Synthesis of 3-Acetamido-3-deoxy-(1→5)-α-D-xylofuranan by Ring-Opening Polymerization of a 1,4-Anhydro-3-azido-α-D-xylopyranose Derivative

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ABSTRACT: A stereoregular 3-acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF) was synthesized by the synthetic route starting from selective ring-opening polymerization of 1,4-anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose (A3ASX). First, A3ASX was polymerized by BF_3·OEt_2 catalyst at −20 to −40 °C to give 3-azido-2-*O*-*tert*-butyldimethylsilyl-(1→5)-α-D-xylofuranan (3AzSXF) with $\bar{M}_n$ of 11.1×10^4−17.8×10^4 and $[\alpha]_D$ of +200−212°. A polymer prepared by $SbCl_5$ catalyst had a mixed structure consisting of 1,5-α- and 1,5-*β*-xylofuranosidic units. 3AzSXF was reduced with $NaBH_4$ in a THF−ethanol mixture to afford 3-amino-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AmSXF). After 3AmSXF was acetylated at its amino groups to produce a 3-acetamidoxylofuranan derivative (3AAdSXF), desilylation of 3AAdSXF gave 3AAdXF with $\bar{M}_n$ of 7.8×10^3 and $[\alpha]_D$ of +212°. The structure analysis was performed using ^{13}C and ^1H NMR spectroscopies, IR spectroscopy, and optical rotation measurements.

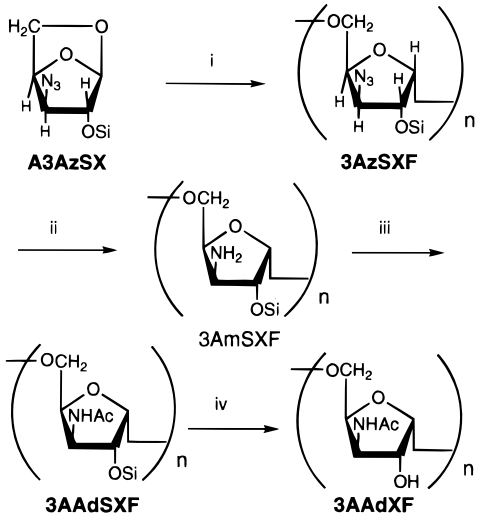
Introduction

Ring-opening polymerizations of anhydro sugars have provided a number of stereoregular polysaccharides such as 1,6-α-linked hexopyranans, 1,4-*β*-linked cellulose-type polysaccharides, and 1,5-α-linked glycofuranans having hydroxyl and acyl groups as the functional group.[1−4] 1,6-α-Linked dextran-type polysaccharides possessing azido, amino, and sulfamide groups in addition to the hydroxyl group were also synthesized.[5] The polysaccharides containing sulfamide and sulfate groups exhibited high anticoagulant activities. Recently, a few new amino-containing polysaccharides, such as 1,5-α-linked xylofuranans and ribofuranans, were synthesized by a synthetic route starting from the selective ring-opening polymerization of azido group containing 1,4-anhydro sugars (=1,5-anhydro sugars).[6,7]

Since it was found that sulfated polysaccharides have anti-HIV (human immunodeficiency virus) activity,[8] various sulfated polysaccharides with high anti-HIV activities were synthesized by the sulfation of natural polysaccharides and of synthetic polysaccharides obtained by the ring-opening polymerization of 1,4-anhydro sugars.[9−13] Since curdlan sulfate had the most potent anti-HIV activity and low side effects,[10] its phase I/II test for an AIDS drug was carried out.[14]

Recently, biological activities of the acetamide group in polysaccharides have attracted much attention since it was found that acetamide group containing natural polysaccharide chitin and chitin oligosaccharides have a wide variety of biological activities, such as wound-healing effects on animals,[15] the induction of neutrophil migration,[16] a drug-carrying ability with sustained release,[17] an activation for morphogenetic events in yeast,[18] and the induction of plant defense response.[19]

Scheme 1. Synthesis of 3-Acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF) by Conversion of Azidoxylofuranan 3AzSXF via Both Aminoxylofuranan 3AmSXF and Acetamidoxylofuranan 3AAdSXF



In this study, we report for the first time the synthesis of a new acetamide group-containing polysaccharide, as shown in Scheme 1.

The synthesis starts from selective ring-opening polymerization of 1,4-anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose providing a stereoregular azido group containing (1→5)-α-D-xylofuranan. The azido group in the polysaccharide was reduced to an amino group, which was then acetylated to give acetamido and *tert*-butyldimethylsilyl groups containing polysaccharide. After removal of the OH-protective *tert*-butyldimethylsilyl group, 3-acetamido-3-deoxy-(1→5)-α-

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Table 1. Ring-Opening Polymerization 1,4-Anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose (A3ASX)[a]

						polymer structure		
no.	A3ASX, g	catalyst[b]	temp, °C	time, h	yield, %	$\bar{M}_n$[c] × 10^4	$[\alpha]^{20}_D$,[d] deg	1,5-α-furanosidic unit,[e] %
1	0.11	$BF_3.OEt_2$	0	4	86	1.2[f]	+174	100
2	0.21	$BF_3{\cdot}OEt_2$	−20	20	92	17.8	+200	100
3	0.20	$BF_3{\cdot}OEt_2$	−40	50	62	11.1	+212	100
4	0.20	$BF_3{\cdot}OEt_2$	−60	100	0			
5	0.22	PF_5	−60	3	95	3.7	+178	98
6	0.13	$SbCl_5$	−10	20	94	1.5	+42	29[g]

[a] Solvent: CH_2Cl_2, 0.5 mL. [b] Amount: 5 mol % to the monomer. [c] Determined in $CHCl_3$ by GPC. [d] Measured in $CHCl_3$ (*c* 1.0%). [e] Determined by ^{13}C NMR. [f] Determined in THF. [g] The remaining 71% is composed of 1,5-*β*-xylofuranosidic units.

D-xylofuranan was successfully synthesized. The structure analysis was performed using NMR and IR spectroscopies and optical rotation measurements.

Results and Discussion

Ring-Opening Polymerization of 1,4-Anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose (A3ASX) and Structure of the Polymers. The azido-containing monomer A3ASX was successfully synthesized by Walden inversion at the C4 carbon of an anhydro-α-D-ribose derivative. The azido monomer A3ASX was polymerized with a few kinds of Lewis acids as catalysts at low temperatures under high vacuum. The result of polymerizations is summarized in Table 1.

When A3ASX was polymerized with $BF_3{\cdot}OEt_2$ as catalyst at temperatures ranging from 0 to −40 °C, polymers were obtained in 62−92% yields. These polymers had high number-average molecular weights of 1.2×10^4−17.8×10^4. However, this catalyst gave no polymer at −60 °C. On the other hand, in the polymerization with PF_5 as catalyst at −60 °C, a polymer with a molecular weight of 3.7×10^4 was produced in 95% yield. Polymerization by $SbCl_5$ catalyst at −10 °C also gave a polymer with a molecular weight of 1.5×10^4 in 94% yield.

When the polymerization result of the *tert*-butyldimethylsilylated anhydroazidoxylose was compared with that of a benzylated anhydroazidoxylose homologue[6] by $BF_3{\cdot}OEt_2$ catalyst, the yield (62−92%) of the former was higher than that (29−48%) of the latter. Molecular weights of the silylated polymers were considerably higher than those of the benzylated polymers prepared in similar conditions. Furthermore, in the polymerization of a *tert*-butyldimethylsilylated 1,4-anhydroazidoribose by $BF_3{\cdot}OEt_2$ catalyst, the polymer was obtained in a high 85% yield.[7] Such high polymerizabilities for the silylated azido monomers might be ascribed to steric and electronic effects of the *tert*-butyldimethylsilyl group at the C2 position.

Since a bicyclic compound 1,4-anhydro-α-D-xylopyranose is equally regarded as 1,5-anhydro-*β*-D-xylofuranose, the ring-opening polymerization of the monomer has a possibility that at most four monomeric units are included in the polymer backbone by causing 1,4- and 1,5-scissions.[20,21] To elucidate mechanism of the polymerization, the polymer structure was examined by measuring the optical rotation and ^{13}C NMR spectrum. Specific rotations of the polymers are shown in Table 1. Several ^{13}C NMR spectra are exhibited in Figure 1.

The polymers (3AzSXF's) prepared by $BF_3{\cdot}OEt_2$ catalyst at −20 and −40 °C exhibited high specific rotations of +200° and +212°, respectively, indicating that those polymers are composed of an α structure. In ^{13}C NMR spectra of both polymers, all absorptions due to five carbons constituting xylose residues appeared as five sharp peaks, representing that the polymers consist of a completely stereoregular structure.[20]

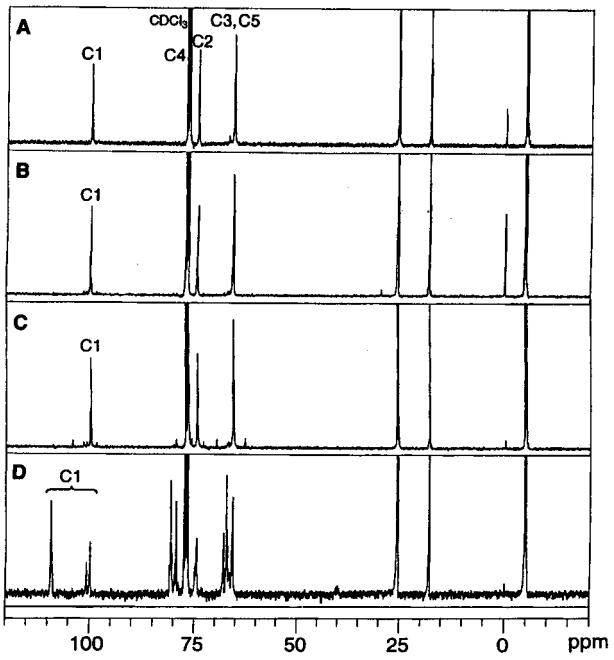

Figure 1. ^{13}C NMR spectra of poly(1,4-anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose)s polymerized by (A) $BF_3{\cdot}OEt_2$ catalyst at −20 °C (=3AzSXF), (B) $BF_3{\cdot}OEt_2$ catalyst at −40 °C (=3AzSXF), (C) PF_5 catalyst at −60 °C, and (D) $SbCl_5$ catalyst at −10 °C (in $CDCl_3$; TMS as reference zero).

^{13}C NMR absorptions of a stereoregular 3AzSXF were assigned using two-dimensional H−H COSY−FG and C−H MHQC spectra. The assignments and chemical shifts of 3AzSXF are shown in Table 2. The assignment of C1 absorption at 100.36 ppm (in CD_2Cl_2) and at 100.01 ppm (in $CDCl_3$) was based on the previous observation that a C1 absorption of 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan appears at 99.98 ppm.[20]

When the high specific rotation and the stereoregular structure indicated by NMR was taken into account, it was revealed that selective ring-opening polymerization occurred via 1,5-α-scission of the 1,4-anhydro sugar and the polymer obtained by $BF_3{\cdot}OEt_2$ catalyst in the temperature range of 0 to −40 °C was 3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AzSXF). This structure was the same as that of 3-azido-2-*O*-benzyl-3-deoxyxylose.[6] It has also been reported that in the cationic ring-opening polymerization of 1,4-anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-ribopyranose a (1→5)-α-ribofuranan derivative was formed.[7]

Table 2. ^{13}C Chemical Shifts of 3-Azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AzSXF), 3-Amino-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AmSXF), 3-Acetamido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AAdSXF), and 3-Acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF)

polymer designation	C1	C2	C3	C4	C5	$Si(CH_3)_2C(CH_3)_3$			$CONCH_3$		solvent
						$C(CH_3)_3$	$C(CH_3)_3$	$(CH_3)_2$	$C{=}O$	CH_3	
3AzSXF	100.36	74.88	66.36	77.26	66.30	25.85	18.31	−4.62			CD_2Cl_2
3AmSXF	100.80	75.64	56.66	77.84	65.48	25.32	17.15	−5.13			DMSO-d_6
3AAdSXF	101.78	75.08	55.57	76.11	67.84	25.47	18.06	−4.80	170.57	23.35	$CDCl_3$
3AAdXF	103.38	76.50	56.98	78.20	69.31				177.54	24.45	D_2O

Table 3. Conversion of 3-Azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AzSXF) into 3-Acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF) via Both 3-Amino-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AmSXF) and 3-Acetamido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AAdSXF)

(A) Reduction of 3AzSXF into 3AmSXF

							3AmSXF		
							yield		
run no.	mg	3AzSXF $\bar{M}_n \times 10^4$	$NaBH_4$, g	THF/EtOH, mL/mL	temp, °C	time, h	mg	%	convn,[a] %
1	420	17.8	0.5 × 2	(40/40) × 2	64	50	323	80	85
2	260	11.1	0.5 × 4	(20/30) × 4	64	160	122	52	100

(B) Acetylation of 3AmSXF into 3AAdSXF

					3AAdSXF			
					yield			
3AmSXF,[b] mg	CH_3COCl, mL	THF/pyridine, mL/mL	temp, °C	time, h	mg	%	convn,[c] %	$\bar{M}_n$,[c] %
120	2.0	20/2	30	6	140	70	100	1.3×10^4

(C) Desilylation of 3AAdSXF into 3AAdXF

					3AAdXF				
					yield				
3AAdSXF, mg	$(Bu)_4NF$, mL	THF, mL	temp, °C	time, h	mg	%	convn,[d] %	$\bar{M}_n$	$[\alpha]^{20}_D$, deg
100	3.0	5	r.t.	1.5	58	95	100	7.8×10^3	+212

[a] Conversion of azido groups into amino groups determined by NMR. [b] The molecular weight was not measured. [c] Conversion of amino groups into acetamido groups. [d] Conversion of *tert*-butyldimethylsilyl groups into hydroxyl groups.

In the polymer (no. 1) prepared by $BF_3{\cdot}OEt_2$ catalyst at 0 °C, a positive specific rotation of +174°, which is a little lower than that of the polymers obtained at −20 and −40 °C, might be due to a little lower molecular weight of the polymer. On the other hand, the polymer (no. 6) prepared by a strong Lewis acid, antimony pentachloride, had two C1 absorptions composed of 29% of 1,5-α-xylofuranosidic and 71% of 1,5-β-xylofuranosidic units at 99.96 and 109.21 ppm, respectively, indicating that this polymer was composed of a mixed 1,5-linked structure.

In the ring-opening polymerization of 1,4-anhydro sugar derivatives such as 1,4-anhydro-α-D-ribopyranose,[21,22] 1,4-anhydro-6-deoxy-β-L-talopyranose,[23] and 1,4-anhydro-α-D-glucopyranose,[24] both 1,4- and 1,5-scissions occurred depending on the kind of 2- and 3-substituents and the catalyst. On the other hand, it was reported that 1,4-anhydroxylopyranoses such as 1,4-anhydro-2,3-*O*-benzyl-α-D-xylopyranose[20] and 1,4-anhydro-3-azido-3-deoxy-2-*O*-benzyl-α-D-xylopyranose[6] did not cause the 1,4-scission but did exclusively cause the 1,5-scission. The selective 1,4-scission took place when the anhydro sugars satisfied both conditions that the sugar has a ribose or talose configuration and that protective groups for the 2- and 3-hydroxyls must be groups causing the coordination of Lewis acid catalyst among O2, O3, and O4 oxygens. In the case of 1,4-anhydro-3-azido-3-deoxy-2-*O*-benzyl-α-D-xylopyranose[6] and -ribopyranose,[7] the 3-azido group did not function as this kind of protective group. Thus, in the ring-opening polymerization of the 2-O-*tert*-butyldimethylsilylated 1,4-anhydroxylopyranose, it is reasonable to consider that the $BF_3{\cdot}OEt_2$ catalyst is exclusively coordinated to O5 but not O4, leading to the selective 1,5-scission.

Conversion of 3AzSXF into 3-Acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF). A stereoregular 3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-xylofuranan was converted into 3-acetamido-3-deoxy-(1→5)-α-xylofuranan via an intermediate 3-amino-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-xylofuranan (3AmSXF) (Scheme 1).

It has been reported that reduction of an azido group included in a *tert*-butyldimethylsilylated polysaccharide with lithium aluminum hydride gave a low yield.[7] In this study, however, it was found that the reduction of the azido group in 3AzSXF with sodium borohydride was very slow in THF. Thus, the reduction was performed in a THF−ethanol mixture at refluxing temperature for a long time. The reduction was completed by repeating twice, producing 3AmSXF in considerably high yields. Results of the reduction are summarized in Table 3.

The ^{13}C NMR spectrum of the resulting polymer (3AmSXF) as well as that of 3AzSXF measured in CD_2Cl_2 is shown in Figure 2. Except for a broad absorption due to C1 carbon which might be attributable to low solubility in the NMR solvent, all carbon absorptions appeared as individual peaks. Therefore, it was revealed that the polymer is 3AmSXF having the amino

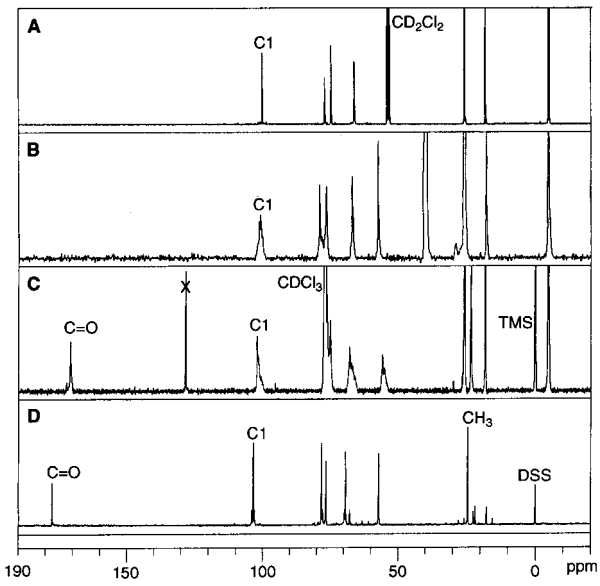

Figure 2. ^{13}C NMR spectra of (A) 3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (in CD_2Cl_2), (B) 3-amino-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (in DMSO-d_6), (C) 3-acetamido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (in $CDCl_3$), and (D) 3-acetamido-3-deoxy-(1→5)-α-D-xylofuranan (in D_2O).

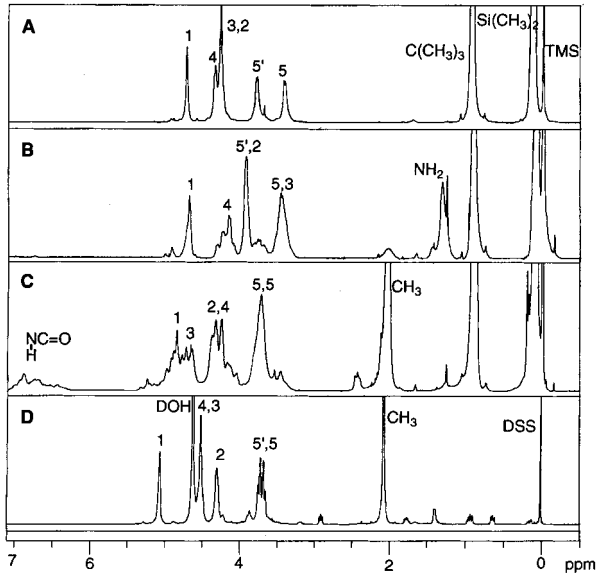

Figure 3. ^{1}H NMR spectra of (A) 3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (in $CDCl_3$), (B) 3-amino-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (in $CDCl_3$), (C) 3-acetamido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (in $CDCl_3$), and (D) 3-acetamido-3-deoxy-(1→5)-α-D-xylofuranan (in D_2O).

group at the C3 position. Assignments of the ^{13}C chemical shifts are shown in Table 2.

Subsequently, the aminoxylofuranan 3AmSXF was acetylated with acetyl chloride to give 3-acetamido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-(1→5)-α-D-xylofuranan (3AAdSXF) with $\bar{M}_n$ of 1.3×10^4. Results of the acetylation are summarized in Table 3. The ^{13}C NMR spectrum (Figure 2) and chemical shift assignments of 3AAdSXF clearly represent that the acetylation of amino groups was completed.

The reason the *tert*-butyldimethylsilyl group was chosen as the 2-OH protective group is that since the acetylation of the 3-amino polymer is performed in organic solvent and the protective group is removed after acetylation, the 3-amino polymer must have such a 2-OH protective group as *tert*-butyldimethylsilyl. The benzyl group was not used for the 2-OH protection, because its removal with sodium in liquid ammonia might cause side reactions in which the acetamide group participates.

Desilylation of 3AAdSXF was carried out with tetra-*n*-butylammonium fluoride at room temperature. Results of the desilylation are also shown in Table 3. ^{13}C NMR and ^{1}H NMR spectra revealed that the resulting polymer is 3-acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF) in which complete desilylation took place, with the C1 absorption appearing at 101.46 ppm as a single peak (Figure 2). The peak of H1 of 3AAdXF appeared at 5.05 ppm, and the three protons (CH_3) of the acetamide group appeared at 2.07 ppm (Figure 3D). 3AAdXF had $\bar{M}_n$ of 7.8×10^3 and $[\alpha]^{20}_D$ of +212°. The ^{13}C chemical shifts assigned by use of 2D NMR are exhibited in Table 2.

In conclusion, a stereoregular acetamido group containing xylofuranan, i.e., 3-acetamido-3-deoxy-(1→5)-α-D-xylofuranan, was for the first time synthesized by four-step reactions starting from the polymerization of a 1,4-anhydroazidoxylose derivative.

Experimental Section

Materials and Measurements. Lithium azide was prepared by the reaction of sodium azide with lithium hydroxide according to the literature.[25] Solvents were distilled before use. 400-MHz ^{1}H and 100-MHz ^{13}C NMR spectra were taken on sample solutions in $CDCl_3$ or D_2O by use of a JEOL Lambda 400 spectrometer. The two-dimensional H−H COSY−FG and C−H MHQC measurements were used to assign the ^{1}H and ^{13}C absorptions. Tetramethylsilane (TMS) and sodium 3-trimethylsilyl-1-propanesulfonate were used as internal standards for organic solvents and water, respectively. Specific rotations were measured in a chloroform or water solution at 20 °C by use of a Perkin-Elmer 240 polarimeter. Molecular weights of polymers were determined by gel permeation chromatography using THF or water as the solvent and standard polystyrenes or pullulans as references.

Synthesis of 1,4-Anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose (A3ASX). The monomer A3ASX was prepared by a synthetic route starting from partial *tert*-butyldimethylsilylation of 1,4-anhydro-α-D-ribopyranose according to a modification of our method applied to the synthesis of a ribose homologue.[7] 1,4-Anhydro-α-ribopyranose was obtained by pyrolysis of ribose according to the method of Köll et al.[26] 1,4-Anhydro-2-*O*-*tert*-butyldimethylsilyl-α-D-ribopyranose was prepared by reacting 1,4-anhydro-α-D-ribopyranose (13.2 g, 0.1 mol) with *tert*-butyldimethylsilyl chloride (23 g, 0.15 mol) in the presence of silver nitrate (17 g, 0.1 mol) at room temperature for 12 h. After workup, 1,4-anhydro-2-*O*-*tert*-butyldimethylsilyl-α-D-ribopyranose (9.4 g, 0.038 mol) was obtained in 38% yield.

1,4-Anhydro-2-*O*-*tert*-butyldimethylsilyl-α-D-ribopyranose (1.6 g, 6.5 mmol) was reacted with trifluoromethanesulfonic anhydride (2.0 g, 7.0 mmol) in pyridine (20 mL) at room temperature. After chromatographic purification, 1,4-anhydro-2-*O*-*tert*-butyldimethylsilyl-3-*O*-trifluoromethanesulfonyl-α-D-ribopyranose (2.46 g, 6.4 mmol) was obtained in 98% yield.

1,4-Anhydro-3-azido-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-α-D-xylopyranose was prepared by reacting 1,4-anhydro-2-*O*-*tert*-butyldimethylsilyl-3-*O*-trifluoromethanesulfonyl-α-D-ribopyranose (2.0 g, 5.3 mmol) with lithum azide (1.2 g, 18.5 mmol) in dry dimethylformamide (10 mL) at 65 °C for 10 h.[6] After workup, purification of crude A3ASX was finally carried out by silica gel column chromatography using a hexane−ethyl acetate mixture (6:1 volume ratio) as an eluent. A3ASX (0.98

g, 3.6 mmol) was obtained in 68% yield. $[\alpha]^{20}_D$: −48.3° (*c* 1% in $CHCl_3$). ^{13}C NMR (in $CDCl_3$) (ppm from TMS): C1 (104.20), C2 (75.92), C3 (69.87), C4 (79.59), C5 (62.89), Si[C(−4.82)-$H_3]_2$C(17.97)[C(25.69)$H_3]_3$.

Polymerization. Cationic ring-opening polymerizations of A3ASX were carried out by use of a high-vacuum technique.[27−29] A3ASX was polymerized with Lewis acids such as BF_3·OEt_2, PF_5, and $SbCl_5$ as catalysts in methylene chloride at low temperatures. The resulting polymers were purified by dissolution−reprecipitation with a chloroform−methanol system three times and freeze-dried from benzene. IR (KBr): $\nu = 2107$ cm^{-1} (N_3). ^{13}C NMR data are shown in Table 2.

Reduction. To a 3AzSXF (0.42 g) solution in THF (40 mL) was added a sodium borohydride (0.5 g) solution in ethanol (30 mL), followed by stirring for 24 h. An amino polymer 3AmSXF was recovered by pouring the reaction solution into water. The polymer was purified by dissolution−reprecipitation using THF−water twice and finally freeze-dried from benzene. The reduction was repeated twice. IR (KBr): $\nu =$ 3500−3000 (NH_2). ^{13}C NMR data are shown in Table 2.

***N*-Acetylation.** 3AmSXF (120 mg) was acetylated with acetyl chloride (2 mL) in THF (20 mL) at 30 °C under a nitrogen atmosphere for 6 h. After workup, 3-acetamido-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-(1→5)-α-D-xylofuranan (3AAdSXF) (140 mg, 70% yield) was obtained. ^{13}C NMR data of 3AAdSXF are shown in Table 2.

Desilylation. *tert*-Butyldimethylsilyl groups in 3AAdSXF (100 mg) were removed by reacting it with tetra-*n*-butylammonium fluoride (3.0 mL) in THF (5 mL) at room temperature for 1.5 h. After water was added, THF was evaporated. Then, the aqueous polymer solution was dialyzed with water for 3 days. 3-Acetamido-3-deoxy-(1→5)-α-D-xylofuranan (3AAdXF) (58 mg, 96% yield) was obtained by freeze-drying from water. ^{13}C chemical shifts of 3AAdXF are shown in Table 2.

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