Synthesis of a Novel Cellulose-Type Hexopyranan 6-Deoxy-(1→4)-α-L-talopyranan by Selective Ring-Opening Polymerization of 1,4-Anhydro Sugar Derivatives

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ABSTRACT: Selective ring-opening polymerization of 1,4-anhydro-6-deoxy-β-L-talopyranose derivatives was investigated. 2,3-*O*-Isopropylidene monomer (AIDT) was polymerized in a stereoregular manner by both phosphorus pentafluoride and antimony pentachloride as catalysts at −40 °C to give a 6-deoxy-2,3-*O*-isopropylidene-(1→4)-α-L-talopyranan, i.e., a cellulose-type polysaccharide. The structure of poly(AIDT) was determined by specific rotation and ^{13}C NMR spectroscopy. 2,3-*O*-Cyclohexylidene monomer (ACDT) was also stereoselectively polymerized by phosphorus pentafluoride to give a (1→4)-linked talopyranan derivative. Deisopropylidenation of the stereoregular poly(AIDT) and decyclohexylidenation of the stereoregular poly(ACDT) gave 6-deoxy-(1→4)-α-L-talopyranan, which is the first synthetic hexopyranan with cellulose-type structure. On the other hand, the polymerization of 2,3-*O*-benzylidene monomer (ABDT) gave an irregular polymer, containing the mixture of (1→4)-α-L-talopyranosidic and (1→5)-β-L-talofuranosidic units. Poly(ABDT) has deprotected by reduction. The mechanism of ring-opening polymerizations of 1,4-anhydrodeoxytalose derivatives is discussed.

Introduction

Although a cellulose-type polysaccharide, that is, a trans-(1→4)-linked polysaccharide, has been obtained by ring-opening polymerization of anhydroribose derivatives,[1,2] cellulose itself has not been synthesized even by using the same polymerization method.[3,4] In the biosynthesis of cellulose, activated monomers such as UDP–glucose[5] and GDP–glucose[6] are used, and stepwise polymerization takes place. Numerous attempts to synthesize cellulose chemically using stepwise polymerization failed to afford a polysaccharide with a stereoregular structure and a high molecular weight.[7]

Ring-opening polymerization of a 1,4-anhydro-D-glucopyranose derivative, which is equally regarded as a 1,5-anhydro-D-glucofuranose derivative because of its bicyclic structure, has given a new furanan-type polymer, i.e., (1→5)-α-D-glucofuranan derivative,[4] although in theory the monomer can be polymerized into cellulose. Micheel and co-workers reported that the cationic ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose readily proceeded to give (1→4)-D-glucopyranans, which consist of mixed structures of (1→4)-β-linked and (1→4)-α-linked D-glucopyranosidic units.[3,8,9] However, we revealed that these polymers are composed mostly of glucofuranosidic units.[4]

In the polymerization of 1,4-anhydro-L-arabinopyranose and 1,4-anhydro-D-galactopyranose derivatives, Kops and Schuerch reported that the polymerization proceeds via an oxacarbenium ion mechanism.[10]

On the other hand, when an appropriate combination of a protective group and an initiator is used in the polymerization of 1,4-anhydro-D-ribose derivatives, selective ring-opening polymerization takes place.[2] 2,3-*O*-Alkylidene,[1] 2,3-di-*O*-methyl,[2] and 2,3-di-*O*-*tert*-butyldimethylsilyl[11] groups can be used as OH-protective groups. The obtained ribose polymer has been revealed to be the first cellulose-type polysaccharide.

The ribose configuration of the monomer is the first requisite. 1,4-Anhydro-α-D-ribopyranose has a bicyclic structure in which the 1,4-anhydro oxygen and O-2 and O-3 oxygens are on the same plane of the pyranose ring. On the other hand, since, in 1,4-anhydro-α-D-lyxopyranose, the 1,4-anhydro oxygen is on the opposite side from the O-2 and O-3 oxygens in relation to the plane of the pyranose ring, the lyxopyranose monomer was not polymerized into the cellulose-type polysaccharide but afforded a (1→5)-α-D-lyxofuranan.[12]

In this study, we report the synthesis of 6-deoxy-(1→4)-α-L-talopyranan, the first synthetic cellulose-type hexopyranan, by selective ring-opening polymerization of 1,4-anhydro-6-deoxy-2,3-*O*-isopropylidene(or cyclohexylidene)-β-L-talopyranose, followed by removal of the protective group. In addition, the polymerization of a 2,3-*O*-benzylidene derivative is also studied. Structure analysis of the synthetic polysaccharide is performed by ^{13}C NMR spectroscopy and optical rotation.

Results and Discussion

Polymerization of 1,4-Anhydro-6-deoxy-2,3-*O*-isopropylidene-β-L-talopyranose (AIDT). AIDT was polymerized by various cationic catalysts at low temperatures. The results are summarized in Table I, exhibiting that the conversion was generally low. When the polymerization was carried out with phosphorus pentafluoride as catalyst at −40 °C for 2–3 h, polymers with negative specific rotations of −40.1° to −42.4° were obtained in 21–37% yields (nos. 1–3). The polymer yields showed a tendency to decrease with longer polymerization time (no. 4). Number-average molecular weights of the polymers were in the range of 1.1×10^4–1.8×10^4. For the isopropylidene-protected polymer, the specific rotation of −42.4°, which indicates the polymer stereoregularity, seems to be the largest negative value, and a polymer with a smaller $[\alpha]_D$ value was obtained with lower polymerization temperature (−60 °C).

When antimony pentachloride was used, the polymerization at −40 °C for 24 h gave a polymer with a specific rotation of −41.1° in 27% yield.

On the other hand, the polymerization with other cationic catalysts such as boron trifluoride etherate and niobium pentachloride, which were good catalysts for the polymerization of 1,4-anhydroribose derivatives,[1,2] hardly gave any polymer.

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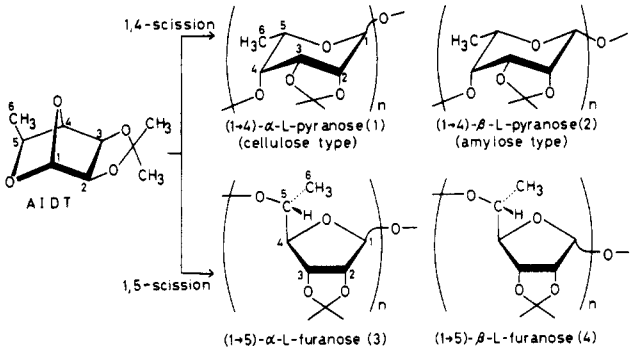
Table I
Cationic Ring-Opening Polymerization of 1,4-Anhydro-6-deoxy-2,3-*O*-isopropylidene-β-L-talopyranose (AIDT)[a]

no.	catalyst kind	catalyst mol %	temp, °C	time, h	yield, %	$[\alpha]_D$,[b] deg	$10^{-4}\bar{M}_n$[c]
1	PF_5	3	−40	2	37.2	−40.4	1.8
2	PF_5	5	−40	2	25.5	−40.1	1.5
3	PF_5	3	−40	3	20.8	−42.4	1.1
4	PF_5	3	−40	16	trace		
5	PF_5	3	−60	2	38.5	−7.7	3.8
6	$SbCl_5$	3	0	24	trace		
7	$SbCl_5$	3	−40	24	26.8	−41.1	1.3
8	$BF_3{\cdot}OEt_2$	3	0	22	trace		
9	$BF_3{\cdot}OEt_2$	3	−60	24	trace		
10	$NbCl_5$	3	0	96	trace		

[a] Monomer, 0.2–1.0 g, was polymerized. Monomer concentration, 50 w/v %; solvent, CH_2Cl_2. [b] Measured in chloroform at 25 °C (c 1%). [c] Determined by GPC (polystyrene standard).

Scheme I



AIDT is a 5-*C*-methyl derivative of 1,4-anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose (AIRP).[1] Therefore, lower polymerizability of AIDT than that of AIRP is considered to be due to the steric hindrance of the methyl group.

Structure of Poly(AIDT). There are four possible monomeric units in the poly(6-deoxy-L-talose) prepared by the ring-opening polymerization of AIDT, i.e., (1→4)-α- (**1**) and (1→4)-β-L-talopyranosidic (**2**) units and (1→5)-α- (**3**) and (1→5)-β-L-talofuranosidic (**4**) units (Scheme I).

Structure of the synthetic polysaccharide was examined by ^{13}C NMR spectroscopy and optical rotation. ^{13}C NMR spectra of poly(AIDT)s with specific rotations of −42.4° and of −7.7° are shown in Figure 1. The assignments of poly(AIDT) are shown in Table II. In the spectrum in Figure 1A, which was assigned with the C–H COSY technique, individual carbon absorptions due to the sugar moiety appear as single peaks, indicating that the polymer is a stereoregular polysaccharide.

Methyl 6-deoxy-α- and -β-L-talofuranoside derivatives, which are considered to be model compounds for a polymer with a L-talofuranose backbone, show $[\alpha]_D$ of −37° and +107°, respectively,[13] while methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talopyranoside[14] and the benzyl-β-L-talopyranoside derivative,[15] which are regarded as model compounds for a polymer with a L-talopyranose backbone, show $[\alpha]_D$ of −49° and +54°, respectively. Taking into account the negative specific rotation of −42°, this poly-L-talose must have an α configuration.

Since a stereoregular structure can be attained by a trialkyloxonium ion mechanism,[1] it was concluded that this poly(AIDT) was exclusively composed of 2,3-*O*-isopropylidene-6-deoxy-(1→4)-α-L-talopyranan. The similarity of the spectrum in Figure 1A (C-1, 108.9; C-2, 85.7; C-3, 81.0 ppm) to the ^{13}C NMR spectrum of 2,3-*O*-isopropylidene-(1→4)-β-D-ribopyranan[1] measured in $CDCl_3$ (C-1, 108.7; C-2, 85.1; C-3, 81.9 ppm) also suggested the (1→4)-α structure of the poly(AIDT).

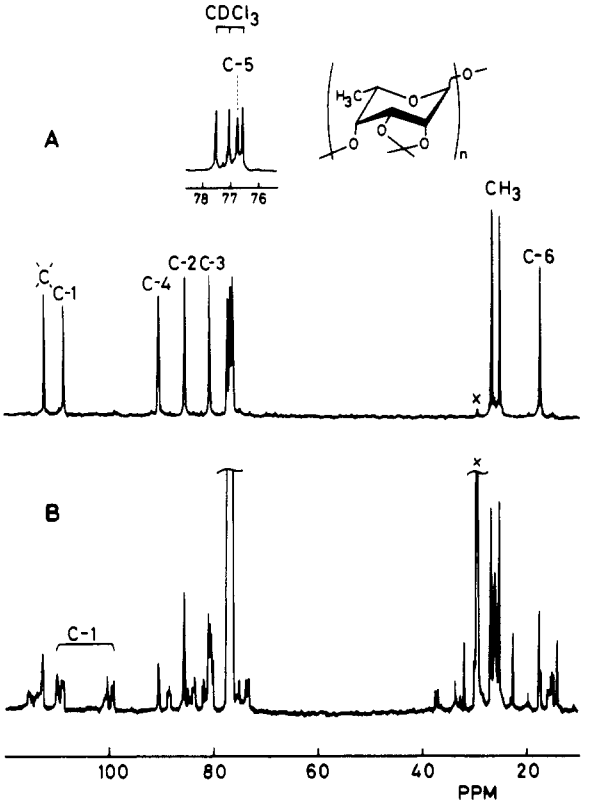


Figure 1. ^{13}C NMR spectra of (A) 6-deoxy-2,3-*O*-isopropylidene-(1→4)-α-L-talopyranan (no. 3 in Table I) and (B) irregular poly(AIDT) (no. 5 in Table I).

In the ^1H NMR spectrum of the stereoregular poly(AIDT), an absorption of the H-1 proton was a singlet, showing that the coupling constant between H-1 and H-2, $J_{1,2}$, is almost zero. Taking into account the dihedral angle between two protons,[16] the value of $J_{1,2}$ indicates that the conformation of the pyranose ring is $^1C_4$ in which H-1 and H-2 protons are both equatorial. If the conformation of (1→4)-α-L-talopyranan was $^4C_1$, the dihedral angle between H-1 and H-2 would be 180°, and, therefore, $J_{1,2}$ would have to be more than 7 Hz.

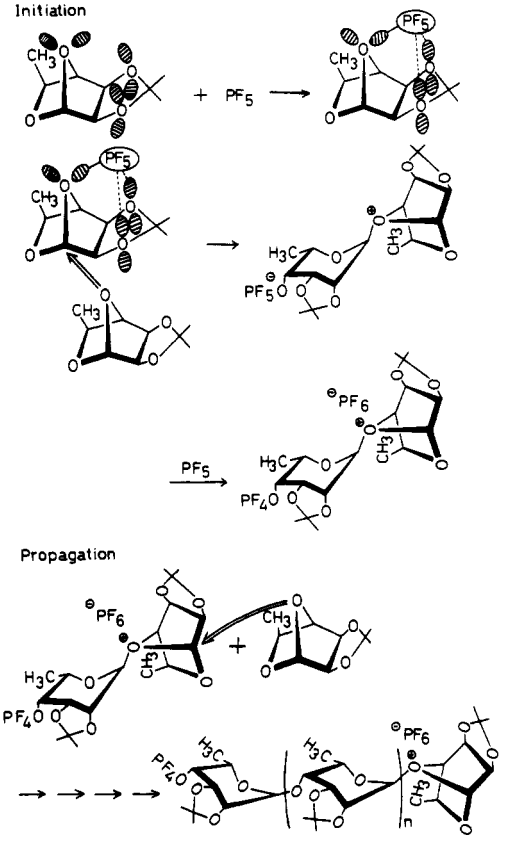
For the polymer with a specific rotation of −7.7°, the ^{13}C NMR spectrum shows that the backbone of the polymer is composed of two kinds of monomeric units. One is found to consist of an α-L-talopyranosidic unit by comparing the spectrum of Figure 1B with that of the stereoregular poly(AIDT) (spectrum in Figure 1A). Considering the specific rotation of the polymer and the similarity of the spectrum in Figure 1B to that of 2,3-*O*-isopropylidene-D-ribose polymer,[1] which is composed of (1→4)-β-D-ribopyranosidic and (1→5)-α-D-ribofuranosidic units, we conclude

Table II
^{13}C Chemical Shifts of Ring Carbons of 6-Deoxy-2,3-*O*-protected Poly(L-taloses) and 6-Deoxy-(1→4)-α-L-talopyranan

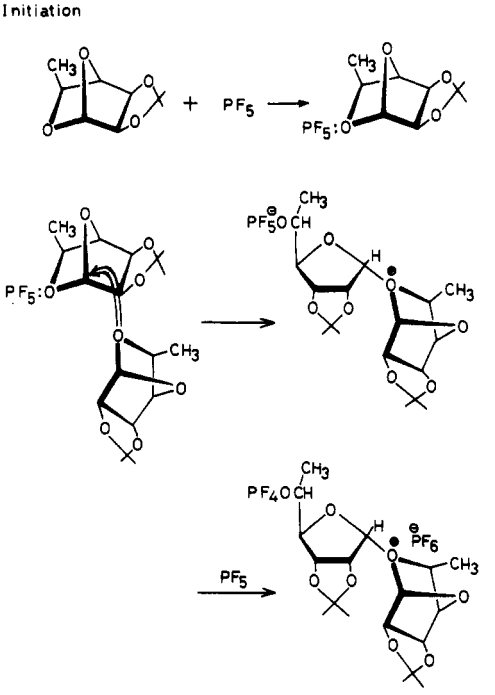
	C-1	C-2	C-3	C-4	C-5	C-6
6-deoxy-2,3-*O*-isopropylidene-(1→4)-α-L-talopyranan	108.82	85.62	80.91	90.67	76.72	17.48
poly(6-deoxy-2,3-*O*-isopropylidene-L-talose) with mixed structures[a]	109.76 (P)[b]	85.72 (P)	80.97 (P)	90.49 (P)	ca. 77 (P)[c]	17.56 (P)
	100.20 (F)	80.67 (F)	80.67 (F)	83.65 (F)	73.67 (F)	14.08 (F)
6-deoxy-2,3-*O*-cyclohexylidene-(1→4)-α-L-talopyranan	109.14	85.26	80.58	90.95	77.00	17.58
poly(6-deoxy-2,3-*O*-cyclohexylidene-L-talose) with mixed structures	110.39 (P)	85.33 (P)	80.58 (P)	90.56 (P)	ca. 77 (P)[c]	17.62 (P)
	100.34 (F)	80.11 (F)[d]	79.64 (F)[d]	83.82 (F)	73.87 (F)	15.81 (F)
poly(6-deoxy-2,3-*O*-benzylidene-L-talose) with mixed structures	108.26 (P)	85.11 (P)	80.17 (P)	88.55 (P)	74.77 (P)	17.63 (P)
	99.51 (F)	80.17 (P)	80.17 (F)	83.05 (F)	71.89 (F)	14.73 (F)
(1→4)-α-L-talopyranan	110.03	80.29	77.12	87.41	73.88	19.88

[a] Each absorption of the polymer with mixed structures showed the splitting that may be caused by tacticity. [b] P, pyranosidic unit; F, furanosidic unit. [c] Overlapped with the absorption of chloroform-*d*. [d] The assignment might be interchanged.

Scheme II



Scheme III



that the other structure of poly(AIDT) consists of β-L-talofuranosidic units. The splitting of individual C-1 carbon absorption is considered to be due to the neighboring monomeric units.

Mechanism of Polymerization of AIDT. By elucidation of the polymerization mechanism, it has been shown that a selective ring-opening polymerization consisting of selective 1,4-scission and β stereoregulation was caused by two factors: (1) complexation of a Lewis acid among a 1,4-linked oxygen and O-2 and O-3 oxygens in an initiation step and (2) formation of an oxonium ion at the O-4 oxygen in a propagation step. Antimony pentahalides and niobium pentahalides are suitable Lewis acid catalysts for the 2,3-*O*-alkylidene-protected monomer, while phosphorus pentafluoride and acryloyl chloride–antimony hexafluoride complex catalyst are appropriate for the 2,3-di-*O*-methyl and 2,3-di-*O*-*tert*-butyldimethylsilyl monomers, respectively.[1,2,11]

A stereoregular structure consisting exclusively of (1→4)-α-L-talopyranosidic units can be attained by a trialkyloxonium ion mechanism, as shown in Scheme II. (1→5)-β-L-Talofuranosidic units in the irregular poly(AIDT) can also be attained by an oxonium ion mechanism, as shown in Scheme III.

In the polymerization of 1,4-anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose,[1] $SbCl_5$ catalyst gave a stereoregular cellulose-type polysaccharide, while PF_5 catalyst gave a polymer with mixed structures. In contrast to the case of ribose, stereoregular cellulose-type poly(AIDT) was obtained with both $SbCl_5$ and PF_5 catalysts. It is considered that the repulsion between the methyl group (C-6) and the 1,4-linked oxygen in AIDT monomer at the initiation step causes the coordination of 1,4-linked oxygen even with the smaller Lewis acid (PF_5), achieved by the space that is formed by the three oxygen atoms, namely, O-2, O-3, and 1,4-linked oxygen. Therefore, both PF_5 and $SbCl_5$ catalyzed the polymerization of AIDT to provide a cellulose-type polysaccharide.

Polymerization of 1,4-Anhydro-2,3-*O*-cyclohexylidene-β-L-talopyranose (ACDT) and Structure Analysis of the Polymer. In the polymerization of AIDT, the smaller coordination space by the effect of the methyl group (C-6) selected PF_5, as well as $SbCl_5$, to form the cellulose-type polysaccharide. To elucidate further the role of the coordination site on the stereoregularity, we polymerized 1,4-anhydro-2,3-*O*-cyclohexylidene-β-L-talopyranose (ACDT) with cationic catalysts. Results are summarized in Table III.

Polymerization of ACDT with PF_5 as catalyst at −40 and −60 °C gave polymers with specific rotations of −43.8°

Table III
Cationic Ring-Opening Polymerization of 1,4-Anhydro-2,3-*O*-cyclohexylidene-6-deoxy-β-L-talopyranose (ACDT)[a]

no.	catalyst: kind	catalyst: mol %	temp, °C	time, h	yield, %	$[\alpha]_D$,[b] deg	$10^{-3}\bar{M}_n$[c]
1	PF_5	3	−40	2	27.5	−43.8	6.7
2	PF_5	3	−60	24	29.0	−43.6	5.6
3	$SbCl_5$	3	−40	2	37.3	−33.0	10.5
4	$SbCl_5$	3	−60	26	60.8	−27.0	12.7
5	$SbCl_5$	3	−78	3	50.0	+0.8	19.0
6	$BF_3{\cdot}OEt_2$	3	−20	45	19.7	−23.4	13.3
7	$CH_2{=}CHCOCl + AgPF_6$	3	−40	1	61.7	−40.2	15.2
8	$CH_2{=}CHCOCl + AgPF_6$	3	−78	3	26.8	−0.9	16.4

[a] Monomer, 0.2 g, was polymerized. Monomer concentration, 50 w/v %; solvent, CH_2Cl_2. [b] Measured in chloroform at 25 °C (c 1%). [c] Determined by GPC (polystyrene standard).

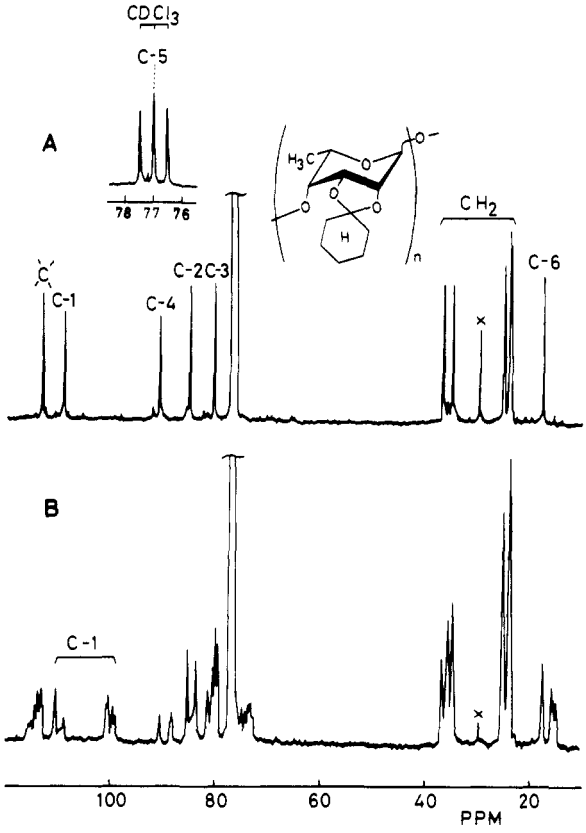


Figure 2. ^{13}C NMR spectra of (A) 2,3-*O*-cyclohexylidene-6-deoxy-(1→4)-α-L-talopyranan (no. 1 in Table III) and (B) irregular poly(ACDT) (no. 5 in Table III).

and −43.6°, respectively. Number-average molecular weights of polymers were 6.7×10^3 and 5.6×10^3. The ^{13}C NMR spectrum of the poly(ACDT) (Figure 2A) shows single peaks for individual carbon absorptions, indicating that the polymerization proceeded in a stereoregular manner. Close resemblance of ^{13}C NMR chemical shifts between stereoregular poly(ACDT) and (1→4)-α-linked poly(AIDT) as shown in Table II and the negative specific rotation of poly(ACDT) indicate that the stereoregular poly(ACDT) also has a cellulose-type structure.

When $SbCl_5$ was used as catalyst, polymers with specific rotations of +0.8° to −33.0° were obtained. ^{13}C NMR spectrum of the polymer (Figure 2B) shows that the poly(ACDT) prepared with $SbCl_5$ had mixed monomeric units, which can be considered to be (1→4)-α-L-talopyranosidic and (1→5)-β-L-talofuranosidic units. Lowering the polymerization temperature increased the formation of (1→5)-β-structure, which was confirmed by the positive specific rotation. The poly(ACDT) with mixed structures was also obtained with $BF_3{\cdot}OEt_2$, which did not catalyze the polymerization of AIDT.

When acryloyl chloride–silver hexafluorophosphate was used as catalyst, the stereoregularity of the obtained polymer was lower but the molecular weight was higher, compared with the case of PF_5 catalyst.

Also in the polymerization of ACDT, it is considered that the PF_5 coordinates with the 1,4-linked oxygen to give a stereoregular polysaccharide. However, in ACDT, the coordination space that consists of 1,4-linked oxygen, O-2, and O-3 might be smaller than that of AIDT. Therefore, the larger initiator $SbCl_5$ was not able to coordinate with the 1,4-linked oxygen, and a stereoregular polymerization did not occur.

Polymerization of 1,4-Anhydro-2,3-*O*-benzylidene-6-deoxy-β-L-talopyranose (ABDT) and Structure Analysis of the Polymer. Polymerization of the benzylidene derivative of the anhydrodeoxytalose monomer was also attempted. Since the benzylidene group can be removed by reduction, main-chain scission might not occur during deprotection.

Poly(ABDT)s with mixed structures, namely, (1→4)-α-L-talopyranosidic and (1→5)-β-L-talofuranosidic units, were obtained with both PF_5 and $SbCl_5$ catalysts (Table IV). When the polymerization catalyst was $SbCl_5$, which catalyzed the polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose to provide a stereoregular (1→4)-β-type (cellulose-type) polysaccharide,[1] contents of (1→4)-α-L-talopyranosidic units of the obtained poly(ABDT)s were 38 and 45%, which were determined from the C-1 absorption in ^{13}C NMR spectra. When PF_5 was used as catalyst, calculated values of (1→4)-α-contents of poly(ABDT)s from ^{13}C NMR spectra were 41 and 50%, which were somewhat higher than those in the case of the polymerization of benzylidenated anhydroribose monomer.[1]

Deprotection of Polymers into Free Polysaccharides. Deisopropylidenation of poly(AIDT) and decyclohexylidenation of poly(ACDT) were carried out by hydrolysis with trifluoroacetic acid and water (9:1 v/v). Results of deisopropylidenation are shown in Table V. When the reaction time was 3 min, an isopropylidene group was eliminated and the polymer yield was nearly quantitative. The ^{13}C NMR spectrum of stereoregular 6-deoxy-(1→4)-α-L-talopyranan measured in deuterium oxide is shown in Figure 3. This polysaccharide is the first synthetic hexopyranan with cellulose-type structure. When the reaction time was longer (10 min), the polymer yield was low. The number-average molecular weight of free talopyranan was 2.3×10^3, indicating that the main-chain scission occurred during the reaction. Low polymer yield also suggested the main-chain scission.

Decyclohexylidenation of poly(ACDT) was carried out in the same manner as deisopropylidenation. After the reaction for 10 min at room temperature, the cyclohexylidene group was mostly removed (>95%).

Table IV
Cationic Ring-Opening Polymerization of 1,4-Anhydro-2,3-O-benzylidene-6-deoxy-β-L-talopyranose (ABDT)[a]

no.	catalyst kind	catalyst mol %	temp, °C	time, h	yield, %	$[\alpha]_D$,[b] deg	$10^{-3}\bar{M}_n$[c]
1	PF_5	3	−40	3	19.8	+18.2	6.4
2	PF_5	6	−60	5	27.4	+21.1	4.3
3	$SbCl_5$	6	−40	22	11.6	+15.8	6.9
4	$SbCl_5$	6	−60	24	45.0	+31.1	7.9
5	$BF_3{\cdot}OEt_2$	6	−20	47	trace		

[a] Monomer, 0.2 g, was polymerized. Monomer concentration, 25–33 w/v %; solvent, CH_2Cl_2. [b] Measured in chloroform at 25 °C (c 1%). [c] Determined by GPC (polystyrene standard).

Table V
Deisopropylidenation of Poly(AIDT)

no.	polymer,[a] mg	TFA,[b] mL	time, min	yield, %	$[\alpha]_D$,[c] deg	$10^{-3}\bar{M}_n$[d]
1	50	0.5	3	97	−47.0	4.4
2	100	1.0	3	84	−40.1	6.2
3	50	0.5	10	43	−32.6	2.3

[a] Starting polymer, no. 3 in Table I. [b] Trifluoroacetic acid:water = 9:1 (v/v). [c] Measured in water at 25 °C (c 0.4–1%). [d] Determined by GPC (dextran standard).

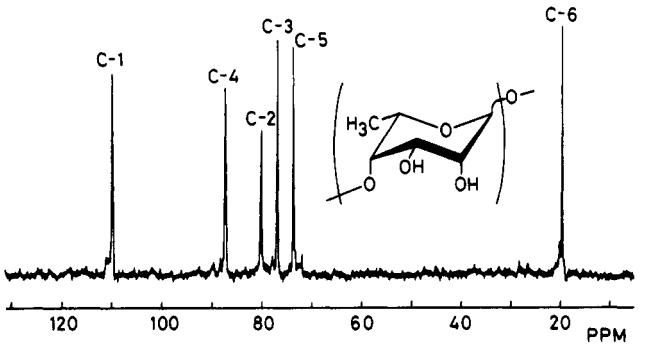


Figure 3. ^{13}C NMR spectrum of 6-deoxy-(1→4)-α-L-talopyranan.

Debenzylidenation of poly(ABDT) was carried out with sodium in liquid ammonia. ^1H and ^{13}C NMR spectra of the obtained polymer showed that the deprotection was complete and the free polysaccharide had two kinds of monomeric units, namely, 6-deoxy-(1→4)-α-L-talopyranosidic and 6-deoxy-(1→5)-β-L-talofuranosidic units.

Experimental Section

1,4-Anhydro-6-deoxy-2,3-O-isopropylidene-β-L-talopyranose (AIDT). AIDT was prepared from L-rhamnose (8.8 g) as the starting material, according to the method of Brimacombe,[17-19] and finally recrystallized from petroleum benzin. Yield: 0.7 g (7.8%). Mp: 67.5–69.0 °C (lit.[17] mp 71–73 °C).

1,4-Anhydro-6-deoxy-2,3-O-cyclohexylidene-β-L-talopyranose (ACDT). Syrupy benzyl α-L-rhamnopyranoside,[17] which was prepared from 2.0 g of L-rhamnose monohydrate, was dissolved in cyclohexanone (26.7 mL) and benzene (11.1 mL), and the solution was heated by using a Dean-Stark trap. After distillation of solvent, p-toluenesulfonic acid (22.3 mg) was added and the mixture was refluxed for 3.5 h with vigorous stirring. The reaction mixture was neutralized with 1.5 N ammonium hydroxide, washed with water, and dried (Na_2SO_4). After concentration, benzyl 2,3-O-cyclohexylidene-α-L-rhamnopyranoside was chromatographed on silica gel, with hexane–ethyl acetate (4:1, v/v) as eluant. The yield was 1.1 g (30.0%). ^1H NMR: δ 1.30 (d, 3 H, H-6), 1.5–1.8 (m, 10 H, $(CH_2)_5$), 3.41 (ddd, 1 H, H-4), 3.73 (dq, 1 H, H-5), 4.10 (dd, 1 H, H-3), 4.17 (d, 1 H, H-2), 4.52 (d, 1 H, CH_2Ph), 4.72 (d, 1 H, CH_2Ph), 5.07 (s, 1 H, H-1), 7.3–7.4 (m, 5 H, Ph). Methanesulfonyl chloride (20 mL) was added to a solution of benzyl 2,3-O-cyclohexylidene-α-L-rhamnopyranoside (12.8 g) in dried pyridine (290 mL), and the mixture was allowed to stand for 2 days at room temperature. Ice and water (600 mL) were added, and the mixture was added to ether (600 mL), which was washed with water (2 × 600 mL) and dried (Na_2SO_4). After Darco treatment, benzyl 2,3-O-cyclohexylidene-4-O-(methanesulfonyl)-α-L-rhamnopyranoside was purified with silica gel column chromatography (eluant: hexane–ethyl acetate (5:1, v/v)). The yield was 12.4 g (80.9%). ^1H NMR: δ 1.33 (d, 3 H, H-6), 1.5–1.9 (m, 10 H, $(CH_2)_5$), 3.20 (s, 3 H, CH_3SO_2), 3.85 (dq, 1 H, H-5), 4.21 (d, 1 H, H-2), 4.27 (dd, 1 H, H-3), 4.37 (dd, 1 H, H-4), 4.53 (d, 1 H, CH_2Ph), 4.70 (d, 1 H, CH_2Ph), 5.11 (s, 1 H, H-1), 7.3–7.4 (m, 5 H, Ph). Debenzylation of the rhamnoside (12.1 g) was performed by refluxing with 10% Pd/C (10.7 g) and ammonium formate (9.2 g) in acetone (350 mL) for 2 h. After removal of catalyst, 2,3-O-cyclohexylidene-4-O-(methanesulfonyl)-α-L-rhamnopyranose was chromatographed on silica gel with hexane–ethyl acetate (3:1, v/v) as eluant. The yield was 8.0 g (84.6%). ^1H NMR: δ 1.30 (d, 3 H, H-6), 1.5–1.9 (m, 10 H, $(CH_2)_5$), 3.23 (s, 3 H, CH_3SO_2), 4.04 (dq, 1 H, H-5), 4.21 (d, 1 H, H-2), 4.22–4.41 (m, 2 H, H-3 and H-4), 5.42 (s, 1 H, H-1). A solution of 2,3-O-cyclohexylidene-4-O-(methanesulfonyl)-α-L-rhamnopyranose (8.0 g) in dry pyridine (125 mL) containing acetic anhydride (125 mL) was allowed to stand for 24 h at room temperature. Workup gave 1-O-acetyl-2,3-O-cyclohexylidene-4-O-(methanesulfonyl)-α-L-rhamnopyranose. The yield was 6.2 g (68.6%). ^1H NMR: δ 1.35 (d, 3 H, H-6), 1.5–1.9 (m, 10 H, $(CH_2)_5$), 2.18 (s, 3 H, CH_3CO), 3.22 (s, 3 H, CH_3SO_2), 3.86 (dq, 1 H, H-5), 4.15 (dd, 1 H, H-2), 4.30 (dd, 1 H, H-3), 4.40 (dd, 1 H, H-4), 6.34 (s, 1 H, H-1). 1-O-Acetyl-2,3-O-cyclohexylidene-4-O-(methanesulfonyl)-α-L-rhamnopyranose (2.6 g) was reacted with sodium azide (2.6 g) in dimethylformamide (65 mL) for 3 h at 140 °C. After cooling, water (200 mL) and ether (200 mL) were added. Extract from the water layer with ether (3 × 200 mL) was added to the ether layer. The ether solution was washed with water, dried with sodium sulfate, and evaporated to dryness. 1,4-Anhydro-2,3-O-cyclohexylidene-6-deoxy-β-L-talopyranose was chromatographed on silica gel with hexane–ethyl acetate (4:1, v/v) as eluant and finally recrystallized from petroleum benzin. The yield was 1.3 g (80.5%). ^1H NMR: δ 1.15 (d, 3 H, H-6), 1.5–1.7 (m, 10 H, $(CH_2)_5$), 3.53 (q, 1 H, H-5), 4.24–4.31 (m, 3 H, H-2, H-3, and H-4), 5.43 (s, 1 H, H-1). The overall yield from L-rhamnose was 11.3%. Mp: 73.5–74.5 °C. $[\alpha]^{25}_D$: −41.8° (c 1, $CHCl_3$).

1,4-Anhydro-2,3-O-benzylidene-6-deoxy-β-L-talopyranose (ABDT). L-Rhamnose monohydrate (25 g) was dissolved in allyl alcohol (200 mL) containing HCl (3 mL), and the solution was allowed to stand for 3 days at room temperature. After neutralization by concentrated ammonium hydroxide, the solution was evaporated to dryness. To the obtained syrup, α,α-dimethoxytoluene (23.5 mL), DMF (110 mL), and p-toluenesulfonic acid (68.7 mg) were added. The reaction was carried out under vacuum for 3 h at 60 °C. After the addition of water (500 mL) containing sodium bicarbonate (3 g), the product was extracted with chloroform. Concentration of the chloroform solution followed by silica gel column chromatography with hexane–ethyl acetate (3:1, v/v) as eluant gave allyl 2,3-O-benzylidene-L-rhamnopyranoside. Mesylation of the allyl rhamnoside was carried out as described in the previous experiment. Allyl 2,3-O-benzylidene-4-O-(methanesulfonyl)-L-rhamnopyranoside having an asymmetric benzylidene methine carbon was obtained as a mixture of 58% anti and 42% syn isomers. ^1H NMR: δ 1.36 (d, 3 H × 0.42, H-6 (syn)), 1.39 (d, 3 H × 0.58, H-6 (anti)), 2.98 (s, 3 H × 0.42, CH_3SO_2 (syn)), 3.20 (s, 3 H × 0.58, CH_3SO_2 (anti)), 3.91 (dq, 1 H, H-5), 3.97–4.25 (m, 2 H, $CH_2CH{=}CH_2$), 4.19 (dd, 1 H × 0.58, H-2 (anti)), 4.31 (dd, 1 H × 0.42, H-2 (syn)), 4.38–4.47

(m, 2 H × 0.42, H-3 (syn) and H-4 (syn)), 4.53 (dd, 1 H × 0.58, H-4 (anti)), 4.61 (dd, 1 H × 0.58, H-3 (anti)), 5.10 (s, 1 H × 0.58, H-1 (anti)), 5.20 (s, 1 H × 0.42, H-1 (syn)), 5.28 (m, 2 H, CH_2-CH=CH_2), 5.90 (m, 1 H, CH_2CH=CH_2), 5.91 (s, 1 H × 0.42, CHPh (syn)), 6.24 (s, 1 H × 0.58, CHPh (anti)), 7.3–7.5 (m, 5 H, Ph). Deallylation of the allyl rhamnoside (6.1 g) was performed by the reaction with acetic acid (32 mL), sodium acetate (5.4 g), water (1.5 mL), and palladium chloride (3 g) for 24 h at room temperature with stirring. Acetylation and ring-closing reaction were carried out as described in the previous section. 1,4-Anhydro-2,3-*O*-benzylidene-6-deoxy-β-L-talopyranose was recrystallized from petroleum benzin. The overall yield from L-rhamnose was 10.1%. ^{1}H NMR: δ 1.16 (d, 3 H, H-6), 3.68 (q, 1 H, H-5), 4.49, 4.50, and 4.51 (s, s, and s, 3 H, H-2, H-3, and H-4), 5.60 (s, 1 H, H-1), 6.15 (s, 1 H, CHPh), 7.3–7.4 (m, 5 H, Ph). Mp: 119–120 °C. $[\alpha]^{25}_D$: −47.4° (*c* 1, $CHCl_3$).

Polymerization of AIDT, ACDT, and ABDT. Polymerization was carried out under high vacuum at low temperature as described previously.[1,2,11,12]

Deprotection of Poly(AIDT) and Poly(ACDT). Deisopropylidenation of poly(AIDT) and decyclohexylidenation of poly(ACDT) were carried out by the same procedure. To 50 mg of the poly(AIDT) (or poly(ACDT)) was added 0.5 mL of trifluoroacetic acid–water (9:1, v/v). The solution was stirring for 3–10 min at room temperature, diluted with 25 mL of water, and dialyzed with running water for 2 days in a cellulose tube. The free polysaccharide was freeze-dried from water.

Debenzylidenation of Poly(ABDT). Debenzylidenation of poly(ABDT) was carried out with sodium in liquid ammonia as described previously.[1] The water-soluble polysaccharide was freeze-dried from water.

Measurement. 270-MHz ^{1}H NMR and 67.8-MHz ^{13}C NMR spectra were measured on the polymer solutions by means of a JEOL GX-270 spectrometer. Specific rotations of polysaccharides were measured on the solutions by means of a Perkin-Elmer 241 polarimeter using a 1-dm cell. Gel permeation chromatography was run on 5% solutions of polymers in tetrahydrofuran at elevated temperature by means of a Toyo Soda high-speed liquid chromatograph (Model HLC 802 UR).

Conclusion

In the polymerization of AIDT, the repulsion between the methyl group (C-6) and the 1,4-linked oxygen caused the coordination of 1,4-linked oxygen not only with $SbCl_5$ but also with PF_5 to afford a stereoregular cellulose-type polysaccharide. Since, in the ACDT monomer, the coordination space that consists of 1,4-linked oxygen, O-2, and O-3 might be smaller than that of AIDT, the larger Lewis acid ($SbCl_5$) was not able to coordinate with the 1,4-linked oxygen, while PF_5 gave a cellulose-type polysaccharide. The polymerization of ABDT did not give a stereoregular polymer. An appropriate combination of a protective group and an intiator was necessary so that the stereoregular polymerization can occur.

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Registry No. AIDT, 18422-81-6; poly(AIDT), 131684-92-9; ACDT, 131684-87-2; poly(ACDT), 131684-93-0; *anti*-ABDT, 131684-90-7; *syn*-ABDT, 131684-91-8; poly(ABDT), 131725-06-9; L-rhamnose, 3615-41-6; benzyl α-L-rhamnopyranoside, 3359-35-1; benzyl 2,3-*O*-cyclohexylidene-α-L-rhamnopyranoside, 131684-83-8; benzyl 2,3-*O*-cyclohexylidene-4-*O*-(methanesulfonyl)-α-L-rhamnopyranoside, 131684-84-9; 2,3-*O*-cyclohexylidene-4-*O*-(methanesulfonyl)-α-L-rhamnopyranose, 131684-85-0; 1-*O*-acetyl-2,3-*O*-cyclohexylidene-4-*O*-(methanesulfonyl)-α-L-rhamnopyranose, 131684-86-1; L-rhamnose monohydrate, 10030-85-0; *anti*-allyl 2,3-*O*-benzylidene-L-rhamnopyranoside, 131725-03-6; *syn*-allyl 2,3-*O*-benzylidene-L-rhamnopyranoside, 131725-04-7; *anti*-allyl 2,3-*O*-benzylidene-4-*O*-(methanesulfonyl)-L-rhamnopyranoside, 131684-88-3; *syn*-allyl 2,3-*O*-benzylidene-4-*O*-(methanesulfonyl)-L-rhamnopyranoside, 131684-89-4.