Ring-Opening Polymerization of a 1,4-Anhydro Xylose Derivative Having an Azido Group and Synthesis of Stereoregular 3-Amino-3-deoxy-(1→5)-α-D-xylofuranan

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ABSTRACT: A new 1,4-anhydro pentose monomer having an azido group, 1,4-anhydro-3-azido-2-*O*-benzyl-3-deoxy-α-D-xylopyranose (A3ABX), was synthesized by benzylation of 1,4-anhydro-α-D-ribopyranose at the C2 hydroxyl group and subsequent trifluoromethylsulfonylation at the C3 hydroxyl group, followed by S_N2 replacement of the trifluoromethylsulfonyl group with the azido group with lithium azide. Ring-opening polymerization of A3ABX was attempted with Lewis acid catalysts such as boron trifluoride etherate, phosphorus pentafluoride, and antimony pentachloride at different temperatures between −60 and −20 °C. Boron trifluoride etherate catalyst gave a polymer with a positive specific rotation and with a single C1 absorption at 99 ppm in the ^{13}C NMR spectrum, indicating that the resulting polymer had a stereoregular 1,5-α furanosidic structure. When the polymerization was carried out by antimony pentachloride at −60 °C, the polymer obtained had a negative specific rotation and the C1 absorption shifted downfield to around 107 ppm, suggesting that the polymer might be composed of a 1,5-β furanosidic unit. Reduction of the azido group to an amino group and the benzyl group to a hydroxyl group gave 3-amino-3-deoxy-(1→5)-α-D-xylofuranan. The structural analysis of the polysaccharides was performed by means of high-resolution ^{1}H and ^{13}C NMR spectroscopies including the two-dimensional spectra of H−H COSY, NOESY, and FGHMQC.

Introduction

Poly- and oligosaccharides having amino groups are widely distributed in nature and play important roles as specific inhibitors with biological activities.[1] Heparin with sulfamide groups derived from the amino group is a mucopolysaccharide having a strong anticoagulant activity.[2] Chitin and chitosan are 1,4-β-linked mucopolysacharides composed of 2-acetamido- and 2-amino-2-deoxy-D-glucopyranoses, respectively, alone found in crustaceans, in insects, and in the cell walls of bacteria. It was reported that a water-soluble chitin derivative, CM-chitin, has unique biological activities: CM-chitin was shown to be an effective antitumor agent[3] and its biodegradability allowed to serve as a drug carrier.[4]

There are several reports on the chemical synthesis of polysaccharide derivatives having amino groups. Treatment of 2,3-anhydro derivatives of cellulose with ammonia gave a cellulose derivative substituted with an amino group at the C2 or C3 position; however, the selectivity and the degree of substitution were low.[5] It was reported that the synthesis of polysaccharide-type polymers having amino groups was carried out by ring-opening polymerization of 6,8-[3.2.1]oct-3-ene. The obtained polymer, poly(5,6-dihydro-2*H*-pyran-6,2-diyloxymethylene), was epoxidized and then the resulting epoxide was treated with ammonia to give an amino group-containing polymer.[6] Previously, we reported the first total synthesis of (1→6)-α-D-glucan derivatives having an amino group at the C2, C3, or C4 position by ring-opening polymerization of the 1,6-anhydro-2-, 3-, or 4-azidoglucopyranose derivative.[7] Although the 3-azido monomer was polymerized easily to give the high molecular weight polymer, 2- or 4-azido monomer provided only oligomers. Furthermore, it was found that the sulfated derivatives of the 3-amino polysaccharides had high anticoagulant activities and low cytotoxicities.[8]

We have synthesized a number of stereoregular polysaccharides by ring-opening polymerization of anhydro pentose and hexose derivatives.[9] Recently, it was found that sulfated polysaccharides obtained by sulfation of the stereoregular polysaccharides[10] and the natural 1,3-β-glucans lentinan[11] and curdlan[12,13] inhibited completely the infection of the AIDS virus at concentrations as low as 3.3 μg/mL in vitro. In this paper, we wish to report the synthesis and ring-opening polymerizability of a new pentose monomer having an azido group, 1,4-anhydro-3-azido-2-*O*-benzyl-3-deoxy-α-D-xylopyranose. The obtained polymer was derivatized to 3-amino-3-deoxy-(1→5)-α-D-xylofuranan by the reduction of the azido and benzyl groups to the amino and hydroxyl groups, respectively. In addition, polymer structures were examined by means of two-dimensional NMR spectra and specific rotations.

Experimental Section

Materials. D-Ribose was kindly supplied by Messrs. T. Mimura and Y. Kaneko of Ajinomoto Co. Ltd. 1,4-Anhydro-α-D-ribopyranose was prepared by vacuum pyrolysis of D-ribose.[14] Lithium azide was synthesized from sodium azide and lithium hydroxide according to the method given in the literature.[15] Other reagents were used without further purification.

1,4-Anhydro-3-azido-2-*O*-benzyl-3-deoxy-α-D-xylopyranose (A3ABX). To 26.4 g (0.2 mol) of 1,4-anhydro-α-D-ribopyranose in 40 mL of dry DMF were added 33.2 g (55% oil dispersion) of sodium hydride and 49 mL of benzyl chloride. The mixture was heated at 90 °C under nitrogen for 30 min and then cooled to room temperature. The reaction mixture was poured into water, and the organic layer was extracted with chloroform. The chloroform layer was washed with water several times and dried over anhydrous sodium sulfate. The

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solvent was evaporated, and the residue was chromatographed on a silica gel column eluted with hexane−ethyl acetate (6:4) to give 20.5 g (44%) of 1,4-anhydro-2-*O*-benzyl-α-D-ribopyranose (A2BR). Other products were 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose (ADBR) (8.2 g, 18%) and 1,4-anhydro-3-*O*-benzyl-α-D-ribopyranose (12.3 g, 26%).

A2BR (11.1 g) was dissolved in 15 mL of dry pyridine. A pyridine (15 mL) solution of trifluoromethanesulfonic anhydride (10 mL) was added dropwise to the cooled A2BR solution (−15 °C). The reaction mixture was stirred for 2.5 h at room temperature and then poured into 200 mL of 10% sodium bicarbonate solution. The organic layer was extracted with chloroform, washed with water several times, and dried. The chloroform was evaporated to give 17.7 g (94%) of 1,4-anhydro-2-*O*-benzyl-3-*O*-(trifluoromethyl)sulfonyl-α-D-ribopyranose (A2B3TR) after purification by silica gel chromatography (eluent, hexane:ether = 2:1).

Lithium azide (5 g, 0.10 mol) was added to a dry DMF (50 mL) solution of A2B3TR (3.5 g, 0.01 mol), and the mixture was stirred at 60 °C for 12 h. The reaction mixture was poured into ice water, followed by extraction of the organic layer with chloroform. The chloroform layer was washed, dried, and evaporated to give 2.3 g (95%) of pure A3ABX after silica gel chromatography (eluent, hexane:ethyl acetate = 7:3). Further purification for the polymerization was carried out by HPLC (column, silica gel) eluted with a hexane−ethyl acetate (1:1) solvent system. $\alpha_D^{25} = -7.1°$ (*c* 1%, $CHCl_3$). IR (neat): ν 2107 cm^{-1} ($-N_3$). ^1H NMR ($CDCl_3$): δ 3.38 (br, H5′), 3.59 (s, methylene of benzyl group), 3.85 (br, H3 and H5), 4.55 (s, H2), 4.70 (m, H4), 5.41 (s, H1), and 7.29 ppm (br, methylene of benzyl group). ^{13}C NMR ($CDCl_3$): δ 63.5 (C5), 67.0 (C3), 72.1 (C2), 76.1 (C4), 85.5 (CH_2), 102.2 (C1), 118−119 (phenyl), 137.0 ppm (phenyl). Elemental analysis calcd for $C_{12}H_{13}O_3N_3$: C, 58.29; H, 5.30; N, 16.99. Found: C, 59.06; H, 5.11; N, 16.21.

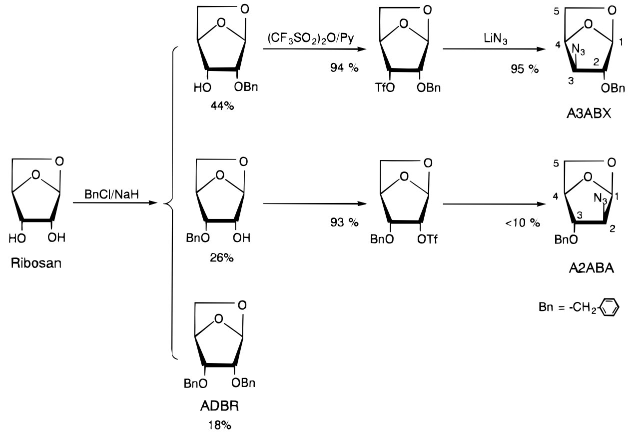
1,4-Anhydro-2-azido-3-*O*-benzyl-2-deoxy-α-D-arabinopyranose (A2ABA) was also prepared from 1,4-anhydro-3-*O*-benzyl-α-D-ribopyranose following the same procedures as above. However, the yield of A2ABA from ribosan was below 2%. IR (neat): ν 2105 cm^{-1} ($-N_3$). ^1H NMR ($CDCl_3$): δ 3.45 (d, H2), 3.60 (br, H5, H5′, and H3), 4.58 (q, methylene of benzyl group), 4.78 (s, H4), 5.57 (s, H1), 7.18 ppm (br, phenyl). ^{13}C NMR ($CDCl_3$): δ 65.5 (C5), 70.5 (C2), 71.0 (CH_2), 80.2 (C4), 82.0 (C3), 99.5 (C1), 127−129 (phenyl), 136.5 ppm (phenyl). Elemental analysis calcd for $C_{12}H_{13}O_3N_3$: C, 58.29; H, 5.30; N, 16.99. Found: C, 57.85; H, 5.34; N, 16.84.

Polymerization. A3ABX was polymerized with Lewis acid catalysts under high vacuum (10^{-5}−10^{-6} mmHg) at low temperatures according to the previous paper.[16] After polymerization was terminated by addition of methanol, the resulting polymer was dissolved in chloroform. The chloroform layer was neutralized with sodium bicarbonate, washed with water several times, dried, and concentrated. Purification was carried out by dissolution−reprecipitation three times by using a chloroform−methanol system, and the polymer was freeze-dried from benzene.

Reduction of the Azido Group to the Amino Group. $NaBH_4$ (0.2 g) was added to a clear solution of 3-azido-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan (0.14 g) in THF (40 mL). The mixture was stirred under reflux for 5 h and then cooled to room temperature. The reaction mixture was poured into ice water, and the organic layer was extracted with chloroform. The chloroform layer was washed with water several times, dried over anhydrous sodium sulfate, and concentrated. The obtained polymer was isolated by freeze-drying from benzene to give 0.11 g of an azido-reduced polymer.

Debenzylation. Powdery 3-amino-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan (0.10 g) was added to 40 mL of liquid ammonia containing 0.2 g of sodium at −78 °C under a nitrogen atmosphere. After the ammonia solution was stirred for 30 min at the same temperature, the reaction was terminated by addition of anhydrous ammonium chloride until a dark blue color disappeared, followed by addition of a small amount of methanol. After evaporation of ammonia, 50 mL of water was added and then the aqueous solution was extracted with methylene chloride. A small amount of 0.05 N HCl solution was added to the water solution. The water layer was dialyzed against deionized water for 1 day. The dialysate was concentrated to approximately 20 mL and freeze-dried to give 0.05 g of an amino polysaccharide.

Scheme 1. Synthesis of the Azido Monomers, 1,4-Anhydro-3-Azido-2-*O*-benzyl-3-deoxy-α-D-xylopyranose (A3ABX) and 1,4-Anhydro-2-azido-3-*O*-benzyl-2-deoxy-α-D-arabinopyranose (A2ABA)



Measurements. ^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a JEOL GX-270 spectrometer in $CDCl_3$ solution. The COSY and NOESY experiments were performed with the JEOL-supplied pulse sequences. The size of the matrix was 128 × 128 and zero-filled into 512 × 512 data points. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken on solutions in $CDCl_3$ or D_2O by means of a JEOL α400 spectrometer. Two-dimensional heteronuclear multiple quantum coherence (FGHMQC) and C−H COSY measurements were used to assign the carbon absorptions. TMS or DSS was used as an internal reference. Specific rotations were measured in chloroform or water at 25 °C by Perkin-Elmer 241 and JASCO DIP-140 polarimeters. Molecular weights were measured at 40 °C on a GPC apparatus with THF, DMSO, or water as solvent and standard polystyrene or pullulan as reference (columns: Toso TSK-gel, G3000H_{XL}, G4000H_{XL}, and G5000H_{XL} for THF, GMH$_{HR}$-M(S) for DMSO, and G2500SW and G3000SW for water).

Results and Discussion

Synthesis of A3ABX. The starting monomer, 1,4-anhydro-3-azido-2-*O*-benzyl-3-deoxy-α-D-xylopyranose (A3ABX) was successfully synthesized by the following reactions: 2-*O*-benzylation of 1,4-anhydro-α-D-ribopyranose (ribosan) with benzyl chloride and then 3-*O*-trifluoromethylsulfonylation of 1,4-anhydro-2-*O*-benzyl-α-D-ribopyranose with trifluoromethanesulfonic anhydride, followed by the S_N2 replacement of the trifluoromethylsulfonyl group at the C3 position with lithium azide (Scheme 1). Finally, HPLC was used for the purification of A3ABX as a polymerizable monomer. By the same procedure, a 2-azido monomer, 1,4-anhydro-2-azido-3-*O*-benzyl-2-deoxy-α-D-arabinopyranose (A2ABA), was prepared from 1,4-anhydro-3-*O*-benzyl-α-D-ribopyranose.

Both A3ABX and A2ABA were new compounds. The structure of A3ABX and A2ABA were identified by IR, NMR, and elemental analysis. Figure 1 shows the IR and C−H COSY spectra of A3ABX. In the IR analysis, the appearance of a strong absorption at 2107 cm^{-1} was assigned to the N_3 stretching vibration peak and no OH stretching vibration was observed over 3000 cm^{-1}, suggesting that the hydroxyl group at the C3 position was replaced with the N_3 group. H−H and C−H COSY spectra were recorded continuously to assign the proton and carbon absorptions in the ^1H and ^{13}C NMR spectra. From Figure 1B, the H3 peak appeared by overlapped

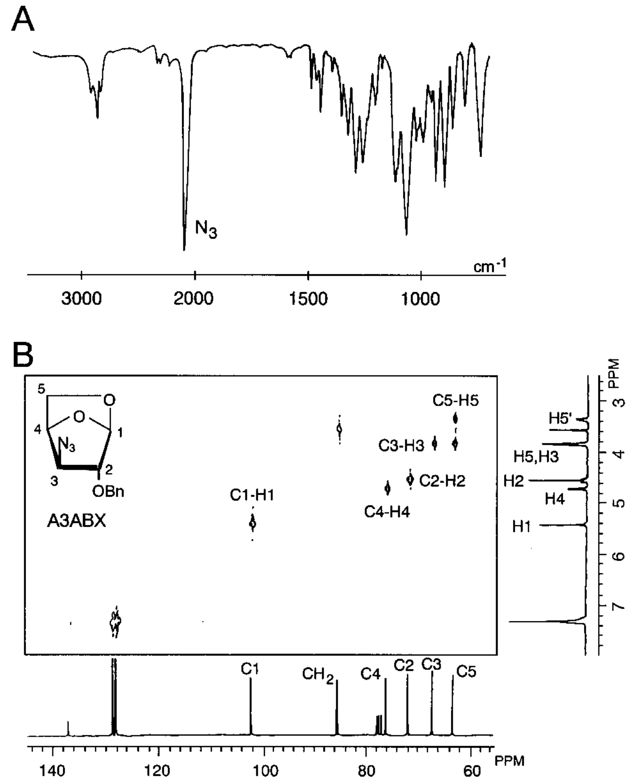


Figure 1. IR (A) and C−H COSY (B) spectra of A3ABX.

Table 1. Ring-Opening Polymerization of A3ABX

no.[a]	catalyst (mol %)	temp °C	time, h	yield, %	$\bar{M}_n$[b] × 10^{-4}	$[\alpha]_D^{25}$ [c], deg	α-content[d] %
1	BF_3OEt_2 (3)	-40	2	29	1.3	+14.8	100
2	BF_3OEt_2 (3)	−40	3	32	3.7	+19.6	100
3	BF_3OEt_2 (5)	−40	5	48	2.3	+16.8	100
4	PF_5 (5)	−20	0.25	86	3.9	+17.7	100
5	PF_5 (5)	−40	0.25	91	2.9	+14.0	100
6	PF_5 (5)	−60	0.25	72	4.4	+21.2	100

[a] Monomer, 0.24−0.29 g; solvent, CH_2Cl_2, 0.5 mL. [b] Determined by GPC. [c] Measured in $CHCl_3$ (*c* 1%). [d] From ^{13}C NMR spectrum.

the H5 peak at 3.85 ppm, and the C3 absorption was observed at 66.6 ppm. The elemental analysis of A3ABX was in agreement with calculated one, indicating support for the structure depicted in Figure 1B. The structure of A2ABA was identified by the same way as A3ABX. However, since the yield of A2ABA from 1,4-anhydro-3-*O*-benzyl-2-*O*-(trifluoromethylsulfonyl)-α-D-ribopyranose was low, the A2ABA monomer was not used for the polymerization. Further studies are currently in progress to seek the reason for the low yield and to learn how to increase the yield.

Ring-Opening Polymerization of A3ABX by Lewis Acid Catalysts. Polymerization of A3ABX was performed with cationic catalysts in the temperature range from −20 to −60 °C to give poly(A3ABX)s with specific rotations ranging from positive to negative in moderate to high yields. Table 1 shows the result of ring-opening polymerizations by boron trifluoride etherate and phosphorus pentafluoride as catalysts. When boron trifluoride etherate was used −40 °C, polymerization for 2−5 h gave polymers with number-average molecular weights ($\bar{M}_n$) of 1.3 × 10^4 to 3.7 × 10^4, which were determined by GPC using polystyrene standards, and specific rotations of +14.8° to +19.6°. When 3 mol % of boron trifluoride etherate was used (no. 1), the yield and molecular weight of the obtained polymer were 29% and 1.3 × 10^4 in 2 h. A little longer polymerization time of

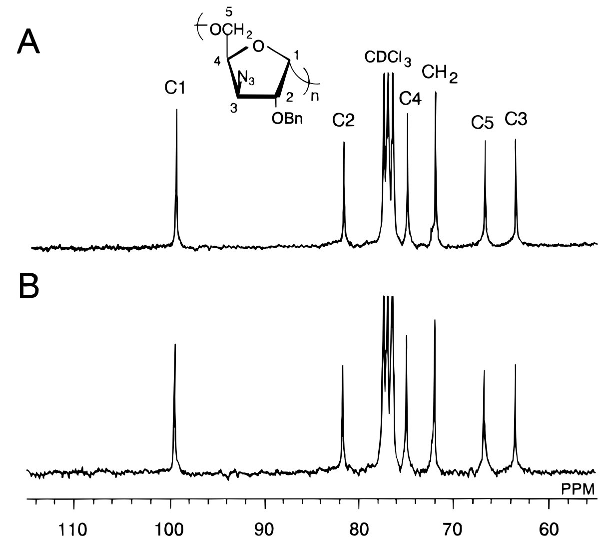


Figure 2. 67.8 MHz ^{13}C NMR spectra of 3-azido-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan prepared by (A) BF_3OEt_2 at −40 °C and (B) PF_5 at −60 °C ($CDCl_3$ as solvent).

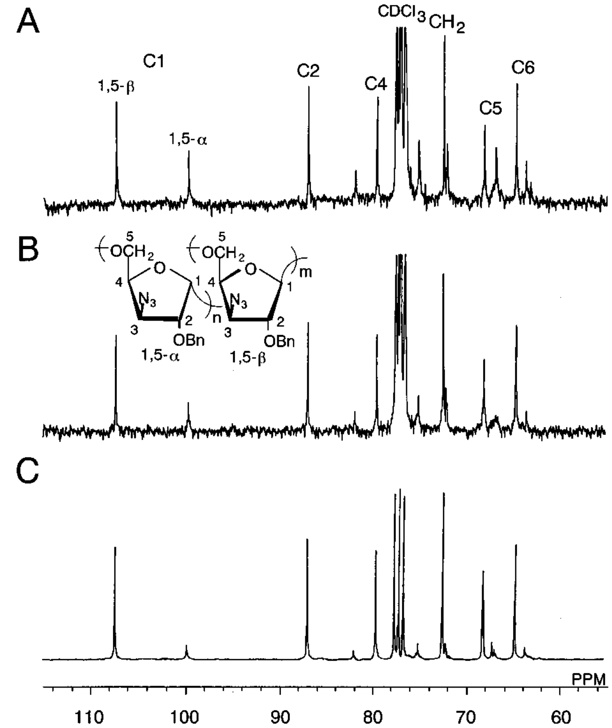


Figure 3. 67.8 MHz ^{13}C NMR spectra of poly(A3ABX) prepared by $SbCl_5$ at (A) −20, (B) −40, and (C) −60 °C ($CDCl_3$ as solvent).

3 h provided a polymer with a slightly higher yield (32%) and higher molecular weight ($\bar{M}_n$ = 3.7 × 10^4) (no. 2). With a higher concentration of boron trifluoride etherate and longer polymerization time (5 h), the polymer yield increased to 48%, but the molecular weight decreased to 2.3 × 10^4 (no. 3). The polymers had a complete 1,5-α stereoregularity as revealed by NMR measurements as described later.

Polymerization of A3ABX by PF_5 catalyst in a short polymerization time (15 min) gave polymers having high molecular weights of $\bar{M}_n$ = 2.9 × 10^4 to 4.4 × 10^4 in high yields. The resulting polymers also had positive specific rotations of +14.0 to +21.2°, suggesting a 1,5-α specificity. However, when the polymerization was carried out at −20 °C, in the ^{13}C NMR spectrum of the resulting polymer, a few small unidentified peaks ap-

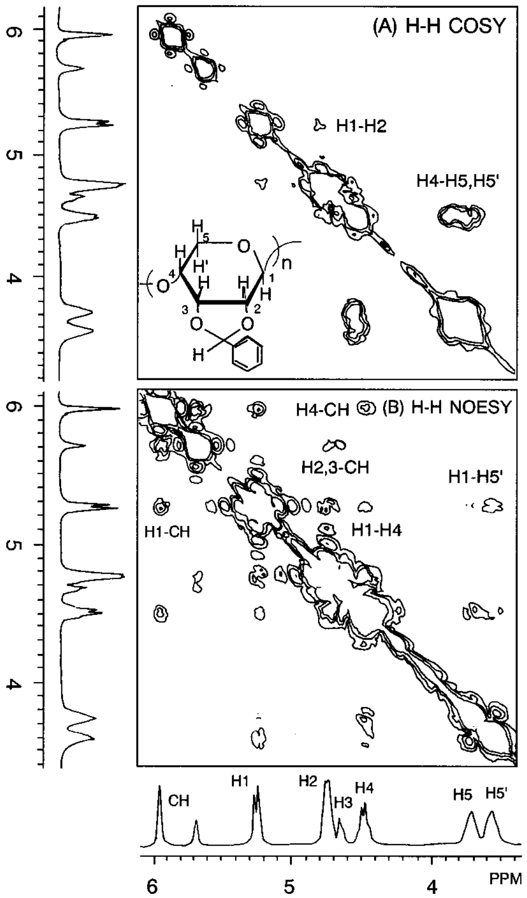


Figure 4. H−H COSY (A) and NOESY (B) spectra of 2,3-*O*-benzylidene-(1→4)-*β*-D-ribopyranan ($CDCl_3$ as solvent).

Table 2. Ring-Opening Polymerization of A3ABX by $SbCl_5$

no.[a]	temp, °C	time, h	yield, %	$\bar{M}_n$[b] × 10^{-4}	$[\alpha]_D^{25}$,[c] deg	α-content[d] %
7	−20	3	74	1.8	+2.8	45
8	−40	3	54	1.1	+1.3	25
9	−60	2.5	42	3.2	-4.2	10

[a] Monomer, 0.24−0.29 g; $SbCl_5$, 3 mol %; solvent, CH_2Cl_2, 0.5 mL. [b] Determined by GPC. [c] Measured in $CHCl_3$ (*c* 1%). [d] From ^{13}C NMR spectrum.

peared in the range of 60−80 ppm. It was assumed that a partial decomposition or elimination of the azido group occurred with the higher polymerization temperature and with the strong PF_5 catalyst.[7]

Table 2 summarizes the results of polymerization by antimony pentachloride as catalyst. Polymerization behaviors were somewhat different from the polymerization by $BF_3{\cdot}OEt_2$ and PF_5 catalysts. The polymerization was carried out at −20, −40, and −60 °C to give polymers with molecular weights of $\bar{M}_n = 1.1 \times 10^4$ to 3.2×10^4. The yield of polymer decreased with decreasing polymerization temperature, while the molecular weight increased. The specific rotations were lower than those of polymers obtained with $BF_3{\cdot}OEt_2$ and PF_5 catalysts. When polymerization was carried out at −60 °C, the resulting polymer had a negative specific rotation of −4.2°, suggesting that the structure of the polymers possessed a lower 1,5-α stereoregularity with an increasing *β* stereoregularity.

Structure of Polymers. ^{13}C NMR spectra of poly(A3ABX)s prepared by $BF_3{\cdot}OEt_2$ at −40 °C and PF_5 at −60 °C are shown in Figure 2. These polymers had positive specific rotaions of (A) +19.6° and (B) +21.2°. Taking into account the highly positive specific rotation and the appearance of five sharp carbon absorptions due to the sugar unit, it was concluded that the polymers were stereoregular 3-azido-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan. All absorptions were assigned by means of two-dimensional NMR spectroscopy.

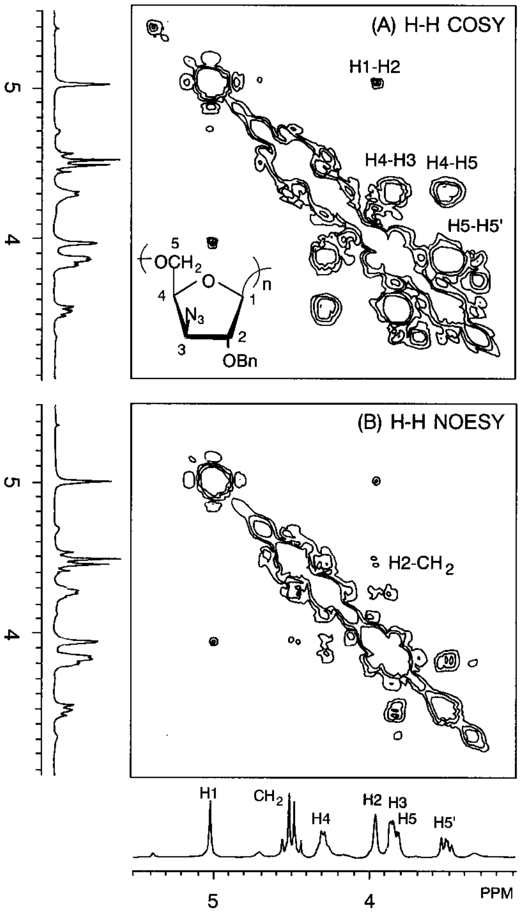


Figure 5. H−H COSY (A) and NOESY (B) spectra of 3-azido-2-*O*-benzyl-(1→5)-*β*-D-xylofuranan ($CDCl_3$ as solvent).

Figure 3 shows the ^{13}C NMR spectra of poly(A3ABX)s obtained by $SbCl_5$ catalyst at polymerization temperatures of (A) −20, (B) −40, and (C) −60 °C, respectively. The C1 absorption appeared as two peaks at 99.5 and 107.5 ppm, suggesting that the polymers were composed of two monomeric units. The intensity of the peak at 99.5 ppm due to the C1 absorption of the (1→5)-α-xylofuranosidic unit decreased with decreasing polymerization temperature. In Figure 3C, since the polymer had a negative specific rotation of −4.2°, the absorption at 107.5 ppm might originate from the C1 absorption of the 1,5-*β* furanosidic or 1,4-*β* pyranosidic unit.

Since a bicyclic 1,4-anhydro sugar monomer is equally regarded as a 1,5-anhydro sugar, there are four possible monomeric units formed in the polymer by ring-opening polymerization, that is, 1,5-α and 1,5-*β* furanosidic and 1,4-α and 1,4-*β* pyranosidic units. To elucidate the structure of the polymer prepared by $SbCl_5$ at −60 °C (no. 3 in Table 2), the nuclear Overhauser effect spectroscopy (NOESY) technique was used. Although the H−H COSY measurement affords direct *J*-couplings, the NOESY technique provides information on the spatial neighborhood protons in molecules. Therefore, the NOESY spectrum of the polymers was measured and compared with that of a benzylidenated (1→4)-*β*-D-ribofuranan, which was synthesized previ-

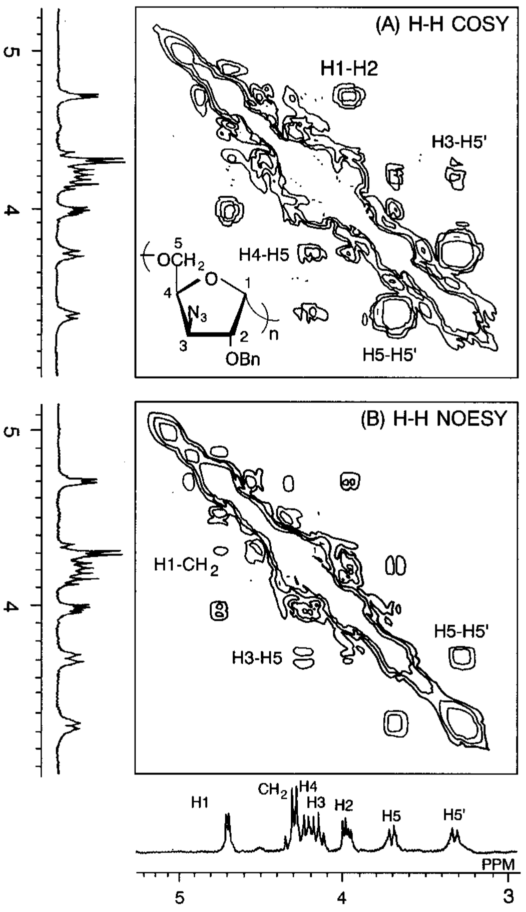


Figure 6. H−H COSY (A) and NOESY spectra of 3-azido-2-*O*-benzyl-(1→5)-α-D-xylofuranan ($CDCl_3$ as solvent).

ously.[17,18] Figures 4−6 show the COSY (A) and NOESY (B) spectra of 2,3-*O*-benzylidene-(1→4)-*β*-D-ribopyranan, poly(A3ABX) prepared by $SbCl_5$ at −60 °C, and 3-azido-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan, respectively. Since the benzylidenated (1→4)-*β*-D-ribopyranan had a 6-membered ring, the H1 proton should be located spatially near H5 and the benzylidene proton (CH). In Figure 4B, the NOESY correlations of the H1 proton between H4, H5, and the benzylidene proton appeared, respectively. On the other hand, no cross peaks between the H1 and H5 protons appeared in Figures 5B and 6B. Furthermore, we previously assigned the structure of (1→5)-α- and (1→5)-*β*-D-xylofuranans, which were obtained by ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose, by comparison with the NMR spectrum of a naturally occurring xylan having a stereoregular 1,4-*β* xylopyranosidic structure.[16] These results suggested that the polymer (no. 3 in Table 2) obtained by $SbCl_5$ at −60 °C is composed of a 1,5-*β* furanosidic unit but not a 1,4-*β* pyranosidic unit.

Reduction of the Azido Group and Deprotection of the Hydroxyl Group of the Polymer. It was reported previously that the reduction of 3-azido-2,4-di-*O*-benzyl-3-deoxy-(1→6)-α-D-glucopyranan with lithium aluminum hydride gave the corresponding 3-amino polymer in good yield.[7] Although 3-azido-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan was reduced with lithium aluminum hydride, the amino polymer was obtained in low yield. Thus, the reduction of the azido group was carried out with $NaBH_4$ in THF to afford 3-amino-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan in a good yield. The IR spectra before and after reduction of the azido group are shown in Figure 7. The strong absorption band at 2106 cm^{-1} due to the azido stretching vibration (Figure 7A) disappeared, while the broad absorption of the amino group appeared between 3000 and 3500 cm^{-1} in Figure 7B, indicating that the reduction of the azido group into the amino group was accomplished. The resulting 3-amino-2-*O*-benzyl-3-deoxy-(1→5)-α-D-xylofuranan was soluble in chloroform, THF, and benzene but insoluble in water and DME. The polymers had molecular weights of 1.0×10^4 to 1.5×10^4 and specific rotations of +4.0° to +8.0° (*c* 1, $CHCl_3$).

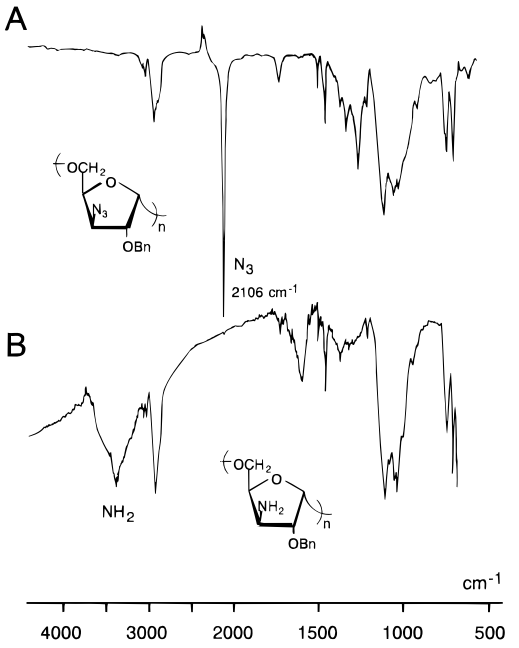


Figure 7. IR spectra of (A) 3-azido-2-*O*-benzyl-(1→5)-α-D-xylofuranan and (B) 3-amino-2-*O*-benzyl-(1→5)-α-D-xylofuranan.

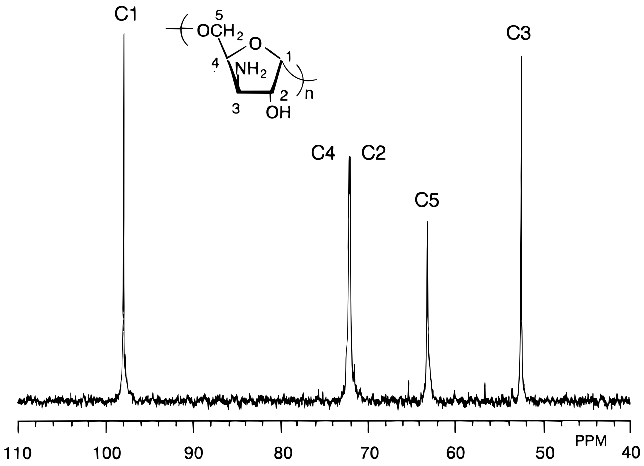


Figure 8. 100 MHz ^{13}C NMR spectrum of 3-amino-3-deoxy-(1→5)-α-D-xylofuranan (D_2O as solvent).

The powdery amino polymer was debenzylated by sodium in liquid ammonia to give an amino polysaccharide containing a free hydroxyl group, i.e., 3-amino-3-deoxy-(1→5)-α-D-xylofuranan, in a good yield. Since the amino xylofuranan was insoluble in water, it was isolated as the HCl salt. Figure 8 shows the ^{13}C NMR spectra of the HCl salt of 3-amino-3-deoxy-(1→5)-α-D-xylofuranan in D_2O. It was found that the benzyl group was removed completely, and the single C1 absorption appeared at 98.0 ppm. The peak assignment was accomplished by measuring such two-dimensional NMR spectra as H−H COSY and FGHMQC. The overlapping peaks at 72.0 ppm were assigned to the C4 (lower field) and C2 (higher field) carbons. The C3 carbon bound by the amino group appeared at the highest field at 52.5 ppm. The molecular weight of the amino xylofuranan was 0.6×10^4 and the specific rotation +5.0° (c 1, H_2O).

The anti-AIDS virus and anticoagulant activities of the amino xylofuranan after sulfation will be investigated.

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