the polymerization medium is carefully dried; a correct stoichiometry (catalyst/ω-hydroxyl polymer) and a complete hydroxyl functionalization are, of course, important factors to avoid the presence of homopolymers. Generally, the polydispersity of the block copolymers prepared in that way is around 1.2. Alternatively, the coupling of these OH-terminated diblock copolymers by means of classical methods (diisocyanates, phosgene) can lead to the preparation of the corresponding PX–PCL–PX triblock materials.

In conclusion, the new polymer-supported bimetallic compounds herein described provide pathways to the synthesis of numerous PCL-based diblock and triblock copolymers. When the hydroxyl-terminated preformed block is prepared by living anionic polymerization, this technique further enables one to tailor a whole set of new materials with a broad range of accurately controlled molecular parameters. Several series of various copolymers have been prepared by applying this new synthetic method; their physico-mechanical behavior,[21,24] their liquid crystalline structures in the presence of a preferential solvent of one block,[30–32] and their role as additives in polymer blends[21,24,33] have been studied and are published elsewhere.

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Polymerization of 1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose, a Substituted 2,6-Dioxabicyclo[3.1.1]heptane

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ABSTRACT: The polymerization of 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose has been studied under a variety of conditions. Cationic and some coordination catalysts caused polymerization; anionic initiators did not. Stereoselectivity and yields were variable and the products were polymers of low viscosity and oligomers. Phosphorus pentafluoride produced good yields of polymer, rich in α-D configuration. Triethylaluminum–water catalyzed production of polymer with a high proportion of β-D configuration. None of the catalysts tested gave completely stereoregular products. The polymerization mechanism and possible causes of low molecular weight are discussed.

Polymerization of bicyclic acetals to produce stereoregular polysaccharides and related polyacetals has been investigated in a number of centers[1–5] and the subject has been recently reviewed.[1–3] Because of the ubiquitous nature of polysaccharides and their important physiological functions, especially involving information transport, the products of these ring-opening polymerizations have been useful model substrates for investigating immunological and allergic reactions, enzyme function, and protein (lectin)–carbohydrate interactions.[3]

Although the structure of the monomers used appears complex, there are a number of simplifying features which make these ring-opening polymerizations amenable to rigorous analysis. Since one uses optically pure monomers, the structural complexities introduced with racemic monomers are avoided, and stereoselectivity can be simply monitored in a series of polymerizations by polarimetry, as well as by NMR spectroscopy. Bond breaking has been

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Table I
Polymerization of 1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose

polymn no.	catalyst	[catalyst] / [monomer], mol %	solvent	[monomer] / solvent vol,[a] g/100 mL	temp, °C	time, h	petroleum ether insoluble fraction % yield	[η], dL/g	$[\alpha]^{25}{}_D$, deg	α,[b] %
61	PF_5	2.0	CH_2Cl_2	43.4	−60	4.5	71.2	0.06	116.6	75
84	PF_5	2.0	CH_2Cl_2	72.1	−60	1.0	64.7	0.09	108.1	73
64	PF_5	3.6	CH_2Cl_2	25.5	−78	42.7	66.0	0.07	112.7	80
78	PF_5	1.8	toluene	49.1	−60	4.0	40.5	0.06	106.0	74
77	PF_5	1.8	toluene	49.1	−78	17.0	>23.4[c]	0.06	101.4	77
62	$BF_3 \cdot OEt_2$	2.0	CH_2Cl_2	43.3	−40					
					~−78	19.0	8.9		87.0	52
63	$SbCl_5$	2.0	CH_2Cl_2	43.3	−60	3.5	61.4	0.05	92.5	57
76	$SbCl_5$	1.8	toluene	49.1	−78	17.5	1.6[d]			
75	Et_3O^+, PF_6^-	5.3	CH_2Cl_2	38.4	0	2.0	1.6			
					−78	46.0				
83	SiF_4	ca. 2	CH_2Cl_2	72.1	−60	1.5	trace			
					−78	16.0				
81	KO-*t*-Bu/ 18-crown-6	2.0	benzene	43.3	−25	46.0	~0			
82	$(TlOEt)_4$	~10	toluene	43.3	25	23.0	~0			
79	1:1 $AlEt_3/H_2O$	2.0	toluene	43.3	25	42.5	74.4	0.08	44.3	9
80	1:1 $ZnEt_2/H_2O$	~10	toluene	43.3	25	42.5	1.9		61.4	

[a] The value of monomer to solvent ratio approximates 1 mol/L in most cases with extremes of 0.59 (no. 64) and 1.67 (no. 83, 84). [b] Percentage of the α-anomeric configuration of the polymer, estimated by comparing two anomeric carbon resonances at 96 and 102 ppm. [c] Portion accidentally lost. [d] The petroleum ether soluble fraction was almost entirely monomeric by GPC analysis.

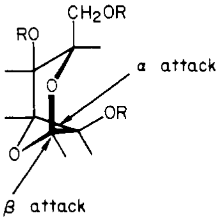
observed to occur only between ring oxygen and the anomeric center, and monomers link always head to tail. As a result the polysaccharides produced have always been completely hydrolyzable and the recovered sugar always has had its original structure. Except in the case of the 2,7-dioxabicyclo[2.2.1]heptanes with two fused five-membered rings, one ring opens preferentially and essentially exclusively. In almost all polymerizations studied to date, ring opening occurs with inversion at the anomeric center or with some degree of racemization. Therefore, except in the case of 1,4-anhydroglycopyranose derivatives or 2,7-dioxabicyclo[2.2.1]heptanes, the only stereochemical problem is to determine the configuration on C-1.

Previously a number of (1→6)-α-D-glycopyranans have been prepared from 1,6-anhydro-β-D-glycopyranose derivatives[3] and a (1→2)-α-D-mannopyran oligomer has been prepared from 1,2-anhydro-3,4,6-tri-*O*-benzyl-β-D-mannopyranose.[6] A few 1,4-anhydroglycopyranose derivatives have been polymerized,[4,7,8] one of which is reported to form stereoregular (1→4)-linked polysaccharide.[8] In contrast, 1,3-anhydroglycopyranose derivatives, which are bicyclic acetals with fused oxetane and pyran ring systems, have only recently been synthesized,[9] and this article reports an exploratory investigation of their polymerization.

Results and Discussion

1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose was polymerized under various conditions as summarized in Table I. All the polymerizations were performed under high vacuum.

The first polymerization was carried out with phosphorus pentafluoride as catalyst, since it has been shown to be the best initiator with 1,6-anhydro-β-D-glycopyranoses.[3] Polymerization with 2 mol % of catalyst at −60 °C gave a relatively high yield (71.2%) of petroleum ether insoluble product in 4.5 h (no. 61). The intrinsic viscosity of the polymer, however, was very low. In spite of the relatively high optical rotation, the stereoregularity was estimated to be not high (~75% α) by comparing the heights of the two anomeric ^{13}C resonances at 102.5 and 96.2 ppm, corresponding to the β and α configurations, respectively (see 1). The position of the β-anomeric C-1 absorption (102.64 ppm) was confirmed by measuring the spectrum of 2,4,6-tri-*O*-benzylpachyman, a β-(1→3)-linked glucan. The petroleum ether soluble fraction was analyzed by analytical liquid chromatography (ALC) and gel permeation chromatography (GPC). The liquid chromatogram showed many overlapping peaks and the GPC showed the presence of low oligomers (probably dimer and trimer) in large quantity and a very small amount of monomeric materials. The ^1H NMR spectrum of the fraction was extremely broad and featureless but did not show signals due to residual monomer. Minor changes in temperature and solvent had only slight influence on the polymerization.



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Polymerization catalyzed by boron trifluoride etherate (no. 62) formed a small amount of petroleum ether insoluble polymer having a lower specific rotation and lower stereoregularity. GPC of the petroleum ether soluble fraction showed the presence of a small amount of low oligomers as well and a large amount of apparently monomeric material. Two sharp major peaks observed at counts 10 and 14 on the liquid chromatogram of the fraction were isolated and shown to be impure methyl 2,4,6-tri-*O*-benzyl-β-D-glucopyranoside and pure methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside. Apparently the quenching agent methanol reacts with residual monomer under acidic conditions to form the corresponding methyl D-glucopyranosides by opening the oxetane ring. Although the formation of cyclic oligomers is one of the characteristic features of the ring-opening polymerization of cyclic ethers such as oxetane derivatives[10,11] and 1,2-epoxides,[12] as well as of cyclic formals,[13] the possibility in the present case appears to be remote because of steric repulsion between the equatorial benzyl groups on C-2 of neighboring units. In addition, no positive evidence of specific cyclic oligomers was detected by ^{1}H or ^{13}C NMR or ALC.

Antimony pentachloride, which has been shown[8] to be regioselective in the polymerization of a 1,5-anhydro-β-D-ribofuranose derivative, proved to give results intermediate between those of phosphorus pentafluoride and boron trifluoride etherate. Triethyloxonium hexafluorophosphate, which is not a very effective catalyst for 1,6-anhydroglycopyranose derivatives at low temperature,[14] was used in relatively large quantity in the present study. Even though the reaction mixture was allowed to remain at 0 °C for 2 h in order to initiate polymerization and kept for 46 h thereafter at −78 °C, the yield of petroleum ether insoluble product was very low, and the petroleum ether soluble fraction contained approximately equal amounts of monomeric glycoside and oligomeric product. Silicon tetrafluoride, which initiates polymerization of 2,6-dioxabicyclo[2.2.2]octane,[15] was even less effective.

In addition to having relatively poor stereoregularity, these cationic polymers are of low viscosity. Low viscosities are also characteristic of the 1,6-linked glycopyranans formed under nonstereoselective polymerization conditions.[3] Lack of stereoregularity in the polymers has usually been interpreted to mean that the reactions have proceeded by way of a carbocation rather than a trialkyloxonium ion mechanism and that the former intermediate is more prone to chain transfer and termination processes.[3] Alternatively, low molecular weights have been found in similar reactions with slow propagation rates.[6] Chain-scission reactions also have been observed to occur on (1→6)-linked anhydroglycopyranans under polymerization conditions.[16] Since the polymerization of this monomer at −60 °C for 1 h (no. 84, Table I) converted more than 90% to products, of which 64.7% were petroleum ether insoluble, the propagation rate is not particularly slow. When preformed petroleum ether insoluble polymer no. 61 was treated with 2 mol % phosphorus pentafluoride in dichloromethane for 4 h at −60 °C, about 9% of the polymer became petroleum ether soluble and the specific rotation of the remaining petroleum ether insoluble material was decreased from +116.6 to 104.4°. The intrinsic viscosity, however, remained almost unchanged. Therefore, although long contact time with catalyst is deleterious, the main reason for the low molecular weights appears to be excessive chain transfer or termination during the polymerization process.

Since the standard cationic initiators did not give configurationally pure polymers, a number of different catalysts were tested. Potassium *tert*-butoxide was complexed with 18-crown-6 and dissolved in benzene. This catalyst is reasonably effective in polymerizing 1,2-anhydro-3,4,6-tri-*O*-benzyl-β-D-mannopyranose.[6] It did not, however, cause significant polymerization in this case. The petroleum ether soluble fraction contained a small amount of oligomeric products as well as the starting 1,3-anhydro sugar derivative (no. 81). Thallous ethoxide was also tested for catalytic activity. It exists as a tetramer and has a distorted cubic structure with thallium and oxygen atoms at the corners.[17] The metal–oxygen–metal linkage is characteristic of a number of stereoselective catalysts and the monovalence of thallium, it was hoped, might avoid the formation of gel sometimes observed with aluminum-based catalysts. However, most of the 1,3-anhydro sugar derivative was unaffected after 1 day of reaction time and only a small amount of oligomeric material was found in the petroleum ether soluble fraction.

Coordination catalysts were also tested. These have been used previously for the polymerization of epoxides and oxetane. Hirano et al. report that the latter should be "anionically polymerizable by a coordination mechanism" on the basis of model calculations by the CNDO/2 molecular orbital method and also report its polymerization by zinc dimethoxide.[18] Diethylzinc–water (1:1) complex, however, produced only a small amount of polymeric material of low optical rotation from the 1,3-anhydro-β-D-glucopyranose derivative. The petroleum ether soluble fraction contained residual monomer and some oligomeric material.

Triethylaluminum modified with 1 molar equiv of water has been effectively used to polymerize epoxides[19] and 3,3-bis(chloromethyl)oxetane.[20] It also caused polymerization of the 1,3-anhydro-β-D-glucopyranose derivative at room temperature to form an ether-insoluble polymer of low viscosity. The petroleum ether soluble fraction was largely oligomeric, and ALC gave no evidence of prominent peaks. The specific rotation of this polymer was remarkably low, and the stereoregularity, as estimated by comparing the relative peak heights of the two anomeric ^{13}C NMR peaks, was quite high in the β sense. This corresponds to largely cis opening of the anhydro ring.

When the specific rotations of the polymers were plotted against their estimated percent of α configuration, an essentially linear relationship (with some scatter) resulted, with extrapolated values of specific rotation for a pure β-(1→3)-linked glucopyranan derivative about +34° and pure α-(1→3)-linked glucopyranan derivative about +134°. For comparison, the fully benzylated pachyman, which is largely β-(1→3)-linked with a few β-(1→6) links,[21] has a specific rotation of +23.7°. A corresponding value for a benzylated α-(1→3)-linked glucopyranan is not available but that of perbenzylated α-(1→6)-linked glucopyranan is +113–114°. The (1→3)-α-D-glucopyranosyl linkage is reported to give higher positive specific rotations than α-(1→6),[22] in agreement with this extrapolation.

The ^{13}C anomeric peak heights may not give precise values for stereoselectivity, but the wide range of specific rotation values indicates a similar wide range of C-1 configurational proportions. If the value for perbenzylated pachyman is considered as indicative of a β-(1→3)-linked linear glucopyranan, then it is possible that the β content of polymer produced with triethylaluminum–water catalyst is as low as 83% β, rather than 91% β estimated from ^{13}C data. This range of values cannot result from simple ionization at the anomeric center during propagation, since the thermodynamically less favored anomer is in this case produced in large excess by a cis opening of the oxetane ring. Clearly different mechanisms must be operational in the polymerizations initiated with various catalyst systems, and it thus appears that trans opening and racemization are not the only modes of ring opening possible in polymerization of bicyclic acetals.

Experimental Section

NMR spectra were measured with a Varian XL-100 spectrometer in deuteriochloroform with tetramethylsilane (Me_4Si) as the internal standard. Chemical shifts are expressed in parts per million (ppm) downfield from the Me_4Si resonance. The configurational proportions of the anomeric carbon of the polymer were estimated by comparing the peak heights of the C-1 peaks at 96 and 102 ppm. Optical rotations were determined in chloroform at 25 °C in a Perkin-Elmer Model 141 polarimeter with a jacketed 1-dm cell. Viscosities were measured in a Cannon-

Ubbelohde semimicroviscometer at 25 °C. Liquid chromatography (ALC) was carried out with a Glenco septumlus injector (Model SV-3), a Glenco pump (Model HPLPS-1), and a Waters differential refractometer (Model R-401). Ethyl acetate–hexane (1:2 v/v) on a silica gel column (Whatman, Partisil M9 10/25) was used at a flow rate of 8 mL/min. A stainless steel column (60 cm × 1.88 cm outside diameter) packed with Styragel (200 Å, Waters Associates) was used for gel permeation separations at a toluene flow rate of 3 mL/min, with use of a Model HPLPS-1 Glenco pump.

Materials. The synthesis of 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose has been reported elsewhere.[9] The monomer was not synthesized in a large quantity at once. The amount sufficient for a few polymerizations was synthesized from 2,4,6-tri-*O*-benzyl-D-glucopyranose via 2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride immediately before the polymerizations. Because the monomer did not crystallize, purification by liquid chromatography was repeated and the resulting pure monomer was dried by distilling benzene from a monomer solution several times on a high-vacuum line; $[\alpha]^{25}_{D}$ +58.0, +61.8, +59.3° (*c* 1, $CHCl_3$).

Dichloromethane, toluene, and benzene were dried by refluxing on calcium hydride, distilled, and then further dried and kept on calcium hydride under high vacuum.

Phosphorus pentafluoride was generated in situ by pyrolysis of *p*-chlorobenzenediazonium hexafluorophosphate crystallized from water or methanol and dried on a high-vacuum line.

Boron trifluoride etherate and antimony pentachloride were distilled three times on a high-vacuum line, with the center cut taken each time, and distributed (by distillation in vacuo) to calibrated capillary tubes connected to a break seal. Triethyloxonium hexafluorophosphate was purified by precipitation in diethyl ether from dichloromethane solution under high vacuum, and the crystals were washed with the mixed solvent by refluxing and dried. After the crystals were weighed under nitrogen, they were dissolved in a known amount of dichloromethane under high vacuum. Then fixed amounts of the solution were transferred to break seals with a syringe under a nitrogen atmosphere. The catalyst solution was kept in a sealed break seal and added to the monomer solution by crushing the break seal under high vacuum.

Silicon tetrafluoride gas was condensed in a glass apparatus, dried under high vacuum, by cooling the apparatus with liquid air. The apparatus was connected to a vacuum line and silicon tetrafluoride was distilled (or sublimed) in vacuo three times from −78 °C to liquid air temperature. The purified silicon tetrafluoride was distributed to break seals by distillation in vacuo.

Commercial triethylaluminum and diethylzinc solutions in toluene (25 w/v %) were placed in a glass apparatus under a nitrogen flow and degassed several times on a high-vacuum line. One molar equivalent of degassed water was distilled into the ampule in vacuo and allowed to react with the organometallic compound with stirring. After being degassed several times, the apparatus was melted off the vacuum line and the solution was transferred under high vacuum through a glass filter to the other ampule connected to a break seal. The catalyst solution was transferred with a syringe to break seals under nitrogen, kept under high vacuum, and added to a monomer solution by crushing the break seal.

Potassium *tert*-butoxide was prepared under high vacuum by the reaction of potassium mirror with *tert*-butyl alcohol dried with sodium hydride, distilled three times on a high-vacuum line, and then thoroughly dried. Bone-dry benzene was introduced by distillation in vacuo, followed by addition of the benzene solution of 18-crown-6, recrystallized from hexane. The *tert*-butoxide was completely solubilized in benzene. The solution was diluted by introduction of the solvent up to the calibration mark. A fixed amount of a solution of known concentration was distributed with a syringe to break seals.

Thallous ethoxide was sealed in a break seal without further purification.

Polymerization. The transfer of the catalysts and solvents and all the polymerizations were carried out under high vacuum as previously reported. Polymerization conditions are summarized in Table I. The cationic polymerizations were terminated at the polymerization temperature by adding cold methanol. Reprecipitation was repeated three times into petroleum ether. The solutions from triethylaluminum–water and diethylzinc–water polymerizations were diluted with toluene and poured into petroleum ether. The recovered polymer was dissolved in chloroform and precipitated in petroleum ether twice after filtering the catalyst residue out. The anionic polymerization solutions were washed with water several times, dried over anhydrous magnesium sulfate, concentrated, and poured into petroleum ether.

All the polymers were freeze-dried from benzene, and the supernatant solutions were concentrated to dryness, further dried under vacuum, and subjected to ^1H NMR, ALC, and GPC.

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