Macromolecules

Volume 14, Number 1 January–February 1981

Selective Ring-Opening Polymerization of 1,4-Anhydro-α-D-ribopyranose Derivatives and Synthesis of Stereoregular (1→4)-β-D-Ribopyranan

Toshiyuki Uryu,* Kissho Kitano, Katsuhiro Ito, Junichi Yamanouchi, and Kei Matsuzaki

Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. *Received June 11, 1980*

ABSTRACT: A new highly stereoregular 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan has been synthesized by selective ring-opening polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose (=1,5-anhydro-2,3-*O*-benzylidene-β-D-ribofuranose) with antimony pentachloride as catalyst in methylene chloride. Other catalysts, such as antimony pentafluoride and niobium pentachloride, also give the polysaccharide derivative with the (1→4)-β-D-ribopyranose structure. The use of the Lewis acids phosphorus pentafluoride, boron trifluoride etherate, and tin tetrachloride as catalysts results in production of polymers whose structures contain a mixture of α-D-ribofuranosidic and β-D-ribopyranosidic units. 1,4-Anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose has also been polymerized by antimony pentachloride to give stereoregular 2,3-*O*-isopropylidene-(1→4)-β-D-ribopyranan. The effects of catalysts, reaction time, and temperatures have been studied, but the highest number-average molecular weights of the polysaccharide derivatives are 43.0×10^3 ($\overline{DP}$ = 213) and 68.6×10^6 ($\overline{DP}$ = 398) for the benzylidene and isopropylidene derivatives, respectively. The mechanism of the stereoregular polymerization is discussed. Removal of the benzylidene group from the polysaccharide derivatives has successfully been carried out with sodium in liquid ammonia to give stereoregular (1→4)-β-D-ribopyranan, which is the first synthetic polysaccharide with the (1→4)-β-D-glycopyranose structure, and to give polyribose containing both (1→5)-α-D-ribofuranosidic and (1→4)-β-D-ribopyranosidic units. Structural analysis of the polymers is performed by ^{13}C NMR spectroscopy and optical rotation.

Until now, stereoregular polysaccharides have been obtained by selective ring-opening polymerization of several kinds of bicyclic anhydro sugars. The ring-opening polymerization of 1,6-anhydro-β-D-aldohexopyranoses proceeds through the ring opening of a five-membered ring similar to that of tetrahydrofuran, leaving a more stable six-membered pyranose ring in the polymer backbone, and provides the stereoregular polysaccharides with 1,6-α-linked D-glucopyranose structures.[1,2] In the previous investigations, we reported that a 5,6-anhydro-α-D-glucofuranose derivative which has both an oxirane ring and a five-membered furanose ring in its molecule[3,4] and a bicyclic 3,5-anhydro-α-D-xylofuranose derivative which has both a four-membered cyclic ether and a five-membered furanose ring[5] yielded stereoregular polysaccharides by ring-opening polymerization of the more reactive smaller cyclic ether ring.

On the other hand, the ring-opening polymerization of 1,4-anhydro sugar derivatives has not succeeded in producing stereoregular polysaccharides. Kops and Schuerch reported that cationic ring-opening polymerizations of 1,4-anhydro-2,3,6-tri-*O*-methyl-α-D-galactopyranose and 1,4-anhydro-2,3-di-*O*-methyl-α-L-arabinopyranose gave polymers with fairly high molecular weight but low stereoregularity, which were composed of a mixture of furanosidic and pyranosidic units in the polymer backbone,[6] in spite of the fact that the method applied was the same method as that for producing completely stereoregular (1→6)-α-D-glucose derivatives.[7,8]

Recently, Micheel et al. investigated ring-opening polymerization of benzylated 1,4-anhydro-α-D-glucopyranose in order to synthesize a 1,4-β-linked polysaccharide with a pyranose backbone.[9,10] The cationic polymerization of the monomer, however, resulted in polymers with fairly high stereoregularity but low molecular weight.

Hall and co-workers demonstrated that cationic polymerization of 2,7-dioxabicyclo[2.2.1]heptane, which is the parent ring compound of 1,4-anhydro-α-D-aldohexopyranose, readily proceeded to give a polymer composed of tetrahydrofuran structures at low temperatures, while polymers with a mixed backbone structure of tetrahydrofuran and tetrahydropyran units were obtained at high temperatures.[11]

Thus, in the ring-opening polymerizations of the 1,4-anhydro sugars and 2,7-dioxabicyclo[2.2.1]heptane, which are bicyclic acetals formed by five-membered and six-membered rings, selective ring-opening polymerization which leads to the formation of polymers with a six-mem-

0024-9297/81/2214-0001$01.00/0

Table I
Ring-Opening Polymerization of 1,4-Anhydro-2,3-*O*-benzylidene-α-D-ribopyranose into Polymers with 1,4-β-D-Ribopyranose Structures[a]

no.	catalyst	mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_D$,[b] deg	$10^{-3}\bar{M}_n$
1	$SbCl_5$	1	20	0.5	87.8	−60.9	37.9
2	$SbCl_5$	10	0	49	33.0	−39.2	2.4
3	$SbCl_5$	1	−40	8	90.6	−60.6	43.0
4[c]	$SbCl_5$	1.5	−40	7.3	76.0	−56.4	17.4
5	$SbCl_5$	2.5	−40	0.33	87.2	−59.2	26.6
6	$SbCl_5$	2.5	−40	1	86.8	−60.9	26.8
7	$SbCl_5$	2.5	−40	3	91.6	−62.2	32.5
8	$SbCl_5$	10	−40	3	56.2	−51.4	4.2
9[d]	$SbCl_5$	3	−78	24	88.4	−60.2	23.1
10	SbF_5	10	−40	0.5	82.3	−50.2	8.0
11	$NbCl_5$	1.4	0	20	17.3	−48.0	2.8
12	$NbCl_5$	2.7	0	77	81.9	−54.9	3.0
13	$NbCl_5$	4.0	0	115	75.7	−51.3	2.4
14	$NbCl_5$	8.1	−50	96	trace		
15	$Ph_3C^+SbCl_6^-$	7.6	0	27	34.6	−51.8	9.4
16	$Ph_3C^+SbCl_6^-$	15.0	0	234	31.2	−27.1	2.6
17	$(CF_3SO_2)_2O$	4.4	0	22	59.9	−8.8	3.0

[a] Monomer (0.2–0.4 g) was polymerized at a 20 w/v % monomer concentration. Solvent CH_2Cl_2. [b] Measured in a $CHCl_3$ solution (10 g/dm³). [c] Monomer (0.2 g) was polymerized in 2 mL of 1:1 $C_2H_5NO_2$–CH_2Cl_2. [d] Monomer concentration 5 w/v %.

bered pyranose backbone structure has not yet been accomplished. Accordingly, in order to prepare 1,4-β-linked polysaccharides with the pyranose backbone structure from anhydro sugars, we considered using a monosaccharide with a specific configuration, the substituents of which would sterically control the ring-opening mode.

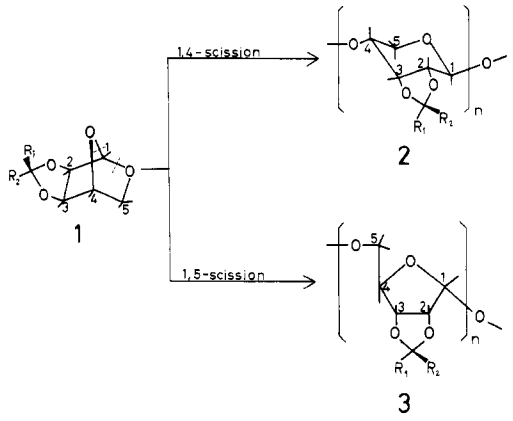
A 1,4-anhydro sugar whose remaining hydroxyls are protected by a benzylidene group is expected to have higher stereoselectivity in the ring-opening polymerization than the benzylated or methylated 1,4-anhydro-α-D-glucose and -L-arabinose because the benzylidene group forms a more rigid, cyclic acetal linkage than the benzyl and methyl ethers. D-Ribose can give a 1,4-anhydro-α-D-ribopyranose derivative in which the hydroxyls at C-2 and C-3 are able to be protected by a benzylidene or isopropylidene group because of their cis relationship. There are a few reports on the synthesis of polyribose in which the polycondensation method was used to give a polyribose bonded mainly by a 1,5-α-linkage[12] and a highly branched polyribose.[13]

In this paper, we report selective ring-opening polymerizations of 1,4-anhydro-2,3-*O*-benzylidene- and 1,4-anhydro-2,3-*O*-isopropylidene-α-D-ribopyranoses into stereoregular 2,3-*O*-benzylidene- and 2,3-*O*-isopropylidene-(1→4)-β-D-ribopyranans, respectively, and also report synthesis of (1→4)-β-D-ribopyranan, which is the first synthetic polysaccharide consisting exclusively of a 1,4-β-linked D-glycopyranose backbone similar to the backbone of cellulose, by removing benzylidene groups from the benzylidenated polymer. In addition, synthesis and structural analysis of polyriboses which are composed of a mixture of α-D-ribofuranosidic and β-D-ribopyranosidic units in the polymer backbone are described.

Results and Discussion

Cationic Polymerization of 1,4-Anhydro-2,3-*O*-benzylidene-α-D-ribopyranose. 1,4-Anhydro-2,3-*O*-benzylidene-α-D-ribopyranose (ABRP) (1) is equally regarded as 1,5-anhydro-2,3-*O*-benzylidene-β-D-ribofuranose. As shown in Scheme I, when the 1,4-anhydro ring of ABRP, the C-1 carbon of which has an α configuration, is stereoregularly opened by an oxonium ion mechanism, as with the polymerization of 1,6-anhydro sugars,[14,15] 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan (2) will be formed by inversion of the C-1 carbon during the ring-opening polymerization, being expected to show negative optical

Scheme I
Ring-Opening Modes of 1,4-Anhydro-α-D-ribopyranose



rotation. On the other hand, when the 1,5-anhydro ring of ABRP, the C-1 carbon of which is regarded to have a β configuration, is stereoregularly opened, 2,3-*O*-benzylidene-(1→5)-α-D-ribofuranan (3), possibly with positive optical rotation, will be obtained.

If the ring opening of the two kinds of anhydro rings in the monomer proceeds through a carbenium ion mechanism, the polymer will be composed of a mixture of (1→4)-α- and (1→4)-β-D-ribopyranosidic and of (1→5)-α- and (1→5)-β-D-ribofuranosidic units.

When polymerizations of ABRP were carried out by cationic initiators in the temperature range from +20 to −78 °C, the monomer was found to be readily polymerized, giving polymers with optical rotations ranging from positive to negative. Although the monomer having an asymmetric benzylidene methine carbon was obtained as a mixture of about 78% anti and 22% syn isomers, it was used for polymerizations without separation of the isomers because no significant difference in the polymerization behavior between the isomers was observed, as described later.

Table I shows the results of polymerizations by catalysts which gave polymers with negative optical rotations. When antimony pentachloride was used at a concentration of 1–2.5 mol % to the monomer, the polymerization for 0.3–3 h at −40 °C gave polymers with specific rotations of −59

Table II
Ring-Opening Polymerization of 1,4-Anhydro-2,3-*O*-benzylidene-α-D-ribopyranose into Polymers with Plus Specific Rotations[a]

no.	catalyst	mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_D$,[b] deg	$10^{-3}\bar{M}_n$
18	PF_5	0.26	0	27.5	13.0	+48.7	5.1
19	PF_5	1	0	1	46.0	+48.1	10.3
20	PF_5	2	0	5.5	46.4	+40.4	5.1
21	PF_5	10	0	66	58.8	+10.6	2.6
22	PF_5	1	−40	18	39.5	+62.8	10.6
23	PF_5	1	−40	41	46.4	+63.2	12.5
24	PF_5	2	−40	1	48.0	+52.8	6.6
25	PF_5	2	−40	3	62.5	+58.9	9.5
26	PF_5	2	−40	11	67.9	+60.9	7.6
27[c]	PF_5	2	−40	22	63.9	+64.5	10.1
28[d]	PF_5	2	−40	18	35.9	+35.1	3.7
29	PF_5	2	−40	41	80.8	+61.3	12.8
30	PF_5	4	−40	1	61.9	+56.1	6.0
31	PF_5	4	−40	19.5	75.7	+61.2	9.8
32	PF_5	6	−40	3	70.9	+62.8	9.2
33	$BF_3 \cdot O(C_2H_5)_2$	2.5	0	7.5	24.2	+47.8	7.8
34	$BF_3 \cdot O(C_2H_5)_2$	10	0	4	56.3	+48.1	19.1
35	$BF_3 \cdot O(C_2H_5)_2$	10	0	22	77.0	+47.9	15.1
36	$BF_3 \cdot O(C_2H_5)_2$	10	−15	22	69.0	+53.4	15.5
37	$BF_3 \cdot O(C_2H_5)_2$	5	−20	59	47.9	+60.6	13.8
38	$SnCl_4$	5	0	23	86.2	+46.7	13.5
39[e]	PCl_5	3	0	168	0		
40[e]	$Ph_3C^+PF_6^-$	11.5	0	27	trace		

[a] Monomer (0.3 g) was polymerized at a 20 w/v % monomer concentration. Solvent CH_2Cl_2. [b] Measured in a $CHCl_3$ solution (10 g/dm³). [c] Monomer (0.4 g) was polymerized in 2 mL of CH_2Cl_2. [d] Monomer (0.2 g) was polymerized in 2 mL of 1:1 $C_2H_5NO_2$-CH_2Cl_2. [e] Monomer (0.2 g) was polymerized in 1 mL of CH_2Cl_2.

to −62° in 76–92% yield (nos. 3, 5–7). Higher catalyst concentration caused a decrease in the polymer yield (nos. 2, 8).

As described in the next section, NMR spectra of the polymers revealed that the polymers with $[\alpha]_D$ ranging from −59 to −62° were composed exclusively of 1,4-β-linked D-ribopyranose units.

Number-average molecular weights of the poly(ABRPs) obtained with $SbCl_5$ catalyst were high. With 2.5 mol % $SbCl_5$, $\bar{M}_n$ ranged from 26.6×10^3 ($\overline{DP}_n$ = 121) to 32.5×10^3 ($\overline{DP}_n$ = 148) and increased with polymerization time, whereas with 10 mol % $SbCl_5$, $\bar{M}_n$ was low, in the range 2.4×10^3 to 4.2×10^3. The highest molecular weight of 43.0×10^3 ($\overline{DP}_n$ = 213) was attained with 1 mol % $SbCl_5$ as catalyst at −40 °C.

Of the various kinds of cationic catalysts for the ring-opening polymerization of 1,6-anhydro-β-D-glucopyranose derivatives, $SbCl_5$ has been known to be a less effective catalyst than the powerful Lewis acids phosphorus pentafluoride and antimony pentafluoride.[16] Antimony pentafluoride catalyst also gave poly(ABRP) with a negative specific rotation (−50.2°), which was about 10° smaller in absolute value than the largest negative $[\alpha]_D$, and with low molecular weight (8.0×10^3) (no. 10). It is assumed that the rate of polymerization by SbF_5 catalyst was too fast to effect complete stereoregulation under the conditions employed.

Stable carbenium ion salts such as triphenylmethyl and tropylium hexachloroantimonates were known to be effective cationic catalysts for alkyl vinyl ethers,[17,18] but in the polymerization of the 1,6-anhydro sugar, triphenylmethyl hexachloroantimonate catalyst provided a polymer with low stereospecificity in low yield.[16] However, the polymerization of ABRP by $(C_6H_5)_3C^+SbCl_6^-$ gave a polymer with specific rotation of −51.8° in 35% conversion, indicating that the triphenylmethyl cation was not as effective as $SbCl_5$ catalyst, but the steric control by the triphenylmethyl hexachloroantimonate catalyst was almost the same as that by $SbCl_5$.

Apparently, bulky gegenanions such as $SbCl_6^-$ and SbF_6^- control the stereoregulation which leads to the formation of polymers with β-D-ribopyranose structures. Since niobium pentachloride is also expected to form the bulky gegenanion $NbCl_6^-$ in the course of the ring-opening polymerization, the polymerization by $NbCl_5$ catalyst was carried out to elucidate the effects of bulkiness of the gegenanion on the stereoregulation. Catalytic behavior of niobium pentachloride, which produced polymers with large negative specific rotations (−48 to −55°), was similar to that of antimony pentachloride, but the former catalyst gave lower molecular weight polymers than the latter catalyst (nos. 11–13). Since a low rate of polymerization by $NbCl_5$ was observed, the low molecular weight might be caused by transfer and termination reactions occurring more often in the polymerization by $NbCl_5$ than by $SbCl_5$.

Table II summarizes the results of polymerizations by catalysts which gave poly(ABRPs) with positive optical rotations. In contrast with $SbCl_5$ catalyst, phosphorus pentafluoride catalyst provided polymers with positive specific rotations ranging from +10.6 to +64.5°. The polymer with high specific rotations (+62.8 to +63.2°) was obtained by 1 mol % PF_5 catalyst at −40 °C, though the polymer yield was low (46%) even for the long polymerization time of 41 h. When the amount of PF_5 was increased to 2 mol %, the highest specific rotation (+64.5°) and the highest polymer yield (81%) were attained at longer polymerization times, but the yield with PF_5 catalyst was lower than that obtained with $SbCl_5$ catalyst.

The cause for the low yield of polymers is attributable to the formation of a dimer, which was formed in approximately 10% yield when the polymerization was performed with 2 mol % PF_5 catalyst. The structure of the dimer was revealed by NMR spectroscopy to be the same as that of a cyclic dimer formed during synthesis of ABRP from D-ribose, that is, di(2,3-*O*-benzylidene-β-D-ribofuranose)-1,5′:1′,5-dianhydride.[19]

Molecular weights of the polymers obtained with PF_5 ranged from 2.6×10^3 to 12.8×10^3 and higher molecular

Table III
^{13}C Chemical Shifts of 1,4-Anhydro-2,3-*O*-benzylidene-α-D-ribopyranose, 2,3-*O*-Benzylidene-Protected Poly(D-riboses), and Poly(D-riboses)

	C-1	C-2	C-3	C-4	C-5	CHC_6H_5
1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose	100.81[a]	81.93	79.98	79.98	63.84[a]	106.76[a]
	99.88[b]	79.98	77.74		63.16[b]	105.63[b]
2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan	108.71	86.22	83.01	85.30	69.35	106.32
		84.86	82.08			104.71
poly(2,3-*O*-benzylidene-D-ribose) with mixed	103.31 (F)[c]	80.49 (F)	79.59 (F)		68.07 (F)	106.74 (F)
structures (mainly 2,3-*O*-benzylidene-(1→5)-	108.58 (P)	86.24 (P)	83.10 (P)	85.43 (P)	69.39 (P)	106.37 (P)
α-D-ribofuranan)		84.84 (P)	82.32 (P)			104.60 (P)
(1→4)-β-D-ribopyranan	107.98	74.62	71.69	81.74	70.13	
poly(D-ribose) with mixed structures (mainly	102.85 (F)	71.54 (F)	70.37 (F)	83.59 (F)	68.57 (F)	
(1→5)-α-D-ribofuranan)	108.17 (P)	74.66 (P)	71.93 (P)	81.69 (P)	70.37 (P)	

[a] Anti. [b] Syn. [c] F, furanosidic unit; P, pyranosidic unit.

weight was attained with lower catalyst concentrations and longer times. However, the molecular weight of dextrorotatory poly(ABRPs) was generally lower than that of levorotatory polymers obtained with $SbCl_5$.

Boron trifluoride etherate catalyst showed somewhat different results from PF_5 catalyst. When the polymerization of ABRP was performed with 5–10 mol % BF_3·OEt_2 catalyst at 0 to −20 °C, the polymer yield (48–77%) was almost equivalent to that for PF_5, but the specific rotation, +47.9 to +60.6°, was a little lower whereas the molecular weight (mostly 13.5×10^3 to 19.1×10^3) was higher than for PF_5 catalyst. Tin tetrachloride catalyst also gave a dextrorotatory polymer with $\bar{M}_n$ of 13.5×10^3.

Evidently large differences in the specific rotation of polymers obtained under various polymerization conditions indicate that the opening mode of anhydro rings mainly depends on the kind of catalyst, and a large negative or positive specific rotation implies that either β-D-ribopyranosidic or α-D-ribofuranosidic units are predominant in the backbone structure of the polymers.

Structure of the Polysaccharide Derivatives. Discrimination between β-D-ribopyranosidic and α-D-ribofuranosidic structures was attempted by means of ^{13}C and ^{1}H NMR spectroscopy. ^{13}C NMR spectra of the monomer and the poly(ABRPs) prepared by $SbCl_5$ and PF_5 catalysts are shown in Figure 1.

Part of the complexity of the NMR spectra resulted from the syn and anti configurations of the asymmetric benzylidene methine carbon. For the monomer, carbons C-1, C-2, C-3, and C-5 exhibit peak splittings in which absorptions for the anti configuration were assigned at lower magnetic field than those for the syn configuration by comparison with the ^{1}H NMR spectra.[20] On the other hand, the ^{13}C NMR spectra of the polymers do not indicate any peak splittings due to the syn and anti configurations. The splitting of the peak due to the benzylidene methine carbon seems to be caused by a conformational difference. A conformational analysis of the polymers obtained from the pure syn and anti monomers is in progress.

Since there was little difference in the rate of polymerization between syn and anti ABRPs, measured from the rate of consumption of the two monomers by means of NMR spectroscopy, it was deduced that polymerizabilities of the isomers varied little with steric structure of the protective group.

The analysis of ^{13}C NMR absorptions of poly(ABRP) was performed by reference to the assignment of ^{13}C NMR spectra of D-ribofuranoses, D-ribopyranoses, and their derivatives,[21–24] as given in Table III.

In spectrum 1B of the poly(ABRP) prepared by $SbCl_5$ catalyst, the C-1 and C-5 carbons each show a single peak, whereas in spectrum 1C of the polymer prepared by PF_5 catalyst the C-1 and C-5 carbons each show two peaks. For

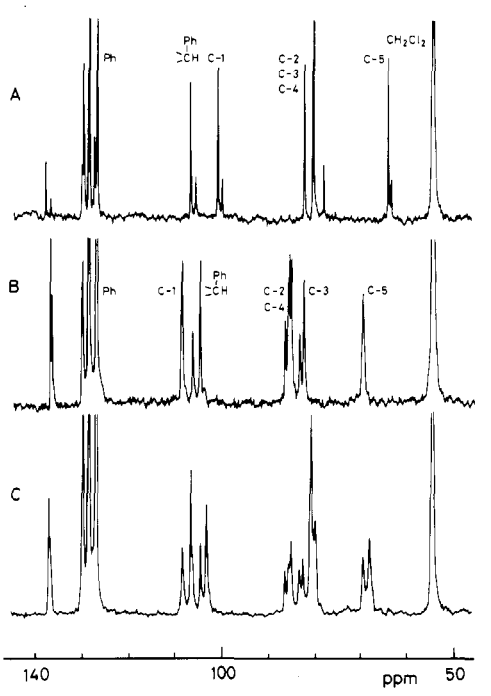


Figure 1. ^{13}C NMR spectra of (A) 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose, (B) 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan prepared by $SbCl_5$ ($[\alpha]_D$ −60.6°), and (C) poly(1,4-anhydro-2,3-*O*-benzylidene-D-ribopyranose) prepared by PF_5 ($[\alpha]_D$ +40.4°) (CH_2Cl_2 as solvent).

the polymers obtained with PF_5 catalyst, absorptions due to C-2, C-3, and C-4 carbons consist of seven peaks ranging from 85.7 to 79.0 ppm, of which five peaks ranging from 85.7 to 81.7 ppm also appear in the spectrum of the polymer prepared by $SbCl_5$ catalyst. Therefore, it was made clear that the levorotatory polymer prepared by $SbCl_5$ catalyst has a stereoregular structure with a D-ribopyranose or D-ribofuranose backbone, whereas the dextrorotatory polymer prepared by PF_5 catalyst has a mixed D-ribofuranosidic and D-ribopyranosidic structure.

^{1}H NMR spectroscopy confirmed the above finding on the polymer structure, as shown in Figure 2. In the monomer spectrum, the benzylidene methine proton signal indicates two peaks at 6.22 and 5.73 ppm due to the anti and syn configurations, respectively.[20] It is seen in the 270-MHz ^{1}H spectrum 2B of the polymer prepared by $SbCl_5$ that, although the benzylidene methine proton shows two peaks at 5.94 and 5.68 ppm in analogy with its ^{13}C NMR absorption and the H-1 proton indicates two closely spaced peaks (5.22 and 5.20 ppm), the polymer has a sterically regular structure. The H-5 and H-5′ protons, which are magnetically nonequivalent, appear separately as multiplets at 3.69 and 3.55 ppm, exhibiting coupling

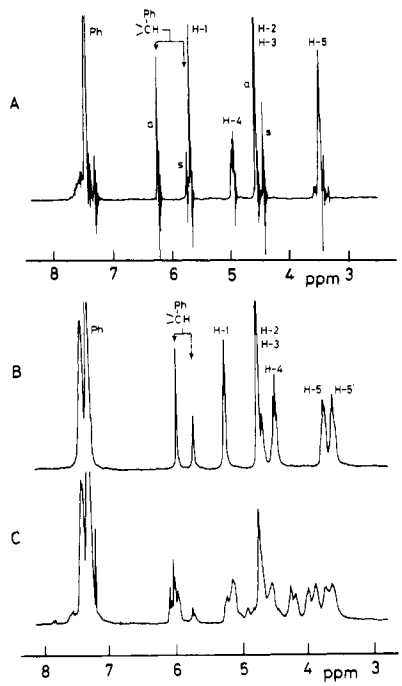


Figure 2. 100-MHz ^{1}H NMR spectrum of (A) 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose and 270-MHz ^{1}H NMR spectra of (B) 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan prepared by $SbCl_5$ ($[\alpha]_D$ −62.2°) and (C) poly(1,4-anhydro-2,3-*O*-benzylidene-D-ribopyranose) prepared by PF_5 ($[\alpha]_D$ +63.2°) ($CDCl_3$ as solvent).

with the H-4 proton. The assignment of the H-4 proton at 4.43 ppm was carried out by means of a decoupling method.

In spectrum 2C of the polymer obtained with PF_5 catalyst, additional absorptions for protons other than those appearing in the spectrum of the polymer obtained with $SbCl_5$ were seen.

Methyl α- and β-D-ribofuranosides, which are considered to be model compounds for a polymer with a D-ribofuranose backbone, show $[\alpha]_D$ of +146 and −63°, respectively, while methyl α- and β-D-ribopyranosides, which are model compounds for a polymer with a D-ribopyranose backbone, show $[\alpha]_D$ of +103 and −105°, respectively.[25]

Hence, the specific rotation of −62° of the stereoregular polymer obtained with $SbCl_5$ catalyst indicates a β configuration. Taking into account the reaction path shown in Scheme I, which leads to the formation of levorotatory polymer, we concluded that this polymer was exclusively composed of 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan. Since the levorotatory polymers prepared by antimony pentafluoride and niobium pentachloride catalysts showed almost the same spectra as those prepared by $SbCl_5$ catalyst, they also have a (1→4)-β-D-ribopyranose backbone.

For the polymer with a specific rotation of +63°, the ^{13}C and ^{1}H NMR spectra show that the backbone of the polymer is composed of two kinds of structures. One structure, a minor structure, is found to consist of β-D-ribopyranosidic units by comparing the spectra with those of the polymer obtained with $SbCl_5$ catalyst. Considering the high positive specific rotation of the polymer and the ease of acidic hydrolysis of the polymer that is characteristic of furanoside polymers,[26] we conclude that the other structure consists of α-D-ribofuranosidic units.

The fraction of the two units was determined by means of ^{13}C NMR spectroscopy. As shown in Figure 3, ^{13}C NMR absorptions of the C-5 carbons of polymers with various specific rotations consist of two peaks of different intensities at 68.67 and 67.40 ppm which are due to C-5 carbons

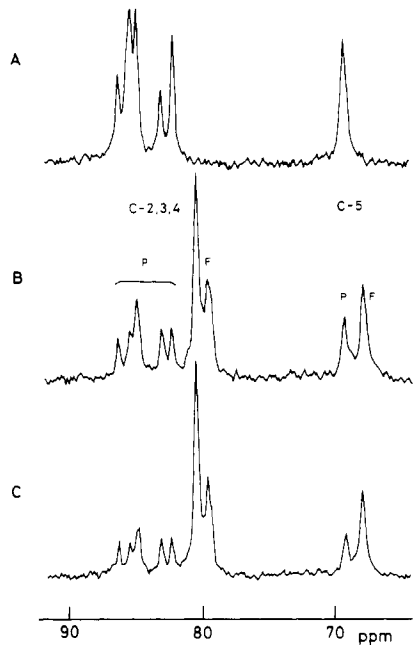


Figure 3. Expanded ^{13}C NMR spectra of poly(1,4-anhydro-2,3-*O*-benzylidene-D-ribopyranoses) prepared by (A) $SbCl_5$ ($[\alpha]_D$ −60.9°), (B) $SnCl_4$ ($[\alpha]_D$ +46.7°), and (C) PF_5 ($[\alpha]_D$ +63.2°). F, furanosidic unit; P, pyranosidic unit (CH_2Cl_2 as solvent).

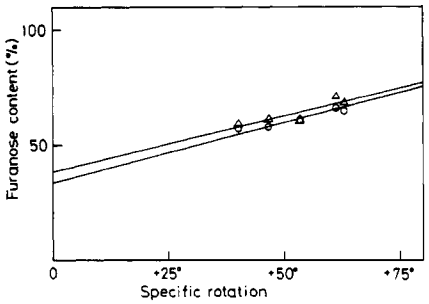


Figure 4. Plot of furanose content determined from ^{13}C NMR absorptions against specific rotation of dextrorotatory poly(1,4-anhydro-2,3-*O*-benzylidene-D-ribopyranoses). (△) from C-5 carbon; (○) from C-2 to C-4 carbons.

in β-D-ribopyranosidic and α-D-ribofuranosidic units, respectively. Similarly, the absorptions due to C-2 to C-4 carbons are divided into two regions representing the β-D-ribopyranosidic and α-D-ribofuranosidic units. The polymers with $[\alpha]_D$ of +40 to +63° had α-D-ribofuranose contents of 57–66%.

In Figure 4, the fractions of α-D-ribofuranosidic units, which were calculated from both the C-5 carbon and C-2 to C-4 carbon absorptions, are plotted against the specific rotation of the polymers, indicating a linear relationship between them. When the fraction of α-D-ribofuranosidic units is extrapolated to zero, the C-5 and C-2 to C-4 carbon absorptions give −78 and −65°, respectively. Since the observed specific rotation for the polymer solely with β-D-ribopyranose structure is −62°, the absorptions due to the C-2 to C-4 carbons can provide more precise α-D-ribofuranosidic content than the C-5 carbon absorptions.

Extrapolation of the fraction of α-D-ribofuranosidic units to unity gave the specific rotation of +127°, which must correspond to a pure α-D-ribofuranose structure.

Polymerization of 1,4-Anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose and Structural Analysis of the Polymer. The finding that there was almost no difference in polymerizability and stereoregulation between the syn and anti isomers of 1,4-anhydro-2,3-*O*-

Table IV
Ring-Opening Polymerization of 1,4-Anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose by Cationic Catalysts[a]

no.	catalyst	mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_D$,[b] deg	$10^{-3}\bar{M}_n$
1	$SbCl_5$	1	−40	20	79.4	−112.3	47.9
2[c]	$SbCl_5$	2	−40	3	54.0	−102.9	32.5
3	$SbCl_5$	1	−60	20	85.4	−109.3	68.6
4[d]	$SbCl_5$	1	−78	20	58.1	−23.3	27.0
5	PF_5	2	−40	3	40.0	−3.3	12.8
6	PF_5	2	−40	20	22.7	−25.3	11.9
7	PF_5	2	−40	45.5	12.9	−31.9	10.3
8	PF_5	1	−60	12	47.9	+7.5	12.6
9	$BF_3 \cdot O(C_2H_5)_2$	5	−30	45.5	78.6	−8.1	35.0

[a] Monomer (0.2 g) was polymerized at a 40 w/v % monomer concentration. Solvent CH_2Cl_2. [b] Measured in a $CHCl_3$ solution (10 g/dm³). [c] Monomer concentration 66.7 w/v %. [d] Monomer concentration 20 w/v.

benzylidene-α-D-ribopyranose suggests that there is almost no participation in the stereoregulation from the C_6H_5CH moiety in the benzylidene group. To elucidate further the role of the substituent of the C-2 and C-3 carbons on the stereoregulation, we carried out ring-opening polymerization of 1,4-anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose (AIRP) with cationic catalysts. The results of polymerizations are shown in Table IV.

With $SbCl_5$ catalyst, poly(AIRPs) with $[\alpha]_D$ of −103 to −112° were obtained in 54–85% conversions, whereas poly(AIRPs) which were prepared by PF_5 and $BF_3 \cdot OEt_2$ catalysts indicate specific rotations ranging from −25 to +7.5°.

The structure of the polymers was examined by ^{13}C NMR spectroscopy. It can be seen from Figure 5 that poly(AIRP) prepared by $SbCl_5$ catalyst has a stereoregular structure because absorptions due to individual carbons appear as single peaks (Figure 5B). Taking into account the specific rotation of −112°, which must correspond to the β configuration, we conclude the poly(AIRP) is 2,3-*O*-isopropylidene-(1→4)-β-D-ribopyranan.

On the other hand, the NMR spectrum (Figure 5C) of the polymer prepared by PF_5 catalyst indicates that absorptions due to individual carbons consist of two to three peaks, one of which has almost the same chemical shift as that of the corresponding carbons of the polymer shown in Figure 5B. Although carbons such as C-5 and quaternary carbon exhibit three absorptions, it seems that there are no more than two kinds of backbone units, that is, α-D-ribofuranosidic and β-D-ribopyranosidic units. For the quaternary carbon, an absorption at 112.66 ppm is clearly due to β-D-ribopyranosidic units, and the other two peaks at 115.49 and 115.10 ppm may be attributable to α-D-ribofuranosidic units with different neighboring sequences. It can be deduced from the peak intensity and optical rotation of the poly(AIRPs) that both peaks at 115.49 and 115.10 ppm correspond to the monomeric units having positive specific rotations.

Accordingly, it was revealed that the 1,4-anhydro-α-D-ribopyranose derivatives in which the C-2 and C-3 carbons are protected by either the benzylidene or isopropylidene group can be polymerized by catalysts such as antimony pentachloride through selective stereoregular 1,4-anhydro ring opening to give the (1→4)-β-D-ribopyranan derivatives.

The molecular weight of poly(AIRPs) obtained by $SbCl_5$, which ranged from 27.0×10^3 to 68.6×10^3 ($\overline{DP}_n$ = 398), was generally higher than that of poly(ABRPs) obtained under similar conditions. This observation may be explained by a greater rate of polymerization of AIRP with smaller protective groups because in the case of 1,6-anhydro sugar very high molecular weight polymers were obtained from an anhydro-D-glucose with small protective groups.[27]

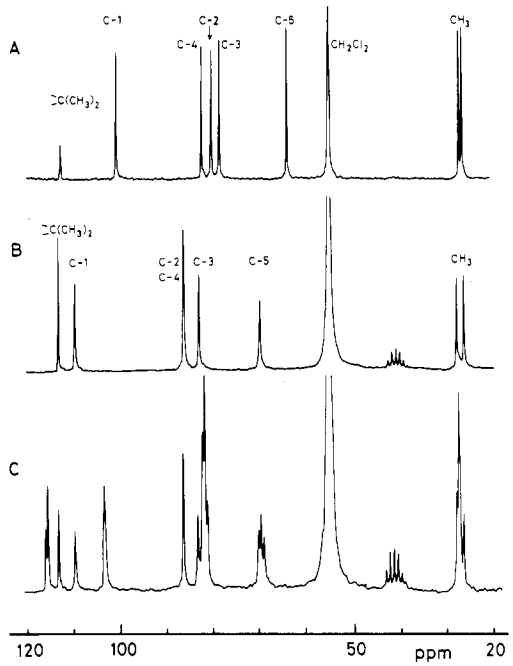


Figure 5. ^{13}C NMR spectra of (A) 1,4-anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose, (B) 2,3-*O*-isopropylidene-(1→4)-β-D-ribopyranan prepared by $SbCl_5$ ($[\alpha]_D$ −112.3°), and (C) poly(1,4-anhydro-2,3-*O*-isopropylidene-D-ribopyranose) prepared by PF_5 ($[\alpha]_D$ +7.5°) (CH_2Cl_2 as solvent).

Mechanism of Polymerization. The formation of stereoregular 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan by $SbCl_5$ catalyst indicates that the polymerization proceeds by an oxonium ion mechanism. Polymerization steps of ABRP by $SbCl_5$ catalyst can be illustrated as in Scheme II.

High stereoselectivity of $SbCl_5$ catalyst is supposed to be caused by (1) selective coordination of bulky $SbCl_5$ to oxygen bonded to the C-1 and C-4 carbons of ABRP, probably because of less steric hindrance of the oxygen, (2) selective ion pairing of $SbCl_6^-$ with the oxonium ion formed by the 1,4-linked oxygen at the growing chain end, and (3) exclusive attachment of the 1,4-linked oxygen of ABRP monomer to the C-1 carbon of growing chain end.

Since $SbCl_5$ has to some extent a tendency to dissociate into $SbCl_4^+$ and $SbCl_6^-$ ions,[28] it is reasonable to consider that complex 4 reacts with $SbCl_5$ to produce the oxonium ion–$SbCl_6^-$ ion pair 5 rather than to assume a reaction of complex 4 with monomer, which occurs in the polymerization of a 1,6-anhydro sugar derivative by PF_5 catalyst.[14,15]

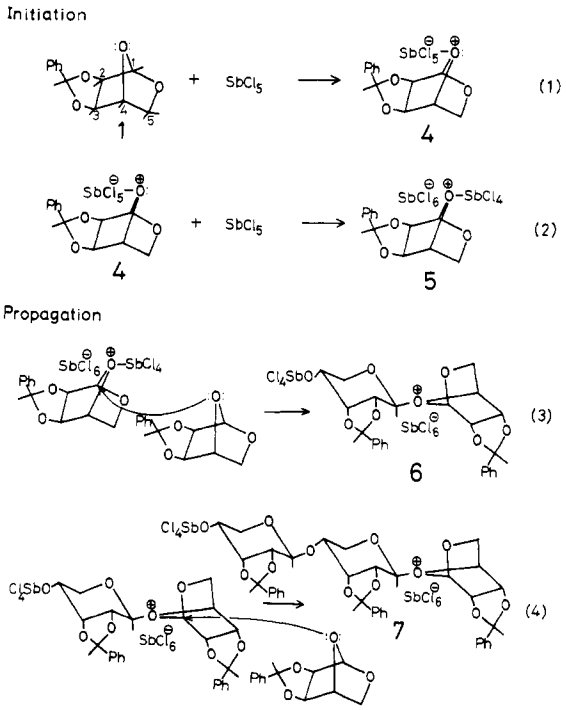
Bulky $SbCl_6^-$ gegenions may control the approaching direction of the monomer to result solely in the attaching of 1,4-linked oxygen to the C-1 carbon of growing chain end.

Table V
Debenzylidenation of Poly(1,4-anhydro-2,3-*O*-benzylidene-D-ribopyranoses) into Free Polysaccharides

	poly(ABRP)				free polysaccharides		
kind of reaction	$[\alpha]^{25}_D$,[a] deg	$\overline{DP}_n$	temp, °C	time, min	yield, %	$[\alpha]^{25}_D$,[b] deg	$[\eta]$,[c] dL/g
hydrolysis[d]	−59.2	120.8	rt[f]	2	67	−62.8	
hydrolysis[d]	+62	46	rt	2	17	+78.9	
reduction[e]	−60	170	−78	90	74	−66.4	0.347
reduction[e]	+56	29	−78	90	74	+93.5	0.131

[a] Measured in a $CHCl_3$ solution (10 g/dm³). [b] Measured in an Me_2SO solution (10 g/dm³). [c] Measured in a 9:1 (v/v) Me_2SO–H_2O solution. [d] With 90 v/v % aqueous trifluoroacetic acid solution. [e] With sodium in liquid ammonia. [f] Room temperature.

Scheme II
Stereoregular Polymerization of ABRP by $SbCl_5$



2,7-Dioxabicyclo[2.2.1]heptane, which can be regarded as a parent ring compound for 1,4-anhydro-α-D-ribopyranose derivatives, was polymerized with various Lewis acid catalysts such as PF_5, BF_3, and SiF_4 at low temperatures to give polymers consisting exclusively of tetrahydrofuran structure,[11] suggesting that the bicyclic acetal has a tendency to cleave at the 1,2-bond with formation of tetrahydrofuran structures.

There would be some interaction of $SbCl_6^-$ with the O-2 and O-3 oxygens of the growing chain end to coordinate the $SbCl_6^-$ ion with the 1,4-linked oxygen because the polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose, in which the configuration at the C-3 carbon and the protective group are different from those in the D-ribose derivatives, did not produce a polymer consisting exclusively of (1→4)-β-D-xylopyranose backbone by $SbCl_5$ catalyst.[29]

On the other hand, the result that cationic catalysts such as phosphorus pentafluoride and boron trifluoride etherate yielded poly(ABRPs) with a backbone composed of a mixture of α-D-ribofuranosidic and β-D-ribopyranosidic units suggests that two kinds of oxonium ions existed in the propagation step, that is, an oxonium ion formed by ionization of 1,5-linked oxygen and one formed by ionization of 1,4-linked oxygen. Since PF_5 is a stronger Lewis acid than $SbCl_5$ and PF_6^- ions are not so bulky as $SbCl_6^-$ ions, the PF_6^- ions may coordinate with both 1,5-linked and 1,4-linked oxygens to form the two kinds of oxonium ions. As no β-D-ribofuranosidic and α-D-ribopyranosidic units were formed in the poly(ABRP) backbone, the polymerization of ABRP could not proceed via a carbenium ion mechanism under the conditions employed in our experiments. The mechanism of the polymerization of 1,4-anhydro sugars with other configurations and protective groups is being investigated in detail and will be reported elsewhere.

Debenzylidenation of Poly(1,4-anhydro-2,3-*O*-benzylidene-D-ribopyranoses) into Free Polysaccharides. Although removal of benzylidene groups from ABRP monomer was successfully carried out by reduction in the presence of palladium black,[19] the reduction of poly(ABRP) in several solvents failed to remove the benzylidene group from the polymer. Therefore, the following methods were used for removal of the protective group.

Hydrolysis with trifluoroacetic acid was effective for removal of benzylidene groups from the levorotatory poly(ABRP) prepared by $SbCl_5$, giving a white powdery poly(D-ribose) in 67% yield after 2 min of reaction. Longer reaction time (5 min) gave a lower polymer yield (about 50%). On the other hand, the acidic hydrolysis of dextrorotatory poly(ABRPs) for 5 min caused degradation of the polymer backbone and gave a trace of polymeric material regardless of the molecular weight of the starting poly(ABRPs), though a small amount of poly(D-ribose) (17% yield) was obtained by hydrolyzing dextrorotatory poly(ABRP) for 2 min.

It is well-known that furanosidic linkages are hydrolyzed faster than pyranosidic linkages,[6,26] and the rate of hydrolysis for methyl β-D-ribofuranoside is a few orders of magnitude larger than that for methyl β-D-ribopyranoside.[30,31] Accordingly, it is reasonable to assume that the levorotatory poly(ABRP), the backbone of which was hardly hydrolyzed under the conditions employed, is composed of β-D-ribopyranosidic units and the dextrorotatory poly(ABRP), which was easily hydrolyzed, is mostly composed of α-D-ribofuranosidic units.

The debenzylidenation of both levorotatory and dextrorotatory poly(ABRPs) was successfully accomplished with sodium in liquid ammonia, which has been used for the debenzylation of synthetic benzylated polysaccharides.[1] The results of debenzylidenations are given in Table V.

Starting from the poly(ABRPs) with $[\alpha]_D$ of +56.0° and −60.6°, the debenzylidenation gave water-soluble white poly(D-riboses) with 74% conversion which showed $[\alpha]_D$ of +93.5° and −66.4°, respectively. Intrinsic viscosities of the dextrorotatory and levorotatory poly(D-riboses) were 0.131 and 0.347 in dimethyl sulfoxide, respectively, indicating good correlations with the degrees of polymerization of 29 and 170 for the starting poly(ABRPs).

^{13}C NMR spectra of poly(D-riboses) and their peak assignment which was attempted by reference to that of D-riboses[21–24] are shown in Figure 6 and Table III. The

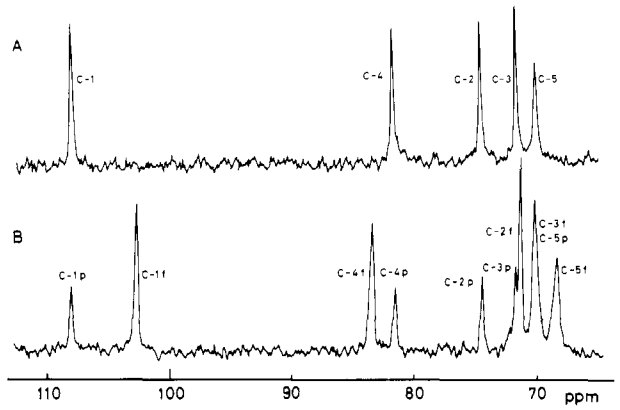


Figure 6. ^{13}C NMR spectra of (A) (1→4)-β-D-ribopyranan ($[\alpha]_D$ −66.4°) and (B) poly(D-ribose) with a mixed structure ($[\alpha]_D$ +93.5°) (deuterium oxide as solvent).

spectra show the formation of free polysaccharides by complete removal of benzylidene groups. In the ^{13}C NMR spectrum of the poly(D-ribose) with $[\alpha]_D$ of −66.4°, six sharp singlets are observed. As shown in Table III, the peaks at 107.98, 81.74, 74.62, 71.69, and 70.13 ppm are attributable to C-1, C-4, C-2, C-3, and C-5, respectively. The chemical shift (107.98 ppm) of the C-1 carbon, which is at rather low magnetic field, shows that this polymer is composed of a β linkage.[21]

In spectrum 1B (Figure 1) of the starting poly(ABRP), the peaks assigned to the C-2, C-3, and C-4 carbons showed splittings, but they became single peaks after debenzylidenation. This observation reveals that the peak splittings observed in spectrum 1B are not due to primary structure but due to higher structure of the polysaccharide derivative (see Note Added in Proof).

As a result, a poly(D-ribose) with $[\alpha]_D$ of −66.4° was found to be highly stereoregular (1→4)-β-D-ribopyranan. This polysaccharide is not known to occur in nature, though D-ribose has been found to be one of constituent monosaccharides in bacterial polysaccharides.[32,33]

On the other hand, the existence of two peaks for respective carbons indicates that a poly(D-ribose) with $[\alpha]_D$ of +93.5° has a backbone structure consisting of 1,5-α-D-ribofuranosidic and 1,4-β-D-ribopyranosidic units, which accords with the NMR analysis on the structure of dextrorotatory poly(ABRP). The composition of the poly(D-ribose) with $[\alpha]_D$ of +93.5° was determined from the NMR spectrum to consist of 72% of the former units and 28% of the latter units. It has been reported that a poly(D-ribose) which was prepared by polycondensation of D-ribose and was bonded mainly with (1→5)-α linkages, showed $[\alpha]_D$ of +35°.[12] Stereoregular (1→5)-α-D-ribofuranan, however, should exhibit much higher specific rotation, that is, approximately +150°, as shown in the previous section.

Experimental Part

Monomer. 1,4-Anhydro-2,3-*O*-benzylidene-α-D-ribopyranose (ABRP) was prepared by treating 20 g of D-ribose with 1000 mL of benzaldehyde, 100 mL of glacial acetic acid, and 100 g of zinc chloride at room temperature according to Vis and Fletcher.[19] ABRP was separated from the resulting white crystals by successive recrystallizations from ether and ethanol and finally purified by recrystallization from *n*-butyl chloride: yield 1.5 g (5%); mp 140.5–142.5 °C (lit.[19] mp 141–146 °C); $[\alpha]^{25}_D$ −56.1° (10 g/dm^3 in $CHCl_3$)(lit.[19] $[\alpha]_D$ −56.6° (10 g/dm^3 in $CHCl_3$)). Since the ABRP obtained was a mixture of syn (lit.[20] $[\alpha]^{23}_D$ −51.5°) and anti (lit.[20] $[\alpha]^{23}_D$ −55.7°) types of diastereoisomers, the composition of the two isomers was determined by means of ^1H NMR spectroscopy from the ratio of peak intensity at 4.56 ppm (H-2 and H-3 protons in anti configuration) to that at 4.42 ppm (H-2 and H-3 in syn). The fraction of anti isomer of ABRP used for the polymerization was in the range 0.71–0.78 (syn, 0.29–0.22).

1,4-Anhydro-2,3-*O*-isopropylidene-α-D-ribopyranose (AIRP) was prepared according to the method of Hughes and Speakman.[34] Thirty-six grams of D-ribose was added to 720 mL of acetone containing 9 mL of concentrated sulfuric acid and the mixture was stirred at room temperature for 1 h. Then, the solution was neutralized with sodium hydroxide solution (18 g/30 mL of H_2O) and concentrated to a syrup. The syrup was chromatographed on a column of silica (250 g), eluting with 9:1 benzene–ether. Several recrystallizations of crude crystals from *n*-pentane gave pure AIRP: yield 2.0 g (5%); mp 61 °C (lit.[34] mp 60.2–61.6 °C); $[\alpha]^{25}_D$ −61.9° (10 g/dm^3 in $CHCl_3$) (lit.[34] $[\alpha]_D$ −62° (7.8 g/dm^3 in methanol)).

Catalyst. Phosphorus pentafluoride was prepared by thermal decomposition of *p*-chlorobenzenediazonium hexafluorophosphate (Ozark-Mahoning Co.). Trifluoromethanesulfonic anhydride was prepared by reacting trifluoromethanesulfonic acid with phosphoric anhydride in vacuo.[35] Commercial boron trifluoride etherate, antimony pentachloride, and antimony pentafluoride were used after purification by trap-to-trap distillation in vacuo.

Solvent. Methylene chloride was purified by extracting impurities with a small amount of concentrated sulfuric acid several times and finally by drying on calcium hydride, followed by distillation.

Polymerization. High-vacuum technique was used for polymerization.[2] ABRP (0.3 g) was polymerized with cationic catalyst in 1.5 mL of methylene chloride. After termination by the addition of methanol, the polymer was purified by reprecipitations, using chloroform–petroleum ether several times and subsequent freeze-drying from benzene, whereby a white fluffy powder was obtained.

Debenzylidenation. Two methods were used for debenzylidenation.

(1) Hydrolysis with Trifluoroacetic Acid–Water. To 500 mg of the poly(ABRP) placed in a flask was added 5.0 mL of 90:10 (v/v) trifluoroacetic acid–water. After stirring for 2 or 5 min, the solution was poured into 100 mL of water and then dialyzed with running water for 3 days. After the aqueous solution was concentrated, the free polysaccharide was freeze-dried from water to give a white powder.

(2) Reduction with Sodium in Liquid Ammonia. This reaction was performed by applying the method of debenzylation of benzylated polysaccharides.[8,36] To 50 mL of liquid ammonia containing 300 mg of sodium, a solution of poly(ABRP) (400 mg) in 10 mL of dimethoxyethane was dropwise added at −78 °C under nitrogen. After 1.5 h of stirring at −78 °C, anhydrous ammonium chloride was added until the blue color disappeared, and then a small amount of water was added. After evaporation of ammonia, the aqueous solution was washed with methylene chloride and dialyzed with water. Finally the polysaccharide was freeze-dried from water.

Measurements. ^1H NMR (270-MHz) and ^{13}C NMR (25-MHz) spectra were measured on the polymer solutions by means of Bruker WH-270 and JEOL PS-100 NMR spectrometers, respectively. Specific rotations of the poly(ABRP) and free polysaccharide were measured on chloroform solution and on dimethyl sulfoxide solution, respectively, by means of a Perkin-Elmer 241 polarimeter. Intrinsic viscosities of the free polysaccharide were measured on 90:10 (v/v) dimethyl sulfoxide–water solution.

Note Added in Proof. From further investigations on the polymerization of each diastereoisomer of ABRP, fast isomerization between the anti and syn configurations was found to occur during the polymerization. Therefore, the peak splittings observed in spectrum 1B can be attributed to the isomeric units in the equilibrium composition.

References and Notes

(1) Schuerch, C. *Acc. Chem. Res.* **1973**, *6*, 184.
(2) Uryu, T.; Tachikawa, H.; Ohaku, K.; Terui, K.; Matsuzaki, K. *Makromol. Chem.* **1977**, *178*, 1929.
(3) Uryu, T.; Kitano, K.; Tachikawa, H.; Ito, K.; Matsuzaki, K. *Makromol. Chem.* **1978**, *179*, 1773.
(4) Uryu, T.; Kitano, K.; Matsuzaki, K. *Makromol. Chem.* **1979**, *180*, 1135.

(5) Uryu, T.; Koyama, Y.; Matsuzaki, K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 673.
(6) Kops, J.; Schuerch, C. *J. Polym. Sci., Part C* **1965**, *No. 11*, 119.
(7) Ruckel, E.; Schuerch, C. *J. Am. Chem. Soc.* **1966**, *88*, 2605.
(8) Ruckel, E.; Schuerch, C. *Biopolymers* **1967**, *5*, 515.
(9) Micheel, F.; Brodde, O.-E.; Reinking, K. *Justus Liebigs Ann. Chem.* **1974**, 124.
(10) Micheel, F.; Brodde, O.-E. *Justus Liebigs Ann. Chem.* **1974**, 702.
(11) Hall, H. K., Jr.; DeBlauwe, F.; Carr, L. J.; Rao, V. A.; Reddy, G. S. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 56*, 101.
(12) Schramm, G.; Grötsch, H.; Pollmann, W. *Angew. Chem.* **1961**, *73*, 619.
(13) Mora, P. T.; Wood, J. W.; McFarland, V. W. *J. Am. Chem. Soc.* **1960**, *82*, 3412.
(14) Ruckel, E.; Schuerch, C. *J. Org. Chem.* **1966**, *31*, 2233.
(15) Uryu, T.; Ito, K.; Kobayashi, K.; Matsuzaki, K. *Makromol. Chem.* **1979**, *180*, 1509.
(16) Zachoval, J.; Schuerch, C. *J. Am. Chem. Soc.* **1969**, *91*, 1165.
(17) Bawn, C. E. H.; Fitzsimmons, C.; Ledwith, A.; Penfold, J.; Sherrington, D. C.; Weightman, J. A. *Polymer* **1971**, *12*, 119.
(18) Ledwith, A.; Chiellini, E.; Solaro, R. *Macromolecules* **1979**, *12*, 240.
(19) Vis, E.; Fletcher, H. G., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 1182.
(20) Grindley, T. B.; Szarek, W. A. *Carbohydr. Res.* **1972**, *25*, 187.
(21) Breitmaier, E.; Jung, G.; Voelter, W. *Chimia* **1972**, *26*, 136.
(22) Perlin, A. S.; Cyr, N.; Koch, H. J.; Korsch, B. *Ann. N.Y. Acad. Sci.* **1973**, *222*, 935.
(23) Gorin, P. A. J.; Mazurek, M. *Can. J. Chem.* **1975**, *53*, 1212.
(24) Ritchie, R. G. S.; Cyr, N.; Korsch, B.; Koch, H. J.; Perlin, A. S. *Can. J. Chem.* **1975**, *53*, 1424.
(25) Bishop, C. T.; Cooper, E. P. *Can. J. Chem.* **1963**, *41*, 2743.
(26) Danishefsky, I.; Whistler, R. L.; Bettelheim, F. A. "The Carbohydrates. Chemistry and Biochemistry"; Academic Press: New York, 1970; Vol. IIA, p 396.
(27) Ito, H.; Schuerch, C. *J. Am. Chem. Soc.* **1979**, *101*, 5797.
(28) Korditz, L. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 4.
(29) Unpublished data from our laboratory.
(30) Augestad, I.; Berner, E. *Acta Chem. Scand.* **1956**, *10*, 911.
(31) Overend, W. G.; Rees, C. W.; Sequeira, J. S. *J. Chem. Soc.* **1962**, 3429.
(32) Kauffman, F.; Jahn, B.; Kruger, L.; Lüderitz, O.; Westpal, O. *Zentralbl. Bakteriol., Parasitenkd., Abt. 1* **1962**, *180*, 509.
(33) Beshkov, M.; Grigorova, D. *Nauchni Tr., Vissh. Inst. Khranit. Vkusova Promst., Plovdiv* **1974**, *21*, 203.
(34) Hughes, N. A.; Speakman, P. R. H. *Carbohydr. Res.* **1965**, *1*, 171.
(35) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 4069.
(36) Uryu, T.; Scheurch, C. *Macromolecules* **1971**, *4*, 342.

Acidolytic Ring Opening of Cyclic Siloxane and Acetal Monomers. Role of Hydrogen Bonding in Cationic Polymerization Initiated with Protonic Acids

Lech Wilczek and Julian Chojnowski*

Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź, 90-362 Łódź, Boczna 5, Poland. *Received March 21, 1980*

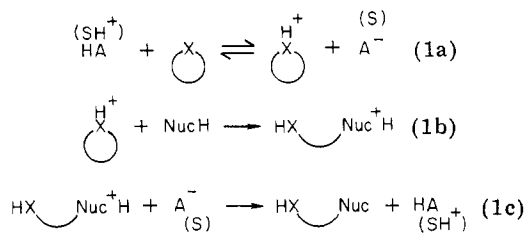
ABSTRACT: The kinetics of ring-opening reactions between trifluoroacetic acid and hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), and dioxolane (DXL) was studied in the inert solvent methylene chloride and in some cases in *n*-heptane. The equilibrium constants of hydrogen-bond formation in the reaction system were determined by an independent method—infrared spectroscopy. Consideration of these constants in kinetic analysis proved to be necessary to obtain a consistent interpretation of the kinetic data. The competition between acid–acid interaction and acid–monomer interaction dominates the kinetic pattern and is suggested as a common phenomenon in cationic polymerization initiated with protonic acids. The role of H-bonded polymeric complexes in the process, including charge stabilization, multifunctional action, and cooperative hydrogen-bond migration, is discussed.

Introduction

The polymerization of a heterocyclic monomer initiated by a protonic acid usually starts with opening of the monomer ring, with the acid acting either as catalyst or simultaneously as both reagent and catalyst. One of the most common schemes of analogous reactions in polar amphiprotic solvents—which is also operative in the acid-catalyzed solvolytic opening of cyclosiloxanes[1,2]—involves the protonation of a heteroatom X followed by nucleophilic attack at the adjacent atom in the ring skeleton, resulting in ring opening, and finally a fast proton return (Scheme I). The solvent may function as the nucleophile and also as the base if HA is the solvent conjugate acid SH^+.

Similar schemes are often applied to cationic polymerization. This may be, however, done only in a formal way. The polymerization usually takes place in a nonpolar aprotic medium, where association phenomena have a strong impact on the process,[3,4] making its kinetics far from being consistent with Scheme I. In particular, the role of acid H-bonding homocomplexation has often been observed in cationic polymerization systems.[5-8] However,

Scheme I



facts concerning the real mechanism are scarce. In order to progress further in understanding the cationic polymerization of heterocycles initiated with a Brønsted acid, kinetic studies of simple ring-opening reactions of heterocyclic monomer rings by acids in nonpolar aprotic and nonbasic solvents (inert solvents) are urgently needed. The reactions of monomers of weak nucleophilicity with an acid of medium strength were chosen here as models.

We have studied the kinetics of the acidolytic cleavage of hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) with trifluoroacetic acid in methylene chloride and in some cases in *n*-heptane. This reaction

0024-9297/81/2214-0009$01.00/0