentafluoride as catalyst at −30 °C decreased in the order: in toluene > dichloromethane > nitromethane > 1,2-dichloroethane (Table 2, experiment nos. 23, 31, 36, and 37), decreased, especially in dichloromethane, with decreasing concentrations of **2** (monomer/solvent (g/mL), 50, 33, and 25) (Table 2, experiment nos. 23–25), and decreased with an increase in the concentration of phosphorus pentafluoride (5, 10, and 15 mol %) (Table 2, experiment nos. 21–23). Compound **2** polymerized more readily than **1** in toluene (see experiment nos. 12 and 31).

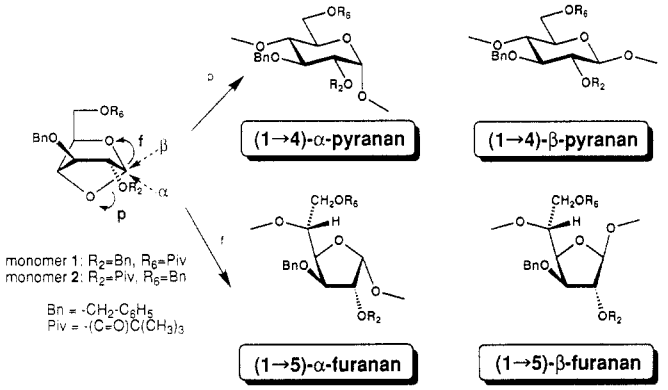


Figure 1. Ring-opening modes of 1,4-anhydro-α-D-glucopyranose derivatives.

Structure of Poly(1)s Synthesized from 1. In general, there are four possible structural units in the poly-(D-glucose) prepared *via* ring-opening polymerization of 1,4-anhydro-α-D-glucopyranose derivatives, namely, the (1→4)-β- ((1→4)-β-P) and (1→4)-α-D-glucopyranosidic ((1→4)-α-P) units and the (1→5)-β- ((1→5)-β-F) and (1→5)-α-D-glucofuranosidic ((1→5)-α-F) units (Figure 1). The structures of these synthetic glucans were determined by means of polarimetry and ^{13}C-NMR spectroscopy reported by Uryu *et al.*[5]

All poly(1)s are dextrorotatory, as shown in Table 1. Taking into account the high positive specific rotation, the poly(**1**) may be a (1→5)-α-D-glucofuranan derivative or a (1→4)-α-D-glucopyranan derivative, *i.e.*, an amylose derivative.

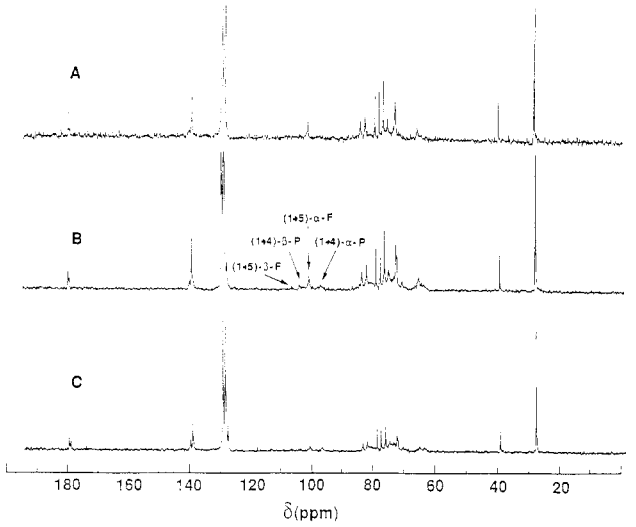


Figure 2. 22.5-MHz ^{13}C-NMR spectra of (A) poly(1) prepared by PF_5 at 0 °C (Table 1, experiment no. 7), (B) poly(1) prepared by PF_5 at −30 °C (Table 1, experiment no. 4), and (C) poly(1) prepared by PF_5 at −78 °C (Table 1, experiment no. 1) ($CDCl_3$ as solvent).

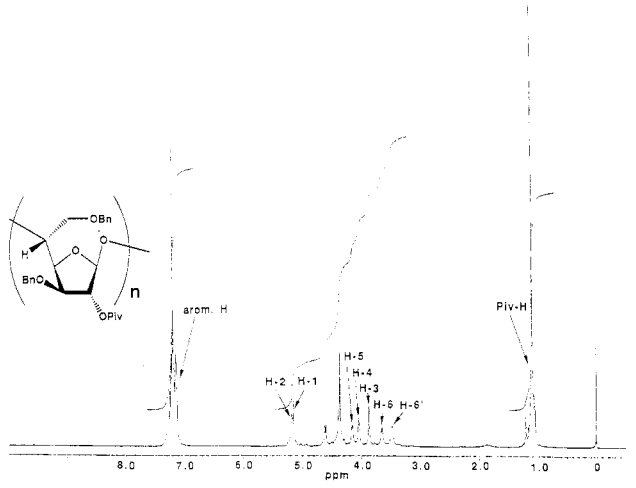


Figure 3. 500-MHz ^{1}H-NMR spectrum of 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan ($CDCl_3$ as solvent).

^{13}C-NMR spectra of poly(1)s synthesized from **1** are shown in Figure 2. In spectrum 2A of poly(1) having $[\alpha]_D$ +83.7° (Table 1, experiment no. 7), the anomeric peak appeared as almost a single peak at 100.2 ppm. In order to assign the peak at 100.2 ppm, the poly(1) having $[\alpha]_D$ +83.7° was desubstituted and acetylated. The anomeric peak of acetylated poly(1) appeared at 100.4 ppm, which is distinctly different from the 95.7 ppm peak of amylose acetate.[12] On the other hand, the anomeric peak of cellulose acetate, *i.e.*, a (1→4)-β-D-glucopyranan derivative, appears at 100.5 ppm.[12] However, the cellulose acetate has $[\alpha]_D$ −21°,[13] which is distinctly different from $[\alpha]_D$ +109° of the acetylated poly(1). Therefore, the anomeric peak at 100.2 ppm was assigned to (1→5)-α-F units.

Spectrum 2B of poly(1) (Table 1, experiment no. 4) shows the four anomeric peaks consisting of 96.7, 100.2, 102.4, and *ca.* 107 ppm. The C-1 peaks of the nonreducing end group of two dimeric model compounds, namely, maltose and cellobiose derivatives[8] with the same protective group system as that of poly(1)s, appeared at 96.7 and 102.4 ppm, respectively; so, the anomeric peaks of poly(1)s at 96.7 and 102.4 ppm were assigned to (1→4)-α-P and (1→4)-β-P units, respectively. Then, the fourth anomeric peak at *ca.* 107 ppm was assigned to (1→5)-β-F units. In spectrum 2C, poly(1) had a structure consisting of (1→4)-α-P and (1→5)-α-F units at −78 °C.

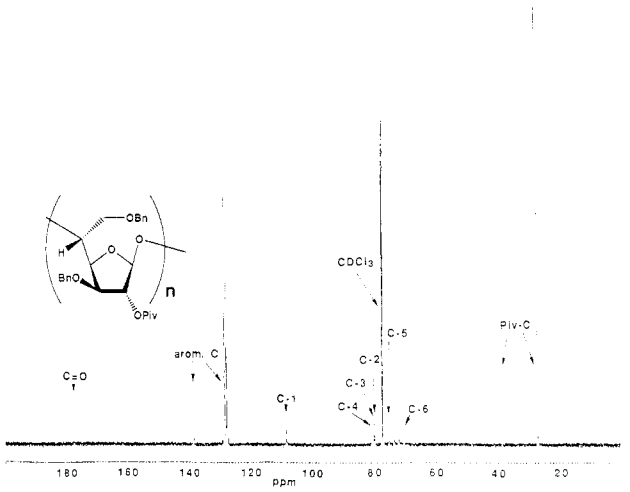


Figure 4. 125-MHz ^{13}C-NMR spectrum of 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan ($CDCl_3$ as solvent).

Table 3. ^{1}H-NMR Chemical Shifts of 3,6-Di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan

	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	benzyl-H
δ, ppm	5.14	5.17	3.87	4.05	4.15	3.64	3.46	4.61, 4.36, 4.38

Table 4. ^{13}C-NMR Chemical Shifts of 3,6-Di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan

	C-1	C-2	C-3	C-4	C-5	C-6	benzyl-C	C=O
δ, ppm	107.95	79.61	79.95	80.41	74.96	70.09	71.67, 73.33	177.13

It turned out that stereoregularities were affected by the catalysts used, concentration of the catalyst, and reaction temperature, as shown in Table 1. The production of (1→5)-α-F units increased with a decrease in the concentration of PF_5 catalyst. Phosphorus pentafluoride, boron trifluoride etherate, and antimony pentachloride gave relatively highly stereoregular poly(1)s. Trifluoromethanesulfonic anhydride, which served as a good catalyst for stereoregular polymerization of the 1,3-anhydro-β-D-glucopyranose derivative,[14] did not cause stereoregular polymerization of **1**.

None of these conditions, however, gave a completely stereoregular polymer. The difference between our present results and those of Uryu *et al.*[5] is the production of (1→4)-α-P units at −78 °C. This fact clearly indicates that the neighboring participation of 6-*O*-pivaloyl groups affects the structures of poly(1)s.

Structure of Poly(2)s Synthesized from 2. All poly(2)s are levorotatory, as shown in Table 2. Taking into account the high negative specific rotation, the poly(2)s may be (1→5)-β-D-glucofuranan derivatives or (1→4)-β-D-glucopyranan derivatives.

^{1}H- and ^{13}C-NMR spectra of poly(2) having $[\alpha]_D$ −69.3° are shown in Figures 3 and 4, respectively. These spectra indicate that the poly(2) has a high degree of stereoregularity. The anomeric peak of stereoregular poly(2) appeared at 108 ppm as a sharp singlet. In order to determine the structure of the stereoregular poly(2), it was desubstituted and acetylated. The anomeric peak of the acetylated poly(2) appeared at 106.2 ppm. On the other hand, anomeric peaks of cellulose acetate, i.e., a (1→4)-β-D-glucopyranan derivative, and amylose acetate, *i.e.*, a (1→4)-α-D-glucopyranan derivative, have appeared at 100.5 and 95.7 ppm,[12] respectively. The chemical shift of

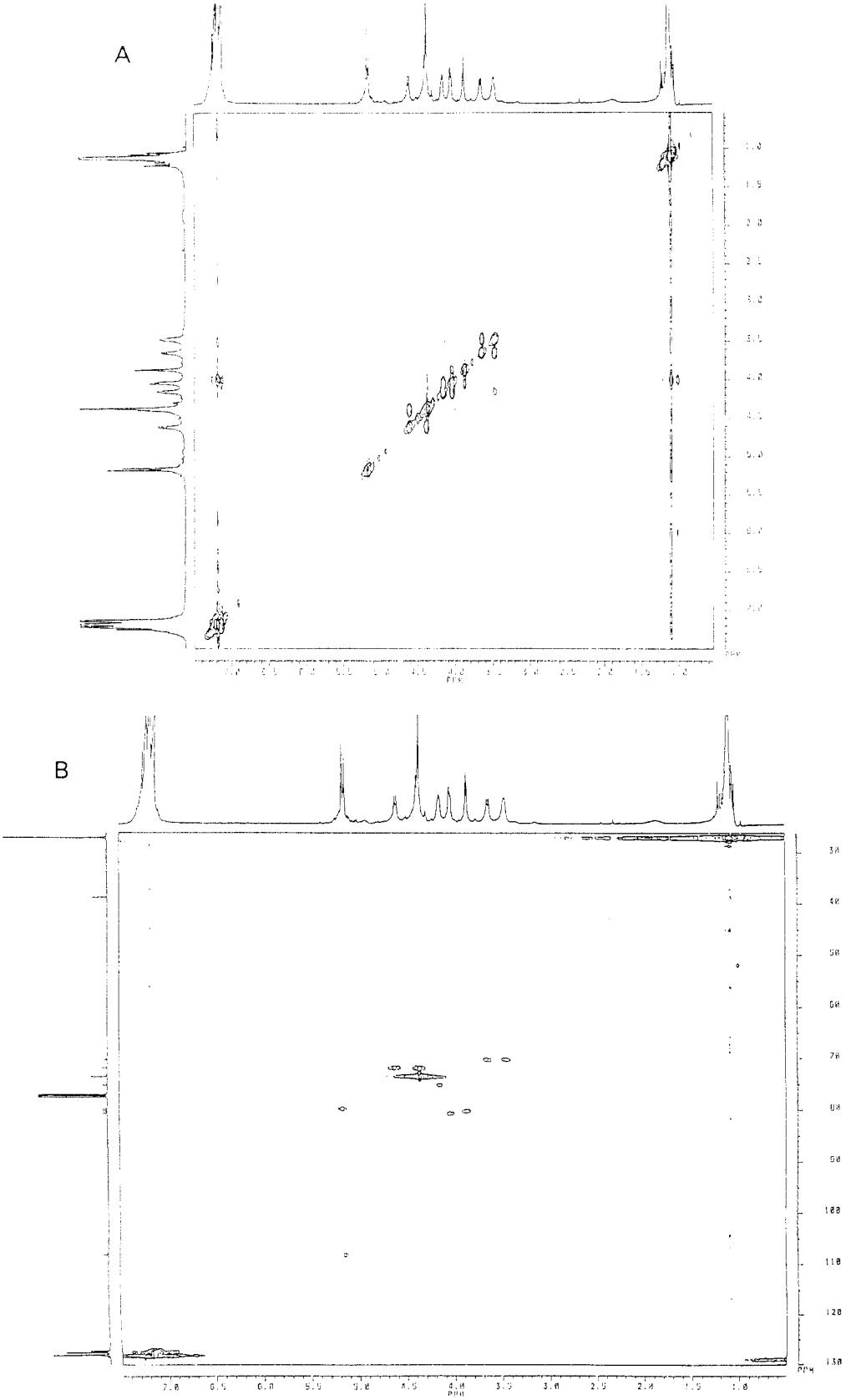
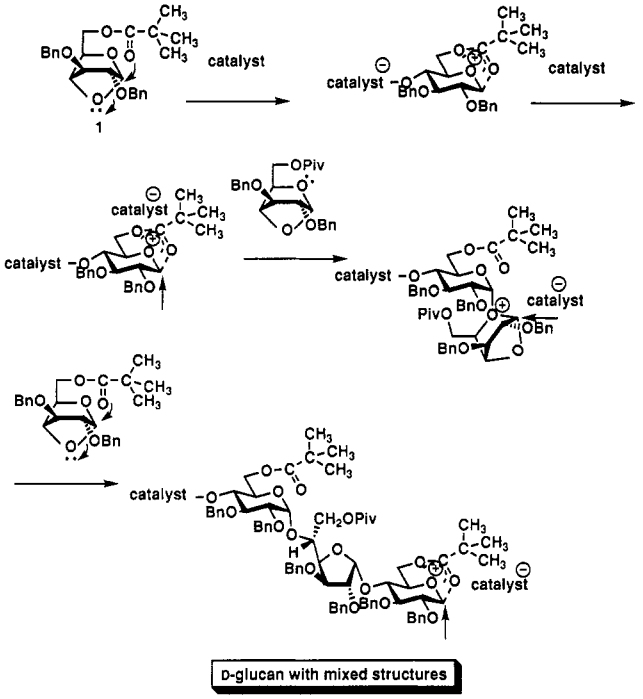


Figure 5. 2D-NMR spectra of 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan (Table 2, experiment no. 31): (A) plot from COSY experiment and (B) plot from HMQC experiment ($CDCl_3$ as solvent).

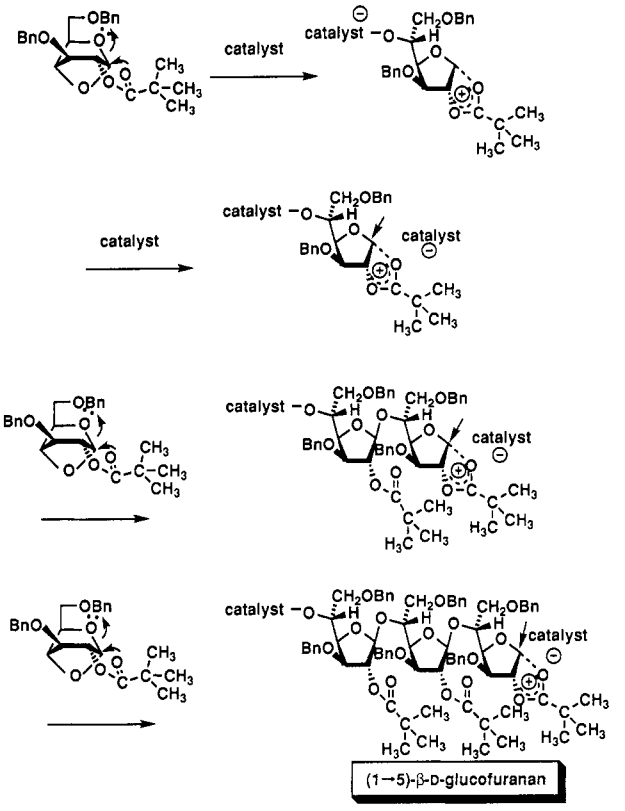
the C-1 resonance of the acetylated poly(**2**) is clearly different from that of cellulose acetate. Therefore, it was concluded that the stereoregular poly(**2**) is 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan. This stereoregular polysaccharide has a high degree of crystallinity and a melting point of *ca.* 120 °C determined by microscopic observation.

The ^1H resonances for the completely stereoregular poly(**2**)s were assigned *via* their cross-peaks in the COSY spectrum (Figure 5A). The ^{13}C resonances were assigned by comparing the ^1H assignments with the ^1H–^{13}C correlation data obtained from an HMQC experiment (Figure 5B). The assignments of proton and carbon peaks are summarized in Tables 3 and 4, respectively.

Scheme 1



Scheme 2



The relationships between reaction conditions and stereoregularity are shown in Table 2. The stereoregular (1→5)-β-D-glucofuranan derivatives were obtained in four kind of solvents. Phosphorus pentafluoride, boron trifluoride etherate, and antimony pentachloride gave stereoregular poly(**2**)s at −30 °C. Trifluoromethanesulfonic anhydride did not cause stereoregular polymerization at −30 °C, as in the case of polymerization of **1**. Stereoregularities of poly(**2**)s increase with a decrease in the concentration of PF_5 catalyst (Table 2, experiment nos. 21–23).

The fact that polymerization of **2** produced a stereoregular β-D-glucofuranan derivative indicates that the neighboring participation of 2-*O*-pivaloyl groups strongly affects the polymerization of **2** to yield stereoregular poly(**2**)s.

Substituent Effects and Mechanism of Polymerizations. Scheme 1 illustrates the proposed propagation mechanism of polymerization of **1** to produce (1→4)-α-P and (1→5)-α-F units. Phosphorus pentafluoride as catalyst coordinates with the acetal oxygen of the 1,4-anhydro ring, the carbonyl oxygen of the pivaloyl group at the 6-O position attacks C-1 from the β-side to form a dioxacarbenium-ion intermediate, and the oxygen of the anhydro ring of the next monomer attacks from the opposite side, *i.e.*, α-side, of the intermediate to form (1→4)-α-P units. Without such neighboring-group participation of the 6-*O*-acyl group, the (1→5)-α-F units are produced as expected from the results of Uryu *et al.*[5]

Scheme 2 illustrates the proposed propagation mechanism of the polymerization of **2** to yield (1→5)-β-D-glucofuranan. The production of (1→5)-β-F units clearly indicates neighboring-group participation of the pivaloyl group at the 2-O position. The catalyst coordinates with the oxygen of the 1,5-anhydro ring, the electron density of which increases due to the electron-donating benzyl group at the 6-O position. This coordination would result in the formation of a (1→5)-β-furanose ring. The carbonyl oxygen of the pivaloyl group at the 2-O position attacks C-1 from the α-side to form a dioxacarbenium-ion intermediate, and then the oxygen of the 1,5-anhydro ring of the next monomer attacks from the opposite side, *i.e.*, β-side, of the intermediate to form (1→5)-β-F sequences.

Deprotection of Substituted Polymers. Stereoregular 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan was debenzylated and depivaloylated with sodium in liquid ammonia to give free (1→5)-β-D-glucofuranan. The IR spectrum of free (1→5)-β-D-glucofuranan was compared with that of the (1→5)-β-D-glucofuranan derivative, as shown in Figure 6. In spectrum 6A of the (1→5)-β-D-glucofuranan derivative, there are bands due to the pivaloyl group at 1740 cm^{-1} and due to benzyl groups at 700 and 740 cm^{-1}. In spectrum 6B of free (1→5)-β-D-glucofuranan, those bands have disappeared. The ^{13}C-NMR spectrum of free (1→5)-β-D-glucofuranan in D_2O is shown in Figure 7. Signals from the protective groups have completely disappeared. The signal of the anomeric peak appears at 108.0 ppm.

Experimental Section

Polymerization. All polymerizations were carried out using a high-vacuum line capable of maintaining a vacuum of 1×10^{-3} Torr. Monomer was dried in a polymerization ampule by evacuating for a few hours. Methylene chloride was dried over P_2O_5, distilled, and degassed by freezing and thawing three times in a high-vacuum line. All solvents were transferred under high vacuum. Phosphorus pentafluoride was generated from *p*-chlorobenzenediazonium hexafluorophosphate by decomposition at 160 °C and transferred to a reaction ampule. $SbCl_5$, BF_3–Et_2O, and $(CF_3SO_2)_2O$ were added into the reaction ampule through the rubber septum by syringe. The reaction apparatus was then separated by melting at a constriction and placed in a bath of the appropriate temperature. Polymerizations were terminated by adding cold methanol at the polymerization temperature. After dilution with ethyl acetate and chloroform (1:1, v/v), the polymer solution was washed with water. The solution was dried over anhydrous sodium sulfate and concentrated to dryness. *n*-Hexane was added to the polymer mixture. The remaining monomer was repeatedly extracted with hot *n*-hexane while applying ultrasonic waves. The residual polymer was finally dried *in vacuo*.

Deprotection. The stereoregular (1→5)-β-D-glucofuranan derivative (25.6 mg) dissolved in toluene (0.2 mL) and 1,2-

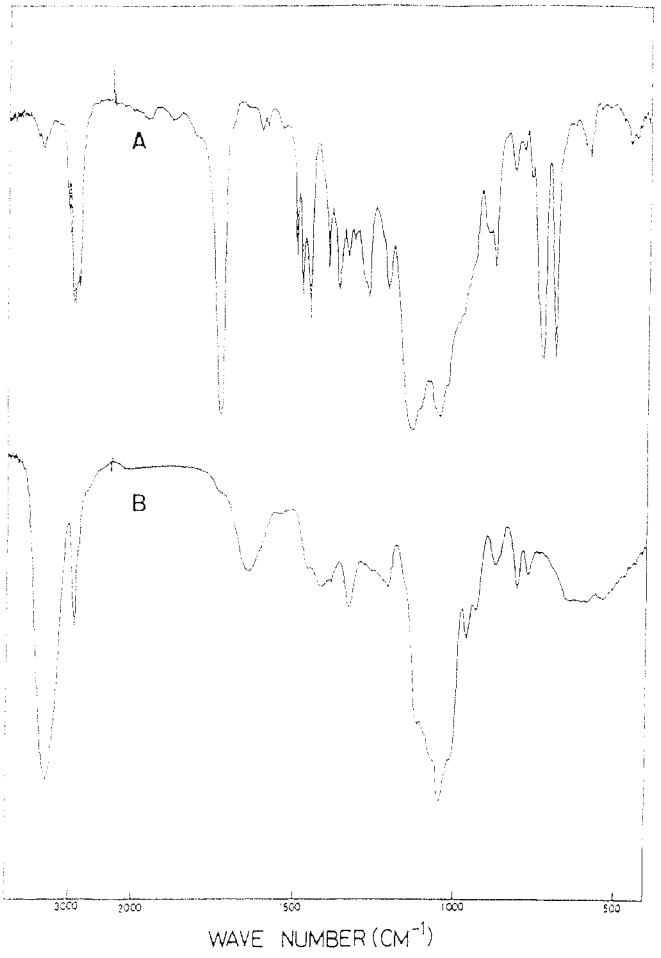


Figure 6. IR spectra of (A) 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-glucofuranan and (B) deprotected (1→5)-β-D-glucofuranan.

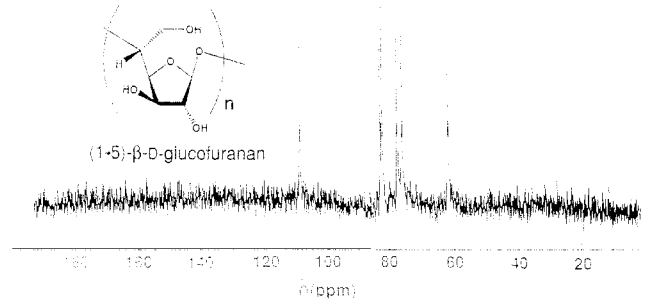


Figure 7. ^{13}C-NMR spectrum of (1→5)-β-D-glucofuranan (in D_2O, DSS as external standard).

dimethoxyethane (0.2 mL) was added dropwise to a solution of small pieces of metal sodium in 5 mL of liquid ammonia at −78 °C. The reaction was allowed to continue for 2 h followed by successive addition of ammonium chloride and several drops of water. Deprotected polymer was dialized with water and freeze-dried (yield, 4.5 mg, 46%). $[\alpha]_D$ −204° (*c* 0.1, H_2O). ^{13}C-NMR (D_2O, DSS as external standard): δ 108.0 (C-1), 82.8, 82.2, 77.4, 75.8 (C-2, C-3, C-4, C-5), 61.5 (C-6). Selected polymers were deprotected by the above-mentioned method.

Acetylation of Deprotected Polymer. The deprotected polymer was acetylated by acetic anhydride/pyridine (3:1, v/v) at 60 °C. After 12 h, the reaction mixture was concentrated to dryness. The acetylated (1→5)-β-D-glucofuranan had $[\alpha]_D$ −76.8° (*c* 0.95, $CHCl_3$). ^{13}C-NMR ($CDCl_3$): δ 106.2 (C-1), 79.9, 79.2, 73.7 (C-2, C-3, C-4, C-5), 62.2 (C-6), 170.6, 169.9, 169.0 (C=O), 20.7 (Ac). Selected polymers were acetylated by the above-mentioned method.

Measurements. The 200-MHz ^1H-NMR and the 22.5-MHz ^{13}C-NMR spectra of substituted glucans were measured in $CDCl_3$ at ambient temperature with tetramethylsilane (Me_4Si) as the internal standard using a Varian XL-200 FT-NMR spectrometer and a JEOL FX-90Q FT-NMR spectrometer, respectively. The chemical shifts are expressed in ppm downfield of the internal Me_4Si absorption. The ^{13}C-NMR spectrum of unsubstituted glucan was recorded in D_2O with DSS as external standard. The structure of the selected stereoregular (1→5)-β-D-glucofuranan derivative was established via two-dimensional homo- and heteronuclear NMR experiments using a Brucker AM-500. Specific rotations were measured with a JASCO Dip-4 digital polarimeter in $CHCl_3$ or H_2O at 25 °C. Infrared spectra were recorded with a Shimadzu FT IR-4000 spectrophotometer. Molecular weight distributions of the substituted polymer were analyzed by gel permeation chromatography in tetrahydrofuran. A Waters universal liquid chromatograph injector (Model U6K), a Waters solvent delivery system (Model 6000A), a Waters refractive index detector (Series R-400), a Waters absorbance detector (Model 440), and Shodex columns (KF802 and KF803) were used. The flow rate was 1.0 mL/min. Calibration curves were obtained by using polystyrene standards (Shodex).

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