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Solid-state polycondensation of natural aldopentoses and 6-deoxyaldohexoses. Facile preparation of highly branched polysaccharide

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Abstract

Solid-state polycondensation of natural aldopentoses and 6-deoxyaldohexoses was found to take place in the presence of H_3PO_4 (5 mol%) at 100–110 °C under a N_2 flow, giving highly branched polysaccharide (Conv. 47–81%, $M_w = 2700–12\,000$, $M_n = 1400–2900$); the reaction mixtures were powdery throughout the polymerization. The product polysaccharide was per-*O*-methylated and subjected to the structure analyses. The acid-hydrolysis, which gave a variety of the partially *O*-methylated monosaccharides, suggested that the product polysaccharides proved to have highly branched structures consisting of both furanose and pyranose units. MALDI-TOF mass analysis revealed that the 1,4-anhydride terminal unit was formed and participated to the polymerization.

Keywords: Solid-state polycondensation; Highly branched polysaccharide; Aldopentose

1. Introduction

There are numerous studies on the polycondensations of natural saccharides and their derivatives [1–9], since they are the most facile methods to prepare artificial polysaccharides. The polycondensation of natural saccharide has been conducted under solid, melt, solution, or suspension conditions with an acid catalyst, producing highly branched polysaccharide. The solid-state polymerization is an attractive way as compared with the other methods. This is green chemistry with a simple process and easy handling; undesirable side reactions will be suppressed due to the lower reaction temperature compared to the melt polymerization. There are known old literatures [8] that deal with the solvent-free polycondensation of natural saccharides in the presence of dry HCl gas, metabolic acid, and ion exchange region, but they have given only insufficient knowledge on the polymerization.

Very recently, we have found that phosphoric acid is an effective catalyst for the solid-state polycondensation of the natural aldohexoses and disaccharides [9], revealing the following features. The reaction mixture is powdery during the polymerization. The product polysaccharide has a highly branched structure, which is composed of the pyranose units with all of possible glycosidic linkages. The 6-OH group takes part in the intramolecular glycosilation to produce the 1,6-anhydride terminal unit, and the acetal exchange reactions take place with the polymerization.

Herein, we have extended this solid-state polycondensation to the natural aldopentoses and 6-deoxyaldohexoses with phosphoric acid. In the old literature, there is only a brief comment; e.g. in the presence of dry HCl gas, D-xylose gives low molecular weight polysaccharide in a very low yield of 5% [8]. In a similar fashion to the aldohexoses, aldopentoses and 6-deoxyaldohexoses were also expected to be polymerized with phosphoric acid in the solid state, however, showing different reaction routes because of the absence of the 6-OH groups. The product polysaccharides were analyzed by MALDI-TOF mass spectroscopy, which was informative for the structure of the repeating and terminal units as well as for the reaction mechanisms. The branched structures were validated by analyzing the hydrolysis products from per-*O*-methylated polysaccharide by means of ^1H NMR and ESI-MS spectroscopy, and HPLC.

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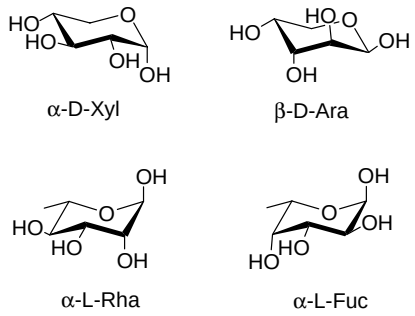


Chart 1. Natural saccharides used as monomers.

2. Results and discussion

2.1. Polymerization

The natural saccharides shown in Chart 1 were ground with H_3PO_4 (5 mol%) in an agate mortar and subjected to polymerization in a test tube under a N_2 flow for 24 h. In the previous paper [9], we have found that the occasional grinding accelerates the solid-state polymerization. Therefore, in a similar manner, the reaction mixtures of runs 1, 3, and 5 in Table 1 were ground in an agate mortar at 1, 3, 5, and 10 h. The monomer conversion and the molecular weight of the product polymer were evaluated by GPC (eluent: 2 mol/L $NaNO_3$ aq., calibration: pulluran standards). Although the molecular weights evaluated here would be smaller than the actual values because of a highly branched structure of the resultant polysaccharide, they can be used as the relative values to follow the polymerization. The good reproducibility of the obtained polysaccharides was confirmed by repeating the experiments several times (runs 1-1, -2, and -3).

α-D-Xyl, β-D-Ara, and α-L-Fuc were polymerized in the solid state at 100 (α-L-Fuc) or 110 °C (α-D-Xyl and β-D-Ara) to produce brownish powder of water-soluble polysaccharide (runs 1, 3, and 5). A little higher temperature by 10 °C made the reaction mixture melted even though the reaction temperatures were lower than their melting points (runs 2, 4, and 6). The water-insoluble and black-colored materials were produced from α-D-Xyl and β-D-Ara by the melt polymerization at 120 °C, indicating that some undesirable side reactions should be involved due to the higher reaction temperature [9]. In contrast, the melt polymerization of α-L-Fuc at 110 °C provided a water-soluble and brown-colored lump of polysaccharide (run 6). As compared to the solid-state polymerization (run 5), run 6 showed the much higher monomer conversion, however, giving the lower molecular polysaccharide. The melt polymerization is favorable for the monomer conversion at the initial stage due to the higher molecular mobility. On the other hand, the generated water could be more easily removed from the powdery mixture to increase the molecular weight (run 5) because of the larger surface area as compared with the melted-resolidified mixture (run 6). These features should lead the above findings. α-L-Rha (mp 89 °C) was unreacted at 70 °C even in the molten state but polymerized at 110 °C, providing brownish polysaccharide (runs 7 and 8). These findings suggest that temperatures higher than about 100 °C are basically required to promote the polymerization.

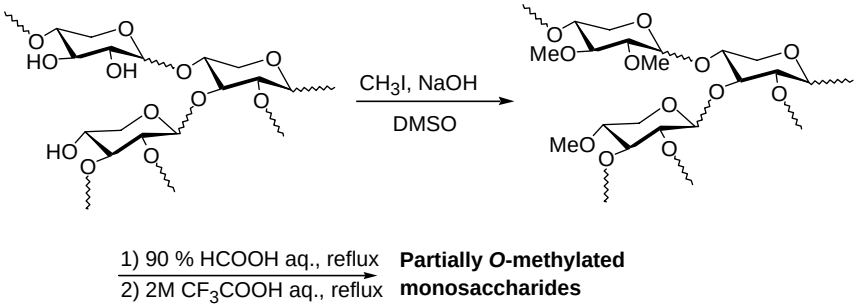
2.2. Hydrolysis analysis

^1H and ^{13}C NMR spectra were not informative to analyze the structure of the obtained polysaccharide due to the broad signals. In order to validate the polymer structure, the polysaccharide was per-*O*-methylated, isolated by reprecipitation, and then hydrolyzed by successive treatment with 90% HCOOH aq. and 2 mol/L CF_3COOH aq. (Scheme 1), producing the mixture of partially *O*-methylated monosaccharides. The polymer structure can be evaluated by characterizing these partially *O*-methylated monosaccharides since their OH groups originate from the glycosidic bonds that form the polymer main chain. Representatively, the polysaccharide obtained from run

Table 1
Solid-state and melt polycondensation of the natural saccharides in the presence of H_3PO_4 (5 mol%) for 24 h under a N_2 flow

Run	Saccharide	Mp[a] (°C)	Temperature (°C)	Appearance	Conv.[b] (%)	M_w[b]	M_n[b]
1-1	α-D-Xyl	148	110	Solid	63	8100	2100
1-2	α-D-Xyl		110	Solid	61	8700	2400
1-3	α-D-Xyl		110	Solid	64	8400	2200
2	α-D-Xyl		120	Melt	A water-insoluble and black-colored material		
3	β-D-Ara	156	110	Solid	81	12 000	2900
4	β-D-Ara		120	Melt	A water-insoluble and black-colored material		
5	α-L-Fuc	142	100	Solid	47	2700	1400
6	α-L-Fuc		110	Melt	83	1500	1100
7	α-L-Rha	89	70	Melt	0		
8	α-L-Rha		110	Melt	84	1300	1200

[a] Evaluated by differential thermal analysis (heating rate: 10 °C/min, under a N_2 flow).
[b] Evaluated by GPC (eluent: 0.2 mol/L $NaNO_3$ aq., calibration: pulluran standards).



Scheme 1. Per-*O*-methylation and subsequent hydrolysis of the product polysaccharide (representatively shown for xylopyranan).

1-1 in Table 1 was analyzed here [10]. Chart 2 shows the products of the partially methylated xylo-pyranoses and -furanoses, which are classified into four groups (A)–(D) by the number of OH groups. The compounds of group (A), 2,3,4-tri-*O*-methylxylopyranose and 2,3,5-tri-*O*-methylxylofuranose, originate from the non-reducing terminal unit of the resultant polysaccharide. Similarly, diols of group (B) are from the linear repeating units or the reducing terminal units, and tri- and tetra-ols of groups (C) and (D) are from the branched repeating units and/or the reducing terminal units.

The mixture of the hydrolysis products, which showed several peaks on a HPLC profile, was roughly fractionated into three parts by column chromatography (Fig. 1). Each of them was identified by ESI-MS spectroscopy to be groups (A), (B), and (C) in Chart 2, respectively. Thus, it is suggested that the product xylan has a branched structure with several kinds of xylose units.

In order to examine the existence of the furanose structures, fraction (A) was reduced by treatment with $NaBH_4$ in 0.5 mol/L NH_3 aq. and then acetylated to obtain the di-*O*-acetyl-tri-*O*-methylxylitol (Scheme 2). In ^{1}H NMR spectrum of the product mixture (Fig. 2), there were observed the multiple peaks at 5.14 ppm, which were assignable to the 4-H (H^a) of 1,4-di-*O*-acetyl-2,3,5-tri-*O*-methylxylitol, indicating that 2,3,5-tri-*O*-methylxylofuranose was contained together with 2,3,4-tri-*O*-methylxylopyranose in fraction (A) (furanoses/pyranose = 1:2.3, calculated by the ^{1}H NMR spectrum) (Scheme 3).

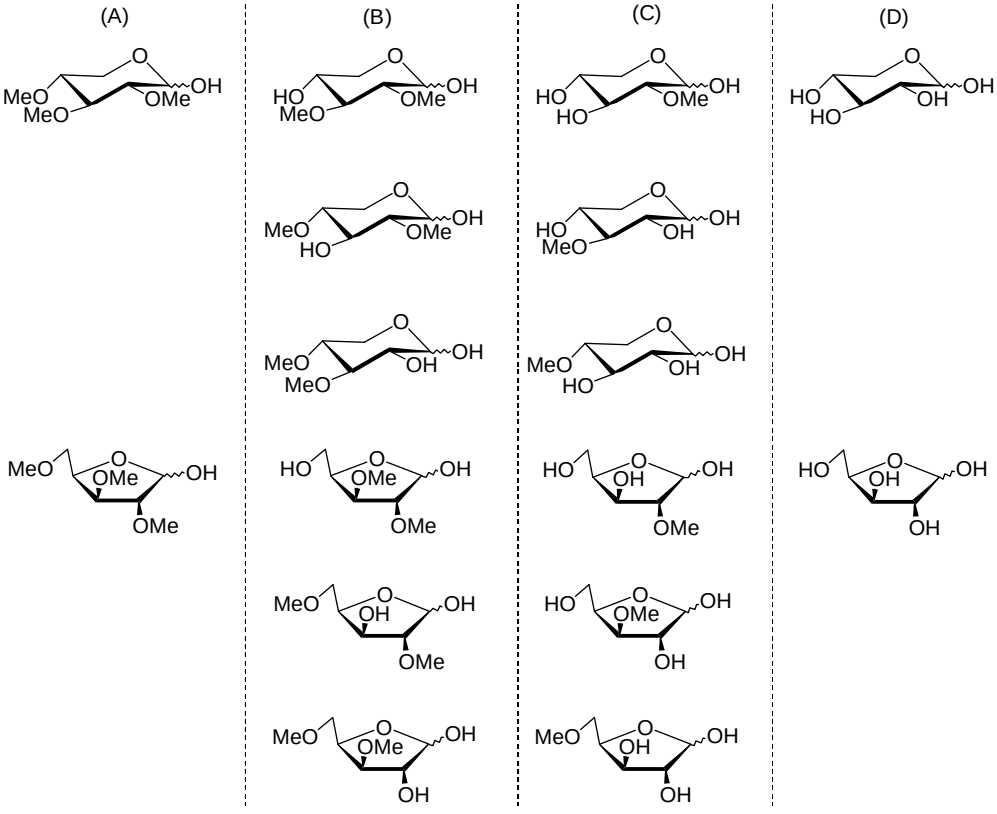


Chart 2. The hydrolysis products from a non-reducing terminal unit (A); reducing terminal and linear units (B); reducing terminal and branched units ((C) and (D)) of the highly branched per-*O*-methyl xylan (run 1-1, Table 1).

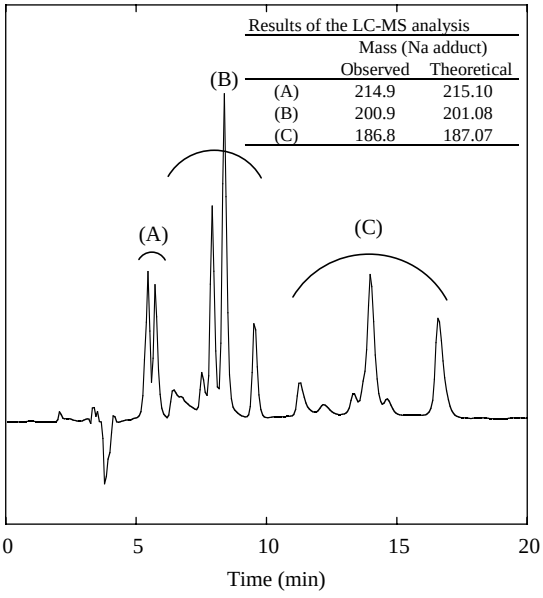


Fig. 1. A HPLC profile (acetone/*n*-exane/MeOH = 1:1:0.01, RI detector) of the hydrolysis product mixture from the per-*O*-methyl polysaccharide obtained at run 1-1 in Table 1.

On the other hand, fraction (B) was acetylated (Scheme 3) and then analyzed by ^{1}H NMR spectroscopy for further investigation on the structure of repeating units of the product xylan (Fig. 3). The spectrum of the diacetylated products showed several kinds of peaks due to the anomeric protons. Peak groups (b) and (d) should be assigned to the α- and β-anomeric protons, respectively, of three diacetylated xylopyranose derivatives, suggested by the chemical shifts of those of the diacetylated glucopyrnaose derivatives [9]. Thus, the other peaks of groups (a) and (c) could be assignable to the anomeric protons of the furanose derivatives. The authentic sample of 1,2-di-*O*-acetyl-3,5-di-*O*-methylxylofuranose was prepared from D-xylose via three steps (Scheme 4). In the ^{1}H NMR spectrum, the α- and β-anomeric protons of this sample showed the identical chemical shifts (δ 6.13 and 6.41) with one of the peaks in groups (a) and (c), respectively.

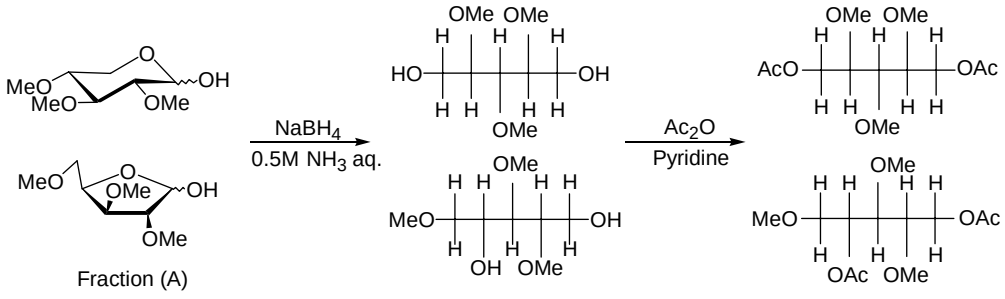
These findings suggest that there are involved both of the pyranose and furanose units with the varieties of the glycosidic bonds in the product xylan. Similarly, the polysaccharides obtained from α-D-Ara and α-L-Fuc (runs 3 and 5 in Table 1) also should have the highly branched structures.

2.3. MALDI-TOF mass analysis

To get more information about the polymer chains, the per-*O*-methylated polysaccharide from run 1-1 in Table 1 was isolated by reprecipitation of the EtOAc solution into hexane (yield: 50%, M_w: 10 500, M_n: 3800, GPC ($CHCl_3$)) and subjected to MALDI-TOF mass analysis (Fig. 4). Two series of peaks, $[A_n+Na]^+$ and $[B_n+Na]^+$ are observed with the regular intervals (ca. 160 u), which are consistent with the mass value of the xylose repeating unit ($C_7H_{14}O_4$: 160.07). The mass values of peak series $[A_n+Na]^+$ are in good agreement with that of the xylan having the methyl glycoside as the reducing terminal unit. As compared with peak series $[A_n+Na]^+$, each peak of series $[B_n+Na]^+$ show the smaller mass value by 46 u, which is consistent with the formula mass of C_2H_6O. This finding means that an ether linkage, which is formed by the intramolecular dehydration between two more hydroxyl groups, is contained as the terminal group in the xylan of peak series $[B_n+Na]^+$. The 1,4-anhydride structure should be reasonably involved in the terminal unit since the furanose units are contained in the product polymer (vide supra). It is noteworthy that the 1,6-anhydride terminal unit is formed in the solid-state polycondensation of natural aldohexoses and disaccharides [9].

Thus, the polymerization reaction takes place through the mechanisms as shown in Scheme 5. An anomeric hydroxyl group is activated by phosphoric acid to generate the carbocation, which undergoes intermolecular (A) and intramolecular (B) addition of a hydroxyl group, producing the polymer chain and the 1,4-anhydride terminal units, respectively. The 1,4-anhydride terminal unit also participates to the further polymerization with the aid of phosphoric acid to provide the furanose and pyranose repeating units.

The peaks corresponding to series $[B_n+Na]^+$ were detected also in the per-*O*-methylated polysaccharides from β-D-Ara and α-L-Fuc, indicating that the intramolecular glycosilation reaction is involved in the polymerizations of these two monomers as well; i.e. the product polysaccharides are composed of both pyranose and furanose units.



Scheme 2. Reduction and subsequent acetylation of fraction (A).

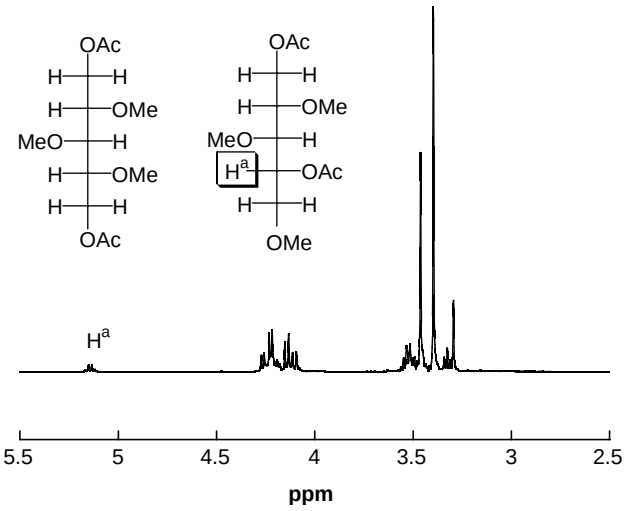


Fig. 2. The ^{1}H NMR spectrum ($CDCl_3$) of the mixture of 1,4-di-*O*-acetyl-2,3,5-tri-*O*-methylxylitol and 1,5-di-*O*-acetyl-2,3,4-tri-*O*-methylxylitol obtained from the fraction (A) (Scheme 2).

3. Experimental

3.1. Material

Commercially available α-D-xylopyranose (α-D-Xyl) and α-L-fucopyranose (α-D-Fuc) were dried at 80 °C under vacuum before use. β-D-Arabinopyranose (β-D-Ara) and α-L-rhamnopyranose (α-L-Rha) were obtained by recrystalization of commercially available D-arabinose and L-rhamnose from 80% EtOH aq. The contents of the α- and β-anomers were determined by ^{1}H NMR spectra in DMSO-d_6 (Table 2). DMSO was fractionally distillated under vacuum and dried over molecular sieves 4A. Powdery NaOH was prepared by the adequate hydrolysis of NaH in dry THF. Other reagents of H_3PO_4, CH_3I, $NaNO_3$, HCOOH, CF_3COOH, $NaBH_4$, and NH_3 aq. were used as received.

3.2. Measurements

Thermogravimetry and differential thermal analyses (TG-DTA) were performed with a Simadzu DTG-60 apparatus (heating rate: 10 °C /min, under a N_2 flow). ^{1}H NMR spectra were recorded with a Bruker DPX300 spectrometer (solvent: $CDCl_3$ or DMSO-d_6, internal standard: Me_4Si). ESI mass spectra were obtained by using a Shimadzu LCMS-QP 8000α system (solvent: MeOH). MALDI-TOF mass spectra were recorded with a KRATOS AXIMA-CFR-S spectrometer (solvent: 0.1 wt% CF_3COOH aq. matrix: 2,5-dihydroxybenzoic acid). Gel permeation chromatography (GPC) was conducted on a TOSOH TSK-GEL ALFA-3000 column (eluent: 0.2 mol/L $NaNO_3$ aq. calibration: pulluran standards) or a Shodex K-804L column (eluent: $CHCl_3$, calibration: polystyrene standards). HPLC analysis was performed on a GL Science Sil-100A column (eluent: acetone/*n*-hexane/MeOH = 1:1:0.01). Silica gel 60N and 60 F_{254} (Merk) were used for column chromatography and TLC, respectively.

3.3. Solid-state polymerization

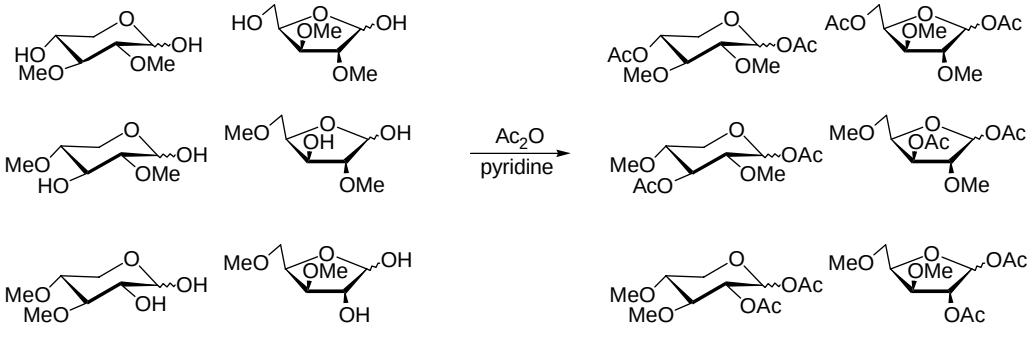
Natural saccharide (300 mg) was ground well with 85% H_3PO_4 aq. (5 mol% for monomer) in an agate mortar and pestle. The mixture in a test tube with a N_2 inlet was heated at 100 or 110 °C on an aluminum block (Eyela dry thermo bath MG-2000) under a N_2 flow. In some cases, the reaction mixture was ground at 1, 3, 5, and 10 h.

3.4. Methylation of the resultant polysaccharide

Into a dry DMSO solution (9 mL) of the above reaction mixture (ca. 300 mg) was suspended powdery NaOH (1.2 g, 0.03 mol) and stirred for 1 h. CH_3I (1.2 mL, 2.7 g, 0.02 mol) was added to this mixture and stirred for another 24 h. The resultant mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was dried with $MgSO_4$ and concentrated. The residue underwent the same methylation process again. Then, the obtained material was dissolved in EtOAc and pored into hexane to give yellow powder of the per-*O*-methylated polysaccharide.

3.5. Hydrolysis of the per-O-methylxylan

The per-*O*-methylyxylan (500 mg) was refluxed for 2 h in 90% HCOOH aq. (30 mL). To the reaction mixture was added 2 mol/L CF_3COOH aq. (30 mL) and then refluxed for another 12 h. The solvent was removed under reduced pressure, giving brown oil of the mixture of the partially *O*-methylated



Scheme 3. Acetylation of fraction (B).

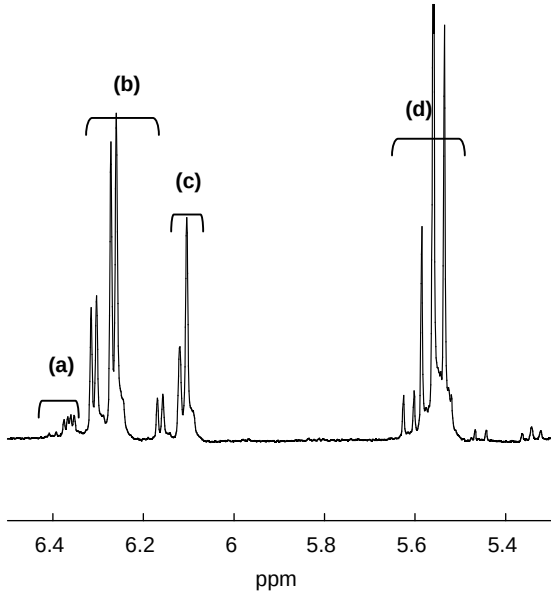


Fig. 3. The ^{1}H NMR spectrum ($CDCl_3$) of the acetylated products from fraction (B) (Scheme 3).

monosaccharides, which were fractionated by column chromatography (acetone/*n*-hexane = 2:1) into fraction (A) (43 mg), (B) (65 mg), and (C) (69 mg) [10].

3.6. Preparation of the tri-O-methylxylitol di-O-acetates from fraction (A)

Into a 0.5 mol/L NH_3 aq. solution (4 mL) of fraction (A) (10 mg) was added an excess amount of $NaBH_4$ (20 mg, 0.53 mmol) and stirred at rt for 12 h. Acetic acid was added to the solution to decompose the residual $NaBH_4$ and then the solvent was evaporated under reduced pressure. Into a pyridine solution (1 mL) of the residue was added acetic anhydride (1 mL) and stirred at rt for 12 h. The solvent was removed under reduced pressure. The residue was dissolved into CH_2Cl_2 (20 mL) and successively washed with 1 mol/L HCl aq. (20 mL), saturated $NaHCO_3$ aq. (20 mL), and saturated NaCl aq. (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to obtain tri-*O*-methylxylitol di-*O*-acetates (12 mg) of fraction (A).

3.7. Acetylation of fraction (B)

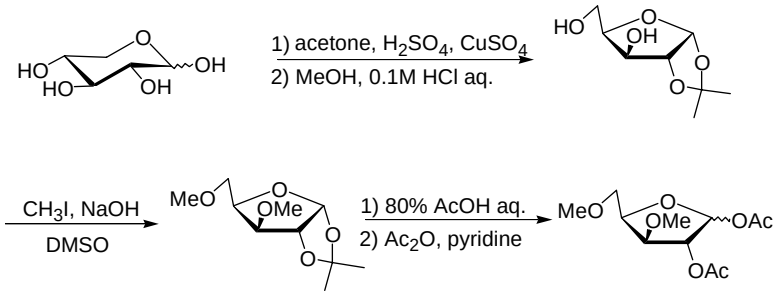
Into a pyridine (1 mL) solution of fraction (B) (10 mg) was added acetic anhydride (1 mL) and stirred at rt for 24 h. The solvent was removed under reduced pressure. The residue was dissolved into CH_2Cl_2 (20 mL) and successively washed with 1 mol/L HCl aq. (20 mL), saturated $NaHCO_3$ aq. (20 mL), and saturated NaCl aq. (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to obtain the acetylated products (14 mg).

3.8. 1,2-O-Isopropylidene-3,5-di-O-methyl-D-xylofuranose

Into a dry DMSO solution (9 mL) of 1,2-isopropylidene-D-xylofuranose (1.0 g, 5.2 mmol) [11] was suspended powdery NaOH (1.2 g, 30 mmol) and stirred for 1 h. CH_3I (1.2 mL, 2.7 g, 20 mmol) was added to this mixture and stirred for another 24 h. The resultant mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography (EtOAc/*n*-hexane = 1:1) to obtain 1,2-*O*-isopropylidene-3,5-di-*O*-methyl-D-xylofuranose (0.51 g, 2.5 mmol, yield: 48%, $R_f = 0.60$ (EtOAc/*n*-hexane = 1:1)). ^{1}H NMR ($CDCl_3$, δ in ppm) δ 5.91 (d, 1H, J = 3.6 Hz, H-1), 4.57 (d, 1H, J = 3.6 Hz, H-2), 4.37–4.32 (m, 1H, H-4), 3.73 (d, 1H, J = 3.6 Hz, H-3) 3.73–3.56 (m, 2H, H-5) 3.41 (s, 3H, OCH_3) 3.40 (s, 3H, OCH_3) 1.49 (s, 3H, CCH_3) 1.32 (s, 3H, CCH_3).

3.8.1. 1,2-O-Diacetyl-3,5-di-O-methyl-D-xyofuranose

1,2-Isopropylidene-3,5-di-*O*-methyl-D-xylofuranose (0.51 g, 2.5 mmol) was dissolved into 80% AcOH aq. (20 mL) and then refluxed for 12 h. The solvent was removed under reduced pressure. Into a pyridine solution (1 mL) of the residue was added acetic anhydride (1 mL) and stirred at rt for 12 h. The solvent was removed under reduced pressure. The residue was dissolved into CH_2Cl_2 (20 mL) and successively washed with 1 mol/L HCl aq. (20 mL), saturated $NaHCO_3$ aq. (20 mL), and saturated NaCl aq. (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc/*n*-hexane = 1:1) to obtain 1,2-*O*-diacetyl-3,5-di-*O*-methyl-D-xyofuranose. (0.28 g, 1.1 mmol, yield: 44%, $R_f = 0.55$ (EtOAc/*n*-hexane = 1:1)) ^{1}H NMR ($CDCl_3$, δ in ppm) δ 6.41



Scheme 4. Synthesis of 1,2-di-*O*-acetyl-3,5-*O*-methylxylofuranose.

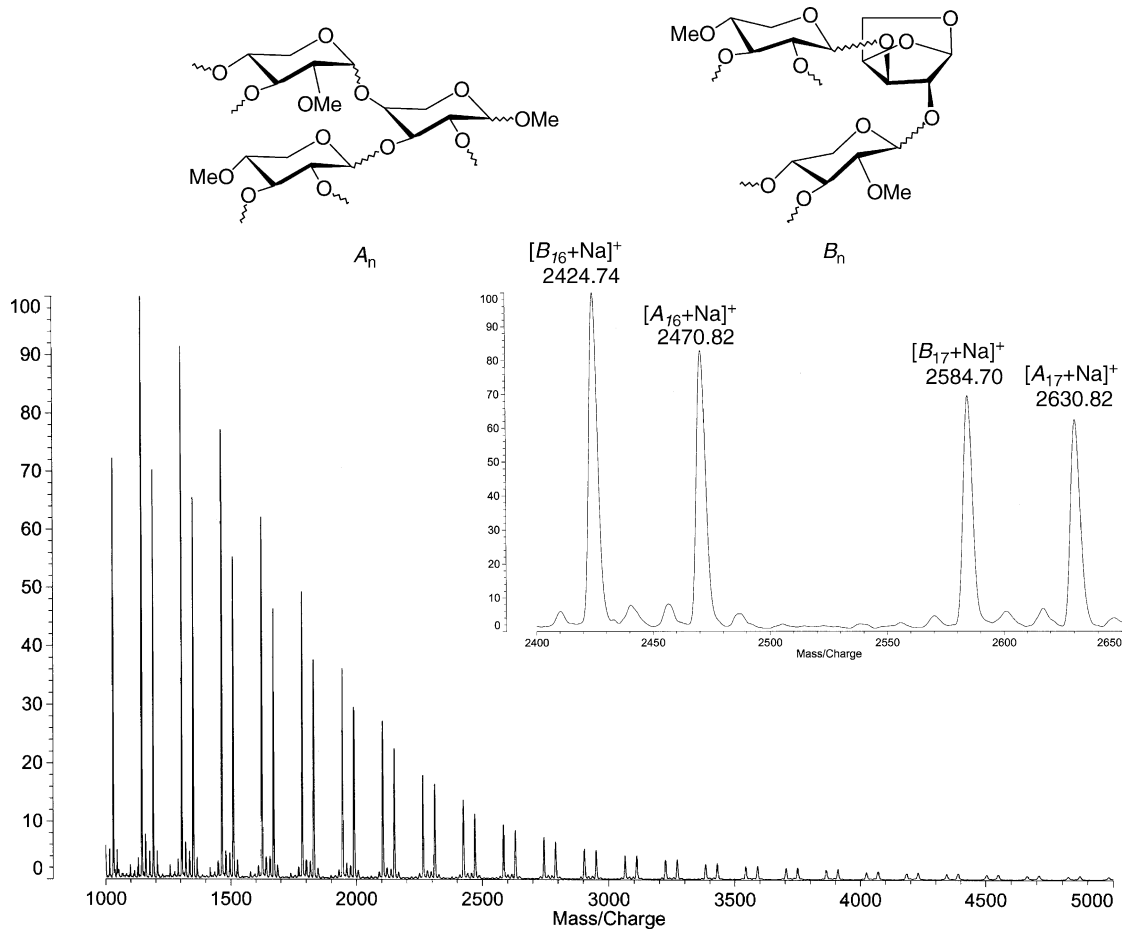
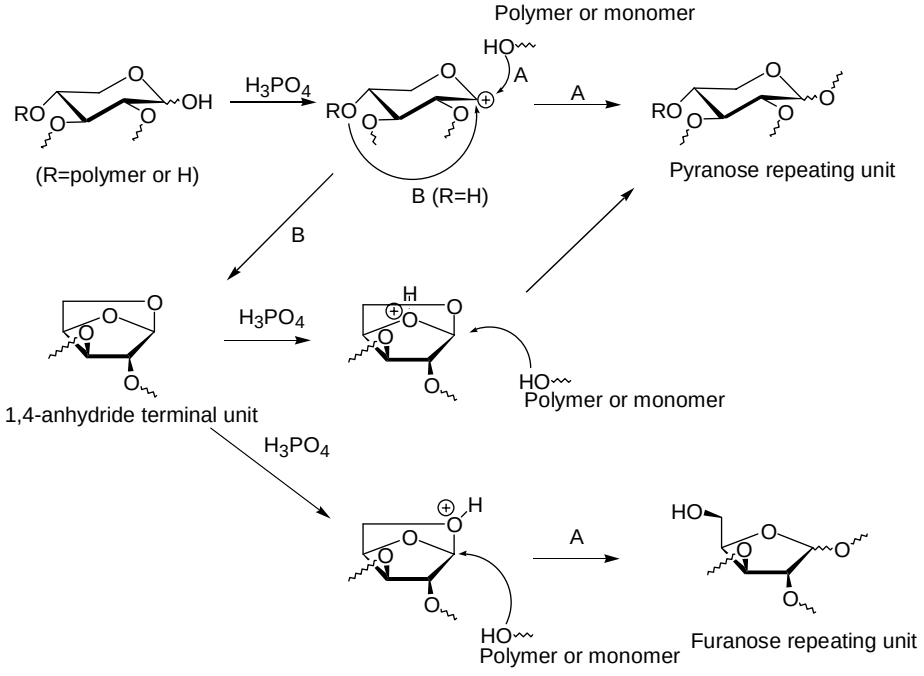


Fig. 4. The MALDI-TOF mass spectrum (matrix: 2,5-dihydroxybenzoic acid) of per-*O*-methyl polysaccharide prepared from α-D-Xyl (run 1-1 in Table 1) (yield: 50%, M_w: 10 500, M_n: 3800) (hexane-insoluble part, GPC (eluent: $CHCl_3$, calibration: PSt standards)).



Scheme 5. The reaction mechanism of the solid-state polycondensation of α-D-Xyl.

Table 2
Purity of the saccharide

Saccharide	α:β[a]
α-D-Xyl	96:4
α-L-Fuc	98:2
β-D-Ara	5:95
α-L-Rha	96:4

[a] The content ratio of the α- and β-anomers was determined by ^{1}H NMR spectrum in DMSO-d_6.

(d, 0.7 H, J=4.5 Hz, H-1 (α-form)), 6.13 (s, 0.3H, H-1 (β-form)), 5.24–5.21 (m, 1H, H-2), 4.46–4.41 (m, 1H, H-4) 4.07–4.03 (m, 0.7H, H-3 (α-form)) 3.81 (d, 0.3H, J=4.5 Hz, H-3 (β-form)) 3.69–3.40 (m, 8H, H-5 and OCH_3) 2.11–2.06 (m, 6H, COCH_3).

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[10] The hydrolysis mixture contained a methanol-insoluble part (11 wt%), which cannot be identified. This part should come from an unknown side reaction during the hydrolysis because the original polymer has proved to have no unidentified unit by MALDI TOFMS analysis. LC-MS analysis has proved that the methanol-soluble part (89 wt%) is exclusively composed of partially methylated monosaccharides as shown in Chart 2. A total yield after silica gel column chromatography was about 40%, which could be caused by losses during the separation (e.g., adsorption onto the silica gel). Thus, this analysis can be used only for the qualitative discussion about the polymer structure.
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