Macromolecules

Volume 19, Number 1 January 1986

Selective Ring-Opening Polymerization of 1,4-Anhydro-α-D-lyxopyranose Derivatives and Synthesis of Stereoregular (1→5)-α-D-Lyxofuranan

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ABSTRACT: A new stereoregular polysaccharide, (1→5)-α-D-lyxofuranan, was synthesized by the selective ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-lyxofuranose (ADBL) (=1,5-anhydro-2,3-di-*O*-benzyl-β-D-lyxofuranose) into 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranan and subsequent removal of the protective benzyl groups. Polymerization of ADBL by phosphorus pentafluoride catalyst gave 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranans with positive specific rotations, while boron trifluoride etherate catalyst gave nonstereoregular poly(ADBL) consisting of (1→5)-α-D-lyxofuranosidic and (1→4)-β-D-lyxopyranosidic structures. In addition, 1,4-anhydro-2,3-di-*O*-methyl-α-D-lyxopyranose (ADML) was polymerized by various Lewis acids as catalyst to give poly(ADMLs), all of which were not stereoregular and were composed of more than two different structural units. 1,4-Anhydro-2,3-*O*-benzylidene-α-D-lyxopyranose (ABLP) was also polymerized by Lewis acid to give poly(ABLP) which consisted mainly of 2,3-*O*-benzylidene-(1→5)-α-D-lyxofuranosidic units. ^{13}C NMR, optical rotation, and hydrolysis were used for structural analysis of polymers. The mechanism of the cationic ring-opening polymerization of ADBL, ADML, and ABLP is discussed.

Introduction

Of four 1,4-anhydro-D-aldopentopyranoses, 1,4-anhydro-α-D-ribopyranose and -α-D-xylopyranose derivatives have been polymerized by the selective ring-opening polymerization and by the subsequent deprotection to give (1→4)-β-D-ribopyranan[1] and (1→5)-α-D-ribofuranan[2] and (1→5)-α-D-xylofuranan,[3] respectively. Recently, these synthetic polysaccharides were successfully converted into biologically active polysaccharides.[4]

Ring-opening polymerization of anhydro sugars has been extensively investigated on 1,6-anhydrohexopyranoses.[5-7] Since a 1,6-anhydrohexopyranose is a bicyclic acetal, there are two possible ring-opening modes. However, the scission of the 1,6-anhydro ring exclusively occurs because of a high reactivity of the 1,6-anhydro ring and the stability of the pyranose-backbone polysaccharide formed by such a ring opening.

On the other hand, 1,4-anhydro-α-D-ribofuranose, which can equally be regarded as 1,5-anhydro-β-D-ribofuranose, gave two kinds of stereoregular polysaccharides depending on both hydroxyl protective groups and polymerization conditions, such as catalyst and temperature. Of several 1,4-anhydroribopyranose and -xylopyranose derivatives, it has been revealed that 1,4-anhydro-α-D-ribopyranoses, the cis hydroxyls of which are protected by dioxolane groups such as benzylidene,[1] methoxybenzylidene,[8] and isopropylidene[1] or by di-*O*-methyl groups[2] with a stereocontrolling function, gave polymers having a (1→4)-β-pyranose backbone, that is, a cellulose-type polysaccharide. Di-*O*-benzylated 1,4-anhydro-α-D-ribopyranose and -α-D-xylopyranose were polymerized by Lewis acid catalysts to give stereoregular polysaccharide derivatives having a (1→5)-α-furanose backbone.

Since D-lyxose, which is a pentose not existing in nature, has cis hydroxyls at C-2 and C-3 carbons, it can provide both di-*O*-benzylated and benzylidenated 1,4-anhydro-α-D-lyxopyranoses.

In this study, we report the first synthesis of 1,4-anhydro-2,3-di-*O*-benzyl-, 1,4-anhydro-2,3-di-*O*-methyl-, and 1,4-anhydro-2,3-*O*-benzylidene-α-D-lyxopyranoses and their cationic ring-opening polymerizations. Since a stereoregular 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranan is obtained, it is debenzylated to give a new polysaccharide, (1→5)-α-D-lyxofuranan. The stereostructure of benzylated, methylated, and benzylidenated poly(D-lyxoses) is studied by 100-MHz ^{13}C NMR spectroscopy, optical rotation, and hydrolysis.

Results and Discussion

Cationic Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-lyxopyranose (ADBL). When ADBL was polymerized with Lewis acids $BF_3 \cdot OEt_2$, PF_5, and $SbCl_5$ as catalysts at 0 to −78 °C in CH_2Cl_2 by using a high-vacuum technique,[4] the polymer was obtained in high conversion. The results are summarized in Table I. The polymers obtained by $BF_3 \cdot OEt_2$ (no. 1 and 2) were

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Table I
Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-lyxopyranose by Cationic Catalysts[a]

no.	catalyst: kind	catalyst: mol %	temp, °C	time, h	polymer: yield, %	polymer: $[\alpha]^{25}_D$,[b] deg	polymer: $\bar{M}_n$[c] × 10^{-3}
1	BF_3·OEt_2	5	−40	6	77.5	+2.4	104
2	BF_3·OEt_2	5	−60	20	43.6	+5.9	107
3	PF_5	5	0	0.2	63.1	*d*	*d*
4[e]	PF_5	10	−40	18	57.7	+27.5[f]	4.5[f]
5	PF_5	5	−60	3	95.2	*d*	*d*
6[g]	PF_5	2	−60	1	22.5	+12.0	5.1
7	PF_5	5	−78	2	97.6	*d*	*d*
8	$SnCl_4$	7.5	0	2	79.2	*h*	*h*
9	$SbCl_5$	5	0	1	75.4	*d*	*d*
10	$SbCl_5$	5	−60	6	77.0	+28.4[f]	2.6[f]
11	NbF_5	10	−60	25	17.5	+0.9	2.4
12	TaF_5	7	−40	33	32.7	+14.4	3.3

[a] Solvent, dichloromethane; monomer-to-solvent ratio, 25–28 w/v %. [b] Measured in chloroform. [c] Measured by GPC using chloroform as solvent. [d] Not determined because of insolubility in chloroform. [e] Monomer-to-solvent ratio, 50 w/v %. [f] Measured after heating at 150 °C in *o*-dichlorobenzene. [g] Copolymerization of ADBL (98%) with 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose (2%). [h] Not determined because of partial insolubility in chloroform.

soluble in chloroform and had number-average molecular weights of about 100 × 10^3. The ^{13}C NMR spectrum of poly(ADBL) (no. 1) is shown in Figure 1C, indicating that the C-1 carbon absorption consists of two peaks and accordingly the polymer obtained with BF_3·OEt_2 is of low stereoregularity. On the other hand, the polymers obtained with PF_5 and $SbCl_5$ as catalysts (no. 3–10) were practically insoluble in dichloromethane, chloroform, cyclohexanone, acetone, and ethyl acetate but were soluble in hot *o*-dichlorobenzene. Figure 1B shows a typical ^{13}C NMR spectrum of $CHCl_3$-insoluble poly(ADBL) (no. 4). The spectrum is very simple and the polymer proved to be highly stereoregular. These $CHCl_3$-insoluble polymers became soluble in chloroform after heating at 150 °C in *o*-dichlorobenzene for 3–20 h, probably because of the partial degradation of the polymer backbone.

The molecular weight of the polymer that was recovered from the *o*-dichlorobenzene solution was measured in a chloroform solution to be 4.5 × 10^3.

The very low solubility of the benzylated polysaccharide is extraordinary, because all the synthetic benzylated (1→6)-α-D-glycans,[7,9] (1→5)-α-D-pentofuranans,[2,3] and (1→4)-β-D-ribopyranan[1] are soluble in such solvents as benzene and chloroform, though the methylated (1→6)-α-D-glucans[10] are scarcely soluble in any solvent. As described later, the stereoregular poly(ADBL) is 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranan, which is expected to show solubility in the above solvents. Although it did not provide a crystalline X-ray diffraction pattern, it is assumed that the polymer backbone is arranged in an ordered structure, which makes the solubility of the polymer decrease. To prove the assumption, copolymerization of ADBL with a few percent of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose was carried out with PF_5 as catalyst. The copolymer was soluble in $CHCl_3$ and showed $[\alpha]^{25}_D$ +12.0° (no. 6). In other polymerizations in which ADBL of low purity was polymerized with PF_5 and $SbCl_5$ as catalyst, the polymers obtained showed solubility in $CHCl_3$. Therefore, only poly(ADBL) with high stereoregularity is insoluble in most organic solvents.

Structure of Poly(ADBL) and Mechanism of Polymerization. Since ADBL, as well as other 1,4-anhydro sugar derivatives, is a bicyclic acetal and possesses fused five- and six-membered heterocycles, ADBL is expected to yield polymers with one or more unit structures as in the case of other 1,4-anhydro sugars.[1-3] The possible polymer structures are (1→5)-α-furanose, (1→5)-β-furanose, (1→4)-β-pyranose, and (1→4)-α-pyranose units. In addition, of these four structural units, the (1→5)-α-furanose unit or (1→4)-β-pyranose unit can exclusively constitute the polymers if the polymerization proceeds via a trialkyloxonium ion mechanism.[7]

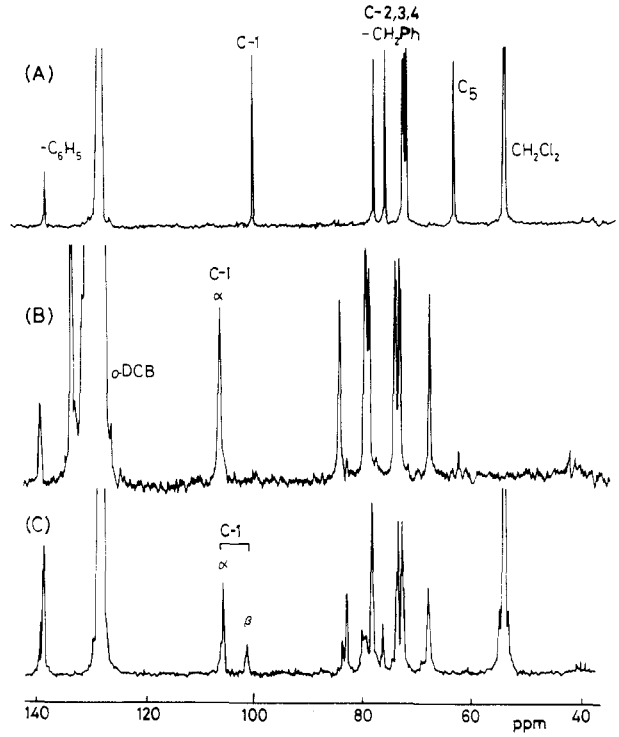


Figure 1. 25-MHz ^{13}C NMR spectra of (A) 1,4-anhydro-2,3-di-*O*-benzyl-α-D-lyxopyranose (solvent, CH_2Cl_2), (B) 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranan (solvent, *o*-dichlorobenzene at 150 °C), and (C) poly(1,4-anhydro-2,3-di-*O*-benzyl-D-lyxopyranose) prepared with BF_3·OEt_2 (solvent, CH_2Cl_2). (Me_4Si as reference zero.)

As mentioned above, the poly(ADBLs) obtained by PF_5 or $SbCl_5$ catalyst had a stereoregular structure. Accordingly, it is considered that the polymerization with PF_5 or $SbCl_5$ proceeded via a trialkyloxonium ion mechanism, which causes inversion at the C-1 carbon, giving poly(ADBLs) consisting of either a (1→5)-α-furanose or (1→4)-β-pyranose unit.

Specific rotations of methyl-D-lyxosides, which can be regarded as model compounds for the possible polymer structures, are reported as follows:[11] methyl-α-D-lyxofuranoside, $[\alpha]_D$ +160°; methyl-α-D-lyxopyranoside, $[\alpha]_D$ +59°; methyl-β-D-pyranoside, $[\alpha]_D$ −127°; no report on the β-D-lyxofuranoside. Taking into account that the stereoregular poly(ADBL) obtained with PF_5 or $SbCl_5$ has a

Table II
Debenzylation of Poly(1,4-anhydro-2,3-di-*O*-benzyl-α-D-lyxopyranose) into Free Polysaccharide

	poly(ADBL)				reaction		yield of free polysaccharide,
no.	no. in Table I	g	NH_3, mL	Na, g	temp, °C	time, h	%
PL-1	1	0.176	50	0.42	−78	2	90.3
	2	0.078					
PL-2	5	0.131	150	1.26	−33	5	40.2
	7	0.172					

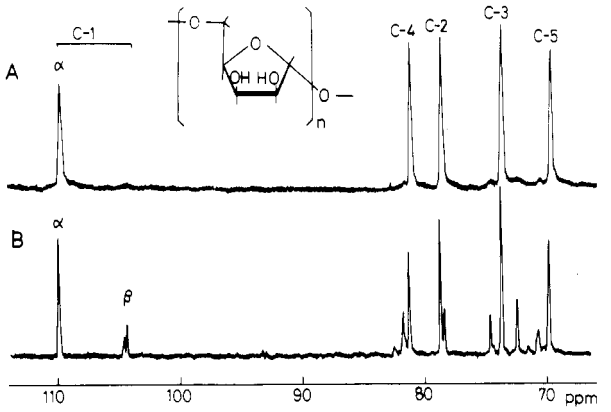


Figure 2. 100-MHz ^{13}C NMR spectra of debenzylated poly(1,4-anhydro-2,3-di-*O*-benzyl-D-lyxopyranoses) prepared by (A) PF_5 ((1→5)-α-D-lyxofuranan) and (B) BF_3·OEt_2 (poly D-lyxose) of mixed structure) measured in D_2O.

relatively high positive specific rotation of +27.5° to +28.4° and that the nonstereoregular ones show a lower positive $[\alpha]_D$ value, ranging from +0.9° to +14.4°, it is assumed that the regular structure is the (1→5)-α-furanose unit. Therefore, it was concluded that 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranan was obtained with PF_5 or $SbCl_5$ as the catalyst by selective 1,5-ring opening via a trialkyloxonium ion mechanism. In addition, the poly(ADBLs) obtained with BF_3·OEt_2 as the catalyst are assumed to consist of mixed structures of the (1→5)-α-furanose unit and one of the two β-units.

Debenzylation of Poly(ADBL) into Free Polysaccharide. Debenzylation of poly(ADBL) was carried out with sodium in liquid ammonia. Reaction conditions and results are summarized in Table II. The debenzylation of both nonstereoregular (PL-1) and stereoregular (PL-2) poly(ADBLs) gave white poly(D-lyxoses), which dissolved in water to show very slightly white muddiness. Although the stereoregular poly(ADBL) was only swollen in toluene–dimethoxyethane, which was a solvent used for debenzylation, the free polysaccharide was obtained in 40% yield. ^{13}C NMR spectra of these poly(D-lyxoses) are shown in Figure 2.

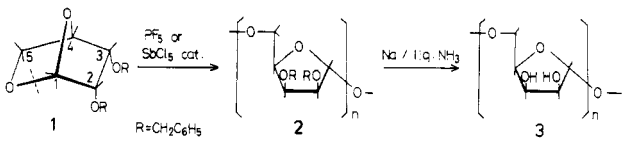
The peak assignment was performed by reference to that of methyl-D-lyxoside.[11] Figure 2A indicates that the individual carbon absorption of a free polysaccharide PL-2 consists of a single peak and therefore the polymer is highly stereoregular. It is clearly found from Table III that the chemical shifts of C-1 (109.71 ppm) through C-4 carbons of the stereoregular polysaccharide are in good accordance with those of the corresponding carbons of methyl α-D-lyxofuranoside rather than those of the β-anomer, except for the C-5 carbon. Taking into account the positive optical rotation of the preceding benzylated polysaccharide and the ^{13}C chemical shift, it was concluded that the stereoregular poly(D-lyxose) is (1→5)-α-D-lyxofuranan (**3**) (Scheme I). Accordingly, the cationic ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-lyxopyranose (**1**) with PF_5 or $SbCl_5$ as the catalyst occurs through the selective scission of 1,5-anhydro ring.

Table III
^{13}C NMR Chemical Shifts of Free Poly(D-lyxoses) and Model Compounds[a]

	chemical shift, ppm				
	C-1	C-2	C-3	C-4	C-5
(1→5)-α-D-lyxofuranan (PL-2)	109.71	78.72	73.76	81.27	69.76
poly(D-lyxose) of mixed structure	109.79	78.46	72.25	81.47	70.55
	104.42	78.52	73.56	81.15	69.76
	104.19		74.43		
methyl α-D-lyxofuranoside[b]	109.2	77.0	72.2	81.4	61.5
methyl β-D-lyxofuranoside[b]	103.3	73.2	71.0	82.1	62.7

[a] Measured in D_2O at room temperature. [b] Reference 11.

Scheme I



A free polysaccharide PL-1 from nonstereoregular poly(ADBL) has three C-1 carbon absorptions at 109.79, 104.42, and 104.19 ppm, the last two of which closely appear and also show two or three peaks for other individual carbons (Figure 2 and Table II). One of the two or three absorption peaks of the nonstereoregular poly(ADBL) is in good accordance with the absorption of the stereoregular (1→5)-α-D-lyxofuranan. Since in the ^{13}C NMR spectrum of the nonstereoregular benzylated polymer, each carbon absorption consists of two peaks, it is concluded that the nonstereoregular poly(D-lyxose) is composed of a mixed structure consisting of (1→5)-α-D-lyxofuranosidic (72%) and (1→4)-β-D-lyxopyranosidic (28%) units. The conclusion of the β-structure was made from the studies on the polymer structure of the methylated poly(D-lyxose) described in the next section.

Cationic Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-methyl-α-D-lyxopyranose (ADML). It has been reported that the di-*O*-methylated 1,4-anhydro-α-D-ribopyranose was polymerized into two completely stereoregular polysaccharide derivatives, that is, di-*O*-methylated (1→4)-β-D-ribopyranan and di-*O*-methylated (1→5)-α-D-ribofuranan, though the di-*O*-benzylated or benzylidenated 1,4-anhydro-α-D-ribopyranose was polymerized into either of the two stereoregular polymers.[2]

Syrupy ADML monomer was polymerized with the Lewis acids PF_5, $SbCl_5$, BF_3·OEt_2, and $SnCl_4$ as catalysts at low temperature in CH_2Cl_2 by using a high-vacuum technique.[12] The results are summarized in Table IV. When ADML was polymerized by the strong Lewis acid PF_5 in a short polymerization time (0.1–0.6 h), poly(ADMLs) with positive specific rotations of +39.9° to +80.7° and with number-average molecular weights from 11.0×10^3 to 24.8×10^3 were obtained in high yield (54.4–85.8%) (no. 1–4 in Table IV).

The polymerization by the $SbCl_5$ catalyst also gave polymers with $[\alpha]^{25}_D$ of +27.6° to +78.6°. However, the catalytic activity of $SbCl_5$ was a little lower than that of

Table IV
Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-methyl-α-D-lyxopyranose by Cationic Catalysts[a]

no.	catalyst		temp, °C	time, h	polymer		
	kind	mol %			yield, %	$[\alpha]^{25}_D$,[b] deg	$\bar{M}_n \times 10^{-3}$
1	PF_5	6.4	0	0.2	85.8	+76.3	11.0
2	PF_5	6.4	−40	0.2	67.9	+80.7	14.7
3	PF_5	6.5	−60	0.1	79.0	+60.0	24.8
4	PF_5	4.6	−78	0.6	54.4	+39.9	20.3
5	$SbCl_5$	5.7	0	16.8	80.7	+78.6	5.2
6	$SbCl_5$	8.1	−40	0.9	59.0	+45.0	6.1
7	$SbCl_5$	5.8	−60	22.3	33.2	+27.6	10.7
8	$SbCl_5$	11.1	−78	46.2	18.4	+41.3	4.0
9	BF_3·OEt_2	6.8	0	14.5	83.4	+85.9	11.3
10	BF_3·OEt_2	9.4	−40	0.5	86.3	+28.2	30.8
11	BF_3·OEt_2	13.4	−60	1.0	17.9	+15.3	45.8
12	BF_3·OEt_2	7.1	−60	29.0	47.0	+2.0	10.1
13	BF_3·OEt_2	7.5	−78	13.0	52.8	+17.5	58.9
14	$SnCl_4$	8.7	0	2.0	87.9	+66.4	6.2
15	$SnCl_4$	8.0	−78	64.0	6.7	+1.9	5.6

[a] *Monomer concentration*, 20 w/v %; *solvent*, CH_2Cl_2. [b] Measured in a 1 w/v % $CHCl_3$ solution.

PF_5 because it resulted in low yield at low temperature and the number-average molecular weights of the polymers obtained were low (4.0×10^3–10.7×10^3).

Boron trifluoride etherate catalyst, which provides high molecular weight polymers from 1,4-anhydro sugars, gave poly(ADMLs) with high molecular weights of 30.8×10^3–58.9×10^3 in the polymerization at −40 to −78 °C. The polymers prepared by BF_3·OEt_2 at low temperature showed low positive $[\alpha]^{25}_D$ values, ranging from +2.0° to +28.2°. Stannic chloride as catalyst also provided a polymer with a low positive $[\alpha]^{25}_D$, +1.9°, in the polymerization at −78 °C, but the molecular weight of the polymers was low.

Structure of Poly(ADML). It was found from ^{13}C NMR spectra of poly(ADMLs) with different specific rotations that all poly(ADMLs) were not stereoregular and that even the poly(ADML) with the highest $[\alpha]^{25}_D$ (+85.9°) showed C-1 absorptions consisting of a main peak at 105 ppm and other small peaks (Figure 3A).

As shown in Figure 3, there are four patterns in the ^{13}C NMR spectra of poly(ADMLs) depending on the specific rotations. Of five backbone-carbon absorptions, the C-1 and C-5 absorptions clearly reflect the difference in stereoregularity, the former ranging from 96.5 ppm to 106 ppm and the latter from 67 ppm to 74 ppm. In addition, the C-1 absorption consists of three absorption regions, that is, absorption at 96.5–98.5, 100.5–101.5, and 104–106 ppm.

It was revealed from the relationship between the specific rotation and NMR absorption intensity that these three absorption regions contribute to positive, negative, and positive optical rotations, respectively. Accordingly, the three absorption regions were assigned (1→4)-α-D-lyxopyranosidic (α-P), (1→4)-β-D-lyxopyranosidic (β-P), and (1→5)-α-D-lyxofuranosidic (α-F) units, respectively. The absorptions due to individual structural units are thought to be split by bonding to different neighboring units.

To confirm that the C-1 absorption is split by the sequential effect, a nonstereoregular poly(1,4-anhydro-2,3-di-*O*-benzyl-D-lyxopyranose) which was polymerized by BF_3·OEt_2 catalyst and has two C-1 absorption peaks was converted into a methylated polymer by debenzylation and subsequent methylation.

As shown in Figure 4, the ^{13}C NMR spectrum of the methylated poly(D-lyxose) derived indicates that the C-1 absorption is composed of two absorption regions at 100.5–101.5 and 104–106 ppm, both of which are further split into a few peaks and shoulders. The spectrum (Figure 4A) was almost the same at that (Figure 4B) of poly(ADML) polymerized by the BF_3·OEt catalyst at −40 °C.

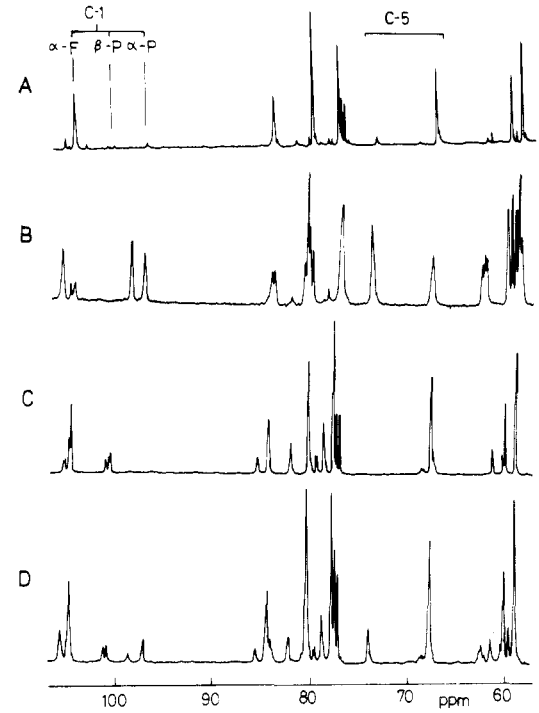


Figure 3. 100-MHz ^{13}C NMR spectra of poly(1,4-anhydro-2,3-di-*O*-methyl-D-lyxopyranoses) prepared by (A) BF_3·OEt_2, 0 °C, ($[\alpha]^{25}_D$ +85.9°); (B) PF_5, 0 °C, ($[\alpha]^{25}_D$ +76.3°); (C) BF_3·OEt_2, −78 °C, ($[\alpha]^{25}_D$ +17.5°); (D) PF_5, −78 °C, ($[\alpha]^{25}_D$ +39.9°).

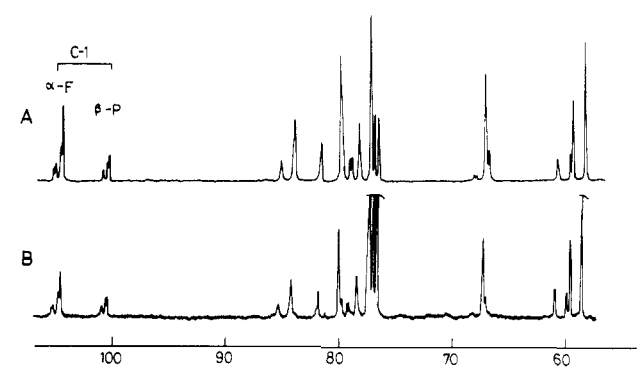


Figure 4. 100-MHz ^{13}C NMR spectra of methylated poly D-lyxoses (A) derived from poly(1,4-anhydro-2,3-di-*O*-benzyl-D-lyxopyranose) and (B) polymerized from 1,4-anhydro-2,3-di-*O*-methyl-α-D-lyxopyranose.

Table V
Ring-Opening Polymerization of 1,4-Anhydro-2,3-*O*-benzylidene-α-D-lyxopyranose by Cationic Catalysts[a]

no.	catalyst kind	catalyst mol %	temp, °C	time, h	polymer yield, %	polymer $[\alpha]^{25}_D$,[b] deg	polymer $\bar{M}_n \times 10^{-3}$	polymer $\bar{M}_w \times 10^{-3}$
1	$SbCl_5$	2	0	1	35.5	+45.4	2.9	5.1
2	$SbCl_5$	7	0	22	50.7	+43.1	3.1	5.3
3	$SbCl_5$	2	−40	3	20.7	+33.0	1.6	2.2
4	$SbCl_5$	2	−60	21	11.2		1.8	2.5
5[c]	$SbCl_5$	7	−60	45	31.9		2.1	3.2
6	PF_5	2	0	42	19.0		5.8	32.9
7	PF_5	7	0	25	52.7	+50.3	4.0	6.7
8	PF_5	2	−40	3	14.9		4.1	6.2
9[c]	PF_5	7	−60	45	43.4	+49.3	3.7	5.6
10	$BF_3{\cdot}OEt_2$	7	0	24	52.6	+47.9	6.8	11.2
11	$BF_3{\cdot}OEt_2$	7	−60	24	0			

[a] Monomer, 0.2 g; solvent, CH_2Cl_2, 1 mL. [b] Measured in a 1 w/v % $CHCl_3$ solution. [c] Monomer, 0.2 g; solvent, CH_2Cl_2, 2 mL.

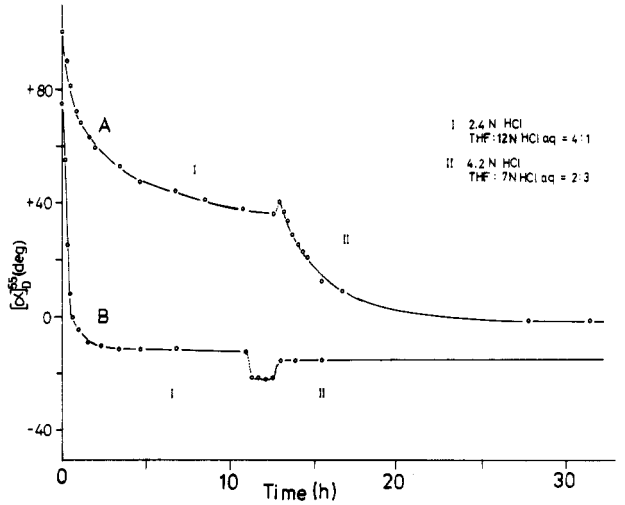


Figure 5. Change in optical rotation during hydrolysis of poly(1,4-anhydro-2,3-di-*O*-methyl-D-lyxopyranoses), obtained by (A) PF_5 at 0 °C ($[\alpha]^{25}_D$ +76.3° (in $CHCl_3$)) and (B) $BF_3{\cdot}OEt_2$ at −40 °C ($[\alpha]^{25}_D$ +28.2° (in $CHCl_3$)).

To determine whether the β-structure is a (1→4)-β-D-lyxopyranosidic or (1→5)-β-D-lyxofuranosidic unit, the hydrolysis of the polymers was carried out, because it is known that the furanosidic linkage is hydrolyzed much faster than the pyranosidic linkage.[13,14] Two poly(ADMLs) with $[\alpha]^{25}_D$ of +76.3° and +28.2° were hydrolyzed (Figure 5), the former having a Figure 3B pattern spectrum and the latter a Figure 3D pattern spectrum. In the initial stage, both polymers were rapidly hydrolyzed, losing positive optical rotation, suggesting that the initially hydrolyzed unit was an α-D-lyxofuranosidic unit. Thus, the poly(ADML) with $[\alpha]^{25}_D$ +28.2° is composed of (1→5)-α-D-lyxofuranosidic and (1→4)-β-D-lyxopyranosidic units, and the C-1 absorptions at 104–106 and 100.5–101.5 ppm are due to the former and the latter units, respectively.

Since after the initial stage the poly(ADML) with the starting $[\alpha]^{25}_D$ of +76.3° still shows positive specific rotation, it can be concluded that this polymer consists of (1→5)-α-D-lyxofuranosidic and (1→4)-α-D-lyxopyranosidic units and that the C-1 absorption at 96.5–98.5 ppm is due to the α-P unit.

Proportions of the three structural units were estimated from the C-1 absorption regions and shown in Figure 6. For the poly(ADMLs) obtained by the $BF_3{\cdot}OEt_2$ catalyst, the α-F unit was predominant in all the polymerization temperatures and 7–26% of the β-P unit was obtained, though small proportions of the α-P unit were produced at 0 °C.

On the other hand, almost equal proportions of the α-F and β-P units were contained in the poly(ADMLs) obtained by the PF_5 catalyst at 0 to −40 °C, and 9–16% of the β-P unit appeared as the temperature was lowered.

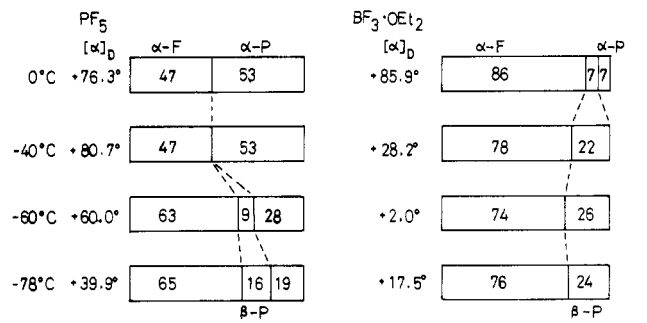
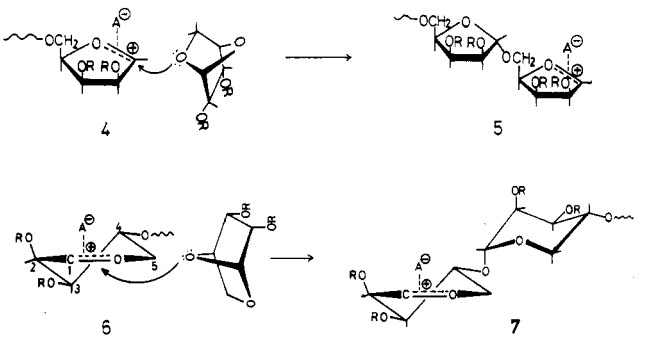


Figure 6. Fractions of α-furanose, β-pyranose, and α-pyranose structure of poly(1,4-anhydro-2,3-di-*O*-methyl-D-lyxopyranoses).

Scheme II



Mechanism of Polymerization. In the polymerization by the mild Lewis acids $BF_3{\cdot}OEt_2$ and $SnCl_4$ at low temperatures, the α-F and β-P units were produced, suggesting that the polymerization proceeded through a trialkyloxonium ion mechanism.[1] On the other hand, from the fact that α-F and α-P were produced in the polymerization by the strong Lewis acids PF_5 and $SbCl_5$ at 0 to −40 °C, the polymerization by these catalysts was believed to proceed through a oxycarbenium ion mechanism.[3,13] The formation of the α-P unit is not accompanied by the β-P unit is explained as that the approaching direction of monomer is strongly restricted probably by the C-2 carbon of the oxycarbenium ion **5** (Scheme II).

It may be reasonable to assume that the α-F unit was formed through the oxonium ion mechanism as well as through the oxycarbenium ion mechanism by PF_5 and $SbCl_5$ catalysts at low temperatures.

Cationic Ring-Opening Polymerization of 1,4-Anhydro-2,3-*O*-benzylidene-α-D-lyxopyranose (ABLP). ABLP was polymerized by a Lewis acid catalyst, as the results are summarized in Table V. When 2 mol % of antimony pentachloride was used as catalyst at 0 to

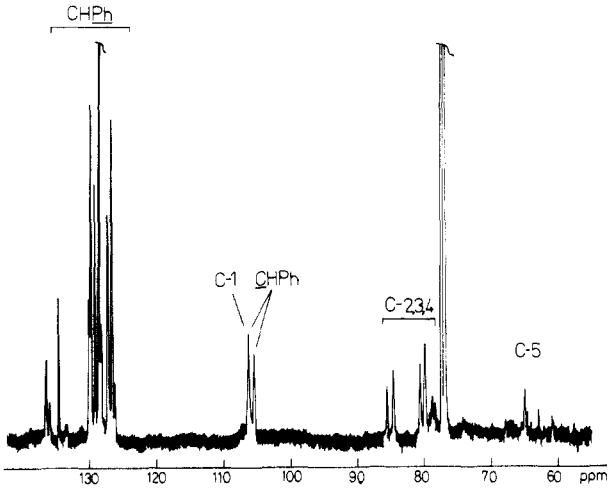


Figure 7. 100-MHz ^{13}C NMR spectrum of poly(1,4-anhydro-2,3-*O*-benzylidene-D-lyxopyranose) prepared by PF_5.

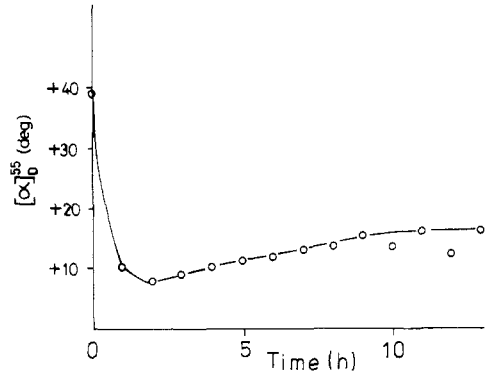


Figure 8. Change in optical rotation during hydrolysis of poly(1,4-anhydro-2,3-*O*-benzylidene-D-lyxopyranose) obtained by BF_3·OEt_2 at 0 °C ($[\alpha]^{25}_D$ +47.9° (in $CHCl_3$)).

−40 °C, poly(ABLPs) with number-average molecular weights ranging from 1.6×10^3 to 2.9×10^3 were obtained in low yield (11.2–35.5%). With 7 mol % of $SbCl_5$ as catalyst, the yield increased to 50.7%, but the molecular weight was still low. Polymerizations by phosphorus pentafluoride and BF_3·OEt_2 catalysts also gave similar results. The highest number-average molecular weight, 6.8×10^3, was obtained by the BF_3·OEt_2 catalyst at 0 °C. In the polymerization by BF_3·OEt_2 at −60 °C, no polymer was formed.

The specific rotation of the poly(ABLPs) ranged from +33.0° to +50.3° and scarcely depended on the polymerization conditions.

Structure of Poly(ABLP). The ^{13}C NMR spectrum of poly(ABLP) which was prepared by the $SbCl_5$ catalyst at 0 °C is shown in Figure 7. Spectra of other polymers were almost the same as that of Figure 7. Since the benzylidene group is chiral, almost all the carbon absorptions are split into two peaks with almost equivalent intensities because of syn- and anti-isomeric structures.

To reveal the structure of poly(ABLP), the hydrolysis of the polymer was performed, and the relationship between $[\alpha]_D$ of the polymer and time during hydrolysis is shown in Figure 8. Rapid decrease in the positive specific rotation in the initial stage reveals that the polymer was composed mainly of α-D-lyxofuranosidic units, although it is assumed that the hydrolysis caused the debenzylidenation as well as the degradation of polymer backbone.

Next, the poly(ABLP) was debenzylidenated to give a free polysaccharide, the structure of which was compared

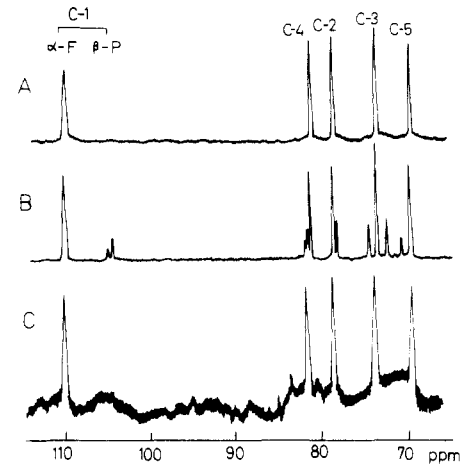


Figure 9. 100-MHz ^{13}C NMR spectra of (A) stereoregular (1→5)-α-D-lyxofuranan obtained by debenzylation of 2,3-di-*O*-benzyl-(1→5)-α-D-lyxofuranan, (B) poly(D-lyxose) obtained by debenzylation of poly(1,4-anhydro-2,3-di-*O*-benzyl-D-lyxopyranose), and (C) debenzylidenated poly(1,4-anhydro-2,3-*O*-benzylidene-D-lyxopyranose).

with that of (1→5)-α-D-lyxofuranan and a free poly(D-lyxose) with a mixed structure using ^{13}C NMR spectroscopy (Figure 9). It is revealed that individual carbon absorptions of the free poly(D-lyxose) obtained from poly(ABLP) (Figure 9C) are in accordance with those of (1→5)-α-D-lyxofuranan (Figure 9A,B), though there are small peaks due to other structural units. Accordingly, the ring-opening polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-lyxopyranose occurred through 1,5-ring scission to provide a benzylidenated polysaccharide consisting mainly of 2,3-*O*-benzylidene-(1→5)-α-D-lyxofuranan.

Unlike 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose, the benzylidene group did not work to give the (1→4)-β-pyranose structure from the D-lyxose homologue.

Experimental Section

1,4-Anhydro-α-D-lyxopyranose. Calcium D-galactonate pentahydrate was prepared by electrolytic oxidation of D-galactose in a 68% yield according to the procedure of Isbell.[15] D-Lyxose was obtained by further oxidation of calcium D-galactonate pentahydrate with hydrogen peroxide, according to Fletcher's method:[16] $[\alpha]^{25}_D$ −12.6° (*c* 0.84 in water at equilibrium). (lit.[16] $[\alpha]^{25}_D$ −14°). D-Lyxose was identified also by means of ^{13}C NMR spectroscopy.[17] 1,4-Anhydro-α-D-lyxopyranose was prepared by vacuum pyrolysis of D-lyxose according to the procedure of Köll and co-workers:[18] $[\alpha]^{25}_D$ −117° (*c* = 0.5 in water) (lit.[18] $[\alpha]^{25}_D$ −113.4° *c* = 0.5 in water).

1,4-Anhydro-2,3-di-*O*-benzyl-α-D-lyxopyranose (ADBL). ADBL was synthesized by benzylation of 1,4-anhydro-α-D-lyxopyranose using a modification of Hakomori's method.[19] A sodium hydride oil dispersion (50%, 5.7 g) and 30 mL of dried *N*,*N*-dimethylformamide were placed in a 300-mL four-necked flask with a drying agent column and vigorously stirred by a magnetic stirrer. To this suspension was added dropwise 1,4-anhydro-α-D-lyxopyranose (5.0 g) solution in 30 mL of dry DMF. After reaction for 1 h at room temperature, 12.5 mL of benzyl chloride solution in 15 mL of dry DMF was dropwise added. The reaction continued overnight and then stopped by pouring into ice water. The organic layer was extracted by chloroform. After being washed with water and dried over anhydrous sodium sulfate, the chloroform solution was concentrated to a yellow syrup. The syrup was purified by column chromatography (silica, benzene:ethyl acetate = 6:1 by volume) to yield a practically colourless syrup of ADBL: yield 9.6 g; $[\alpha]^{25}_D$ −62.3° (c 1.78 in $CHCl_3$).

1,4-Anhydro-2,3-di-*O*-methyl-α-D-lyxopyranose (ADML). ADML was synthesized by the methylation of 1,4-anhydro-α-D-lyxopyranose with a modification of Hakomori's method.[19] A sodium hydride oil dispersion (50%, 3.6 g) and 18 mL of dried DMF were placed in a 100-mL four-necked flask with a drying

agent column and vigorously stirred by a magnetic stirrer. To this suspension was added dropwise a 1,4-anhydro-α-D-lyxopyranose (3.6 g) solution in 18 mL of dry DMF. After reaction for 1 h at room temperature, 4.2 mL of methyl iodide was dropwise added. The reaction was continued overnight, and sodium hydride (1.8 g) was added again. After 1 h, 2.1 mL of methyl iodide was dropwise added. The reaction was continued overnight and then stopped by pouring into ice water. The organic layer was extracted by chloroform. After being washed with water and dried over anhydrous sodium sulfate, the chloroform solution was concentrated to a syrup. The syrup was purified by column chromatography (silica, benzene:methanol = 95:5 by volume) to yield a syrup of ADML: yield 2.76 g (85%); $[\alpha]^{25}_D$ −122.8° (*c* 0.97 in $CHCl_3$).

1,4-Anhydro-2,3-*O*-benzylidene-α-D-lyxopyranose (ABLP). ABLP was synthesized by the benzylidenation of 1,4-anhydro-α-D-lyxopyranose with of modification of Evans' method.[20] 1,4-Anhydro-α-D-lyxopyranose (3.0 g), dimethoxytoluene (3.93 mL), DMF (30 mL), and *p*-toluenesulfonic acid (12 mg) were placed in a 100-ml flask with a reflux condenser connected with an aspirator and vigorously stirred by a magnetic stirrer. The reaction was performed at 60 °C. After 2 h, the reaction was stopped by pouring the mixture into an aqueous solution (150 mL) of $NaHCO_3$ (1 g). The organic layer was extracted with chloroform. After being washed with water and dried over anhydrous sodium sulfate, the chloroform solution was concentrated to a yellow syrup. The syrup was purified by column chromatography (silica, benzene:ethyl acetate = 10:1). The solution was concentrated and crystallized from *n*-butyl chloride: yield 1.5 g (30%); $[\alpha]^{25}_D$ −58.4° (*c* 1 in $CHCl_3$).

Catalyst. Commercial boron trifluoride etherate, stannic chloride, and antimony pentachloride were used after purification by trap-to-trap distillation in vacuo. Phosphorous pentafluoride was prepared by thermal decomposition of chlorobenzenediazonium hexafluorophosphate (Ozark-Mahoning Co.).

Solvent. Dichloromethane was purified by extracting impurities with concentrated sulfuric acid several times and finally by drying on calcium hydride, followed by distillation.

Polymerization. A high-vacuum technique was used for polymerization.[12] The monomer was polymerized with a cationic catalyst in dichloromethane. Termination was performed by the addition of methanol. Two methods were used for polymer purification. For chloroform-soluble polymers, the polymer was purified by reprecipitation with chloroform–petroleum ether several times and subsequent freeze-drying from benzene. For chloroform-insoluble polymers, the polymer was purified by reprecipitation, using hot *o*-dichlorobenzene–methanol once and then using hot *o*-dichlorobenzene–petroleum ether several times, and subsequent vacuum drying at 60 °C.

Debenzylation. To liquid ammonia containing sodium was added dropwise under nitrogen a solution (or suspension for insoluble polymers) of poly(ADBL) in 20 mL of dimethoxyethane. After sufficient stirring, the reaction was terminated by the addition of anhydrous ammonium chloride and then a small amount of water. After the evaporation of ammonia, the aqueous solution was washed with dichloromethane and dialyzed with water. Finally the polysaccharide was freeze-dried from water.

Debenzylidenation. This reaction was carried out in almost the same procedure as the debenzylidenation described in ref 1.

Measurement of Optical Rotation during Hydrolysis. Hydrolysis of poly(ADML) and poly(ABLP) was performed according to Schuerch's method.[13] After poly(ADML) (3 mg) was dissolved with a small amount of tetrahydrofuran (THF) in a 2-mL volumetric flask, 0.4 mL of 12 N HCl was added to the flask and then THF was added to give the 2-mL solution having the concentration of 2.4 N HCl. The measurement of optical rotation was carried out on the solution using a Perkin-Elmer 241 polarimeter at 55 °C. In the second stage where the hydrolysis was performed at higher acid concentration, the concentration was increased by adding an additional 12 N HCl. In the case of poly(ABLP), 11.4 N HCl was used and the acid concentration in the initial stage was 1.1 N.

Measurements. 100-MHz ^{13}C NMR and 25-MHz ^{13}C NMR spectra were recorded for the polymer solutions by means of JEOL GX-400 and PS-100 NMR spectrometers, respectively. Specific rotations were measured by means of a Perkin-Elmer 241 polarimeter. The molecular weight was measured by gel permeation chromatography with standard polystyrenes as reference.

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