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Synthesis of D-xylopyranan by the ring-opening polymerization of 3-*O*-benzyl-α-D-xylopyranose 1,2,4-orthopivalate. Attempts to synthesize a stereoregular polymer

Michiko Hori, Fumiaki Nakatsubo*

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

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Abstract

3-*O*-Benzyl-α-D-xylopyranose 1,2,4-orthopivalate (**1**) was newly synthesized and polymerized under cationic polymerization reaction conditions in order to synthesize stereoregular (1→4)-β-D-xylopyranan. Although the polymerization of orthopivalate **1** was carried out under various reaction conditions, a non-stereoregular polymer, but mainly consisting of (1→4)-β-xylopyranose units, was obtained. Comparing these results with those of glucose 1,2,4-orthopivalates, it was revealed that not only the substituents in the C-2 and C-3 positions, but also the CH_2OR group in glucose 1,2,4-orthopivalate, largely contribute to (1→4)-β-glucosidic bond formation by the ring-opening polymerization. © Published by Elsevier Science Ltd.

Keywords: Stereoregular (1→4)-β-D-xylopyranan; 1,2,4-Orthopivalates; Ring-opening polymerization; Substituents of C-2 and C-3 positions; CH_2OR group

1. Introduction

Xylan is present approximately 20–30% by weight in hard woods, and the backbone consists of D-xylopyranose units linked by (1→4)-β-glycosidic bonds. The xylose units in the xylan chain additionally carry (1→2)-linked 4-*O*-methyl-α-D-glucuronic acid residues as a pendant group, on the average of about one uronic acid per ten xylose residues.[1] Because linear (1→4)-β-D-xylopyranan without such pendant groups is difficult to isolate from natural xylan, chemical synthesis is indispensable for getting information on the properties of xylan devoid of uronic acid residues. Stereoregular (1→4)-β-D-xylopyranan will be useful for defining much clearer the role of xylan in woods. Recently, an enzymatic synthesis of stereoregular xylan was reported.[2] However, chemical synthesis has not yet succeeded in spite of attempts by Bochkov and Rodionov and by Kochetkov and co-workers.[3]

We succeeded in the first chemical synthesis of cellulose by the ring-opening polymerization of glucose 1,2,4-orthopivalate[4] and found that both the 3-*O*-benzyl and orthopivaloyl groups are indispensable substituents for the synthesis of a stereoregular (1→4)-β-pyranan.[5,6]

These substituent effects were applied to the ring-opening polymerizations of 2-*O*-acyl-1,4-

* Corresponding author. Fax: +81-75-7536300.
E-mail address: tsubosan@kais.kyoto-u.ac.jp (F. Nakatsubo).

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anhydro-3,6-di-*O*-benzyl-D-glucose and 2-*O*-acyl-1,4-anhydro-3-*O*-benzyl-D-xylose derivatives to give novel stereoregular (1→5)-β-D-glucofuranan[7] and (1→5)-β-D-xylofuranan,[8] respectively. Consequently, it was indicated that the CH_2OBn group in the 1,4-anhydro-D-glucose derivative does not contribute to the stereo- and regioregularities of the resulting polymer, because the analogous stereoregular polymers were obtained from both 1,4-anhydro-D-glucose with the CH_2OBn group and 1,4-anhydro-D-xylose without the CH_2OBn group.

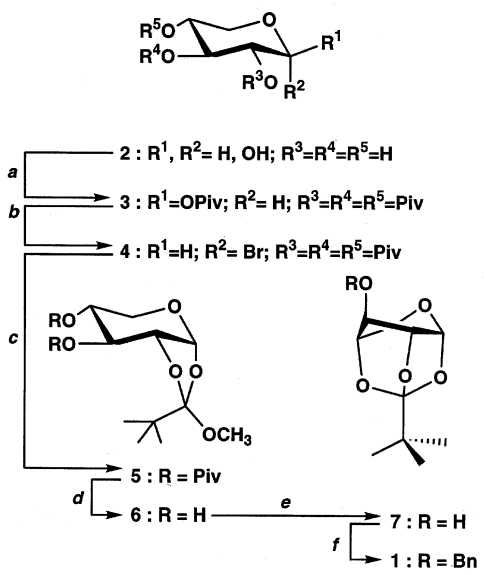
Thus, we expect that the synthesis of stereoregular (1→4)-β-D-xylopyranan is possible by the ring-opening polymerization of xylose orthoester.

In this paper, we report the ring-opening polymerization of the xylose 1,2,4-orthoester derivative in consideration of the substituent effects derived from D-glucose orthoesters to yield a stereoregular (1→4)-β-D-xylopyranan.

2. Results and discussion

*Selection and synthesis of 3-*O*-benzyl-α-D-xylopyranose 1,2,4-orthopivalate* (**1**).— Bochkov and Rodionov reported the ring-opening polymerization of 3-*O*-acetyl-α-D-xylose 1,2,4-orthoacetate at −21 °C in dichloromethane with triphenylcarbonium perchlorate as an initiator.[3a] Detailed structure analyses described that the resulting polymer contained an approximately equal number of (1→4)-β- and (1→2)-α-glycosidic linkages and about equal number of anomeric bonds. According to their scheme of chain growth, the resulting polymer structure is determined by the relative rates of electrophilic attack of an initiator or cation in a living polymer chain to the oxygen at C-2 and C-4 positions in the monomer. That is, because the electron density of the C-4 oxygen is nearly equal that of C-2 oxygen in 3-*O*-acetyl-α-D-xylose 1,2,4-orthoacetate, both (1→4)- and (1→2)-glycosidic linkages are obtained.

Then, we considered that the application of the substituent effects derived from our ring-opening polymerizations of D-glucose 1,2,4-orthoesters[5,6] to xylose orthoesters may enable one to obtain stereoregular (1→4)-β-D-xylopyranan by ring-opening polymerization. Thus, we selected 3-*O*-benzyl-α-D-xylopyranose 1,2,4-orthopivalate (**1**) as a starting material for the ring-opening polymerization.



Scheme 1. Synthetic route for 3-*O*-benzyl-α-D-xylopyranose 1,2,4-orthopivalate. Reagents and conditions: (a) $(CH_3)_3CCOCl$, pyridine, 80 °C, overnight, 92%; (b) HBr (30% in AcOH), $CHCl_3$, 0 °C, 4 h; (c) Et_3N, MeOH, 4 Å MS, dichloroethane, 50 °C, 8 h, 97% overall yield from compound **3**; (d) DBU, MeOH, rt, overnight; (e) *p*-TsOH, 4 Å MS, dichloroethane, rt, 3 h, 95% overall yield from compound **5**; (f) $C_6H_5CH_2Br$, NaH, Bu_4NI, THF, 80 °C, 4 h, 82%.

Bochkov et al. reported the synthetic methods for xylose 1,2,4-orthoester derivatives.[9] However, they have synthesized the orthoacetate and orthobenzoate derivatives, not the orthopivalate. We obtained orthopivalate **1** by a synthetic route of six reaction steps as shown in Scheme 1, which is similar to the method reported by Bochkov et al.[9]

For the preparation of the 1,2-methyl orthoester, Bochkov et al.[9] used 2,6-lutidine as the base in CH_3NO_2 at 37 °C and reported difficulty in the removal of 2,6-lutidine in the work-up procedure. 1,2-*O*-Methylorthopivaloyl-3,4-di-*O*-pivaloyl-α-D-xylopyranose (**5**) was obtained in a low yield (less than 10%) under the same reaction conditions as those of Bochkov et al.[9] Then, we used triethylamine instead of 2,6-lutidine and 4 Å molecular sieves as a dehydrating agent in dichloroethane at 50 °C to obtain compound **5** in 97% yield from compound **3** (reaction *c* in Scheme 1). In subsequent depivaloylation, 1,8-diazabi-

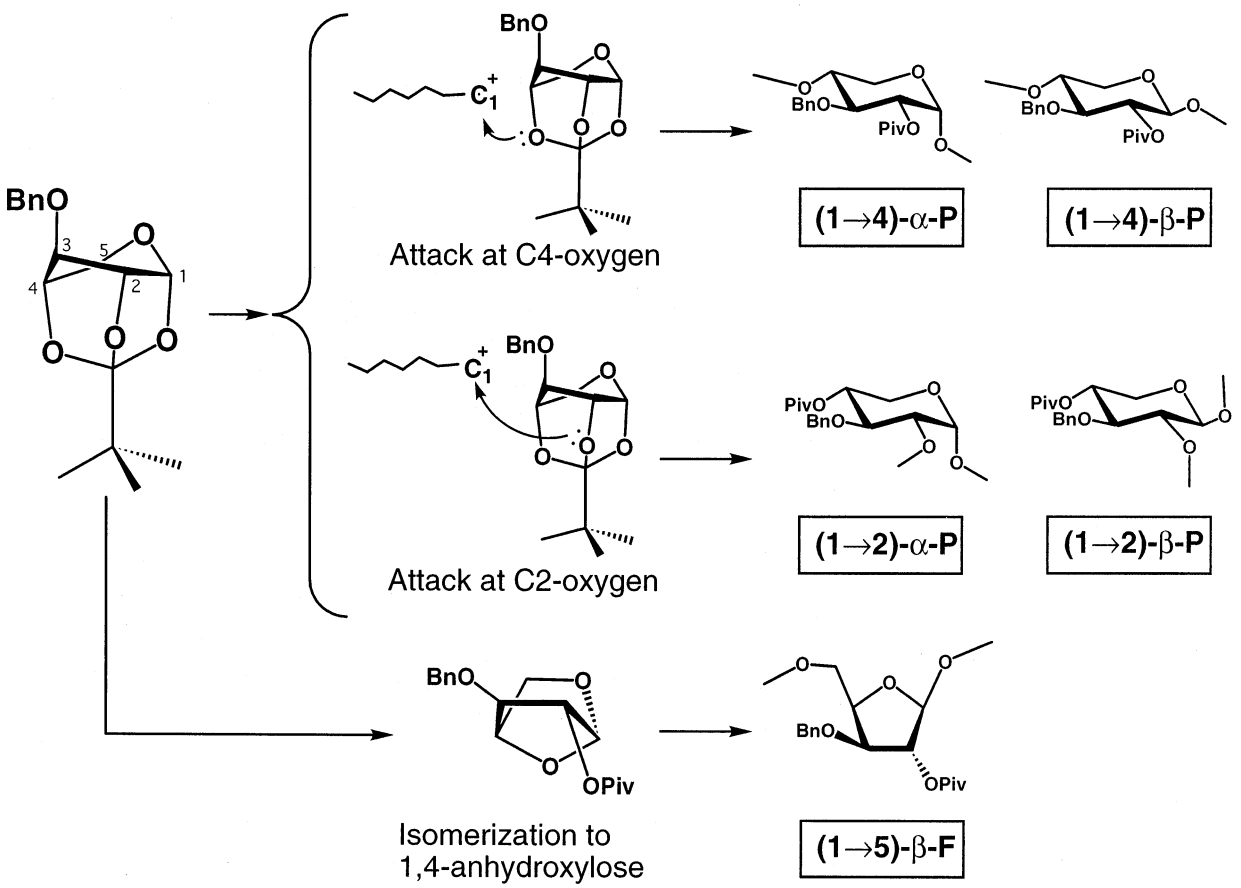


Fig. 1. Possible structures in the ring-opening polymerization of orthopivalate **1**.

cyclo[5.4.0]undec-7-ene (DBU) was used. The above modifications of the reaction conditions gave orthopivalate **1** in 68% overall yields from D-xylose; Bochkov et al.[9] obtained orthoester derivatives in an approximately 22% overall yields from D-xylose.

Possible structures in ring-opening polymerization of xylose orthoester.—As shown in Fig. 1, there are four possible structures in the polymer prepared by the present ring-opening polymerization. That is (1→4)-α-, β- and (1→2)-α-, β-xylopyranose units. In addition, the isomerization of the orthoester may produce the corresponding 1,4-anhydro-D-xylose derivative leading to the (1→5)-β-D-xylofuranose unit. This isomerization has been already reported by Bochkov et al.[10] Actually, in the glycosylations using orthopivalate **1** with various Lewis acids, 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl-α-D-xylopyranose was obtained as a byproduct.[11]

Polymerization of orthopivalate **1** *and their structures.*—Orthopivalate **1** was polymerized under various reaction conditions. Table 1 shows several examples of the polymerization reactions. Unfortunately, the ^{1}H and ^{13}C NMR spectra of each resulting polymer indicated that all polymerizations gave non-stereoregular polymers. The resulting polymer structures could be divided into two types on the basis of the NMR spectral patterns, that is, the spectral patterns of the polymers obtained using Ph_3CBF_4, $BF_3{\cdot}Et_2O$, and $SbCl_5$ as an initiator, and of the polymer using PF_5.

Figs. 2 and 3 show the ^{1}H and ^{13}C NMR spectra of the polymers of entry 1 obtained using Ph_3CBF_4 (spectrum A) and entry 8 obtained using PF_5 (spectrum B), respectively. All ^{13}C NMR spectra of polymers show several small peaks around the carbonyl and ring carbons to indicate that all polymers are non-stereoregular.

Main structural unit of the polymers.—The ^{1}H NMR spectrum of the stereoregular 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-xylofuranan[8] is shown in Fig. 2 (spectrum C). The main

resonances of the spectra of B and C are completely identical. Fig. 4 shows the main resonances of these ^{13}C NMR spectra are also completely identical. These clearly indicate that polymer entry 8 mainly consists of (1→5)-β-D-xylofuranose units.

On the other hand, the ^{13}C NMR spectrum of polymer entry 1 shows the major anomeric peak at δ 100.0 ppm. In addition, the specific rotations of polymer entry 1 were large and negative. These suggest that the polymer entry 1 has β-glycosidic linkages. The main struc-

Table 1
Ring-opening polymerizations of 3-*O*-benzyl-α-D-xylopyranose 1,2,4-orthopivalate [a]

Entry	Initiator	Orthopivalate/solv. (g/100 mL)	Temperature (°C)	Time (h)	Yield [b] (%)	$\overline{DPn}$ [c]	$[\alpha]_D^{25}$ (°)
1	Ph_3CBF_4	71.4	20	3	74.4	13.6	−59.5
2	Ph_3CBF_4	70.0	0	52	75.2	10.8	−87.9
3	Ph_3CBF_4	62.5	−30	52	87.1	7.5	−63.3
4	$BF_3{\cdot}Et_2O$	70.0	20	19	66.2	5.4	−4.2
5	$BF_3{\cdot}Et_2O$	71.4	0	90	89.8	20.3	−36.8
6	$BF_3{\cdot}Et_2O$	71.4	−30	92	88.2	12.9	−47.2
7	$SbCl_5$	70.0	−30	132	38.0	3.0	−12.6
8	PF_5	71.4	−30	141	92.1	21.9	−55.5

[a] Initiator concentration: 5 mol%, solvent–CH_2Cl_2.
[b] Polymer was the insoluble fraction in $CHCl_3$–*n*-hexane (ca. 1:5, v/v).
[c] Molecular weight was calculated from GPC data using polystyrene standards in THF.

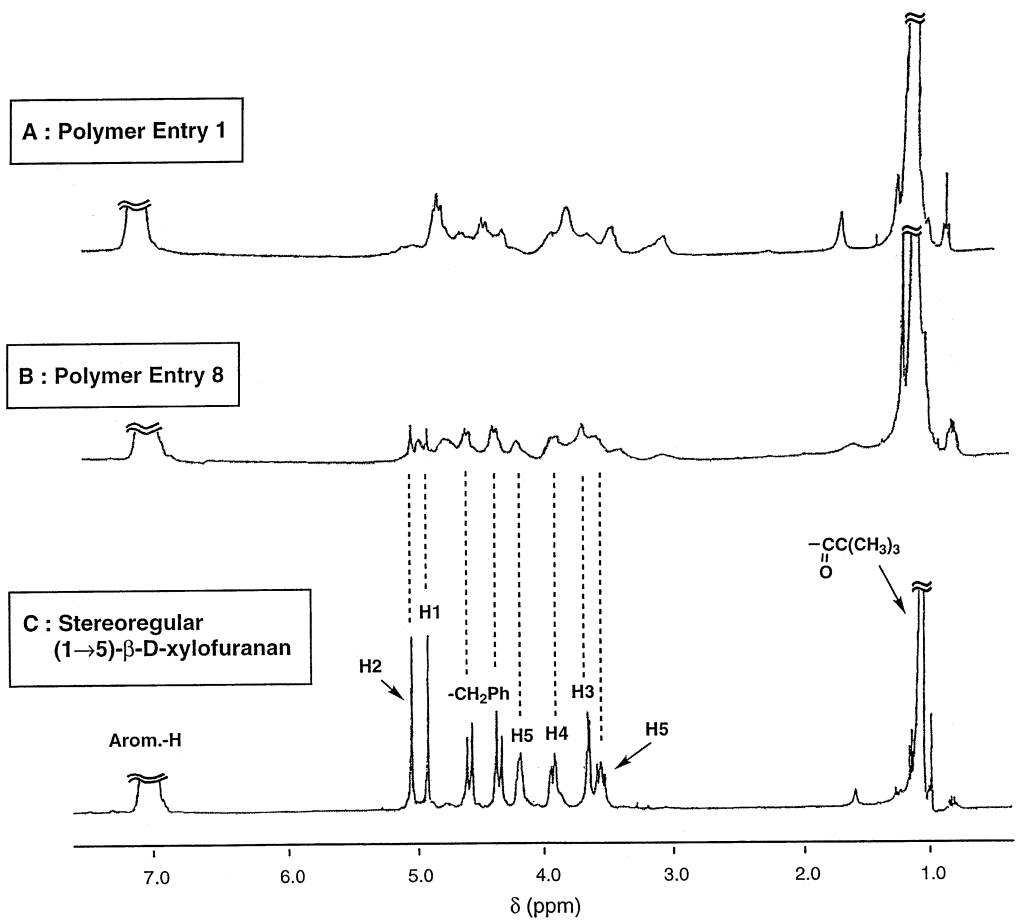


Fig. 2. 300 MHz ^1H NMR spectra of (A) the polymer entry 1 [Initiator: Ph_3CBF_4], (B) the polymer entry 8 [Initiator: PF_5] and (C) stereoregular 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-xylofuranan.[8]

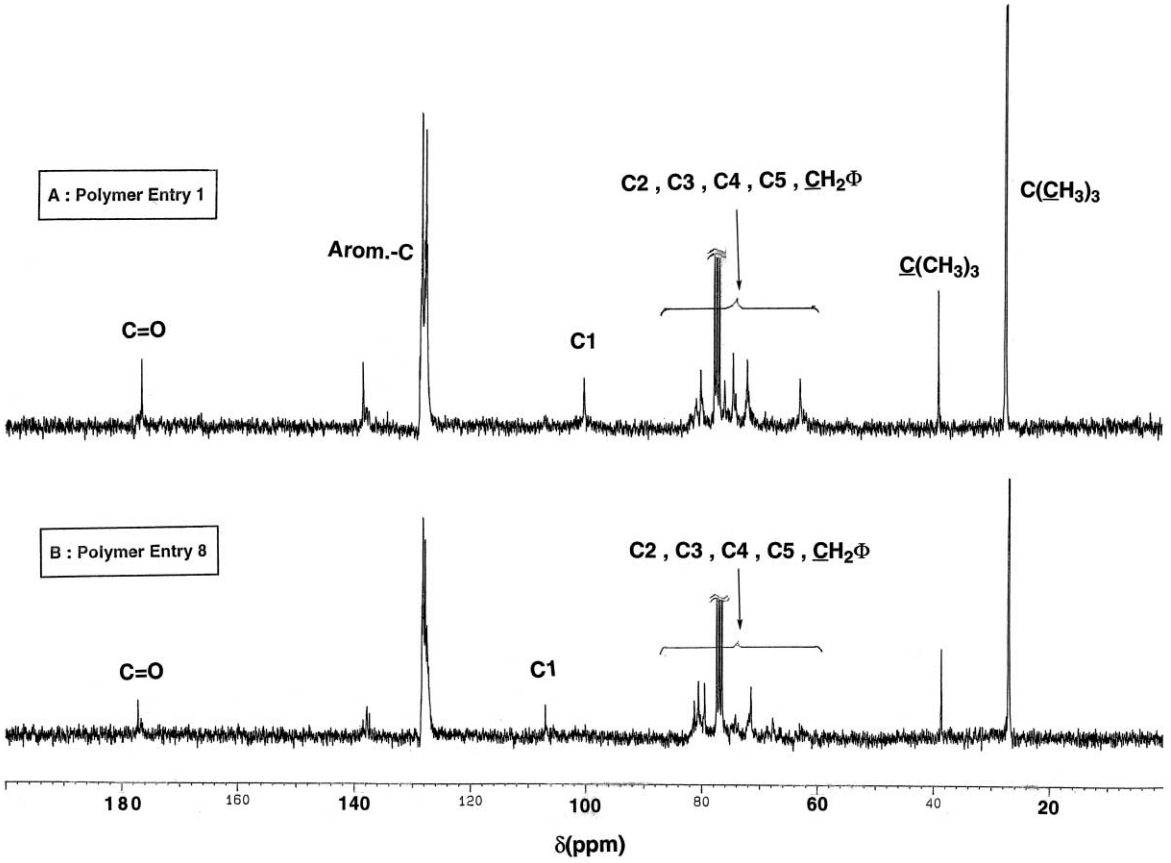


Fig. 3. 75 MHz ^{13}C NMR spectra of (A) stereoregular 3-*O*-benzyl-2-*O*-pivaloyl-(1→5)-β-D-xylofuranan[8] and (B) the polymer entry 8 [Initiator: PF_5].

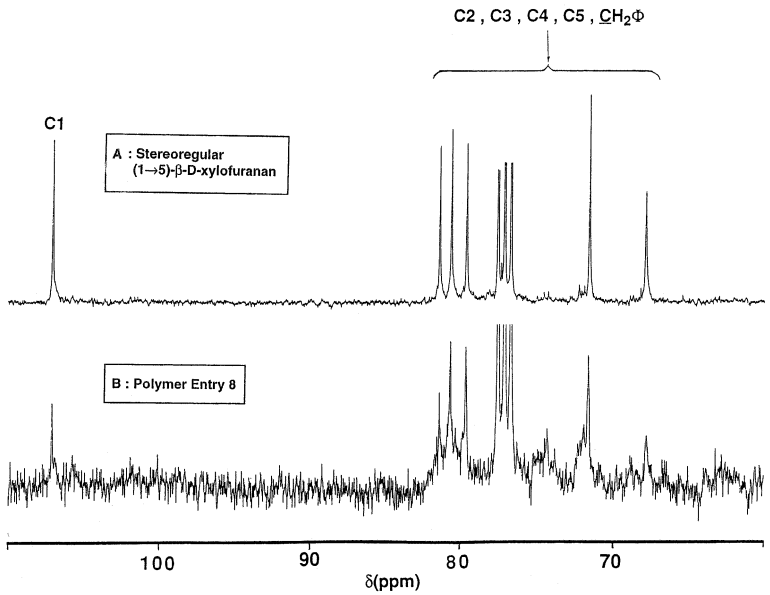


Fig. 4. 75 MHz ^{13}C NMR spectra of (A) stereoregular (1→5)-β-D-xylofuranan and (B) the polymer entry 8.

ture of polymer entry 1 was investigated by the identification of the hydrolysis products. The polymer entry 1 was converted into its per-*O*-methyl derivative via depivaloylation, subsequent methylation, debenzylation, and methylation. The methyl derivative from poly-

mer entry 1 was hydrolyzed with trifluoroacetic acid, and the products were converted into their xylitol acetate derivatives. The ^{1}H NMR spectrum suggests that the main product is 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methylxylitol. Furthermore, in order to compare with the acetylated natural xylan (as the model compound of (1→4)-β-D-xylopyranose unit), polymer entry 1 was deprotected with sodium metal in liquid ammonia and anhydrous tetrahydrofuran as a co-solvent at −50 °C, and subsequently acetylated with acetic anhydride and pyridine at room temperature. GPC analysis indicated that the acetylation was performed with slight depolymerization. The natural xylan from oat-spelts was acetylated by the method of Koshijima and Timell[12] in order to avoid the depolymerization reported by Lebel et al.[13] Fig. 5 shows the ^{1}H NMR spectrum of the natural xylan acetate (spectrum A) and the acetylated derivative from polymer entry 1 (spectrum B). The main resonances in these spectra are completely identical. These results clearly indicate that the polymer entry 1 mainly consists of (1→4)-β-xylopyranose units, but it is not stereoregular.

Substituent effects of the CH_2OR group on ring-opening polymerization of glucose orthoesters.—In the ring-opening polymerization of xylose orthopivalate **1**, unfortunately, stereoregular (1→4)-β-D-xylopyranan was not obtained in contrast to glucose 1,2,4-orthopivalates, which lead to stereoregular (1→4)-β-D-glucopyranan. The difference between the results of D-xylose orthopivalate and those of D-glucose orthopivalate seems to be caused by the presence of the CH_2OR group in D-glucose.

Ring-opening polymerizations have been already performed in our laboratory for several 3-*O*-benzyl-D-glucose orthopivalate derivatives with different substituents at the C-6 position:[14] 6-*O*-methyl-, benzyl-, acetyl-, pivaloyl-, 2-methylbutyloyl-, tosyl-, 6-iodo-, 6-chloro-, and 6-deoxy-derivatives, in order to clarify the effects of the substituents at C-6 position on the ring-opening polymerization. As a result, only 6-*O*-benzyl-, methyl-, pivaloyl-, and 3-*O*-benzyl-6-deoxy-D-glucose orthopivalate derivatives gave stereoregular (1→4)-β-D-pyranan, and it is indicated that the substituent effects of C-6 position is due to an electronic factor increasing the electron density of the C-4 oxygen, not to steric factors.[15]

On the other hand, we polymerized several D-xylose 1,2,4-orthopivalate derivatives with

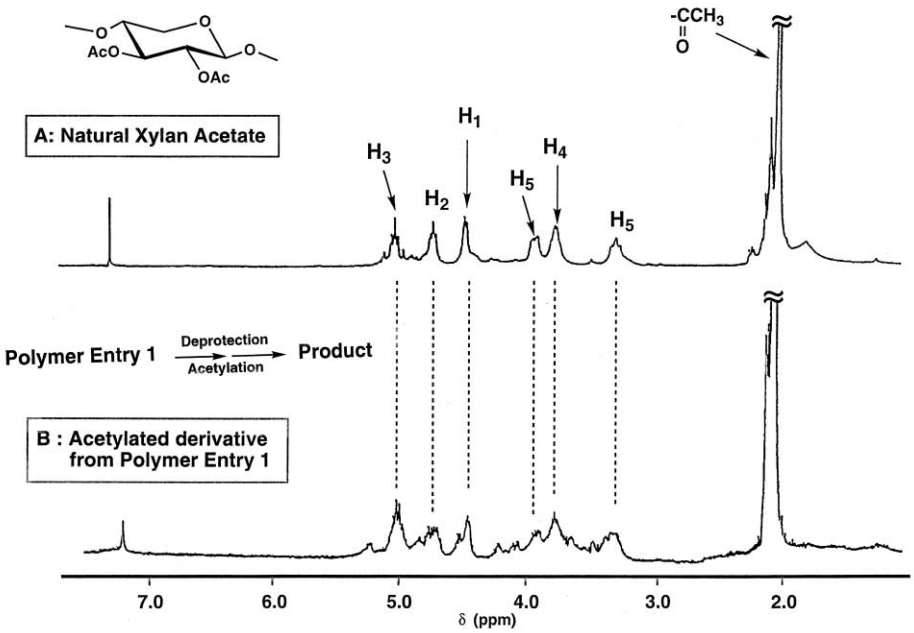


Fig. 5. 300 MHz ^{1}H NMR spectra of (A) the natural xylan acetate and (B) the acetylated derivative from polymer entry 1 [Initiator: Ph_3CBF_4].

different substituents at the 3-*O*-position, that is, methyl, allyl, benzyloxybenzyl, 4-*tert*-butylbenzyl, trimethylsilyl, *tert*-butyldiphenylsilyl, *tert*-butyldimethylsilyl, 4-nitrophenyl and acetyl derivatives, under the same polymerization conditions as that of entry 1 in Table 1. The NMR spectra showed that all resulting polymers consisted of the mixed structures.

Consequently, we confirmed that the CH_2OR and 3-*O*-benzyl groups in orthoesters played an important role in (1→4)-β-D-glycosidic bond formation and were the essential groups for the synthesis of cellulose by a ring-opening polymerization of the D-glucose 1,2,4-orthopivalate.

3. Conclusions

The ring-opening polymerization of orthopivalate **1** selected in consideration of the substituent effects gave the polymer mainly consisting of (1→4)-β-D-xylopyranose units, but not a stereoregular type of polymer. The structure of polymer largely depends on the initiator used.

Comparing these results with those of glucose orthopivalates, it was revealed that, not only the substituents of C-2 and C-3 positions, but also at the CH_2OR group in the D-glucose orthoester contributes to (1→4)-β-D-glucopyranosidic bond formation by the ring-opening polymerization.

Thus, we found that xylose orthopivalate **1**, which lacks the CH_2OR group, hardly gives any stereoregular (1→4)-β-D-xylopyranan. The molecular design of novel starting materials for polymerization will be needed to synthesize stereoregular (1→4)-β-D-xylopyranan.

4. Experimental

General methods.—Anhydrous CH_2Cl_2 was distilled from CaH_2. Preparative thin-layer chromatography (PTLC) was performed on silica gel plates (Kieselgel 60 F254, E. Merck). The standard work-up procedure included diluting the reaction mixture with EtOAc, washing with aq $NaHCO_3$, and brine, drying over Na_2SO_4, and concentration in vacuo. All melting points (mp) are uncorrected. ^1H 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 $CHCl_3$-*d* with Me_4Si as internal standard. Chemical shifts (δ) and coupling constants (J) are given in δ values (ppm) and Hz, respectively. Some chemical shift assignments were assigned using a decoupling method; others were assigned 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 THF. Calibration curves were obtained by using polystyrene standards (Shodex). A Waters universal liquid chromatograph injector (model U6K), a Waters solvent delivery system (model 6000A), a Waters refractive index detector (series R-400), a Waters absorbance detector (model 440), and Shodex columns (KF802 and KF803) were used. The flow rate was 1.0 mL/min.

1,2,3,4-Tetra-O-*pivaloyl*-*β*-D-*xylopyranose* (**3**).—To a solution of D-xylose (5 g, 33.3 mmol) in pyridine (20 mL) was added pivaloyl chloride (25 mL, 0.2 mol), and the mixture was heated at 80 °C overnight. Then 3 mL MeOH was added, and the mixture was worked-up by the standard method. Compound **3** was recrystallized from EtOH to give colorless needles (14.8 g, 91.6% yield): mp 112.5–113.0 °C; $[\alpha]_D^{25}$ −14.9° (*c* 1, in $CHCl_3$). ^1H NMR ($CDCl_3$): δ 5.67 (d, 1 H, $J_{1,2}$ 7.82 Hz, H-1), 5.17 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 5.37 (t, 1 H, $J_{3,4}$ 9.19 Hz, H-3), 5.02 (m, 1 H, $J_{4,5a}$ 5.6 Hz, H-4), 4.11 (dd, 1 H, J_{gem} 11.7 Hz, H-5_a), 3.45 (dd, 1 H, $J_{4,5b}$ 9.85 Hz, H-5_b), 1.13, 1.14, 1.15, 1.19 (s, 9 H, 3 × CH_3); ^{13}C NMR ($CDCl_3$): δ 92.6 (C-1), 77.4, 77.0, 76.6, 68.7, 63.2 (C-2, C-3, C-4, C-5), 38.7 [$C(CH_3)_3$], 26.8–27.1 (CH_3), 177.2, 176.9, 176.6, 176.4 (C=O). Anal. Calcd for $C_{25}H_{42}O_9$: C, 61.71; H, 8.70. Found: C, 61.46; H, 8.44.

2,3,4-Tri-O-*pivaloyl*-*α*-D-*xylopyranosyl bromide* (**4**).—To a solution of compound **3** (3.0 g, 5.98 mmol) in $CHCl_3$ (40 mL) was added a 30% solution of HBr in AcOH (1.8 mL, 20.6 mmol). The mixture was allowed to stand for 4 h at rt. The reaction mixture was worked-up

by the standard method. Compound **4** was recrystallized from EtOH to give crude colorless crystals (2.87 g). Compound **4** was used for the subsequent reactions without further purification because of its instability: ^{1}H NMR ($CDCl_3$): δ 6.59 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.78 (dd, 1 H, $J_{2,3}$ 9.89 Hz, H-2), 5.65 (t, 1 H, $J_{3,4}$ 9.75 Hz, H-3), 5.06 (m, 1 H, $J_{4,5a}$ 5.99 Hz, H-4), 4.03 (dd, 1 H, J_{gem} 11.1 Hz, H-5$_a$), 3.85 (t, 1 H, $J_{4,5b}$ 0 Hz, H-5$_b$), 1.18, 1.17, 1.15 (s, 9 H, 3 × CH_3); ^{13}C NMR ($CDCl_3$): δ 87.9 (C-1), 70.9, 69.0, 67.8, 62.5 (C-2, C-3, C-4, C-5), 38.8, 38.7 [*C*(CH_3)$_3$], 27.1, 27.0 (CH_3), 176.7, 177.3 (C=O).

*1,2-*O*-Methylorthopivaloyl-3,4-di-*O*-pivaloyl-α-*D*-xylopyranose* (**5**).—To a solution of a crude compound **4** (2.87 g) in a mixture of dichloroethane (12 mL), Et_3N (580 μL, 5.98 mmol) and MeOH (202 μL, 7.18 mmol) was added powdered 4 Å molecular sieves (2.5 g) at 50 °C. After 8 h, the reaction mixture was filtered using Celite 535, and the residue was washed with $CHCl_3$. The combined filtrate and washings were diluted with $CHCl_3$, washed with brine, dried over Na_2SO_4 and concentrated in vacuo to give an orange syrup. Compound **5** was purified on a silica gel column (Wakogel C-200), eluting with $CHCl_3$ to give a colorless syrup (2.42 g, 97.3% overall yield from compound **3**): $[\alpha]_D^{25}$ −7.10° (*c* 1, in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.54 (d, 1 H, $J_{1,2}$ 4.99 Hz, H-1), 4.28 (t, 1 H, $J_{2,3}$ 5.67 Hz, H-2), 5.65 (dd, 1 H, $J_{3,4}$ 7.25 Hz, H-3), 4.80 (dd, 1 H, $J_{4,5a}$ 5.78 Hz, H-4), 3.94 (dd, 1 H, J_{gem} 12.6 Hz, H-5$_a$), 3.75 (t, 1 H, $J_{4,5b}$ 5.65 Hz, H-5$_b$), 1.21, 1.19 (s, 9 H, piv-CH_3), 3.27 (s, 3 H, OCH_3), 1.09 (s, 9 H, orthoester-CH_3); ^{13}C NMR ($CDCl_3$): δ 98.6 (C-1), 78.4, 71.0, 68.1, 63.1 (C-2, C-3, C-4, C-5), 50.4 (OCH_3), 27.0, 26.8 (CH_3), 38.7, 38.9 [C(CH_3)$_3$], 127.9 [C-(-O$_3$)], 177.9, 176.7 (C=O). Anal. Calcd for $C_{21}H_{36}O_8$: C, 60.56; H, 8.71. Found: C, 60.42; H, 8.51.

*α-*D*-Xylopyranose 1,2,4-orthopivalate* (**7**).—To a solution of compound **5** (2.42 g, 5.82 mmol) in 40 mL of MeOH was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.74 mL, 11.6 mmol). The solution was stirred at rt overnight. The reaction mixture was concentrated, the yellow residue was dissolved in 60 mL of dichloroethane, and then *p*-toluenesulfonic acid (6.0 mg, 0.03 mmol) was added. The solution was heated for 3 h at reflux temperature with a Dean–Stark trap. The reaction mixture was neutralized with $NaHCO_3$ and concentrated in vacuo. Compound **7** was purified on a silica gel column (Wakogel C-200), eluting with 1:1 EtOAc–*n*-hexane to give colorless crystals (1.19 g, 95.0% overall yield from compound **5**): mp 118.6–119.2 °C; $[\alpha]_D^{25}$ +61.7° (*c* 0.1, in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.74 (d, 1 H, $J_{1,2}$ 4.82 Hz, H-1), 4.38 (dt, 1 H, $J_{2,3}$ 4.43 Hz, H-2), 4.31 (m, 1 H, $J_{3,4}$ 4.75 Hz, H-3), 4.07 (dd, 1 H, $J_{4,5a}$ 0, $J_{2,4}$ 1.77 Hz, H-4), 4.27 (d, 1 H, J_{gem} 12.7 Hz, H-5$_a$), 4.19 (dd, 1 H, $J_{4,5b}$ 4.3 Hz, H-5$_b$), 1.06 (s, 9 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 97.8 (C-1), 74.1, 72.1, 65.8, 64.2 (C-2, C-3, C-4, C-5,), 35.7 [*C*(CH_3)$_3$], 122.4 [C(O-)$_3$], 24.9 (CH_3). Anal Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.59; H, 7.50.

*3-*O*-Benzyl-α-*D*-xylopyranose 1,2,4-orthopivalate* (**1**).—Compound **7** (1.19 g, 5.51 mmol) was dissolved in THF (40 mL). Sodium hydride (264.4 mg, 6.61 mmol, 60% in mineral oil), *n*-Bu_4NI (20 mg) and benzyl bromide (0.79 mL, 6.61 mmol) were added at rt. The mixture was heated at 80 °C under stirring. After 4 h, MeOH was added to the reaction mixture in order to decompose the excess benzyl bromide. The reaction mixture was worked-up by the standard method to give yellow crystals. Compound **1** was recrystallized from MeOH to give colorless crystals (1.38 g, 82.0% yield): mp 91.8–92.0 °C; $[\alpha]_D^{25}$ +42.6° (*c* 0.5, in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.72 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 4.38 (dt, 1 H, $J_{2,3}$ 4.4 Hz, H-2), 4.20 (m, 1 H, $J_{3,4}$ 4.51 Hz, H-3), 3.90 (dd, 1 H, $J_{4,5a}$ 0, $J_{2,4}$ 1.82 Hz, H-4), 4.15 (s, 1 H, J_{gem} 0 Hz, H-5$_a$), 4.14 (s, 1 H, $J_{4,5b}$ 0 Hz, H-5$_b$), 1.04 (s, 3 H, CH_3), 4.69, 4.62 (d, 1 H, each, J_{gem} 12.2 Hz, $C_6H_5CH_2$), 7.30–7.35 (Ar); ^{13}C NMR ($CDCl_3$): δ 97.7 (C-1), 65.4, 70.4, 71.0, 72.0, 72.2, (C-2, C-3, C-4, C-5, $CH_2C_6H_5$), 24.9 (CH_3), 35.6 [C(CH_3)$_3$], 122.4 [C(O-)$_3$], 137.7, 128.5, 128.0, 127.6 (Ar). Anal Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.81; H, 7.29.

Polymerization.—All polymerizations were carried out under a high-vacuum system.[16] Compound **1** was dried in a polymerization ampule by evacuating for ca. 1 day.

Dichloromethane 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. $SbCl_5$ and $BF_3{\cdot}Et_2O$ were added to the reaction ampule through the rubber septum by syringe. Triphenylcarbenium tetrafluoroborate was placed on a small glass plate in the reaction ampule with monomer. The reaction apparatus was then flame sealed and placed in a water bath at 20 °C. The reaction mixture was diluted with $CHCl_3$, washed with satd aq $NaHCO_3$, water, and brine, dried over anhyd Na_2SO_4, and concentrated to dryness. The polymer mixture was dissolved in a small amount of $CHCl_3$. To the solution, *n*-hexane was added, and then the solidified residual polymer was collected by filtration, and finally dried in vacuo.

Conversion of the polymer entry 1 into its per-O-*methyl derivative*.—To a solution of the polymer entry 1 (35 mg) in 10:1 dioxane–MeOH (3 mL), 28% CH_3ONa in MeOH (0.35 mL) was added. The reaction mixture was kept at 50 °C for 24 h. Then, the reaction mixture was treated with Amberlyst 15 ion-exchange resin for neutralization, and then filtered. The resin was washed with 1:4 MeOH–$CHCl_3$. The combined washings and filtrate were concentrated to dryness. The product was treated with MeI (80 μL) and powdered NaOH (51 mg) in DMF (2 mL) at 50 °C overnight. The reaction mixture was neutralized with AcOH, diluted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Water was added to the resultant polymer mixture, and the solidified residual polymer was collected by filtration and dried in vacuo. Depivaloylated polymer (26.9 mg) was dissolved in 1:1 THF–AcOH (5 mL), and palladium hydroxide on charcoal (50 mg) was added. The reaction mixture was kept under H_2 at 50 °C. After about 1 day, the palladium hydroxide on charcoal was filtered off and washed with 1:4 MeOH–CH_3Cl. The combined washings and filtrate were concentrated to dryness. The product was concentrated and treated with Ac_2O and pyridine at 50 °C overnight. Methylation of the product was performed in the same manner as described above to give colorless powder (16.4 mg).

Hydrolysis of the per-O-*methyl derivative from the polymer entry 1*.—The per-*O*-methyl derivative from the polymer entry 1 (16.4 mg) was dissolved in 2 M trifluoroacetic acid (2 mL) in a small ampule. The ampule was sealed under N_2 and kept at 100 °C overnight. After the ampule was cooled to rt, it was opened and the reaction mixture was concentrated in vacuo. The hydrolysate was reduced with $NaBH_4$ and acetylated with Ac_2O and pyridine for NMR analysis. ^1H NMR ($CDCl_3$): δ 4.30 (d, 1 H, $J_{1a,2}$ 4.8 Hz, H-1_a), 3.51 (overlapped, H-2), 3.47 (overlapped, H-3), 5.33 (m, 1 H, H-4), 4.44 (d, 1 H, $J_{5a,4}$ 3.6, J_{gem} 12.0 Hz, H-5_a), 4.17 (overlapped, 2 H, H-1_b, H-5_b), 3.51, 3.47 (s, 3 H, respectively, OCH_3), 2.09, 2.07, 2.05 (s, 3 H, respectively, C=OOCH_3).

Conversion of polymers into acetates.—Each polymer (90 mg) dissolved in anhyd THF (4 mL, distilled over potassium metal–benzophenone) was added dropwise to a solution of small pieces of Na in 4 mL of liquid NH_3 at −50 °C. The reaction was continued for 5 h, followed by successive additions of NH_4Cl and several drops of water. Afterwards, the reaction mixture was placed under a stream of N_2 in order to remove NH_3. The deprotected polymer was dialyzed against distilled water and freeze-dried, and the product was treated with Ac_2O and pyridine at rt overnight. The reaction mixture was concentrated in vacuo at 30 °C. The product was purified by PTLC (eluent: 5:95 MeOH–$CHCl_3$) to give each acetylated polymer.

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