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Chemical Synthesis of a New Polysaccharide. Ring-Opening Polymerization of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-allopyranose and Preparation of Stereoregular (1→6)-α-D-Allopyranan

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ABSTRACT: The cationic ring-opening polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-allopyranose (TBALL) was investigated with phosphorus pentafluoride as catalyst at low temperature to synthesize a new (1→6)-α-linked polysaccharide. Polymerization at a catalyst concentration of more than 4 mol % and at the optimum monomer concentration gave a stereoregular polymer with high molecular weight in high conversion. The calculation of the initiation efficiency of PF_5 and the examination of the ^{31}P NMR spectrum of the polymerization system indicated that complexation of PF_5 with TBALL monomer occurred and that propagating species were produced even several tens of hours after initiation. Polymerizations of TBALL with other Lewis acids as catalysts were also investigated. The polymer structure was determined by optical rotation and ^1H and ^{13}C NMR spectroscopy. In addition, the copolymerization of TBALL (M_1) and a 1,6-anhydroglucose derivative (M_2) was studied and the monomer reactivity ratios calculated by the Kelen–Tüdös method were found to be $r_1 = 0.44$ and $r_2 = 2.69$. Debenzylation of the polymer gave a free polysaccharide that was only soluble in DMF–N_2O_4 mixture. The ^{13}C NMR spectrum and the periodate oxidation of the debenzylated polymer indicated that the polymer was stereoregular (1→6)-α-D-allopyranan.

Three 1,6-anhydro-β-D-hexopyranose derivatives obtained from D-glucose,[1-3] D-mannose,[4] and D-galactose[5] have provided synthetic (1→6)-α-D-hexopyranans with high molecular weights through cationic ring-opening polymerizations. 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-altropyranose in which the configurations at the C-2 and C-3 carbons are different from those of the glucose derivative showed almost no homopolymerizability, though it was found that a copolymer of the 1,6-anhydroaltrose derivative can be obtained when a 1,6-anhydroglucose derivative is chosen as a comonomer.[6]

Schuerch and co-workers reported that the ring-opening polymerizability of tri-*O*-benzylated 1,6-anhydro sugars decreases in the order 1,6-anhydro-β-D-manno- > -D-gluco- > D-galactopyranose.[7,8] The reason for the difference in the polymerizability has been ascribed to steric and energetic factors inherent in the individual monomers.

Of the remaining four D-aldohexoses, D-allose gives 1,6-anhydro-β-D-allopyranose in which two hydroxyls are in axial position and a hydroxyl is in equatorial position according to the X-ray structural analysis of its crystal.[9] Thus, the 1,6-anhydro-β-D-allopyranose derivative is expected to have polymerizability. Recently, it was found that D-allose is a component of a natural polysaccharide.[10]

In this study, to synthesize the fourth (1→6)-α-D-glycan, preparation and cationic ring-opening polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-allopyranose (TBALL) are investigated. Since 2,3,4-tri-*O*-benzyl-(1→6)-α-D-allopyranan with high molecular weight is obtained under appropriate conditions, debenzylation of the polymer into a free polysaccharide is carried out. Structural analysis and solubility data for the free polysaccharide (1→6)-α-D-allopyranan, which is not naturally occurring, are reported. In addition, the relative polymerizability of TBALL is reported from the copolymerization studies of TBALL with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose.

Results and Discussion

Polymerization Behavior with PF_5 Catalyst. Cationic ring-opening polymerization of 1,6-anhydro-2,3,4-

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Table I
Ring-Opening Polymerization of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-allopyranose by PF_5 Catalyst[a]

no.	cat. concn, mol % to monomer	monomer concn, g/100 mL	temp, °C	time, h	conv, %	$[\alpha]^{25}_D$,[b] deg	$10^{-3}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	f[d]
1	4	50	−40	20	7.6	+123.5	38.9	1.76	0.03
2	4	100	−40	23	16.1	+138.6	29.6	1.95	0.12
3	10	100	−40	4	10.5	+131.7	22.5	1.83	0.04
4	4	50	−60	20	25.3	+138.1	45.1	2.01	0.12
5	4	50	−60	100	45.3	+139.1	43.6	1.89	0.22
6	4	100	−60	20	38.9	+134.6	38.6	2.24	0.22
7	4	100	−60	20	17.3	+139.4	33.8	2.02	0.11
8	4	100	−60	100	12.3	+141.0	29.5	1.83	0.09
9	10	100	−60	4	67.1	+139.6	37.1	2.20	0.16
10	4	30	−78	20	13.7	+141.5	63.0	2.07	0.05
11	4	30	−78	100	10.8	+144.1	50.7	2.02	0.05
12	4	50	−78	20	33.6	+146.0	76.8	2.12	0.10
13	4	50	−78	100	70.4	+141.2	62.5	2.38	0.24
14	7	50	−78	20	52.1	+139.2	67.7	2.23	0.10
15	10	50	−78	4	36.7	+143.7	59.6	2.24	0.05
16	10	100	−78	4	27.5	+138.8	31.5	2.32	0.08
17	20	50	−78	20	74.1	+138.1	31.8	2.33	0.10

[a] Solvent, CH_2Cl_2. [b] Measured in $CHCl_3$ (c 1). [c] Determined by gel permeation chromatography. [d] Initiation efficiency defined in eq 1.

tri-*O*-benzyl-β-D-allopyranose (TBALL) was carried out with various Lewis acids as catalysts. The results of polymerizations by PF_5 catalyst are shown in Table I. The conversion was generally low and was sensitive to variations of monomer concentration, catalyst concentration, temperature, and time.

The conversion was extremely low when the concentration of PF_5 catalyst was less than 4 mol % to the monomer or the temperature was above −40 °C. This polymerization behavior was different from that of other 1,6-anhydro sugars. In the initial polymerization experiments, we were not certain that this phenomenon was characteristic of TBALL and suspected that an undetectable impurity in the monomer prevented TBALL from polymerizing. One to two mole percent of PF_5 usually results in an almost quantitative conversion for the polymerization of the 1,6-anhydroglucose derivative.[3]

In the polymerization at the relatively higher temperature of −40 °C, the conversion was low in the range 7.6–16.1% (nos. 1–3). The conversion increased as the temperature was lowered. At −60 °C, a high conversion of 67.1% was obtained in a short polymerization time (4 h) and a high monomer concentration (100 g/100 mL of CH_2Cl_2) (no. 9). As shown later, the polymer was a stereoregular 2,3,4-tri-*O*-benzyl-α-D-allopyranan.

However, high monomer concentration was not effective in the polymerization at −78 °C, because similar conditions, except for the temperature (−78 °C), provided relatively low conversion (27.5%) (no. 16). However, polymerizations at −78 °C at a lower mononmer concentration of 50 g/100 mL gave high conversions of 70.4 and 74.1% with catalyst concentrations of 4 and 20 mol %, respectively (nos. 13 and 17). It seems that the optimum monomer concentrations are 100 g/100 mL and 50 g/100 mL at −60 and −78 °C, respectively.

After the polymerization was terminated, poly(TBALL) and the monomer were recovered from the polymerization mixture, but there were no oligomers.

Number-average molecular weights of the polymers were high, in the range of 22.5×10^3 to 76.8×10^3. The polymerization at −78 °C generally gave higher molecular weight polymers than at higher temperature. Since in the case of the glucose derivative, the optimum temperature providing high molecular weights was −60 °C, TBALL exhibited a somewhat different characteristic on this point.

To elucidate the reason for the low conversion, the initiation efficiency f of PF_5 which was actually used for polymerization was estimated according to the following equation and is shown in Table I.

$$f = \frac{2[\text{moles of polymer}]}{[\text{moles of } PF_5]} = \frac{2Cm_0/100(\overline{DP}_n)}{im_0/100} = \frac{2C}{i(\overline{DP}_n)} \quad (1)$$

where C, i, $\overline{DP}_n$, and m_0 are percent conversion, mol % of a PF_5 precursor, the number-average degree of polymerization, and the number of moles of monomer in feed, respectively. The factor 2 was used because an initiation reaction needs two molecules of PF_5.[11] As the number of moles of PF_5 that is transferred into the polymerization ampule after thermal decomposition of the precursor is less than that of the PF_5 precursor,[11] the f value must be a little higher than that shown in Table I.

The f values ranged from 0.03 to 0.24, and high yields were associated with large f values (nos. 5, 6, 9, and 13). Especially, in the polymerizations for 100 h, which resulted in high conversions (nos. 5 and 13), the f values were large, in the range 0.22–0.24, suggesting that new propagating species were formed even several tens of hours after initiation of polymerization.

Polymerization by Other Lewis Acids. Polymerizations of TBALL were attempted with various other Lewis acids, $SbCl_5$, SbF_5, TaF_5, NbF_5, and $BF_3{\cdot}OEt_2$, and the results are summarized in Table II.

Two to five mole percent antimony pentachloride as catalyst at −78 °C gave fairly high conversions of 30.3–56.6% (nos. 18–21). Since the polymerization of the glucose derivative required 20 mol % of $SbCl_5$ to attain 60% conversion,[12] it was unexpected that such a small amount of $SbCl_5$ could cause the polymerization of TBALL. However, $SbCl_5$ was the best catalyst to polymerize 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose into a (1→4)-β-D-ribopyranan derivative.[13]

However, the molecular weights of the polymers obtained with $SbCl_5$ catalyst ranged from 15.6×10^3 to 30.8×10^3, values considerably lower than those of the polymers obtained with PF_5 catalyst at −78 °C.

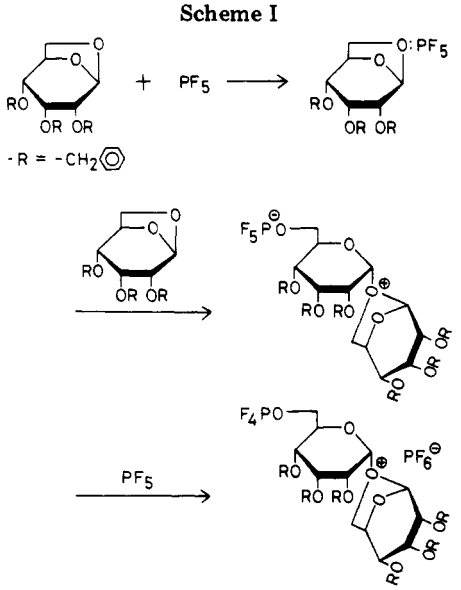
^{31}P NMR Measurement of the Polymerization System. To examine the cationic behavior of PF_5, the ^{31}P NMR spectrum of the polymerization system containing TBALL and PF_5 was recorded at −80 °C for a period of 18.6–19.9 h after initiation of the polymerization at −90 °C, as shown in Figure 1. The assignment of the peaks was carried out according to the previous work.[11]

Table II
Ring-Opening Polymerization of TBALL by Cationic Catalysts[a]

no.	cat.	cat. concn, mol %	temp, °C	time, h	conv, %	$[\alpha]^{25}_D$,[b] deg	$10^{-3}\bar{M}_n$[c]	f[d]
18	$SbCl_5$	2	−78	20	37.2	+141.9	30.8	0.52
19	$SbCl_5$	2	−78	100	30.3	+141.9	29.0	0.45
20	$SbCl_5$	5	−78	20	56.6	+142.6	26.3	0.37
21	$SbCl_5$	20	−78	20	42.7	+141.2	15.6	0.12
22	SbF_5	10	−60	4	28.5	+117.5	11.5	0.21
23	SbF_5	5	−78	50	12.4	+113.5	13.3	0.16
24	TaF_5	28	−78	100	18.5	+143.5	52.8	0.01
25	NbF_5	32	−78	100	5.5	+102.1	9.4	0.02
26	$BF_3{\cdot}OEt_2$	20	−20	100	trace			

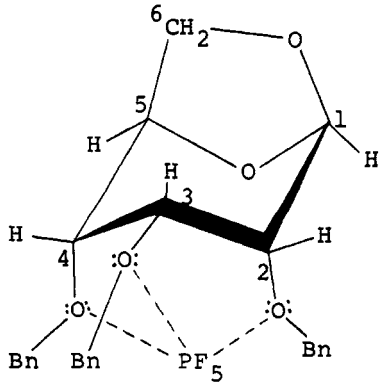
[a] Solvent, CH_2Cl_2; monomer concentration, 50 g/100 mL. [b] Measured in $CHCl_3$ (c 1). [c] Determined by gel permeation chromatography. [d] Initiation efficiency.

Scheme I



There are large sextet absorptions due to a TBALL–PF_5 complex centered at 134.2 ppm as well as small absorptions due to PF_4O– and PF_6^- arising from the propagating species (Scheme I). Such large absorptions of the complex existing a few tens of hours after initiation are characteristic of the TBALL–PF_5 polymerization system and were not observed in the polymerization of the glucose derivative by PF_5 catalyst where the complexation was observed under special conditions.[11]

Since in TBALL the three OBn groups at C-2, -3, and -4 exist on the same side of the pyranose ring, the complexation is assumed to occur between these oxygens and PF_5. Moreover, the sextet absorptions suggest the equivalence of five fluorine atoms on the basis of a fast intramolecular positional exchange.[14]



It is supposed that the complexation prevails over the initiation reaction at PF_5 concentrations of less than 4 mol % and there is no PF_5 used for initiating the polymerization.

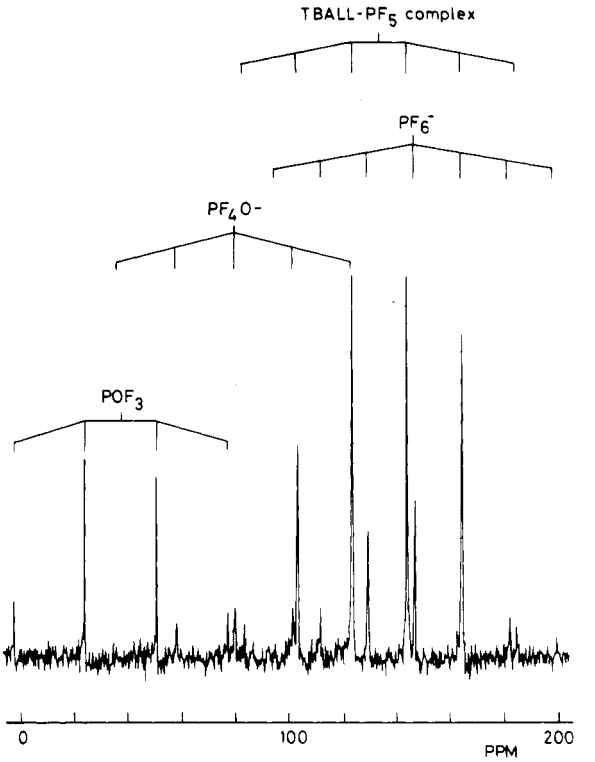


Figure 1. 40-MHz ^{31}P NMR spectrum of the polymerization mixture of TBALL/PF_5 (10:3) in CH_2Cl_2 at −80 °C. Accumulated from 18.6 to 19.9 h after initiation.

There are several reports of complexation of Lewis acids with sugar derivatives, including levoglucosan[15,16] and the complexation of PF_5 with a bicyclic ether.[14]

Polymer Structure. The polymers obtained at −40 °C exhibited large positive specific rotations from +123.5° to +138.6°, and those obtained at −60 to −78 °C showed rotations from +134.6° to +146.0°, indicating a high α-configuration. In Figure 2, 400-MHz ^1H NMR spectra of TBALL and the polymer are shown. In the polymer spectrum, the H-1 proton appears as a single peak at 4.94 ppm and the other protons also appear as separate absorptions, the assignment of which was performed by using the spin–spin decoupling method, clearly indicating that the polymer is composed of a single, stereoregular structure.

As the H-1, H-2, and H-3 protons of the polymer do not exhibit spin–spin splitting, these three protons take dihedral angles calculated by the Karplus equation,[17] that is, approximately 80°.

As the 100-MHz ^{13}C NMR spectra of the monomer and polymer show in Figure 3, all the pyranose-ring carbon

Table III
^1H and ^{13}C Chemical Shifts (ppm) of TBALL and Poly(TBALL)[a]

substance	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
TBALL	5.42 (d)	3.69 (m)	3.60 (t)	3.63 (q)	4.61 (q)	3.47 (q)	3.61 (q)
poly(TBALL)	4.94 (s)	3.28 (s)	3.88 (s)	3.50 (d)	3.78 (d)	3.40 (d)	3.03 (d)

substance	C-1	C-2	C-3	C-4	C-5	C-6	CH_2Ph
TBALL	100.89	75.22	72.85	75.33	74.58	65.13	73.47, 72.62, 71.02
poly(TBALL)	97.15	77.63	74.30	74.76	65.96	65.96	74.96, 71.26, 69.70

[a] Solvent: $CDCl_3$ (^1H), CD_2Cl_2 (^{13}C).

Table IV
Copolymerization of TBALL with 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (LGTBE)[a]

no.	LGTBE feed, g	TBALL feed, g	TBALL feed, mol fract	time, h	conv, %	mol fract of TBALL in copolymer[b]	$[\alpha]^{25}_D$,[c] deg	$10^{-3}\bar{M}_n$[d]
C-1	0.45	0.15	0.25	1.7	23.3	0.11	+114.7	
C-2	0.30	0.30	0.50	23.0	47.3	0.31	+116.5	1.67
C-3	0.15	0.45	0.75	23.0	18.1	0.55	+123.8	1.88
C-4	0.10	0.50	0.83	46.0	7.8	0.67	+124.3	

[a] Catalyst: PF_5, 2 mol % to total monomers; temperature, −60 °C; solvent: CH_2Cl_2, 2 mL. [b] Calculated by ^{13}C NMR spectroscopy. [c] Measured in $CHCl_3$ (*c* 1). [d] Determined by gel permeation chromatography.

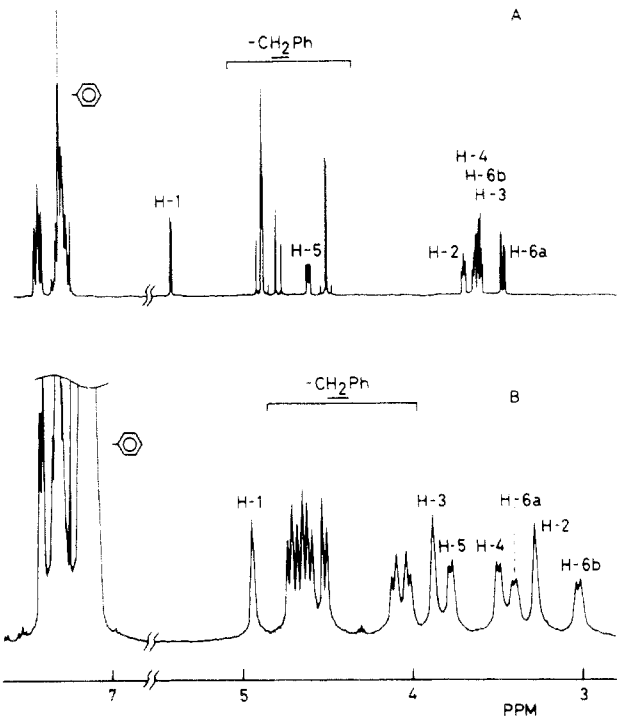


Figure 2. 400-MHz ^1H NMR spectra of (A) TBALL monomer and (B) poly(TBALL) (in $CDCl_3$).

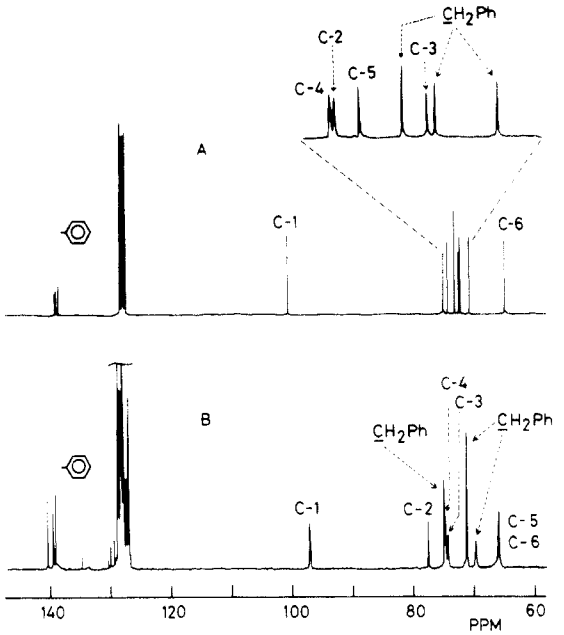


Figure 3. 100-MHz ^{13}C NMR spectra of (A) TBALL monomer and (B) poly(TBALL) (in CD_2Cl_2).

signals of the polymer appear as sharp peaks assignable to a single structure. Peak assignments of the ^1H and ^{13}C NMR spectra are given in Table III. The assignment of the ^{13}C absorptions was carried out by using the heterospin decoupling method.

Taking into account the high positive specific rotation and the structural analysis by NMR, it was concluded that poly(TBALL) is a highly stereoregular 2,3,4-tri-*O*-benzyl-(1→6)-α-D-allopyranan.

Ring-Opening Polymerizability of TBALL. Of the eight possible 1,6-anhydro-β-D-hexopyranoses, the tri-*O*-benzylated 1,6-anhydro-β-D-manno-, -D-gluco-, and -D-galactopyranoses have high polymerizabilities, while the tri-*O*-benzylated 1,6-anhydro-β-D-altropyranose exhibits almost no homopolymerizability. Taking into account the polymer conversion and the degree of polymerization, it was considered that the polymerizability of TBALL is similar to that of the galactose derivative.

Table V
Monomer Reactivity Ratios of Tri-*O*-benzylated (or -*p*-methylbenzylated) 1,6-Anhydro-β-D-hexopyranose Copolymerizations Calculated by the Kelen-Tüdös Method[a]

monomer 1	r_1	r_2[b]	$1/r_2$[c]	ref
mannose	9.58	0.95	1.05	8
galactose	0.31	1.41	0.71	8
altrose	0.06	1.52	0.66	6
allose	0.44	2.69	0.37	this paper

[a] Catalyst, PF_5; solvent, CH_2Cl_2; temperature, −60 °C [b] $=r_{glucose}$. [c] $=k_{21}/k_{22}$

To collect further information on the reactivity, copolymerizations of TBALL and 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (LGTBE) were carried out with PF_5 as catalyst at −60 °C, and the results are summarized in Table IV.

As the mole fraction of TBALL in the feed increased, the conversion decreased and the specific rotation of the

Table VI
Debenzylation of 2,3,4-Tri-O-benzyl-α-D-allopyranan

	starting polymer			debenzylated polymer		
no.	$[\alpha]^{25}_D$,[a] deg	$10^{-3}\bar{M}_n$	reacn scale, mg	yield, %	$[\alpha]^{25}_D$,[b] deg	$[\eta]^{25}$,[b] dL/g
D-1	+138.0	36.7	100	74.4	+80.5	
D-2	+135.8	32.6	217	90.5	+80.9	
D-3	+140.9	53.4	684	82.5	+90.8	0.056

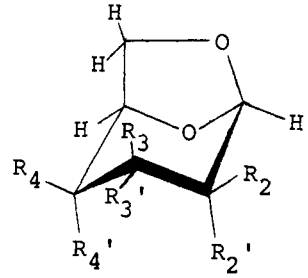
[a] In chloroform. [b] In water, before freeze-drying.

copolymer increased. The mole fraction of the TBALL unit in the copolymer was less than that of TBALL in the feed.

The composition of the copolymers was estimated by using ^{13}C NMR spectra, and the monomer reactivity ratios were calculated by means of the Kelen–Tüdös equation,[18,19] as shown in Table V; also included in Table V are results for other benzylated 1,6-anhydro sugars.

In the copolymerization of TBALL with LGTBE, $r_{TBALL} = 0.44$ and $r_{LGTBE} = 2.69$, meaning that the reactivity of the allose monomer is smaller than that of the glucose monomer.

As shown in Table V, the reciprocal of r_2 ($=k_{21}/k_{22}$), that is, the relative reactivity to the glucose-propagating end, is in the following order: mannose > glucose > galactose > altrose > allose. Except for the altrose derivative, which has no homopolymerizability, this order agrees with the order of reactivity that was obtained from the homopolymerization experiments.



1,6-anhydro sugar

gluco: $R_2 = R_3' = R_4 = H$, $R_2' = R_3 = R_4' = OBn$
manno: $R_2' = R_3' = R_4 = H$, $R_2 = R_3 = R_4' = OBn$
galacto: $R_2 = R_3' = R_4' = H$, $R_2' = R_3 = R_4 = OBn$
altro: $R_2' = R_3 = R_4 = H$, $R_2 = R_3' = R_4' = OBn$
allo: $R_2 = R_3 = R_4 = H$, $R_2' = R_3' = R_4' = OBn$

The three reactive 1,6-anhydro sugars have an axial hydroxyl at the 3-position, while the less reactive allose and altrose derivatives have an equatorial hydroxyl at the 3-position. It might be assumed that there is repulsion between the oxygen of axial 3-OBn and the O-6 oxygen of the 1,6-anhydro ring and that this works to some extent as a driving force of 1,6-anhydro ring scission.

Debenzylation of 2,3,4-Tri-O-benzyl-(1→6)-α-D-allopyranan into (1→6)-α-D-Allopyranan. Debenzylation of the benzylated polymer was carried out with sodium in liquid ammonia, as shown in Table VI.

The free polysaccharide (1→6)-α-D-allopyranan was insoluble in water, dimethyl sulfoxide, and other solvents examined but soluble in dimethylformamide (DMF)–N_2O_4 mixture. Although synthetic (1→6)-α-D-galactopyranan, which was insoluble in many solvents, was soluble in DMF–N_2O_4 and 10% LiOH–0.5% borate,[5] the synthetic (1→6)-α-D-allopyranan was not soluble in the latter solvent.

The ^{13}C NMR spectrum of (1→6)-α-D-allopyranan was measured on the DMF–N_2O_4 solution, as shown in Figure 4. Individual carbons appear as single peaks, indicating

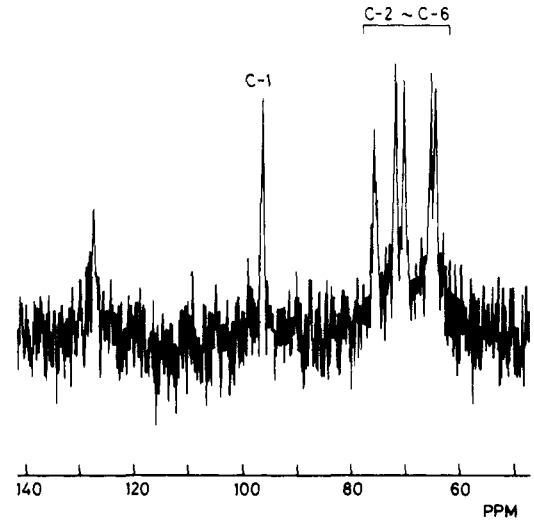


Figure 4. 25-MHz ^{13}C NMR spectrum of (1→6)-α-D-allopyranan (in DMF–N_2O_4 mixture).

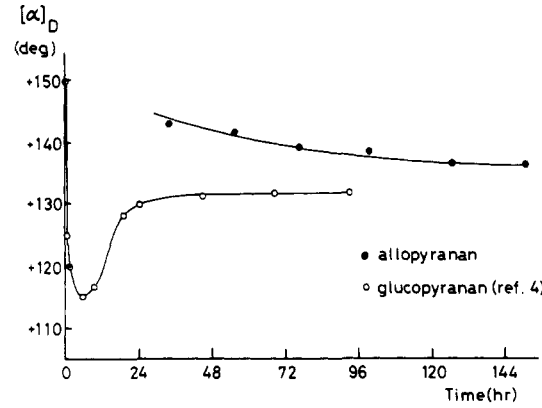


Figure 5. Change in specific rotation during oxidation of 1,6-glycan with sodium periodate.

that the polysaccharide is highly stereoregular.

The (1→6)-α-linkage of the polysaccharide was examined by periodate oxidation, as were (1→6)-α-D-mannopyranan[4] and -galactopyranan,[5] because all the (1→6)-α-D-glycopyranans must give the same oxidized polysaccharide derivative after scission of the C–C bonds between C-2 and C-3 and C-3 and C-4. The $[\alpha]_D$ of the oxidized D-allopyranan approached that of the oxidized (1→6)-α-D-glucopyranan, +134° (Figure 5). This result indicates that the oxidized polymers obtained from both D-allopyranan and (1→6)-α-D-glucopyranan have the same (1→6)-α-linked structure.

Experimental Section

Synthesis of TBALL. 1,2:5,6-Di-O-isopropylidene-α-D-*ribo*-hexofuranose-3-ulose, which had been prepared by the reaction of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose[20] with KIO_4 and RuO_2, was reduced with $NaBH_4$ to afford 1,2:5,6-di-O-isopropylidene-α-D-allofuranose according to the procedure of Baker et al.[21] Hydrolysis of 1,2:5,6-di-O-isopropylidene-α-D-allofuranose gave D-allose.[21] D-Allose was acetylated with acetic anhydride and pyridine to give pentaacetyl-β-D-allopyranose. 1,6-Anhydro-2,3,4-tri-O-benzyl-β-D-allopyranose (TBALL) was synthesized from pentaacetyl-β-D-allopyranose as starting material according to a modification of the method of Zemplén et al.[22] A mixture of 1,6-anhydro-2,3,4-tri-O-acetyl-β-D-allopyranose (6.0 g), benzyl chloride (90 mL), and powdered KOH (20 g) was vigorously stirred at 100–105 °C for 4 h. After a usual workup procedure, crude crystals of TBALL were obtained. Recrystallizations of TBALL were carried out a few times from ethanol and finally from *n*-butyl chloride. Yield based on pentaacetyl-β-D-allopyranose was 3.5%:

mp 95.0–96.0 °C; $[\alpha]^{25}_D$ −47.5° (c 1, $CHCl_3$).

Anal. Calcd for $C_{27}H_{28}O_5$: C, 74.98; H, 6.52. Found: C, 74.92; H, 6.50.

Other Materials for Polymerization. 1,6-Anhydro-2,3,4-tri-O-benzyl-β-D-glucopyranose (LGTBE) was prepared as described previously[3] and finally recrystallized from n-butyl chloride: mp 90.0–91.0 °C (lit.[12] mp 89.5–90.5 °C); $[\alpha]^{25}_D$ −31.6° (c 2.7, $CHCl_3$) (lit.[12] $[\alpha]^{25}_D$ −30.5°).

Polymerization catalysts and methylene chloride were purified as described previously.[3,13]

Polymerization. Polymerization was carried out in methylene chloride using the high-vacuum technique.[3,11] The polymerization was terminated by the addition of methanol. The polymer was purified by dissolution–reprecipitation using chloroform–petroleum ether system and was finally freeze-dried from benzene.

Debenzylation of the Polymer. 2,3,4-Tri-O-benzyl-(1→6)-α-D-allopyranan was dissolved in 1,2-dimethoxyethane, and the solution was added to liquid ammonia containing sodium at −78 °C. The reaction was allowed to continue for 1–1.5 h, followed by successive additions of ammonium chloride and water. The solution of debenzylated polymer in water was dialyzed with running water for several days. The polymer was freeze-dried from water.

Periodate Oxidation. The periodate oxidation of the free polysaccharide was carried out according to the procedure of Frechet and Schuerch.[4]

Measurements. The 40-MHz ^{31}P NMR spectrum of the polymerization system was measured by means of a JEOL PS-100 spectrometer with external phosphoric acid as reference. The 400-MHz ^1H and 100-MHz ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer in chloroform-d and methylene-d_2 chloride, respectively, with tetramethylsilane as internal standard. The 25-MHz ^{13}C NMR spectrum of (1→6)-α-D-allopyranan was measured on the DMF–N_2O_4 solution by means of a JEOL PS-100 spectrometer. Gel permeation chromatography was run on 1% solutions of polymers in chloroform by means of a Toyo Soda high-speed chromatograph (Model HLC 802UR). The number-average molecular weight determined by gel permeation chromatography was based on the standard polystyrene samples and was almost the same as the value determined by membrane osmometry. The optical rotation was measured in chloroform or water at 25 °C using a Perkin-Elmer Model 241 polarimeter.

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Mass Spectral Characterization and Thermal Decomposition Mechanism of Poly(dimethylsiloxane)

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ABSTRACT: The thermal decomposition of poly(dimethylsiloxane) (PDMSi) was studied by direct pyrolysis–mass spectrometry (DP–MS). The mass spectral data show that the pyrolytic breakdown of PDMSi, pure or containing NaOH, leads to the formation of cyclic oligomers through an intramolecular exchange process. An estimate of the pyrolysis product distribution has been performed. It has been ascertained that the addition of a catalyst in the PDMSi lowers its maximum polymer decomposition temperature (PDT) without sensibly altering the relative amounts of pyrolysis products. PDMSi contains a mixture of cyclic oligomers, formed together with the high polymer in the synthesis. The MS analysis allowed the simultaneous detection and identification of these cyclic oligomers.

Introduction

The characterization of polymers by direct pyrolysis in the mass spectrometer yields important structural information and is becoming increasingly appreciated.[1-6] Typical applications of this method include structural identification of polymers, differentiation of isomeric structures, copolymer composition and sequence analysis, identification of oligomers formed in the polymerization reaction, and identification of volatile additives contained in polymer samples.[1] Furthermore, direct pyrolysis in the MS provides unique information on the primary processes of thermal decomposition of polymers.[7-9]

In the DP–MS technique, polymers are introduced via the direct-insertion probe and the temperature is increased gradually to a point at which thermal degradation reactions occur; the volatile compounds formed are then ionized and detected.

The mass spectrum of a polymer obtained under these conditions is therefore that of a mixture of oligomers formed by pyrolysis. An advantage of this technique is that pyrolysis is accomplished under high vacuum and, if polymers contain oligomers formed in the polymerization

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