Selective Ring-Opening Polymerization of Di-*O*-*t*-butyldimethylsilylated and Di-*O*-*p*-bromobenzylated 1,4-Anhydro- α -L-arabinopyranoses and Structural Analysis of Free Arabinans

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ABSTRACT: We report herein studies of ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- α -L-arabinopyranose (ADSA) and 1,4-anhydro-2,3-di-*O*-*p*-bromobenzyl- α -L-arabinopyranose (ADBA) by cationic initiation in methylene chloride. Polymerization of ADSA using phosphorus pentafluoride as initiator at -60°C gave stereoregular (1 $\rightarrow$ 5)- α -L-arabinofuranan derivatives in 85% yield. Polymerization of ADBA with various Lewis acids afforded slightly less stereoregular polymers (α -content 90%) under optimum conditions. Deprotection of both substituted polymers resulted in a free polysaccharide having the same structure, (1 $\rightarrow$ 5)- α -L-arabinofuranan. The polymer structure was characterized by ^{13}C NMR spectroscopy, specific rotation, and the methylation analysis using GC-MS spectroscopy.

KEY WORDS Ring-Opening Polymerization / Cationic Initiation / ^{13}C NMR / 2D NMR / Specific Rotation / Free Polysaccharide / Methylation Analysis / GC-MS Spectroscopy /

Several stereoregular polysaccharides have been synthesized by the selective ring-opening polymerization of 1,4-anhydro pentoses. The synthesis of the cellulose-type polysaccharide, (1 $\rightarrow$ 4)- β -D-ribopyranan, by the selective ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzylidene- α -D-ribopyranose and 1,4-anhydro-2,3-di-*O*-methyl- α -D-ribopyranose with antimony pentachloride in methylene chloride was reported.¹ Stereoregular polysaccharides having a (1 $\rightarrow$ 5)- α -furanosidic structure were also prepared by ring-opening polymerization of 1,4-anhydro- α -D-ribopyranose,² D-xylopyranose,³ and D-lyxopyranose⁴ derivatives with various reaction conditions.

Kops and Schuerch first reported the ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-methyl- α -L-arabinopyranose with Lewis acid as a catalyst.⁵ However, stereoregular

polysaccharide was not obtained under any experimental conditions, and the obtained polymer had a mixed structure of a nearly equal amount of furanosidic and pyranosidic units in the polymer backbone.

On the other hand, a benzylated homolog 1,4-anhydro-2,3-di-*O*-benzyl- α -L-arabinopyranose was polymerized by using various Lewis acid catalysts. Only a maximum of 90% stereoregularity ((1 $\rightarrow$ 5)- α -furanosidic content) could be observed in the best case.⁶

In this study, we report the cationic ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- α -L-arabinopyranose (ADSA) and 1,4-anhydro-2,3-di-*O*-*p*-bromobenzyl- α -L-arabinopyranose (ADBA) to give a stereoregular polymer in the case of ADSA and a slightly less stereoregular polymer in the case of ADBA. The structure of

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the deprotected polymer was also analyzed to propose a new type of polysaccharide consisting of a mixed structure of both five-membered ring units and open-chain units.

EXPERIMENTAL

¹H NMR (270 MHz), ¹³C NMR (67.8 MHz), and 2D NMR spectra were recorded on a JEOL JMN GX-270 spectrometer. Specific rotations were measured on CHCl₃, DMSO, or H₂O solution by means of a Perkin-Elmer M-241 polarimeter. Molecular weights were determined by organic-phase GPC (column, Toyo Soda TSK-gel, G2000H, G3000H, G4000H, G5000H, 7.6 × 600 mm × 4; eluent, THF) using polystyrene standards and by aqueous-phase GPC (columns, Toyo Soda TSK-gel, G2000SW, G3000SW, G4000SW, 7.6 × 600 mm × 3; eluent, 66.7 mmol phosphate buffer, pH = 6.86) using dextran standards. GC-MS spectra were measured at 70 eV with a JEOL JMS DX-300 spectrometer (column, HP OV-1, 0.31 mm × 25 m).

1,4-Anhydro-α-L-arabinopyranose

1,4-Anhydro-α-L-arabinopyranose was obtained in 6.4% yield by pyrolysis of L-arabinose according to the method of Köll, Deyhim, and Heyns.⁷

1,4-Anhydro-2,3-di-O-*t*-butyldimethylsilyl-α-L-arabinopyranose (ADSA) and 1,4-Anhydro-2,3-di-O-*p*-bromobenzyl-α-L-arabinopyranose (ADBA)

Silylation of the anhydro sugar was carried

out by method of Hakimelahi and coworkers.⁸ To a 1,4-anhydro-α-L-arabinopyranose (8 g, 0.06 mol) solution in dry THF (100 ml), dry pyridine (24 g, 0.3 mol) and silver nitrate (31 g, 0.18 mol) were added. The solution was stirred until the silver nitrate completely dissolved. Then, *t*-butyldimethylsilyl chloride (28 g, 0.18 mol) was added and the resulting mixture was stirred for 20 h at room temperature. After filtration, the filtrate was poured into a 5% aqueous NaHCO₃ solution and extracted with CHCl₃ which was dried by anhydrous Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography (hexane: ethyl acetate = 12:1) to give pure ADSA (10.4 g) in 47.7% yield: [α]_D = +102.2° (c 1%, CHCl₃).

ADBA was prepared by the reaction of 1,4-anhydro-α-L-arabinopyranose with *p*-bromobenzyl chloride in the presence of powdered KOH as described in the previous paper.³ Yield 28.1%. [α]_D = +65.5° (c 1%, CHCl₃).

The structure of ADSA and ADBA was confirmed by ¹H and ¹³C NMR spectroscopy.

Polymerization

The polymerization was carried out under high vacuum conditions in sealed glass ampoules as described in the previous paper.⁹ Polymers were purified by reprecipitation using chloroform and methanol, and followed by freeze-drying from benzene.

Deprotection

A solution of poly(ADSA) (0.32 g) in dry

THF (25 ml) was added to a (*n*-Bu)₄NF (1 mol THF solution, 5.3 ml) solution and refluxed for 1.5 h. After dialyzing with distilled water for 5 days, the aqueous solution was concentrated to 1–2 ml and freeze-dried from water to give a free polysaccharide. Yield, 0.11 g (92.1%).

A solution of poly(ADBA) (0.52 g) in 1,2-dimethoxyethane (15 ml) was added to a solution of sodium (1.0 g) in liquid ammonia (100 ml) at -78°C . After reacting for 2 h, anhydrous ammonium chloride was added until the blue color disappeared. The ammonia was evaporated and water was added to the reaction mixture. The aqueous layer was washed twice with dichloromethane, dialyzed with distilled water for 5 days, and then freeze-dried. Yield, 0.07 g (47.0%).

Methylation Analysis of Free Polysaccharide

A free polysaccharide (No. 13 in Table III) (10 mg) was treated with methyl sulfinylcarbanion (10 ml), which was prepared by NaH (55%, 0.8 g, 18.3 mmol) with dry DMSO (15 ml) at 65 – 70°C , under a nitrogen atmosphere and the mixture was stirred overnight by the aid of ultrasonication at 30°C . Then

methyl iodide (5 ml) was added to the reaction mixture, and stirred for 3 h at 30°C . After dialyzing overnight, the methylated polysaccharide was extracted with chloroform. The chloroform layer was dried by anhydrous Na₂SO₄, evaporated, and the residue was dried under vacuum overnight at 60°C . The methylation procedure was repeated until no OH band was detected by the IR spectrum. The permethylated polysaccharide was hydrolyzed by heating at 110°C with 90% formic acid (5 ml) for 16 h, and then with 1% trifluoroacetic acid (5 ml) for 16 h. The methylated polysaccharide in the hydrolysate was converted into alditol acetate by reduction with NaBH₄ and acetylation with acetic anhydride and pyridine at 100°C for 2 h, and the product was analyzed by a JEOL JMS DX-300 GC-MS spectrometer.

RESULTS AND DISCUSSION

Starting monomers, ADSA and ADBA, were synthesized by pyrolysis of L-arabinose and by subsequent protection of hydroxyl groups. These monomers were readily polym-

Table I. Ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- and *p*-bromobenzyl- α -L-arabinopyranoses by cationic catalysts^a

No.	Catalyst		Temp.	Time	Yield	$[\alpha]_D$	$\bar{M}_n^c$	$\bar{M}_w/\bar{M}_n$	(1 $\rightarrow$ 5)- α -F ^d
		mol% to monomer	$^{\circ}\text{C}$	h	%	deg.	$\times 10^{-4}$		%
1	BF ₃ OEt ₂	5	-20	24	76.6	-6.7	5.1	1.35	68.3
2	BF ₃ OEt ₂	5	-40	24	60.1	-9.1	4.0	2.58	71.2
3	SbCl ₅	5	-40	8	32.4	$+12.5$	1.7	3.41	52.2
4	SbCl ₅	5	-60	2	48.0	$+13.2$	2.8	2.71	62.0
5	PF ₅	3	-60	2	83.4	-20.4	6.3	2.97	100
6	SbCl ₅	3	-20	1	72.4	$+12.4$	0.3	1.90	52.6
7	SbCl ₅	3	-60	1.5	54.1	-12.6	0.2	1.77	79.1
8	PF ₅	2	-60	0.5	90.0	-24.5	6.0	1.69	90.0
9	BF ₃ OEt ₂	3	0	20	90.1	-9.7	6.5	2.00	64.7

^a Monomer concentration: 50–80 w/v%, solvent: CH₂Cl₂. Nos. 1–5: 1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- α -L-arabinopyranose. Nos. 6–9: 1,4-anhydro-2,3-di-*O*-*p*-bromobenzyl- α -L-arabinopyranose.

^b Measured in CHCl₃ (*c* 1).

^c Determined by GPC.

^d Calculated from ¹³C NMR spectra.

Figure 1. Ring-opening modes of 1,4-anhydro- α -L-arabinopyranose.

erized by various cationic catalysts at low temperatures to afford high molecular weight polymers. It was first revealed that the di-*O*-*t*-butyl-dimethylsilylated monomer had a high polymerizability. The results of polymerization are summarized in Table I.

Polymerization of ADSA by boron trifluoride etherate gave silylated polymers with $[\alpha]_D = -6.7^\circ$ and -9.1° in 76.6 and 60.1% yield, respectively. Antimony pentachloride as catalyst gave the polymer [poly(ADSA)] with $[\alpha]_D = +12.5^\circ$ in 32.4% yield. When ADSA was treated with phosphorus pentafluoride at -60°C , a completely stereoregular polymer, 2,3-di-*O*-*t*-butyldimethylsilyl-(1 $\rightarrow$ 5)- α -L-arabinofuranan was produced and the specific rotation of the polymer was -20.4° .

Koyama and coworkers reported that in the polymerization of 1,4-anhydro-2,3-di-*O*-benzyl- α -L-arabinopyranose the stereoregularity of the polymer was about 90%.⁶ Recently, Good and Schuerch revealed that for the polymerization of 1,3-anhydroglucose monomers, the obtained *p*-bromobenzylated polymers were more stereoregular than the benzylated polymers prepared under similar conditions.¹⁰ Thus, we used *p*-bromobenzyl group as a protective group of the monomer. Nos. 6–9 in Table I shows the results of the polymerization of ADBA. Antimony pentachloride or boron trifluoride etherate gave *p*-

bromobenzylated polymers with a percentage (52–79%) of α -linkages, but the *p*-bromobenzylated polymer with the highest stereoregularity (90% α) was obtained with phosphorus pentafluoride at -60°C . These results are almost the same as those of the benzylated polymer, and no improvement in the polymer stereoregularity was observed.

The number-average molecular weight of the polymers ranges from 17×10^3 – 65×10^3 and the distribution was symmetrical and narrow. However, the polymers prepared by SbCl_5 catalyst (Nos. 6 and 7) showed low number-average molecular weights.

The ring-opening polymerization of 1,4-anhydro sugar derivatives gives four possible monomeric units in the polymer backbone, as shown in Figure 1. When the 1,5-linkage is opened, the obtained polymers consist of (1 $\rightarrow$ 5)- α - and (1 $\rightarrow$ 5)- β -furanocyclic structures. The negative $[\alpha]_D$ value -20.4° for a completely stereoregular silylated polymer (No. 5) reveals that the polymer is composed of (1 $\rightarrow$ 5)- α -L-furanosidic units. With SbCl_5 as catalyst (Nos. 3, 4, and 6), the obtained polymers showed positive $[\alpha]_D$ values, suggesting that the content of the (1 $\rightarrow$ 5)- β configuration increased in the polymer backbone.

Figure 2 shows 67.8 MHz ^{13}C NMR spectra of poly(ADSA) prepared by (A) PF_5 at -60°C , (B) BF_3OEt_2 at -40°C , (C) SbCl_5 at

Figure 2. 67.8 MHz ^{13}C NMR spectra of (A) 2,3-di-*O*-*t*-butyldimethylsilyl-(1 $\rightarrow$ 5)- α -L-arabinofuranan prepared by PF_5 ($[\alpha]_{\text{D}} -20.4^\circ$) (no. 5 in Table I), (B) poly(1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- α -L-arabinopyranose) prepared by BF_3OEt_2 ($[\alpha]_{\text{D}} -9.1^\circ$) (no. 2 in Table I), (C) poly(1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- α -L-arabinopyranose) prepared by SbCl_5 ($[\alpha]_{\text{D}} +12.5^\circ$) (no. 3 in Table I), and (D) poly(1,4-anhydro-2,3-di-*O*-*p*-bromobenzyl- α -L-arabinopyranose) prepared by PF_5 ($[\alpha]_{\text{D}} -24.5^\circ$) (no. 12 in Table III) (CDCl_3 as solvent).

-40°C , and (D) poly(ADBA) prepared by PF_5 at -60°C , respectively. The stereoregularity of the polymers was determined from the C1 absorptions. Spectrum 2A shows only five absorptions (except for absorptions of solvent and protected groups), indicating that the polymer is of high stereoregularity. Taking

into account the negative optical rotation, it was concluded that the polymer is 2,3-di-*O*-*t*-butyldimethylsilyl-(1 $\rightarrow$ 5)- α -L-arabinofuranan. In spectrum 2C, the C1 carbon appears as two peaks at 108.8 and 103.0 ppm due to the (1 $\rightarrow$ 5)- α and (1 $\rightarrow$ 5)- β configurations. On the other hand, the existence of a number of small

Table II. ^1H and ^{13}C chemical shifts and chemical properties of 1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- (or *p*-bromobenzyl)- α -L-arabinopyranoses and the corresponding polymers^a

		H1, C1	H2, C2	H3, C3	H4, C4	H5, C5	H5'	mp	$[\alpha]_D^{25}$
								°C	deg. ^d
ADSA ^b	^1H	5.32 (d)	3.92 (a)	3.60 (d)	4.43 (m)	3.57 (q)	3.51 (d)	Oil	+102.2
	^{13}C	99.9	85.1	79.8	83.0	65.2			
ADBA ^c	^1H	5.54 (d)	3.80 (q)	3.51 (d)	4.71 (q)	3.64 (q)	3.56 (d)	79.5	+65.5
	^{13}C	98.5	87.7	83.3	79.8	65.4		80.5	
Poly(ADSA)	^{13}C	108.8	84.4	82.0	78.9	66.6			-20.4
Poly(ADBA)	^{13}C	106.3	83.0	88.2	80.4	65.8			-24.5

^a Solvent, CDCl_3 ; ppm from internal tetramethylsilane.^b Proton coupling constants (Hz): $J_{1,2}=2.4$, $J_{2,3}=0.5$, $J_{2,4}=1.8$, $J_{3,4}=0.5$, $J_{4,5}=8.0$, $J_{5,5'}=12.2$ ^c Proton coupling constants (Hz): $J_{1,2}=2.1$, $J_{2,3}=1.0$, $J_{2,4}=1.9$, $J_{3,4}=0.5$, $J_{4,5}=8.0$, $J_{5,5'}=14.0$.^d Measured in CHCl_3 (c 1).**Table III.** Deprotection of poly(1,4-anhydro-2,3-di-*O*-*t*-butyldimethylsilyl- and *p*-bromobenzyl)- α -L-arabinopyranoses) into free polysaccharides

Polymer						Free polysaccharide					
No.		$[\alpha]_{\text{D}}^{25}$ deg.	$\bar{M}_n \times 10^{-4}$	$\overline{\text{DP}}$	Temp	Time	No.	Yield	$[\alpha]_{\text{D}}^{25}$	$\bar{M}_n \times 10^{-4}$	$\overline{\text{DP}}$
					°C	h		%	deg.		
10	Poly(ADSA)	−24.5	6.3	587	refl. ^d	1.5	13	92.1	−20.3	1.8	397
11	Poly(ADSA)	+13.2	2.8	194	refl. ^d	1.5	14	90.9	−25.4		
12	Poly(ADBA)	−24.5	6.0	128	−60 ^e	2	15	47.0	−74.7 ^f	^g	^g

^a Measured in CHCl_3 (c 1). ^b Measured in D_2O (c 1).^c Measured by GPC using phosphate buffer as solvent.^d With $(n\text{-Bu})_4\text{NF}$ in THF. ^e With sodium in liquid ammonia.^f Measured in DMSO (c 0.5). ^g Not determined because of insolubility in H_2O .

peaks in the range of 60–110 ppm in spectra 2B and 2D indicates slightly less stereoregularity.

The assignments of ^1H and ^{13}C NMR spectra of the monomers and the corresponding polymers were carried out using 2D homonuclear shift-correlation (H–H COSY) and heteronuclear shift-correlation (C–H COSY) spectroscopy. The results are given in Table II. The formation of stereoregular and non-stereoregular polymers suggests that the polymerization proceeded *via* trialkyloxonium and carbenium ion intermediates. The trialkyloxonium ion reacts stereospecifically to form α -linkages, while the carbenium ion re-

acts nonstereospecifically to produce a mixture of α and β linkages. Therefore, ADSA was polymerized in a thoroughly stereospecific manner with phosphorus pentafluoride by trialkyloxonium ion mechanism.³

Structural Analysis of Free Polysaccharides

The synthetic polymers, 2,3-di-*O*-*t*-butyldimethylsilyl-(1 $\rightarrow$ 5)- α -L-arabinofuranan with $[\alpha]_D -20.4^\circ$ and $+13.2^\circ$ and 2,3-di-*O*-*p*-bromobenzyl-(1 $\rightarrow$ 5)- α -L-arabinofuranan with $[\alpha]_D -24.5^\circ$, were deprotected with $(n\text{-Bu})_4\text{NF}$ in THF and with sodium in liquid ammonia, respectively, to give free polysaccharide having the same structure, (1 $\rightarrow$ 5)- α -L-arabinofura-

Figure 3. 67.8 MHz ^{13}C NMR spectra of (A) poly(L-arabinose) ($[\alpha]_D -20.3^\circ$) in D_2O (no. 13 in Table III), (B) poly(L-arabinose) ($[\alpha]_D -25.4^\circ$) in D_2O (no. 14 in Table III) (C) poly(L-arabinose) ($[\alpha]_D -74.7^\circ$) in $\text{DMSO}-d_6$ (no. 15 in Table III), and (D) poly(D-ribose) in D_2O .

nan. Table III summarizes the results of the deprotection. The $[\alpha]_D$ values of the free polysaccharides, however, were different from the reported value, $[\alpha]_D -146^\circ$, of natural α -L-arabinofuranan.¹¹

As shown in Figures 3A, 3B, and 3C, the ^{13}C NMR spectra of the deprotected polymers were very similar and non-ascribable absorptions appeared in the range of 97–110, 75–77, 67–72, and 61–65 ppm as well as the absorptions assignable to α -L-arabinofura-

nosidic units. The proportion of the former absorption was estimated from the C5 absorptions to be about 50%. The ^{13}C NMR spectrum of (1 $\rightarrow$ 5)- α -D-ribofuranan which was obtained by deprotection of 2,3-di-*O*-benzyl- or 2,3-di-*O*-*t*-butyldimethylsilyl-(1 $\rightarrow$ 5)- α -D-ribofuranan showed only five absorptions corresponding to the α -D-ribofuranosidic structure and did not give the non-ascribable absorptions (Figure 3D). We assumed an "open-chain" type polymer which was

partially cleaved at C1–O–C4 linkage in the polymer backbone produced during the de-protection.

To determine the structure, methylation analysis was performed. The deprotected polymer with $[\alpha]_D = -20.3^\circ$ (No. 13 in Table III) was fully methylated by Hakomori method.¹²⁾ The methylated polysaccharide was converted into partially methylated alditol acetates by the usual method and then analyzed by GC-MS spectroscopy. If the open-chain type structure is present in the polymer backbone, the structure demonstrated in Figure 4B will be given by GC-MS spectrum.

Figure 5 shows the results of the methyl-

Figure 4. The fragmentation of alditol acetates.

Figure 5. GC-MS spectra of poly(L-arabinose) (no. 13 in Table III). (A) Total ion chromatogram, (B) mass spectrum of (1) in (A), and (C) mass spectrum of (2) in (A).

ation analysis. The mass spectra were measured at 70 eV and the injection temperature was 180°C. Spectrum 5A is a total ion chromatogram of the methylated products. Spectra 5B and 5C are the mass spectral charts of peaks 1 and 2 in Figure 5A, respectively. Spectrum 5C showed primary fragments, m/e 233, 189, 161, 117, and 73, and secondary fragments, m/e 129 (189–60), 101 (161–60), 87 (117–30), 71 (101–30), and 57 (117–60), formed from the primary fragment by single or consecutive eliminations of acetic acid (m/e 60) or formaldehyde (m/e 30). Thus, spectrum 5C corresponds to the structure of Figure 4A which was led from (1 $\rightarrow$ 5)- α -L-arabinofuranan. Spectrum 5B showed primary fragments, m/e 161, 117, and 73, and secondary fragments, m/e 147 (205–60+2H), 131 (205–73–H), 130 (205–73–2H), 101 (161–60), 87 (117–30), 71 (101–30), and 57 (117–60), formed from the primary ones by the elimination. If the open-chain type structure exists, the difference of the alditol acetate 4A and 4B should appear at C4; that is, (1 $\rightarrow$ 5)- α -arabinofuranan gives 4-acetate and the open-chain product affords 4-OMe alditol acetate, as shown in Figure 4. Lindberg and coworkers reported alditol acetate having 2,3,4-OMe gives primary fragments, m/e 117 and 161, and having 2,3-OMe affords m/e 117 and 189.¹³ Therefore, we considered the structure of spectrum 5B (peak 1 in Figure 5A) to be 2,3,4-OMe alditol acetate which comes from the open-chain structured unit on the basis of the above GC-MS results and the literature.

The ratio of peaks 1 and 2 from GC-MS spectra (Figure 5A) was not in agreement with the results of ¹³C NMR spectra. The reason

for this difference may be due to the unstability of the mixed structure. The open-chain type monomeric units might exist randomly in the polymer chain so that several corresponding absorptions appear in the ¹³C NMR spectra. A synthetic polysaccharide containing this type of open-chain unit is, as far as we know, limited to the arabinose polymer.

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