CH_2Cl_2 solution. It was shown from the $^{31}P\{^1H\}$ NMR spectrum that this dealkylation agent is not selective for the side groups, as required, and reacts with the methoxy group as well as with a polymer chain.

Registry No. 1, 106-61-6; 2, 83999-29-5; 3, 83999-30-8; 4, 71638-12-5; 5, 71638-15-8; 5 (homopolymer), 83999-31-9; 5 (repeating unit), 84108-18-9; PCl_3, 7719-12-2; teichoic acid, 9041-38-7.

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Selective Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose and Synthesis of Stereoregular (1→5)-α-D-Xylofuranan

Toshiyuki Uryu,* Junichi Yamanouchi, Shuji Hayashi, Hidehiko Tamaki, and Kei Matsuzaki

Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.

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ABSTRACT: A new stereoregular polysaccharide, (1→5)-α-D-xylofuranan, was synthesized by selective ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose (ABXP) (1,5-anhydro-2,3-di-*O*-benzyl-β-D-xylofuranose) into 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan and subsequent removal of the protective benzyl groups. Polymerizations of ABXP by boron trifluoride etherate catalyst gave 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranans with $[\alpha]_D$ values of +151 to +158° and number-average molecular weights of 26×10^3 ($(\bar{DP})_n = 83$) to 149×10^3 ($(\bar{DP})_n = 477$). Catalysts such as stannic chloride, silicon tetrafluoride, phosphorus pentafluoride, and niobium pentafluoride also gave poly(ABXPs) with high positive specific rotations. On the other hand, antimony pentachloride as catalyst provided poly(ABXPs) with mixed structures depending on the polymerization conditions. After debenzylation, stereoregular (1→5)-α-D-xylofuranan and xylofuranans with mixed structures consisting of (1→5)-α- and (1→5)-β-D-xylofuranosidic units were obtained. ^{13}C NMR spectra of a natural xylan consisting of (1→4)-β-D-xylopyranosidic units and of the synthetic xylans were measured to determine the structures of the xylans. The mechanism of the cationic ring-opening polymerization of ABXP is discussed.

Highly stereoregular polysaccharides of the dextran-type (1→6)-α-glycan have been synthesized by ring-opening polymerization of 1,6-anhydro sugars.[1,2] It has been possible to prepare a synthetic dextran with regioselective branching.[3] Furthermore, (1→6)-α-linked heteropolysaccharides were obtained by ring-opening copolymerization of different 1,6-anhydro sugars.[4,5] The chemical synthesis has also been attempted for the cellulose-type polysaccharide (1→4)-β-glycopyranose, which is the most naturally abundant polysaccharide, using the polycondensation of unsubstituted[6] and substituted saccharides,[7] though successful results have not been achieved.

Recently, we reported the first synthesis of a (1→4)-β-linked stereoregular polysaccharide by selective ring-opening polymerization of 1,4-anhydroribopyranose derivatives.[8] Since (1→4)-β-D-ribopyranan does not occur in nature, the physical properties and structure of the polysaccharide could not be compared with those of a natural polysaccharide of the same structure.

It is known that wood xylan, which is contained as the second most abundant polysaccharide next to cellulose in hardwoods and has the (1→4)-β-linked xylopyranose structure,[9] cannot be synthesized by the polycondensation of D-xylose.[10] However, the ring-opening polymerization of a 1,4-anhydro-α-D-xylopyranose derivative might provide a stereoregular synthetic (1→4)-β-D-xylopyranan if the selective opening of the 1,4-anhydro ring occurs during polymerization as in the case of 1,4-anhydroribopyranose.

Until now, only the ring-opening polymerization of 1,4-anhydro-α-D-glucopyranose,[11,12] -β-D-galactopyranose,[13] and -α-L-arabinopyranose[13] derivatives was investigated, resulting in the formation of nonstereoregular polysaccharide derivatives. Since 1,4-anhydro-α-D-glucopyranose can be regarded as 1,5-anhydro-β-D-glucofuranose, in which there are two possible ring-opening modes of 1,4- and 1,5-ring scissions, it is difficult to find monomer structures and polymerization conditions that will lead to the selective ring-opening polymerization. A model compound of the 1,4-anhydro sugar, 2,7-dioxabicyclo[2.2.1]heptane, has been polymerized by cationic catalysts to give a polymer with the backbone structure containing five-membered rings (furanose rings in the

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Table I
Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-O-benzyl-α-D-xylopyranose 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	$BF_3{\cdot}O(C_2H_5)_2$	5	−20	20	83.3	+151.2	28.8
2	$BF_3{\cdot}O(C_2H_5)_2$	7	−40	4	65.3	+153.6	34.1
3	$BF_3{\cdot}O(C_2H_5)_2$	3	−60	30	79.1	+155.1	119
4	$BF_3{\cdot}O(C_2H_5)_2$	5	−60	20	79.3	+154.7	149
5	$BF_3{\cdot}O(C_2H_5)_2$	7	−60	20	51.3	+158.4	26.3
6	SiF_4	c	0	188	55.1	+140.2	28.7
7	SiF_4	c	−40	615	11.3	+126.0	
8	PF_5	1	−20	20	59.2	+44.0	15.0
9	PF_5	1	−40	20	79.9	+111.5	28.3
10	PF_5	3	−60	20	93.3	+135.3	20.9
11	NbF_5	8	−40	4	73.3	+121.9	13.7
12	NbF_5	11	−60	20	73.8	+138.8	21.1
13	SbF_5	5	−40	4	74.0	+131.7	22.3
14	TaF_5	10	−40	20	36.4	+66.9	5.0
15	$TiCl_4$	7	−40	72	0.8		
16	$SnCl_4$	3	−40	21	83.9	+149.4	69.3

[a] Solvent, CH_2Cl_2. [b] Measured in $CHCl_3$ (c 1%). [c] Not determined.

Table II
Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-O-benzyl-α-D-xylopyranose by Antimony Pentachloride Catalyst[a]

no.	catalyst conc, mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_D$,[b] deg	$10^{-3}\bar{M}_n$	polymer structure,[c] % (1→5)-β	(1→5)-α
17	2	0	20	52.8	+44.2	10.0		
18	1	−20	20	46.1	+44.4	21.9	55	45
19	3	−30	4	83.4	+42.7	24.5		
20	1	−40	2	69.0	+29.3	40.8		
21	2	−40	20	86.2	+26.5	31.4	72	28
22	3	−40	4	89.3	+99.3	29.4	37	63
23	6	−40	20	82.8	+72.5	13.6	41	59
24	1	−50	4	84.8	+48.4	43.0		
25[d]	3	−60	4	66.3	+100.6	33.2	20	69
26	6	−60	20	68.4	+105.0	25.2		
27[e]	6	−78	20	42.6	+134.0	31.5	6	80

[a] Solvent, CH_2Cl_2. [b] Measured in $CHCl_3$ (c 1%). [c] Determined from the proportion of C-1 absorptions in ^{13}C NMR spectrum of poly(ABXP). [d] The remaining proportions are assigned to the C-1 absorptions at 104.76 ppm (4%) and 101.39 ppm (7%). [e] The C-1 absorptions at 104.76 ppm (5%) and 101.39 ppm (9%).

technical carbohydrate term).[14]

In this study, we report the first synthesis of 1,4-anhydro-2,3-di-O-benzyl-α-D-xylopyranose and its cationic ring-opening polymerization, which gives a stereoregular 2,3-di-O-benzyl-(1→5)-α-D-xylofuranan through selective 1,5-ring opening and poly(dibenzylxyloses) with mixed structures. It is also reported that a new polysaccharide (1→5)-α-D-xylofuranan is prepared by debenzylation of stereoregular 2,3-di-O-benzyl-(1→5)-α-D-xylofuranan. In addition, the structure of synthetic and natural xylans is studied by ^{13}C NMR spectroscopy.

Results and Discussion

Cationic Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-O-benzyl-α-D-xylopyranose (ABXP). ABXP was readily polymerized by various cationic catalysts at low temperatures from 0 to −78 °C, as the results in Table I indicate. With boron trifluoride etherate as catalyst, poly(ABXPs) with high positive specific rotations of +151 to +158° were obtained in high yield. Stannic chloride as catalyst also gave poly(ABXP) with $[\alpha]_D$ +149° in 84% yield, and metal fluoride catalysts SiF_4, PF_5, NbF_5, and SbF_5 provided polymers with somewhat lower $[\alpha]_D$ values (+111 to +139°). A mild Lewis acid, silicon tetrafluoride, as catalyst for the first time caused ring-opening polymerization of an anhydro sugar. Although SiF_4 was a good catalyst for stereoregular polymerization of the model compound 2,7-dioxabicyclo[2.2.1]heptane,[14] it could not cause the polymerization of 1,4-anhydro-2,3-O-benzylidene-α-D-ribopyranose.[15] When the polymerization was carried out with PF_5 as catalyst at the higher temperature of −20 °C or with TaF_5 as catalyst, poly(ABXPs) with lower $[\alpha]_D$ values were obtained.

Number-average molecular weights of the polymers were in the range 14×10^3 ($(\bar{DP})_n = 45$) to 149×10^3 ($(\bar{DP})_n = 477$), and they were especially high for the polymers obtained with 3–5 mol % $BF_3{\cdot}OEt_2$ as catalyst at −60 °C (nos. 3 and 4). The polymer prepared by $SnCl_4$ catalyst also had a high number-average molecular weight, $\bar{M}_n = 69 \times 10^3$ ($(\bar{DP})_n$ 222). As these catalysts also produced high molecular weight polymers from the 1,4-anhydroribopyranose derivative, it was found that they are good catalysts for producing high molecular weight poly(1,4-anhydropentopyranoses).

Table II outlines the results of polymerizations by $SbCl_5$ catalyst. The specific rotation of poly(ABXPs) prepared by $SbCl_5$ catalyst ranged from +26.5 to +134.0°, changing considerably with temperature, time, and catalyst concentration. It is noteworthy that poly(ABXPs) with low $[\alpha]_D$ values from +26.5 to +29.3° were obtained with 1–2 mol % $SbCl_5$ as catalyst at −40 °C. In contrast, the polymerization of 1,4-anhydro-2,3-O-benzylidene-α-D-ribopyranose by $SbCl_5$ catalyst exclusively caused 1,4-ring opening, to give (1→4)-β-D-ribopyranan derivatives with almost identical $[\alpha]_D$ values irrespective of polymerization temperature and catalyst concentration. Number-average

Table III
^{13}C Chemical Shifts of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose, 2,3-Di-*O*-benzyl-Protected Poly(D-xyloses), and Poly(D-xyloses)

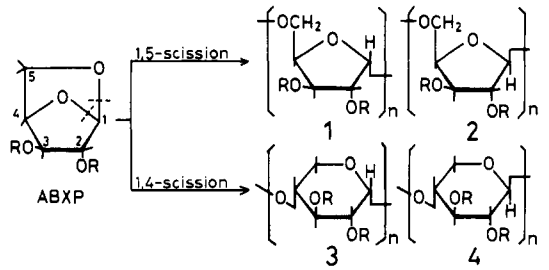
		C-1	C-2	C-3	C-4	C-5	*$CH_2C_6H_5$
1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose		102.46	(85.35, 84.22, 75.93)[a]			62.91	73.01, 71.69
2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan		99.98	75.83	81.78	84.22	67.01	72.67, 72.28
poly(2,3-di-*O*-benzyl-D-xylose)	(1→5)-α	100.02	75.79	82.13	84.22	67.01	
with mixed structures	(1→5)-β	108.17	80.61	82.13	86.86	68.67	72.23, 72.03
(1→5)-α-D-xylofuranan[b]		103.34	78.32	76.61	78.32	68.28	
(1→5)-α-D-xylofuranan[c]		101.83	77.15	75.30	77.40	67.50	
poly(D-xylose) with mixed structures[d]	(1→5)-α	103.73	78.57	77.01	78.76	68.62	
	(1→5)-β	111.53	82.23	77.79	82.47	69.20	
natural (1→4)-β-D-xylopyranan[e]		102.95	75.54	74.08	76.71	63.99	

[a] Not individually assigned. [b] Measured in 0.7 N NaOH aqueous solution. [c] Measured in D_2O. [d] Measured in 1 N NaOH aqueous solution. [e] Measured in 1.3 N NaOH aqueous solution.

molecular weights of the polymers prepared by $SbCl_5$ were fairly high and were in the range 10×10^3 to 4×10^3 ($(\bar{D}\bar{P})_n$ = 32–138).

In summary, it was revealed that the mild catalysts BF_3·OEt_2, SiF_4, NbF_5, and $SnCl_4$ produced poly(ABXPs) with high positive specific rotations, while the strong Lewis acids $SbCl_5$ and PF_5 gave polymers with low specific rotations at relatively high temperatures.

Structure of Poly(1,4-anhydro-2,3-di-*O*-benzyl-D-xylopyranose). There are four possible monomeric units in the poly(D-xylose) prepared by the ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose, namely, the (1→5)-α- (1) and (1→5)-β-D-xylofuranosidic (2) units and the (1→4)-α- (3) and (1→4)-β-D-xylopyranosidic (4) units.



^{13}C NMR spectra of poly(ABXPs) with different specific rotations as well as the spectrum of ABXP monomer are shown in Figure 1. In spectrum 1B, the spectrum of the poly(ABXP) having $[\alpha]_D$ +156°, individual carbon absorptions due to the sugar moiety appear as single peaks, indicating that the polymer has high stereoregularity. Taking into account the high positive specific rotation and the mechanism of ring-opening polymerization leading to a stereoregular polymer which will be described later, one can conclude that this poly(ABXP) is 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan (1).

On the other hand, spectrum 1C, the spectrum of the poly(ABXP) with $[\alpha]_D$ +26.5°, shows that individual absorptions due to carbons C-1–C-5 appear as two peaks except for one carbon. The resonances correspond to new signals due to carbons at lower fields together with signals identical with those of 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan shown in spectrum 1B. Considering that the intensity of the lower field peaks increased with decreasing specific rotation of poly(ABXP), the lower field peaks are attributable to a β configuration. The proportions of the α and β configurations were determined from the C-1 absorptions, as shown in Table II.

Since there are two possible monomeric units with negative specific rotations, that is, the 2,3-di-*O*-benzyl-(1→5)-β-D-xylofuranosidic (2) and -(1→4)-β-D-xylopyranosidic (4) units, that structure 2 is present and not 4 will be established in the next section.

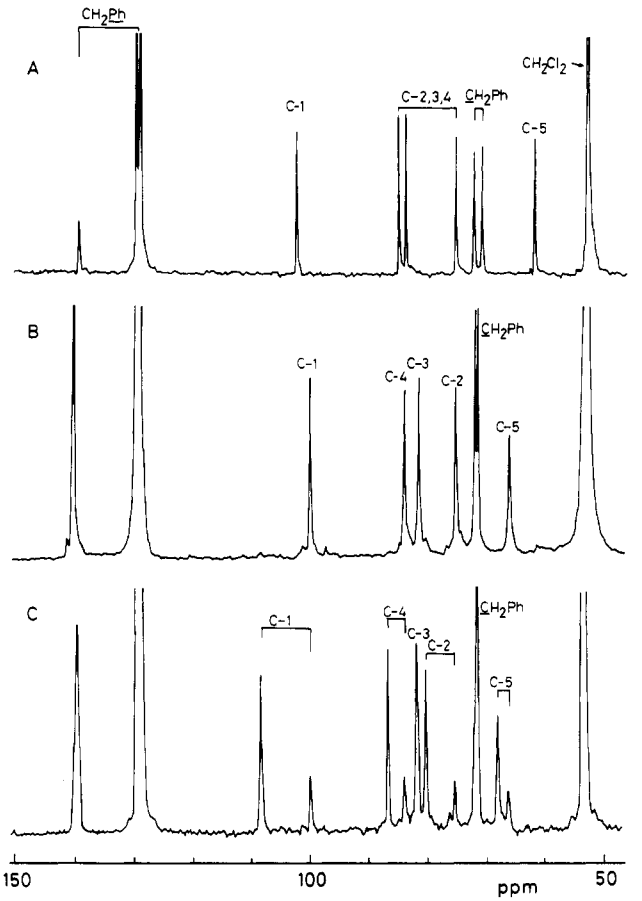


Figure 1. ^{13}C NMR spectra of (A) 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose, (B) 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan prepared by $BF_3O(C_2H_5)_2$ ($[\alpha]_D$ +156.2°), and (C) poly(1,4-anhydro-2,3-di-*O*-benzyl-D-xylopyranose) prepared by $SbCl_5$ ($[\alpha]_D$ +26.5°) (Me_4Si as reference zero).

^{13}C chemical shifts and assignments of the peaks are shown in Table III. The assignments of the ^{13}C NMR absorptions were based on comparison with the chemical shifts shown in methyl α- and β-xylofuranosides,[16] assuming that there are minor differences due to etherification and solvent change.

Figure 2 exhibits that in ^{1}H NMR spectrum 2B, the spectrum of the poly(ABXP) with $[\alpha]_D$ +154.7°, individual proton resonances appear as quartets (H-5 and H-2) and a doublet (H-1) (4.85 ppm). The assignment of the H-2 proton was carried out by the decoupling method. Spectrum 2C, the spectrum of the polymer with low $[\alpha]_D$ value, also exhibits that this polymer is composed of two kinds of monomeric units. For example, the H-1 proton appears as two absorptions at 4.85 ppm (doublet) and 5.07 ppm (doublet which is detectable from the expanded spectrum)

Table IV
^{1}H Chemical Shifts and Coupling Constants of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose and 2,3-Di-*O*-benzyl-(1→5)-α-D-xylofuranan [a]

	chemical shift, ppm							
	H-1	H-2	H-3	H-4	H-5ex	H-5en	$2CH_2C_6H_5$	
1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose (ABXP)	5.42 d	3.61 d	3.91 q	4.69 q	4.06 d	3.39 o	4.55 d 4.51 d	4.51 d 4.47 d
2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan (PXF)	4.85 d	3.98 q	4.15–4.35		3.79 q	3.52 q	4.58 d 4.44 d	4.44 d 4.25 d

	coupling constant, Hz								
	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{3,5en}$	$J_{4,5ex}$	$J_{4,5en}$	$J_{5en,5ex}$	$J_{CH_2C_6H_5}$
ABXP	0	0.92	1.53	4.88	1.22	0	3.36	6.71	11.76
PXF	4.59	0	6.48	nd	0	5.94	4.59	10.80	11.88

[a] d, doublet; q, quartet; o, octet. In the assignment of PXF, H-5ex is designated to be the proton farther from the C C_1-O-C_4 oxygen than H-5en.

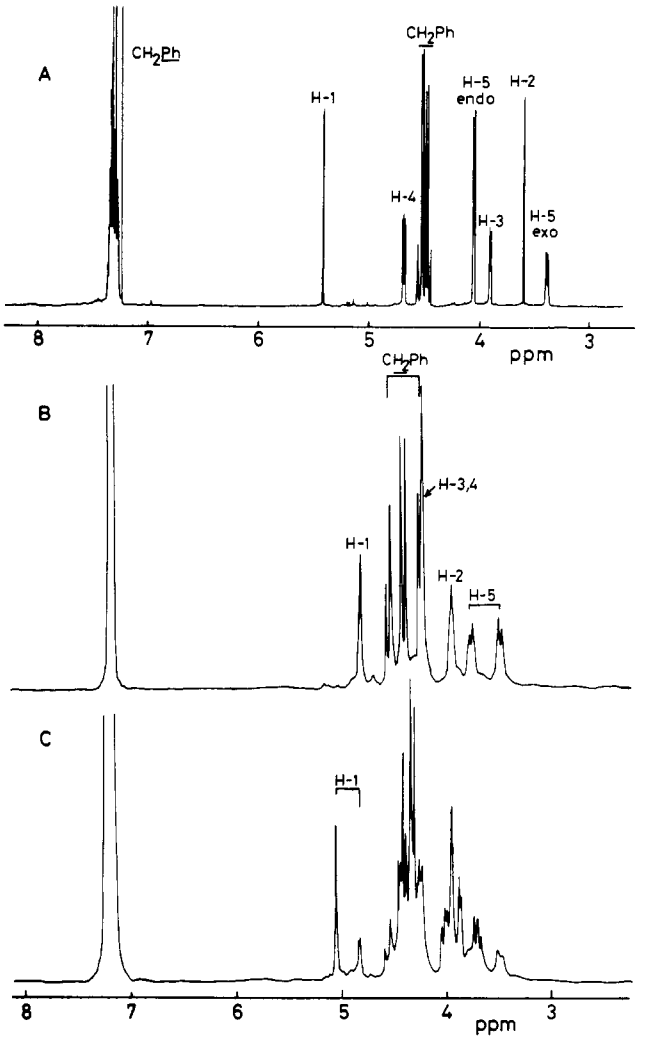


Figure 2. (A) 400-MHz ^{1}H NMR spectrum of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose and 270-MHz ^{1}H NMR spectra of (B) 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan prepared by $BF_3{\cdot}O(C_2H_5)_2$ ($[\alpha]_D$ +154.7°) and (C) poly(1,4-anhydro-2,3-di-*O*-benzyl-D-xylopyranose) prepared by $SbCl_5$ ($[\alpha]_D$ + 42.7°) (Me_4Si as reference zero).

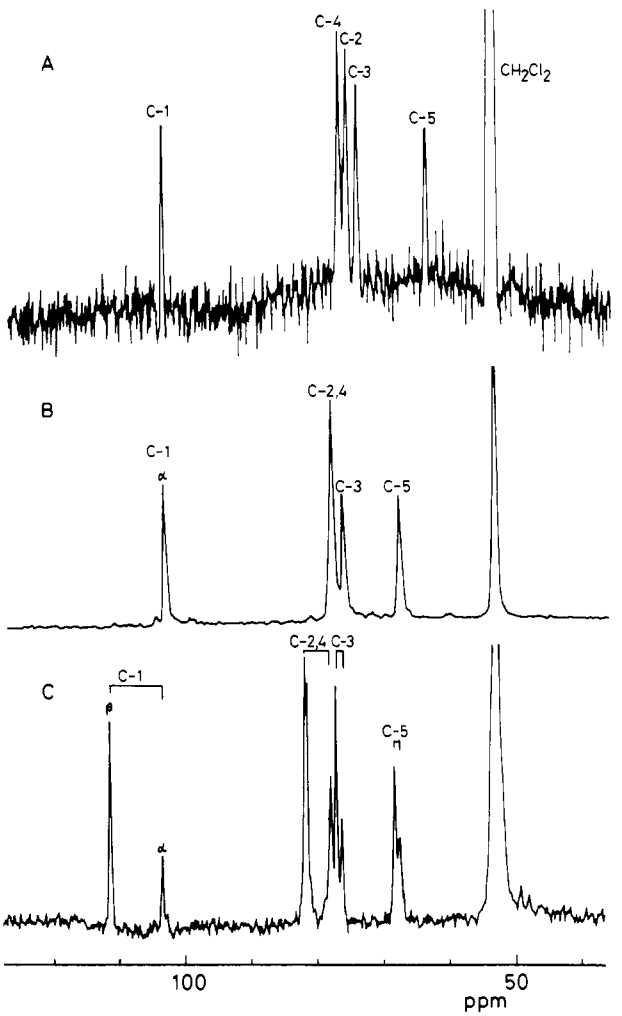


Figure 3. ^{13}C NMR spectra of (A) natural (1→4)-α-D-xylopyranan ($[\alpha]_D$ −80°), (B) synthetic (1→5)-α-D-xylofuranan ($[\alpha]_D$ +177.4°), and (C) synthetic poly(D-xylose) with a mixed structure ($[\alpha]_D$ −13.6°) (Me_4Si as reference zero).

due to the α and β configurations, respectively. ^{1}H chemical shifts and coupling constants for the ABXP monomer and 2,3-di-*O*-benzyl-(1→5)-α-D-xylofuranan are shown in Table IV, indicating that in ABXP there is no coupling between H-1 and H-2, but a small coupling between H-1 and H-3 as in the case of 1,4-anhydro-2,3-di-*O*-acetyl-α-D-xylopyranose.[17]

Structural Analysis of Free Xylans. The synthetic xylan derivatives were debenzylated with sodium in liquid ammonia to give free polysaccharide xylans in order to determine their structure. The results are summarized in Table V. Natural xylans, which are produced as hemicellulose in wood, are known to consist of a (1→4)-β-D-xylopyranose backbone.[9] To our knowledge, there are no ^{13}C NMR spectra of xylans in the literature. Since natural xylans extracted from wood often include other carbohydrate units,[18,19] the structure of two kinds of natural xylans

Table V
Debenzylation of
Poly(1,4-anhydro-2,3-di-O-benzyl-D-xylopyranoses)
into Free Polysaccharide Xylans[a]

	poly(ABXP)				free polysaccharide	
no.	wt, g	$[\alpha]^{25}_D$,[b] deg	Na, g	time, h	yield, %	$[\alpha]^{25}_D$,[c] deg
1	0.58	+154.5	0.30	2.5	71.6	+177.4
2	0.56	+29.5	0.53	2.0	94.2	−13.6

[a] Solvent, liquid ammonia; temperature, −78 °C. [b] Measured in $CHCl_3$ solution (10 g/dm³). [c] Measured in water (10 g/dm³).

was examined. The ^{13}C NMR spectrum of a xylan with $[\alpha]_D$ −80° which was found by a chemical method to be exclusively composed of xylose units[20] is shown in Figure 3 together with the spectra of synthetic ones.

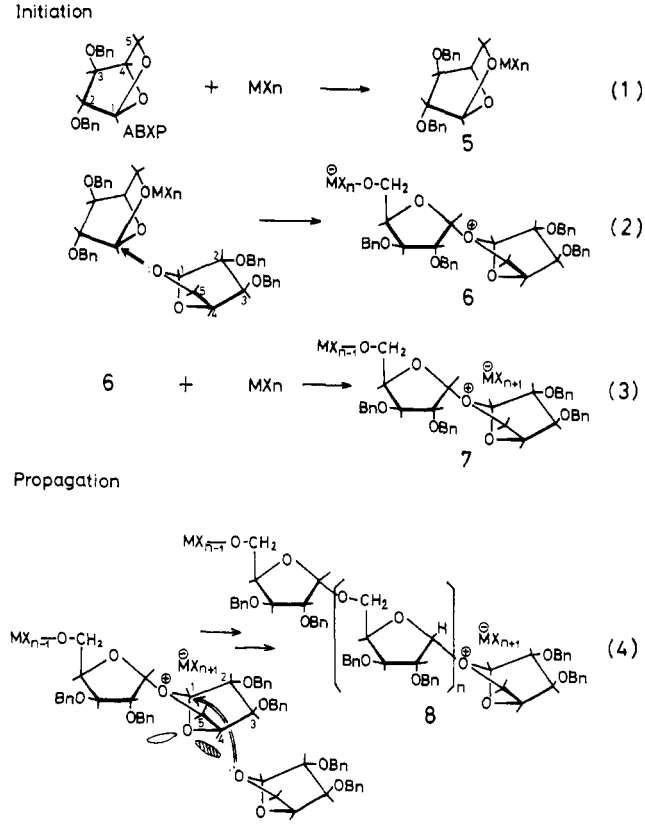
Spectrum 3A of the natural xylan is completely different from spectrum 3B of the synthetic xylan. For instance, the C-1 absorptions of the natural xylan, that is, (1→4)-β-D-xylopyranan, and of a synthetic xylan with a high positive specific rotation, that is, (1→5)-α-D-xylofuranan, appear at 102.95 and 103.34 ppm, respectively. In addition, there is a large chemical shift difference in the C-5 absorption between the natural and synthetic xylans, exhibiting absorptions at 63.99 and 68.28 ppm, respectively. Chemical shifts of other carbons are also different between the xylans, as shown in Table III.

It was revealed by ^{13}C NMR spectroscopy that a xylan which was extracted from Japanese beech pulp according to the literature[18] contained a considerable amount of carbonyl groups as glucuronic acid branches, but the other NMR absorptions were almost identical with those of the natural linear xylan.

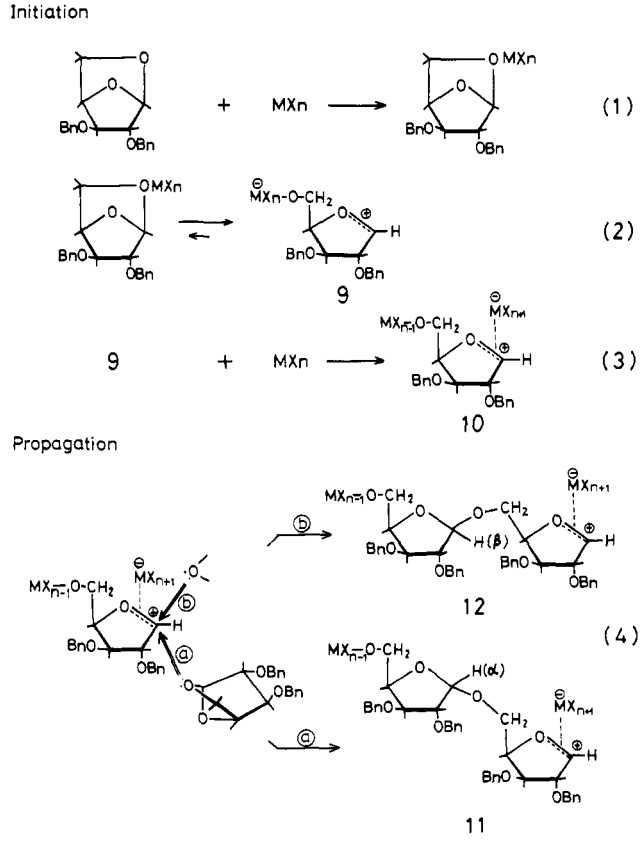
On the other hand, a synthetic xylan with $[\alpha]_D$ −13.6° shows two peaks due to the C-1 carbon at 103.73 and 111.54 ppm, indicating that there are two kinds of monomeric units in the polymer backbone (spectrum 3C). The former (103.73 ppm) is attributable to the same carbon as that (103.34 ppm) of the synthetic (1→5)-α-D-xylofuranan, though a small difference in chemical shift arises from different concentrations of NaOH in NMR solvent. The absorptions appeared more downfield with increasing NaOH concentration. Figure 3 and Table III clearly indicate that the monomeric unit with a β configuration in the synthetic xylan is different from that in natural (1→4)-β-D-xylopyranan and must be the (1→5)-β-D-xylofuranosidic unit. Therefore, it was concluded that the synthetic xylan with a mixed structure is composed of (1→5)-α-D-xylofuranosidic and (1→5)-β-D-xylofuranosidic units. For a xylan with $[\alpha]_D$ −13.6°, the proportions of (1→5)-α- and (1→5)-β-D-xylofuranosidic units were determined from the ^{13}C NMR spectrum to be 28 and 72%, respectively.

Mechanism of Polymerization. A stereoregular structure consisting exclusively of (1→5)-α-D-xylofuranosidic units can be attained by an oxonium ion mechanism, as shown in Scheme I. The selective 1,5-ring opening of the ABXP is reasonably interpreted by the following two reasons. (1) The 1,5-linked oxygen is more nucleophilic than the 1,4-linked oxygen, which leads to the preference of C_1–O^+–C_5 oxonium ions. (2) The selective 1,5-ring cleavage may be explained by applying the antiperiplanar theory of Deslongchamps et al.[21] As indicated in Scheme I, one of the p orbitals of oxygen of the C_1–O^+–C_4 linkage is antiperiplanar to the C_1–O^+ bond of the C_1–O^+–C_5 linkage to be cleaved, whereas no p orbital

Scheme I



Scheme II



of oxygen of the C_1–O–C_5 linkage is antiperiplanar to the C_1–O^+ bond of the C_1–O^+–C_4 linkage even if this oxonium ion is formed.

On the other hand, Scheme II indicates that a mixed structure consisting of (1→5)-α- and (1→5)-β-D-xylofuranosidic units can be formed by a carbenium ion

mechanism. The reaction might proceed in the following steps. Complexation of $SbCl_5$ to the 1,5-linked oxygen of ABXP occurs, followed by scission of the 1,5 ring because of the strong Lewis acidity of $SbCl_5$. An initiating carbenium ion **10** may be approached by the 1,5-linked oxygen of ABXP from two directions a and b, giving (1→5)-α-linked (**11**) and (1→5)-β-linked (**12**) xylofuranose structures. The reason that the (1→5)-β units increased with increasing temperature is considered to be due to the favored approaching direction b over the direction a on account of weakened interaction between ion pairs. A similar mechanism has been proposed for the ring-opening polymerization of the 1,4-anhydro-α-L-arabinopyranose derivative.[13]

When the polymerization of ABXP was performed with $SbCl_5$ catalyst at −60 to −78 °C, the C-1 resonance of poly(ABXP) exhibited four peaks, two peaks of which appeared at the same chemical shifts as those attributed to (1→5)-α- and (1→5)-β-xylofuranosidic units. Thus, the remaining two peaks at 104.76 and 101.39 ppm with several percent proportions might be due to the possible 1,4-linked xylopyranosidic units (Table II, nos. 25 and 27).

We proposed the polymerization mechanism leading to the (1→5)-α-D-xylofuranan derivative by selective 1,5-ring opening of ABXP, which is completely different from the mechanism leading to the (1→4)-β-D-ribopyranan derivative by selective 1,4-ring opening of 1,4-anhydro-2,3-*O*-benzylidene(or isopropylidene)-α-D-ribopyranose.[8] It might be considered that the selective 1,4-ring opening in the benzylidene- or isopropylidene-protected monomer is due to the rigidity and steric hindrance of the protective groups. The difference in stereoregulation between the benzylidene and benzyl protective groups will be reported in detail elsewhere in the polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose.

Experimental Section

1,4-Anhydro-α-D-xylopyranose. D-Xylose (150 g) was pyrolyzed under vacuum according to the method of Köll, Deyhim, and Heyns.[17] A dark brown syrup was dissolved in methanol and treated with activated carbon. After filtration, the filtrate was heated in the presence of 150 g of Amberlite IRA-400 at 60 °C for 10 h, followed by concentration to dryness to give a brown syrup; yield 8%.

1,4-Anhydro-2,3-di-*O*-acetyl-α-D-xylopyranose. 1,4-Anhydro-α-D-xylopyranose syrup (20 g) was acetylated with 126 mL of acetic anhydride and 200 mL of pyridine. After a workup procedure, the acetylated compound was separated by means of silica gel column chromatography, using 93:7 benzene–methanol once and 4:1 benzene–ethyl acetate two times: yield of the yellow syrup, 44%; $[\alpha]^{25}_D$ +13.1° (*c* 1%, $CHCl_3$) (lit.[17] $[\alpha]_D$ +12.3° (*c* 1%, $CHCl_3$)).

1,4-Anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose (ABXP). 1,4-Anhydro-2,3-di-*O*-acetyl-α-D-xylopyranose (12 g) was benzylated with 133 mL of benzyl chloride and 28 g of powdered KOH at 100–105 °C for 3 h and then for a further 1.5 h after addition of 65 mL of benzyl chloride and 14 g of KOH according to a modification of the method of Zemplen, Csürös, and Angyal.[22] After excess benzyl chloride was evaporated, 150 mL of chloroform and 150 mL of water were added to the reaction mixture, followed by separation of the chloroform layer. The concentrated chloroform solution was subjected to steam distillation. The benzylated compound was separated by means of silica gel column chromatography, using 99:1 benzene–methanol once and 9:1 benzene–ethyl acetate two times. Then it was separated by preparative gel permeation chromatograph and finally eluted on a silica gel column; yield of the slightly yellow syrup, 16%. The structure of ABXP was confirmed by ^1H and ^{13}C NMR spectroscopy. $[\alpha]^{25}_D$ −13.0° (*c* 1%, $CHCl_3$).

Polymerization. High-vacuum technique was used. ABXP was dried in a polymerization ampule by evacuating for several hours and dissolving in dry methylene chloride, followed by distilling the methylene chloride off the monomer solution. When SiF_4 (Matheson Co.) was used as catalyst, the gas was introduced by bubbling into the monomer solution under nitrogen. Other procedures were the same as before.[2] Polymers were purified by reprecipitations, using chloroform and petroleum benzin and subsequent freeze-drying from benzene.

Debenzylation. About 1.5 g of poly(ABXP) dissolved in 10 mL of dimethoxyethane was added dropwise to a solution of 0.5 g of sodium in 80 mL of liquid ammonia, and the reaction was allowed to continue for 2 h, followed by successive addition of ammonium chloride and 10 mL of water.[23] Free polysaccharide was dialyzed with running water for 4–5 days, concentrated to 1–2 mL of solution, and freeze-dried from water.

Natural Xylan. Japanese beech pulp (350 g) prepared by the sulfite method was extracted with 2.7 L of 17.5% NaOH aqueous solution according to the literature.[18] To an extracted solution 150 mL of Fehling solution was added, followed by separation the precipitate by means of a centrifuge. Then 360 mL of Fehling solution was added to the supernatant solution to precipitate a xylan: yield about 2%; $[\alpha]^{25}_D$ −81.2° (*c* 0.5%, 1.0 N NaOH aqueous solution).

A linear natural xylan was extracted from bleached kraft pulp made from domestic (Japanese) mixed hardwoods by Ohsawa and coworkers[20] and was kindly supplied to us; $[\alpha]^{25}_D$ −80° (*c* 0.2%, 1.5 N NaOH aqueous solution). Other properties and structure will be reported by them.

Measurements. The 400-MHz ^1H NMR spectrum of ABXP was measured on a 1% solution in $CDCl_3$ by means of a JEOL GX-400 spectrometer. The peak assignment was performed by the decoupling method.[5] The 270-MHz ^1H NMR and 25-MHz ^{13}C NMR spectra of poly(ABXPs) were measured on $CDCl_3$ solution and on CH_2Cl_2 solution by means of JEOL FX-270 and PS-100 spectrometers, respectively. ^{13}C NMR spectra of synthetic xylans were measured on 0.7–1 N NaOH aqueous solution and on D_2O solution and those of natural xylans on 1.3 N NaOH aqueous solution. Specific rotations of poly(ABXP), synthetic xylan, and natural xylan were measured on chloroform solution (10 g/dm^3), aqueous solution (10 g/dm^3), and 1.0 N NaOH solution (5.0 g/dm^3), respectively, using a Perkin-Elmer model 241 polarimeter. For a linear natural xylan with low solubility, specific rotation was measured on 1.5 N NaOH solution (about 2 g/dm^3), exhibiting approximately −80°, but the value might be a little higher. Molecular weights of poly(ABXPs) were determined by means of a Toyo Soda HLC-802UR gel permeation chromatograph using standard polystyrenes as reference and tetrahydrofuran as solvent. For this kind of polymers, the molecular weights determined by the GPC method are known to agree with those by the osmotic method.[24]

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Fluorescence and Absorbance of Polystyrene in Dilute and Semidilute Solutions

John M. Torkelson,[1a] Sanford Lipsky,[1b] Matthew Tirrell,*[1a] and David A. Tirrell[1c]

Department of Chemical Engineering and Materials Science and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, and Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received April 28, 1982*

ABSTRACT: The fluorescence and absorbance of polystyrene in solution have been measured over a wide concentration range for several molecular weights and solvents. The absorbance at wavelengths below 280 nm for these molecular weights and solvents is found to be insensitive to the transition between dilute and semidilute solutions. Self-absorption of the fluorescence results in a much reduced observed monomer emission at high concentration. When this is corrected, the ratio of excimer to monomer fluorescence intensity, I_E/I_M, is essentially constant at low concentrations and at most increases only very slowly and smoothly at higher concentrations. No significant molecular weight or solvent effects on the concentration dependence of I_E/I_M are manifested for these molecular weights and solvents over the concentration range studied. Contrary to previous reports, fluorescence spectroscopy reveals no abrupt transition between dilute and semidilute solutions.

Introduction

Intermolecular excimer formation by polymers in solution is similar to intramolecular excimer formation by nonadjacent chromophores in that both rely on diffusion of significant portions of the polymer molecules rather than single-bond rotation for the photophysical reaction to occur. Recently, we reported a study in which we found that intramolecular excimer formation by nonadjacent chromophores, or remote intramolecular excimer formation, was insignificant in dilute solutions of polystyrene.[2] We now report on a study in which both the fluorescence and the absorption spectra of polystyrene are investigated over a wide range of concentration and in which the conditions are more favorable for remote intramolecular and intermolecular excimer formation.

A number of concentration studies on the fluorescence of polystyrene in solution have been reported. An early concentration study was done by Vala et al.,[3] who found that the ratio of excimer to monomer fluorescence intensity, I_E/I_M, was insensitive to small changes of concentration in a very dilute solution. Later, Nishihara and Kaneko[4] did an extensive study of polystyrene in six solvents. Contrary to Vala et al.,[3] they indicated that I_E/I_M increased linearly with concentration even at concentrations approaching infinite dilution. Roots and Nyström[5] reported the concentration dependence of the fluorescence of three molecular weights of polystyrene and found that the curve representing I_E/I_M showed an apparent upward curvature at $c[\eta] \simeq 1$ for all molecular weights. They concluded that fluorescence spectroscopy was of value in determining the critical concentration, c^*, for the transition from dilute to semidilute solution behavior. This concentration is, to within a numerical constant of order one, $1/[\eta]$.[6,7] They also claimed that the value of c^* determined by fluorescence depended on molecular weight as $c^* \sim M^{-0.8}$, in agreement with predictions from theoretical scaling arguments.[8,9] Renyuan,[10] also studying polystyrene fluorescence, reported two critical concentrations in the curve representing I_E/I_M; both critical concentrations were almost independent of molecular weight.

Clearly, there is little agreement among the various studies of the concentration dependence of polystyrene fluorescence. A possible contributor to this lack of agreement is that at high polymer concentration the effect of self-absorption of monomer fluorescence by the sample may become significant. If these self-absorption corrections are not made or are made improperly, the different geometries used in each of the studies may be responsible for the discrepancies.

Recently, two studies have reported on the concentration dependence of the absorption spectrum of polystyrene solutions. Destor et al.[11] made absorption measurements of poly(oxyethylene) in water and poly(vinyl acetate) in acetonitrile as well as of polystyrene in chloroform. For the first two polymers they found a critical concentration at which there was a break in the absorbance vs. concentration curve. They interpreted this concentration to be c^* and found $c^* \sim M^{-0.75\pm0.10}$. For polystyrene, the curve was linear at low concentrations ($c < 0.6\%$) but became progressively curved for the highest concentration used ($0.6\% < c < 1\%$). They explained their results as being due to changes in polarizability of the medium with increasing polymer concentration. The replacement of a solvent molecule by a monomer alters the polarity and consequently the absorption frequency and molar absorptivity. The diminished effect in polystyrene was interpreted to result from the reduced monomer–monomer interactions between the bulky phenyl groups and from the fact that the absorption bands originate from π–π^* transitions, which are not very sensitive to the medium's polarity. Lee, Waddell, and Casassa[12] have repeated these measurements. While they found seemingly critical con-

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