Ring-Opening Polymerization of 1,4-Anhydro-3-*O*-benzyl-2-*O*-acyl-α-D-xylopyranose and Synthesis of Stereoregular (1→5)-*β*-D-Xylofuranan

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ABSTRACT: Ring-opening polymerizations of both 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl- (**1**) and 1,4-anhydro-3-*O*-benzyl-2-*O*-acetyl-α-D-xylopyranose (**2**) gave their respective (1→5)-*β*-D-xylofuranan derivatives. Subsequent removal of the protective groups gave stereoregular (1→5)-*β*-D-xylofuranan for the first time. Polymerization of monomer **1** by PF_5 gave 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-*β*-D-xylofuranan with $[\alpha]_D^{25}$ −87.4° and a number-average molecular weight of 16.9×10^3 ($\overline{DPn} = 55$). Polymerization of monomer **2** by PF_5 gave 3-*O*-benzyl-2-*O*-acetyl-(1→5)-*β*-D-xylofuranan with $[\alpha]_D^{25}$ −121.1° and a number-average molecular weight of 6.4×10^3 ($\overline{DPn} = 24$). Removal of the acyl and benzyl groups gave nonnatural new stereoregular polysaccharide (1→5)-*β*-D-xylofuranan.

Introduction

Uryu et al. reported the ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose.[1] Stereoregular (1→5)-α-xylofuranan was obtained only when $BF_3 \cdot Et_2O$ was used as an initiator at 7 mol % concentration at −60 °C. Polymer consisting of a mixture of (1→5)-α- and (1→5)-*β*-xylofuranosic linkages was obtained when other Lewis acids, e.g., SiF_4, PF_5, NbF_5, SbF_5, TaF_5, $TiCl_4$, and $SnCl_4$, were used. Stereoregular (1→5)-*β*-xylofuranan was never obtained by their method.

On the other hand, we found in our stepwise synthesis of cellulose derivatives that both benzyl and pivaloyl groups introduced into 3-*O*- and 2-*O*-positions of glucose, respectively, are indispensable for highly stereoselective (1→4)-*β*-glycosidic bond formation.[2] These substituent effects were applied to the ring-opening polymerizations of 1,4-anhydroglucose derivatives to give stereoregular (1→5)-*β*-glucofuranan.[3]

The key mechanism is believed to be the result of the neighboring group participation of 2-*O*-acyl group to provide stereoregular (1→5)-*β*-glucosidic bond formation.[3] Since (1→5)-*β*-xylofuranan does not occur in nature, its physical properties, structure, and biological activities are of great interest. Therefore, we selected 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl- (**1**) and 1,4-anhydro-3-*O*-benzyl-2-*O*-acetyl-α-D-xylopyranose(**2**) as starting materials for the ring-opening polymerizations to synthesize stereoregular (1→5)-*β*-xylofuranan. We expect that these 1,4-anhydroxylose derivatives with 2-*O*-pivaloyl group or 2-*O*-acetyl group will induce stereoselective *β*-glycosidic bond formation by the same mechanism.

Results and Discussion

Polymerizations of Monomers. Compounds **1** and **2** were synthesized by our novel synthetic method.[4] Their polymerizations were carried out under the same reaction conditions: −30 °C for 40 h in CH_2Cl_2 using PF_5 as an initiator. The results are summarized in Table 1. Number-averaged molecular weights of the polymer from compound **1** (poly(**1**)), 2-*O*-pivaloyl derivative, and the polymer from compound **2** (poly(**2**)), 2-*O*-acetyl derivative, determined by gel permeation chromatography (GPC) in chloroform using polystyrene standards, were 16 900 ($\overline{DPn} = 55$) and 6400 ($\overline{DPn} = 24$), respectively. Interestingly, poly(**1**) showed the relatively high solubility in $CHCl_3$, CH_2Cl_2, EtOAc, and so on, while poly(**2**) showed the poor solubility in spite of having a lower molecular weight than poly(**1**), and dissolved only in chloroform.

Table 1. Polymerization of 1,4-Anhydroxylopyranose Derivatives[a]

monomer	*T* (°C)	*T* (h)	yield (%)	$[\alpha]_D^{25}$ (deg)	$\overline{DPn}$[c]	10^{-3} M_{GPC}	M_W/M_N
1	−30	40	75	−87.4	55	16.9	1.5
2	−30	40	57[b]	−121.1	24	6.4	1.8

[a] Initiator: PF_5, initiator concentration 5 mol %; solvent CH_2Cl_2; monomer/solvent 50 g/100 mL. [b] Polymer was the insoluble fraction in chloroform/*n*-hexane (∼1/5, v/v). [c] Molecular weight was calculated from GPC data using polystyrene standard in chloroform.

Structure of Polymers. Generally, there are four possible structural units in the polymer prepared by the ring-opening polymerization of 1,4-anhydro-α-D-xylopyranose derivatives, namely, (1→5)-α- and (1→5)-*β*-D-xylofuranose units and the (1→4)-α- and (1→4)-*β*-D-xylopyranose units. The polymer may have one stereoregular linkage or may contain a mixture of these linkages.[1]

No ^{1}H-NMR spectrum of any (1→5)-*β*-D-xylofuranan derivative has been recorded since this is the first time any (1→5)-*β*-D-xylofuranan derivative was synthesized. However, Uryu et al.[1] published the spectrum of (1→5)-α-D-xylofuranan and that of 2,3-di-*O*-benzyl-xylofuranan consisted of a mixture of both (1→5)-α- and (1→5)-*β*-linkages. From these spectra, the characteristics signals of the (1→5)-*β*-D-xylofuranan derivative can be deduced. Uryu et al. were also able to assign the chemical shifts of (1→5)-*β*-D-xylofuranan derivatives on the basis of the ^{13}C-NMR spectra of the above two polymers.

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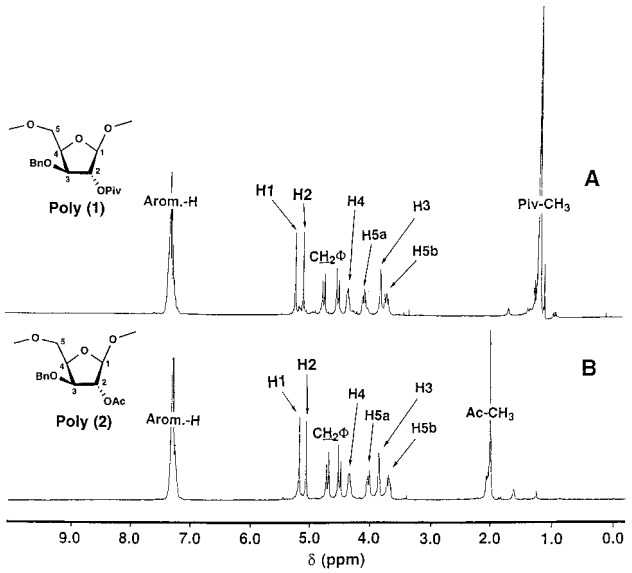


Figure 1. ^{1}H-NMR spectra (300 MHz) of (A) 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-*β*-D-xylofuranan (poly(**1**)) and (B) 3-*O*-benzyl-2-*O*-acetyl-(1→5)-*β*-D-xylofuranan (poly(**2**)) ($CDCl_3$ as solvent).

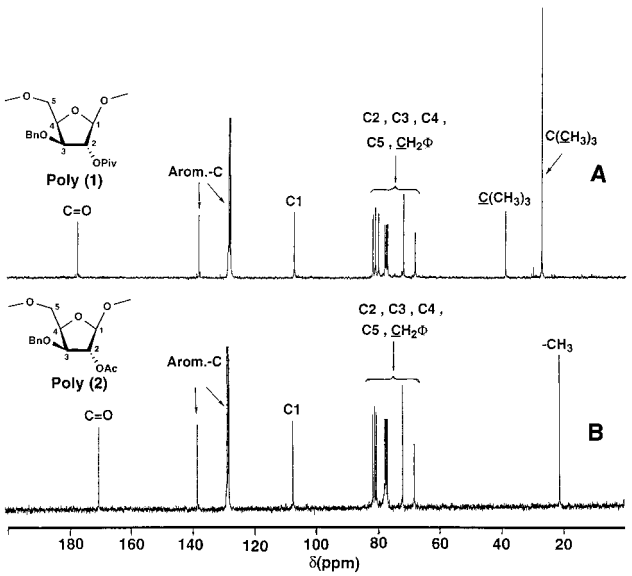
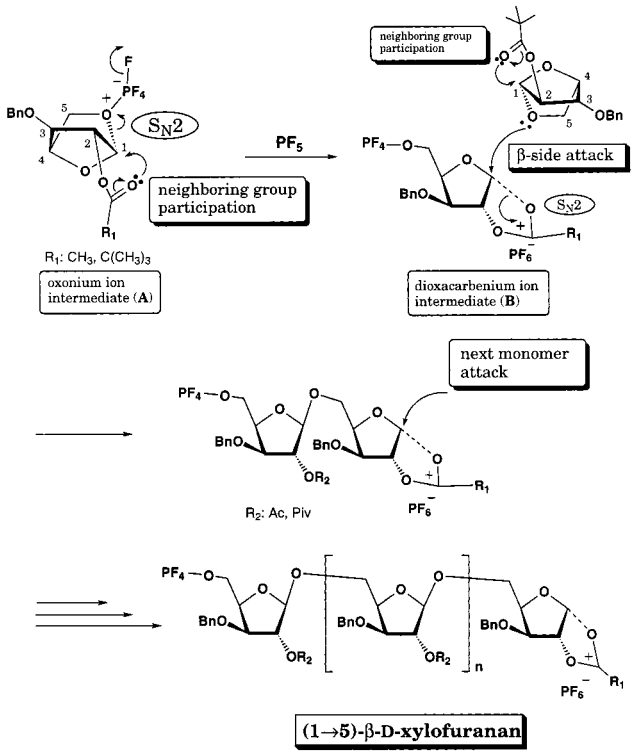


Figure 2. ^{13}C-NMR spectra (300 MHz) of (A) 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-*β*-D-xylofuranan (poly(**1**)) and (B) 3-*O*-benzyl-2-*O*-acetyl-(1→5)-*β*-D-xylofuranan (poly(**2**)) ($CDCl_3$ as solvent).

^{1}H- and ^{13}C-NMR spectra of poly(**1**) and poly(**2**) are shown in Figures 1 and 2, respectively. The ^{1}H-NMR spectra show very clear resonance for each ring proton. The ^{13}C-NMR spectra showed only one single peak for anomeric carbon at about 107 ppm. These results clearly indicate that both poly(**1**) and poly(**2**) are highly stereoregular and consist of only one intermonomeric linkage. By comparing these spectra with those of 2,3-di-*O*-benzylxylofuranan derivatives[1] and taking into considerations the substituent effects of the acyl groups at the 2-*O*-positions, it is clear that both poly(**1**) and poly(**2**) consist exclusively of (1→5)-*β*-D-xylofuranosidic linkages. For example, the signals of the anomeric protons appear as singlets at δ 5.04 and 5.05 ppm, respectively. This indicates that these polymers consist exclusively of *β*-xylofuranose repeating units. An α-furanose units would have appeared as a doublet with a coupling constant of about 4.59 Hz.[1] The stereoregularity is also supported by a single sharp peak assigned

Scheme 1. Mechanism of the Polymerization of 1,4-Anhydroxylopyranose Derivatives



to the C1-carbon appearing at 107 ppm in ^{13}C-NMR of each polymer (Figure 2) rather than at 100 ppm for the α-derivative.[1]

In addition, the specific rotations of both poly(**1**) ($[\alpha]_D^{25}$ −87.4°) and poly(**2**) ($[\alpha]_D^{25}$ −121.1°) were large negative in spite of these molecular weights. This suggests that these polymers have *β*-glycosidic linkages; stereoregular (1→5)-α-D-xylofuranan derivative has large positive specific rotation ($[\alpha]_D^{25}$ + 158.4°)[1].

Thus, all above results strongly indicate that both polymers prepared by the polymerizations of the present starting monomers **1** and **2** are stereoregular polysaccharides, (1→5)-*β*-D-xylofuranan derivatives.

These results of the present polymerizations are consistent with those of the ring-opening polymerizations of 1,4-anhydro-α-D-glucopyranose derivatives, giving (1→5)-*β*-D-glucofuranan.[3,5] These results reconfirm the preferential 1,5-acetal bond scission to give (1→5)-furanosidic linkages in the case of the ring-opening polymerizations of 1,4-anhydro sugars.

Mechanism of Polymerization. Scheme 1 illustrates the proposed propagation mechanism of the polymerization of 1,4-anhydro-2-*O*-acyl-3-*O*-benzyl-α-D-xylopyranose derivatives to yield (1→5)-*β*-D-xylofuranan. Phosphorus pentafluoride as initiator coordinates with the 1,5-linked oxygen as suggested by Uryu et al.,[1] which is more nucleophilic than the 1,4-linked oxygen, to afford the C1−O$^+$−C5 oxonium ion intermediate (**A**) preferentially. The carbonyl oxygen of the acyl group at the 2-*O*-position attacks C-1 from the α-side, and then the dioxacarbenium ion intermediate (**B**) occurs via C1−O$^+$ bond breaking by intramolecular S_N2 reaction mechanism. The 1,5-linked oxygen of the next monomer can attack the C1-carbon of **B** only from the opposite side, i.e., *β*-side, to give only (1→5)-*β*-linkage. Thus, this polymerization indicates that the neighboring group participation of the pivaloyl (acetyl) group at the 2-*O*-

Table 2. ^{13}C Chemical Shifts[a] of (1→5)-β-D-Xylofuranan and Poly(D-xylose) with Mixed Structures

	C-1	C-2	C-3	C-4	C-5
(1→5)-β-D-xylofuranan[b]	110.60	81.27	76.80	81.50	68.26
poly(D-xylose) with mixed structures					
(1→5)-β-xylofuranosidic units[c]	111.53	82.23	77.79	82.47	69.20
(1→5)-α-xylofuranosidic units[c]	103.73	78.57	77.01	78.76	68.62

[a] Measured in 1 N NaOH aqueous solution. [b] 1,4-Dioxane was used as an internal standard. [c] Tetramethylsilane was used as an internal standard.

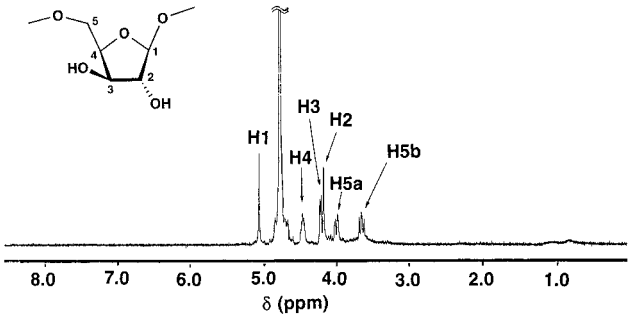


Figure 3. ^{1}H-NMR spectrum (300 MHz) of (1→5)-β-D-xylofuranan (D_2O as solvent).

position greatly affects the stereoregularity of the polymerization. This ring-opening polymerization with neighboring group participation was first proposed by Ichikawa et al. in 1988 and supported by a later study (Kobayashi et al. in 1998) for the polymerization of 1,6-anhydrogalactose derivatives.[6,7] Our recent results of the polymerization of 1,4-anhydro-α-D-glucopyranose derivatives also support this mechanism.[3]

Conversion of the Polymers into Free (1→5)-β-D-Xylofuranan. poly(**1**) and poly(**2**) were subjected to deacylation with Super-Hydride,[8] potassium triethyl borohydride, and subsequent debenzylation with $Pd(OH)_2$/C. However, the ^{1}H-NMR spectra of these products showed the residual benzyl groups in these polymers. The debenzylation reaction was then carried out at higher temperature and/or by the addition of acetic acid. However, the stereoregular (1→5)-β-D-xylofuranan skeleton was found to be easily depolymerized at temperature over 40 °C or under the mild acidic conditions, e.g., a small amount of acetic acid.

Thus, both debenzylation and deacylation of 3-*O*-benzyl-2-*O*-acyl-(1→5)-β-D-xylofuranan derivatives were conducted with sodium in liquid ammonia at about −50 °C, resulting in free (1→5)-β-D-xylofuranan without any depolymerization. The ^{1}H-NMR spectrum of free (1→5)-β-D-xylofuranan in D_2O indicates that the benzyl and acyl groups were completely removed (Figure 3). The ^{1}H resonance was assigned via their cross-peaks in the COSY spectrum (Figure 4). The signal of the anomeric peak appears at 103.8 ppm in ^{13}C-NMR spectrum (Figure 5): the C1-carbon of free (1→5)-α-D-xylofuranan appears at 101.8 ppm.[1] The ^{13}C resonance was assigned by 1. Table 2 shows the ^{13}C chemical shifts, measured in ref 1 N NaOH aqueous solution, of synthesized free (1→5)-β-D-xylofuranan and polymer with mixed structures,[1] which is a model compound of (1→5)-α- and (1→5)-β-xylofuranosidic units. The chemical shifts of synthesized free (1→5)-β-D-xylofuranan are close to those of the (1→5)-β-xylofuranosidic units, although a small difference (~1 ppm) may arise from different internal standards. These results strongly indicate that stereoregular polysaccharide (1→5)-β-xylofuranan was first synthesized.

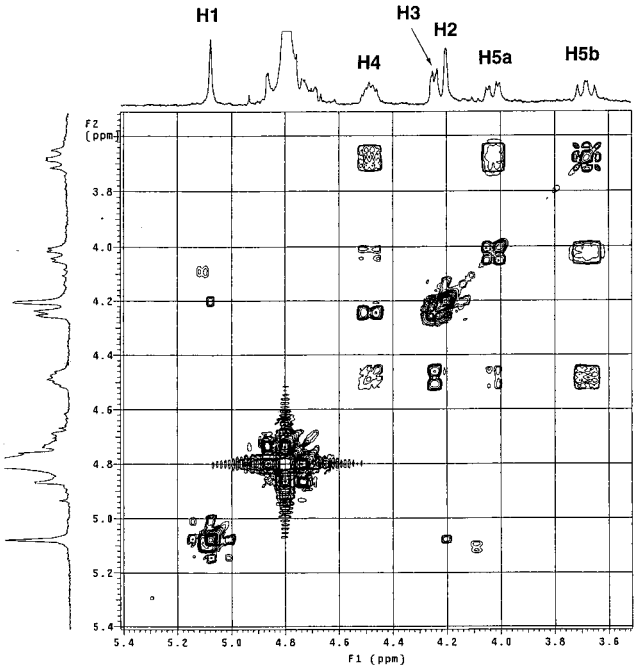


Figure 4. H−H COSY spectrum of (1→5)-β-D-xylofuranan (D_2O as solvent).

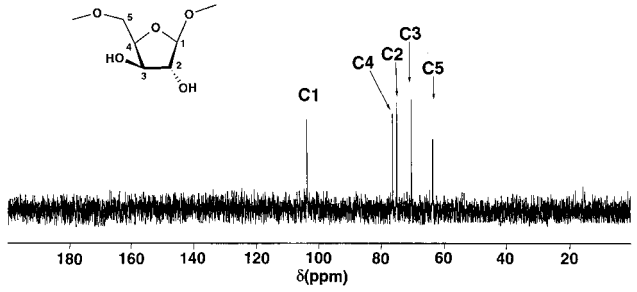


Figure 5. ^{13}C-NMR spectrum (300 MHz) of (1→5)-β-D-xylofuranan (D_2O as solvent).

The present results from these xylose derivatives coincides with those from glucose derivatives. Consequently, in the ring-opening polymerizations of 1,4-anhydroglucose and 1,4-anhydroxylose derivatives having the 2,7-dioxabicyclo[2.2.1]heptane system from model experiments of Hall et al.,[7] it is concluded that the bond breaking of 1,5-acetal linkage precedes that of 1,4-acetal linkage as expected. Thus, the CH_2OR group at the C6-position of glucose may not contribute to the regioregularity in the ring-opening polymerization, because the analogous stereoregular polymers were obtained from both 1,4-anhydroglucose with CH_2OR and 1,4-anhydroxylose without CH_2OR.

Conclusions

The novel stereoregular polysaccharide (1→5)-β-D-xylofuranan was synthesized as planned by ring-opening polymerization of two 1,4-anhydroxylopyranose

derivatives selected with consideration given to the substituent effects derived from the results of the polymerization of 1,4-anhydroglucopyranose derivatives.

Experimental Section

Polymerization. All polymerizations were carried out under a high-vacuum system.[2f] The monomer was dried in a polymerization ampule by evacuating for approximately a day. Methylene chloride was distilled from CaH_2 and degassed by freezing and thawing three times in a high-vacuum line. The solvent was transferred under high vacuum. Phosphorus pentafluoride was generated from *p*-chlorobenzenediazonium hexafluorophosphate by decomposition at 160 °C and transferred to a reaction ampule. The reaction apparatus was then separated by melting off and placed in an ethanol bath at −30 °C. The reaction mixture was diluted with chloroform; washed with saturated aqueous $NaHCO_3$, water, and brine; dried over anhydrous sodium sulfate; and concentrated to dryness. 3-*O*-Benzyl-2-*O*-pivaloyl-(1→5)-*β*-D-xylofuranan was purified on silica gel column (Wakogel C-200) eluted with ethyl acetate/*n*-hexane (1/2, v/v), yield 75 %. The polymer mixture from monomer **2** was dissolved in a small amount of chloroform. To the solution was added *n*-hexane, and precipitated polymer 3-*O*-benzyl-2-*O*-acetyl-(1→5)-*β*-D-xylofuranan was then collected by filtration, and finally dried in vacuo, yield 57 %.

3-*O*-Benzyl-2-*O*-pivaloyl-(1→5)-*β*-D-xylofuranan [Poly-(1)]. $\overline{DPn}$ = 55 (determined by GPC in chloroform using polystyrene standards); $[\alpha]_D^{25}$ −87.4° (*c* = 1, in chloroform); ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* = 5.04 (s, 1H, $J_{1,4}$ = 0 Hz, C1−H), 5.17 (s, 1H, $J_{2,3}$ = 0 Hz, C2−H), 3.77 (d, 1H, $J_{3,4}$ = 5.09 Hz, C3−H), 4.31 (dt, 1H, $J_{4,5a}$ = 3.70 Hz, C4−H), 4.05 (d, 1H, J_{gem} = 10.9 Hz, C5−Ha), 3.67 (m, 1H, $J_{4,5b}$ = 7.66 Hz, C5−Hb), 1.14−1.18 (C═OC(CH_3)$_3$), 4.71, 4.47 (d, 1H, *J* = 12.1 Hz, respectively, CH_2C$_6$H$_5$), 7.21−7.27 (aromatic); ^{13}C-NMR (300 MHz, $CDCl_3$) *δ* = 107.0 (C-1), 81.3, 80.5, 79.5, 71.5, 67.8 (C-2, C-3, C-4, C-5, *C*H$_2$C$_6$H$_5$), 27.0 (C═OC(*C*H$_3$)$_3$), 38,6 (C═O*C*(CH$_3$)$_3$), 137.8, 128.2, 128.0, 127.8, 127.5 (aromatic), 177.2 (C = O). Anal. Calcd for $(C_{17}H_{22}O_5 \cdot 0.5H_2O)_{55} \cdot H_2O$: C, 64.51; H, 7.34. Found: C, 64.65; H, 7.10.

3-*O*-Benzyl-2-*O*-acetyl-(1→5)-*β*-D-xylofuranan [Poly(2)]. $\overline{DPn}$ = 24 (determined by GPC in chloroform using polystyrene standards); mp 186.3−192.1 °C; $[\alpha]_D^{25}$ −121.1° (*c* = 0.5, in chloroform); ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* = 5.05 (s, 1H, $J_{1,4}$ = 0 Hz, C1−H), 5.16 (s, 1H, $J_{2,3}$ = 0 Hz, C2−H), 3.86 (d, 1H, $J_{3,4}$ = 5.09 Hz, C3−H), 4.35 (dt, 1H, $J_{4,5a}$ = 3.70 Hz, C4−H), 4.03 (d, 1H, J_{gem} = 10.9 Hz, C5−Ha), 3.70 (m, 1H, $J_{4,5b}$ = 7.66 Hz, C5−Hb), 2.0 (C═OCH$_3$), 4.69, 4.50 (d, 1H, *J* = 12.1 Hz, respectively, CH_2C$_6$H$_5$), 7.31−7.33 (aromatic); ^{13}C-NMR (300 MHz, $CDCl_3$) *δ* = 107.0 (C-1), 81.3, 81.0, 80.2, 71.7, 67.9 (C-2, C-3, C-4, C-5, *C*H$_2$C$_6$H$_5$), 20.9 (CH$_3$), 137.8, 128.3, 127.8, 127.6 (aromatic), 170.0 (C═O). Anal. Calcd for $(C_{14}H_{16}O_5 \cdot 0.6H_2O)_{24.4} \cdot 4H_2O$: C, 60.5; H, 7.09. Found: C, 60.8; H, 6.92.

(1→5)-*β*-D-xylofuranan. The stereoregular 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-*β*-D-xylofuranan [$\overline{DPn}$ = 14 (determined by GPC in chloroform using polystyrene standards)] (50 mg) dissolved in THF (1.5 mL) dried over metal potassium was added dropwise to a solution of small pieces of sodium metal in 3 mL of liquid ammonia at −50 °C. The reaction was continued for 5 h followed by successive addition of ammonium chloride and several drops of water. After the reaction mixture was allowed under a stream of nitrogen gas in order to remove ammonia deprotected polymer was dialyzed with water and freeze-dried (13.7 mg, 54.9 % yield): mp 178−189 °C $[\alpha]_D^{25}$ −44.6° (*c* = 0.1, in H_2O); Anal. Calcd for $(C_5H_8O_4)_{14.4}H_2O$: C, 45.03; H, 6.17. Found: C, 45.06; H, 6.13. The same deprotected polymer was obtained from 3-*O*-benzyl-2-*O*-acetyl-(1→5)-*β*-D-xylofuranan [$\overline{DPn}$ = 22 (determined by GPC in chloroform using polystyrene standards)] by the same manner as described above: mp 181−189 °C $[\alpha]_D^{25}$ −69.3° (*c* = 0.1, in H_2O); ^{1}H-NMR (300 MHz, D_2O) *δ* = 5.07 (s, 1H, $J_{1,4}$ = 0 Hz, C1−H), 4.20 (s, 1H, $J_{2,3}$ = 0 Hz, C2−H), 4.24 (d, 1H, $J_{3,4}$ = 5.4 Hz, C3−H), 4.49 (m, 1 H, C4−H), 4.03 (dd, 1H, J_{gem} = 11.1 Hz, $J_{4,5a}$ = 3.6 Hz, C5−Ha), 3.68 (dd, 1H, $J_{4,5b}$ = 7.8 Hz, C5−Hb); ^{13}C-NMR (300 MHz, D_2O) *δ* = 103.8 (C-1), 75.2 (C-2), 70.5 (C-3), 76.6 (C-4), 63.7 (C-5). Anal. Calcd for $(C_5H_8O_4)_{22.3} \cdot H_2O$: C, 45.18; H, 6.13. Found: C, 45.11; H, 6.18.

Measurements. All melting points (mp) are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC300 FT-NMR (300 MHz) spectrometer and a Varian INOVA300 FT-NMR (300 MHz) spectrometer, in chloroform-*d* or D_2O with tetramethylsilane (TMS) and 1,4-dioxane, respectively, as internal standards. Chemical shifts (*δ*) and coupling constants (*J*) are given in *δ* values (ppm) and Hertz, respectively. Some chemical shifts were assigned using a decoupling method; others were assigned by an analogy with values in the literature and by analogy with model compounds. Optical rotations were measured at 25 °C using a JASCO Dip-1000 digital polarimeter. Molecular weight distributions of the substituted polymer were analyzed by gel permeation chromatography (GPC) in chloroform. Calibration curves were obtained by using polystyrene standards (Shodex). A Shimadzu liquid chromatograph injector (LC-10ATvp), a Shimadzu column oven (CTO-10Avp), a Shimadzu UV-VIS detector (SPD-10Avp), a Shimadzu refractive index detector (RID-10A), a Shimadzu communication bus module (CBM-10A), a Shimadzu LC workstation (CLASS-LC10), and Shodex columns (KF802, KF802.5 and KF803) were used. The flow rate was 1.0 mL/min.

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References and Notes

(1) Uryu, T.; Yamanouchi, J.; Hayashi, S.; Tamaki, H.; Matsuzaki, K. *Macromolecules* **1983**, *16*, 320−325.
(2) (a) Takano, T.; Nakatsubo, F.; Murakami, K. *Cellul. Chem. Technol.* **1988**, *22*, 135−145. (b) Takano, T.; Harada, T.; Nakatsubo, F.; Murakami, K. *Cellul. Chem. Technol.* **1990**, *24*, 333−342. (c) Takano, T.; Harada, T.; Nakatsubo, F.; Murakami, K. *Mokuzai Gakkaishi* **1990**, *36*, 212−217; *Chem. Abstr.* **1990**, *114*, 134389u. (d) Nishimura, T.; Takano, T.; Nakatsubo, F.; Murakami, K. *Mokuzai Gakkaishi* **1993**, *39*, 40-47; *Chem. Abstr.* **1993**, *119*, 162634n. (e) Nishimura, T.; Takano, T.; Nakatsubo, F.; Murakami, K. *Mokuzai Gakkaishi* **1994**, *40*, 44−49; *Chem. Abstr.* **1994**, *121*, 282437p. (f) Nishimura, T.; Nakatsubo, F. *Carbohydr. Res.* **1996**, *294*, 53−64. (g) Nishimura, T.; Nakatsubo, F. *Tetrahedron Lett.* **1996**, *37*, 9215-9218. (h) Nishimura, T.; Nakatsubo, F. *Cellulose* **1997**, *4*, 109−130.
(3) Kamitakahara, H.; Nakatsubo, F.; Murakami, K. *Macromolecules* **1994**, *27*, 5937−5942.
(4) Hori, M., Nakatsubo, F. *Carbohydr. Res.*, in press.
(5) Hori, M. Unpublished data.
(6) Ichikawa, H.; Kobayashi, K.; Sumitomo, H. *Carbohydr. Res.* **1988**, *179*, 315−320.
(7) Kobayashi, K.; Isii, T.; Okada, M.; Shuerch, C. *Polymer J.* **1993**, *25* (1), 49−57.
(8) Danishefsky, S. J.; Armistead, D. M.; Wincott, E.; Selnick, H. G.; Hungate, R. *J. Am. Chem. Soc.* **1989**, *111*, 2967−2980.
(9) Hall, H. K., Jr.; DeBlauwe, F.; Carr, L. J.; Rao, V. S.; Reddy, G. S. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 101.

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