Articles

Synthesis of (1→3)-α-D-Glucopyranan by Stereoregular Cationic Polymerization of Substituted 2,6-Dioxabicyclo[3.1.1]heptanes: 1,3-Anhydrotri(*p*-substituted-benzyl)-β-D-glucopyranoses

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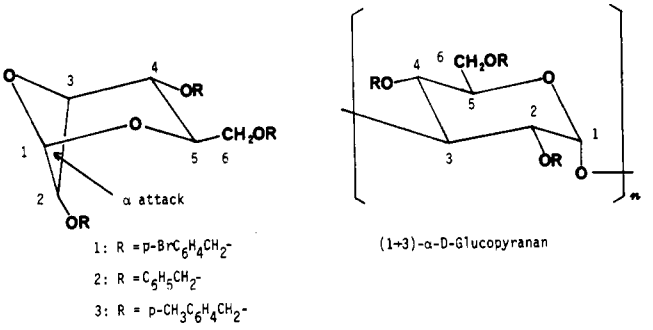
ABSTRACT: The influence of initiator, solvent, and temperature on the polymerization of 1,3-anhydro-2,4,6-tri-*O*-(*p*-bromobenzyl)-β-D-glucopyranose (**1**), 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose (**2**), and 1,3-anhydro-2,4,6-tri-*O*-(*p*-methylbenzyl)-β-D-glucopyranose (**3**) was investigated. Polymerization of **1** using trifluoromethanesulfonic anhydride or silver trifluoromethanesulfonate as initiator gave stereoregular (1→3)-α-D-glucopyranan derivatives, while other initiators were less stereoselective. Polymerization of **2** produced slightly less stereoregular polymers under the best conditions found. Compound **3** afforded only oligomers. Substituted polymers were characterized by ^{13}C NMR spectroscopy, polarimetry, gel permeation chromatography, vapor-phase osmometry, and intrinsic viscosity. Debenzylation or debromobenzylation of the substituted polymers afforded unsubstituted linear (1→3)-D-glucopyranans which were characterized by ^{13}C NMR spectroscopy, polarimetry, and complete hydrolysis to glucose by trifluoroacetic acid.

Introduction

The (1→3)-α-D-glucopyranan structure is a cell wall component of several species of fungi, yeasts, and lichen.[1] It is also produced extracellularly by *Streptococcus* species which have been implicated in the causes of dental caries[2,3] and certain heart infections. Synthetic polysaccharides have been used as model compounds to elucidate the relationship between molecular structure and function of natural polysaccharides and to investigate enzyme, antibody, and lectin reactions.[4] Therefore, the synthesis of (1→3)-α-D-glucopyranan might provide a useful model compound for biological and immunological studies.

We recently reported syntheses,[5-8] a conformational analysis,[9] and polymerizations[10,11] of substituted 1,3-anhydro-β-D-glucopyranose and -β-D-mannopyranose derivatives. In a previous preliminary investigation[10] of the polymerization of 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose (**2**) none of the initiators afforded completely stereoregular polymer. Polymerization of **2** using Lewis acids gave polymers with varied stereoregularity, while polymerization using triethylaluminum–water afforded polymer with 90% β-linkages, corresponding to cis opening of the anhydro ring. Anionic initiators failed to polymerize **2**. Recent results[11] with 1,3-anhydro-β-D-mannopyranose derivatives have shown that "nonmetal halide" initiators, such as tris(4-bromophenyl)aluminum hexachloroantimonate, triphenylcarbenium perchlorate, and trifluoromethanesulfonic anhydride, afforded polymers with higher stereoregularity and molecular weight than metal halide initiators, such as phosphorus pentafluoride and antimony pentachloride. We now report the use of these and other initiators for the polymerization of **2** and **3**, and the stereoregular polymerization of **1**. Unsubstituted (1→3)-D-glucopyranans of different stereoregularities were synthesized by the debenzylation or debromobenzylation of the resultant polymers.



Results and Discussion

When monomer **3** was treated with trifluoromethanesulfonic (triflic) anhydride or phosphorus pentafluoride at −60 or −78 °C for 2–10 h, only a trace of petroleum ether insoluble material was produced. The soluble fraction was identified by ^1H NMR and gel permeation chromatography as low molecular weight oligomers, presumably (1→3)-linked dimers and trimers. The stereoregularity of the methylbenzylated oligomers was not determined. No unreacted monomer was detected. The major effort was therefore directed toward the polymerization of monomers

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Table I
Polymerization of 1,3-Anhydroglucose Derivatives

monomer[a]	initiator	concn, mol %	solv	monomer/solv, g/(100 mL)	temp, °C	time, h	yield,[b] %	$[\alpha]^{23}_D$,[c] deg	α,[d] %	$10^{-3}\bar{M}_{GPC}$[e]	$\bar{M}_w/\bar{M}_n$	$10^{-3}\bar{M}_{OSM}$[f]	$[\eta]$,[g] dL/g	$[\alpha]^{23}_D$-(desub),[h] deg
1	$(CF_3SO_2)_2O$	2.0	CH_2Cl_2	50	−78	4.0	59	62.8	95	1.9	2.9			
1	$(CF_3SO_2)_2O$	2.0	CH_2Cl_2	50	−60	6.0	67	62.5	95	20.0	2.3		0.31	+228
1	$(CF_3SO_2)_2O$	2.0	CH_2Cl_2	50	−40	2.0	94	61.0	94	8.4	6.8			
1	$(CF_3SO_2)_2O$	2.0	CH_2Cl_2	50	0	2.0	90	52.2	95	5.2	9.3			
1	$(CF_3SO_2)_2O$	2.0	toluene	30	−40	0.5	69	64.5	100	16.1	1.7		0.12	+252
1	$(CF_3SO_2)_2O$	2.0	toluene	30	0	2.0	86	59.4	92	9.7	4.0	29.9		
1	$(CF_3SO_2)_2O$	2.0	benzene	30	0	3.5	74	62.6	94	3.5	3.1			
2	$(CF_3SO_2)_2O$	2.0	CH_2Cl_2	50	−60	6.0	46	103.3	73	2.7	2.1		0.07	+185
2	$(CF_3SO_2)_2O$	2.0	CH_2Cl_2	50	0	6.0	45	107.5	80	3.6	1.8		0.14	+205
2	$(CF_3SO_2)_2O$	2.0	toluene	40	−40	4.5	86	119.2	93	6.4	1.6		0.22	
2	$(CF_3SO_2)_2O$	2.0	toluene	40	0	4.5	92	112.9	91	2.3	2.2		0.07	+232
2	$(CF_3SO_2)_2O$	2.0	benzene	40	0	4.5	88	119.6	92	2.4	1.8	19.1	0.10	
1	$AgCF_3SO_3$	2.0	benzene	30	RT[i]	18	100	61.4	100	31.0	1.8		0.39	+259
2	$AgCF_3SO_3$	2.0	benzene	40	RT[i]	21	94	114.7	90	2.1	1.8	10.6	0.10	
2	$(C_6H_5)_3CCl$	2.0	toluene	33	−25	23	10.5			3.1	2.1			
2	$(C_6H_5)_3CCl$	2.0	toluene	33	0	22	59	113.4	89	3.7	1.8		0.13	
2	$(C_6H_5)_3CCl$	2.0	benzene	33	RT[i]	21	95	121.5	95	4.4	2.2	22.7	0.19	
2	$(C_6H_5)_3CCl$	2.0	benzene	33	50	38	trace							
2	$(C_6H_5)_3CClO_4$	2.0	toluene	33	−55	26	6	91.6		1.3	1.4			
2	$(C_6H_5)_3CClO_4$	2.0	CH_2Cl_2	50	−55	26	76	103.9	70	1.2	1.7		0.09	
2	$(C_6H_5)_3CClO_4$	2.0	CH_2Cl_2	50	−15	26	81	110.3	87	0.9	1.9		0.03	
2	$(C_6H_5)_3CClO_4$	2.0	CH_2Cl_2	50	RT[i]	18	80	74.3	50	0.5	1.5	4.0	0.05	
2	$(p\text{-}BrC_6H_5)_3NSbCl_6$	2.0	CH_2Cl_2	50	−15	54	53	93.8	69	1.5	1.8		0.06	
2	$(p\text{-}BrC_6H_5)_3NSbCl_6$	2.0	CH_2Cl_2	50	RT[i]	18	75	88.9	60	0.7	1.5		0.08	
1	PF_5	2.0	CH_2Cl_2	50	−95	3.5	33	59.1	75	0.8	1.5			
1	PF_5	4.7	CH_2Cl_2	50	−78	3.5	96	49.2	84	1.7	3.4	8.0	0.11	
1	PF_5	4.7	CH_2Cl_2	50	−60	3.5	94	58.7	73	2.3	2.9		0.10	
1	$SbCl_5$	6.0	CH_2Cl_2	50	−60	3.5	89	62.7	60	0.9	2.0	4.0	0.06	

[a] Arabic numeral 1 indicates bromobenzylated monomer (150 mg for each polymerization), 2 benzylated monomer (200 mg for each polymerization). [b] Yield of petroleum ether insoluble material, in percent. [c] Determined in $CHCl_3$. [d] Estimated by ^{13}C NMR. [e] $\bar{M}_n$ as determined by GPC using polystyrene standards. [f] $\bar{M}_n$ as determined by vapor-phase osmometry. [g] Determined in $CHCl_3$ at 25 °C. [h] Desubstituted (1→3)-D-glucan. [i] Room temperature.

1 and 2, and several initiators were tested for their catalytic activity (Table I). The polymers were isolated as fluffy white powders with relatively low molecular weights and low intrinsic viscosities.

Phosphorus pentafluoride and antimony pentachloride, which have been shown to be stereospecific initiators for 1,6-anhydro-[4] and 1,4-anhydroglycopyranose[12,13] derivatives, respectively, afforded bromobenzylated polymers of low molecular weight and stereoregularity as has been shown previously[10] for the polymerization of monomer 2. Triflic anhydride in toluene at −40 °C and silver triflate in benzene at room temperature produced completely stereoregular bromobenzylated polymers from 1, but none of the initiators gave completely stereoregular benzylated polymers. Polymerization of 2 using triflic anhydride or silver triflate afforded benzylated polymers with a high percentage (73–93%) of α-linkages, but the benzylated polymer with the highest stereoregularity (95% α) was obtained with triphenylchloromethane at room temperature in benzene. Triphenylcarbenium perchlorate and tris(4-bromophenyl)amminium hexachloroantimonate gave low molecular weight nonstereoregular benzylated polymers.

The formation of both stereoregular and nonstereoregular polymers suggests that propagation proceeds by way of trialkyloxonium ion and carbocation intermediates; the former reacts stereospecifically to produce α linkages, the latter nonstereospecifically to produce both α- and β-linkages. The amount of the thermodynamically more favored α anomer which forms depends on polymerization conditions.

Counterions derived from nonmetal halide initiators such as triflic anhydride interact much more strongly with a carbocation than counterions derived from metal halides such as phosphorus pentafluoride and antimony pentachloride.[14] Apparently, increased interaction between propagating intermediate and counterion increases the stereospecificity of polymerization, possibly by stabilizing the trialkyloxonium ion or alternatively by shielding a C-1 carbocation. The similar stereoregularities of polymers produced by triflic anhydride and silver triflate are consistent with stereoregulation by the counterion.

The rate and stereospecificity of polymerization were generally greater, and the molecular weight distribution of the polymers was usually narrower in aromatic solvents than in dichloromethane.

Optimal polymerization temperature range must be determined for each monomer and initiator. At lower temperatures, polymerization is sluggish. At higher temperatures, polymer stereoregularity decreases, possibly because of increased carbocation character in the propagating species, and molecular weight decreases and molecular weight distribution broadens, probably due to enhanced chain-transfer reactions.

The stereoregularity of the substituted polymers was estimated by ^{13}C NMR spectroscopy by comparing the anomeric peak areas at δ 102.7 and 96.2, corresponding to the β and α configurations, respectively. Generally, bromobenzylated polymers were more stereoregular than benzylated polymers prepared under similar conditions.

A plot of specific rotation vs. estimated percentage of α-linkages for the benzylated polymers revealed an essentially linear relationship: $[\alpha]^{23}_D = 0.94$ (% α-linkages) + 31.5°. The extrapolated values of specific rotation for a perbenzylated (1→3)-β-D-glucopyranan derivative and a perbenzylated (1→3)-α-D-glucopyranan derivative are +31.5° and +125.4°, respectively. The accuracy of the extrapolated value of specific rotation for a (1→3)-β-D-glucopyranan derivative is limited by the lack of data for benzylated glucopyranans with less than 50% α-linkages.

For comparison, a fully benzylated pachyman, which consists mainly of (1→3)-β-D-glucopyranose residues,[15] has a specific rotation of +23.7°.[10] A corresponding value for a perbenzylated (1→3)-α-D-glucopyranan is not available, but a perbenzylated (1→6)-α-D-glucopyranan has a specific rotation of +113–114°.[16,17] The (1→3)-α-D-glucopyranosyl linkage is reported to give higher optical rotations than the (1→6)-α-D-glucopyranosyl linkage,[18] in agreement with this extrapolation. The specific rotations of the bromobenzylated polymers ranged from +49.2° to +64.5°, but there was no consistent relationship between specific rotation and estimated anomeric configuration.

The number-average molecular weight of the substituted glucopyranans, determined by gel permeation chromatography (GPC) using polystyrene standards ($\bar{M}_{GPC}$), ranged from 5.0×10^2 ($\overline{DP}_n \simeq 1$) to 6.4×10^3 ($\overline{DP}_n \simeq 15$) for the benzylated glucopyranans and from 8.0×10^2 ($\overline{DP}_n \simeq 1$) to 3.1×10^4 ($\overline{DP}_n \simeq 46$) for the bromobenzylated glucopyranans. The absolute number-average molecular weight of a few selected benzylated and bromobenzylated glucopyranans was determined by vapor pressure osmometry ($\bar{M}_{OSM}$). The calculated values of $\bar{M}_{OSM}$ were 5–8 times greater than the corresponding values of $\bar{M}_{GPC}$ for the benzylated polymers and 3–4 times greater than the corresponding values of $\bar{M}_{GPC}$ for the bromobenzylated polymers. The ratio of $\bar{M}_{OSM}/\bar{M}_{GPC}$ appeared to be related to stereoregularity: the more stereoregular the polymer, the smaller the ratio of $\bar{M}_{OSM}/\bar{M}_{GPC}$. Polymers having some β-linkages apparently pack more tightly than polymer with α-linkages.

The molecular weight distribution, analyzed by GPC, was essentially symmetrical for the benzylated polymers and narrower than for most of the bromobenzylated polymers. The calculated values of $\bar{M}_w/\bar{M}_n$ ranged from 1.4 to 2.2 for the benzylated polymers and from 1.5 to 9.3 for the bromobenzylated polymers.

The intrinsic viscosity of the benzylated and bromobenzylated polymers was low, ranging from 0.03 to 0.22 dL/g for benzylated polymers and from 0.03 to 0.39 dL/g for bromobenzylated polymers. Intrinsic viscosity did not correlate well with $\bar{M}_{GPC}$, possibly because of differences in the molecular weight distributions of the polymers.

The low molecular weight and low intrinsic viscosity of these polymers may result from the carbocation character of the propagating species. Chain-transfer and termination reactions tend to be enhanced for carbocation relative to oxonium ion intermediates.[4] Alternatively, the low molecular weight may result from a slow propagation rate. Since the polymerization of 1 with triflic anhydride at −40 °C for 2 h converted 94% into petroleum ether insoluble products, the rate of propagation is not particularly slow. Therefore, the main reason for the low molecular weight appears to be excessive chain transfer or termination during polymerization.

A comparison of the results obtained for the three monomers reveals that molecular weight and polymerizability are affected by monomer substitution and decrease in the order **1 > 2 > 3** and that stereoregularity decreases in the order **1 > 2**. The initiator undoubtedly complexes with the ring and ether oxygens. The effective initiator concentration and therefore the rate of initiation depend upon the position of the complexation equilibrium between ring and ether oxygens. Electron-donating substituents, like the *p*-methyl group, enhance the basicity of the ether oxygens and shift the equilibrium away from the ring oxygen, whereas electron-withdrawing substituents, like the *p*-bromine atom, reduce the basicity of the ether oxygens and shift the equilibrium toward the ring oxygen. It is difficult to predict the effect of monomer substitution on the rate of propagation. Although electron-donating substituents should increase the nucleophilicity of the monomer, they should also stabilize the propagating chain end. Copolymerization studies necessary to further evaluate the effect of substituent structure on monomer reactivities have not yet been performed. Although little is known about the mechanism of termination or chain transfer of anhydro sugars, these processes appear also to be strongly influenced by monomer substitution. Compared to electron-donating substituents, electron-withdrawing substituents tend to increase stereospecificity and decrease chain-transfer and termination reactions.

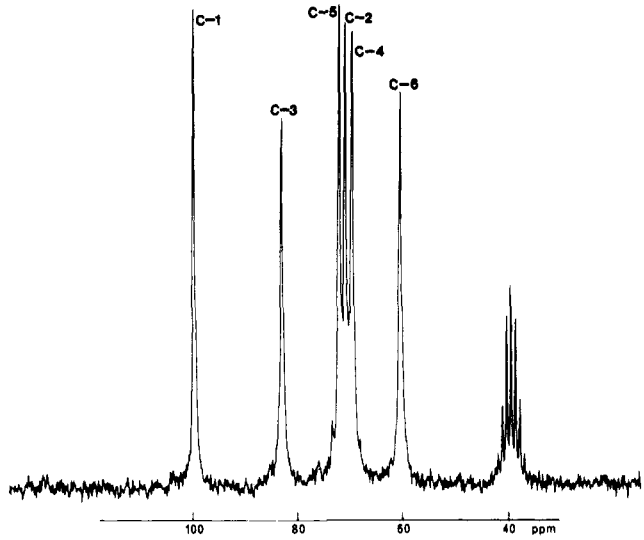

Figure 1. ^{13}C NMR spectrum of stereoregular unsubstituted linear (1→3)-α-D-glucopyranan produced by using silver triflate in benzene at room temperature.

It is also interesting to compare the results of this investigation with those obtained from the polymerization of 1,3-anhydromannose derivatives. Although triflic anhydride caused stereoregular polymerization of both 1,3-anhydroglucose and 1,3-anhydromannose derivatives, optimal polymerization conditions must be determined for each monomer. In general, mannopyranans were more stereoregular than glucopyranans formed under similar conditions, possibly because of the difference in monomer configuration at C-2. In contrast to the equatorial arrangement of the C-2 substituent in the anhydromannose derivative, axial arrangement of the substituent in the anhydroglucose derivative may hinder the approach of the monomer from the α direction to the growing end of the polymer.[9]

The mannopyranans generally had higher molecular weights than the glucopyranans, but the intrinsic viscosities were similar. The 1,3-anhydroglucose and 1,3-anhydromannose derivatives polymerized at similar rates, but a copolymerization study to evaluate monomer reactivities has not been carried out.

In order to clarify the structures of the polymers, representative polymers with varying molecular weights and stereoregularities were debenzylated or debromobenzylated, and then hydrolyzed. The hydrolysate was analyzed by paper and liquid chromatography. In all cases glucose was the only sugar present. Neither its C-3 epimer, allose, nor nonhydrolyzable disaccharides were detected, indicating that the polymers must be (1→3)-D-glucopyranans.

The ^{13}C NMR spectra of the unsubstituted glucans (Figure 1) were assigned by comparison with the spectra recorded for naturally occurring (1→3)-α- and (1→3)-β-

D-glucopyranans. The spectrum of a (1→3)-α-D-glucopyranan from *Penicillium patulum* (pD 14, 50 mg/mL, 32 °C, D_2O; C-1 (δ 101.3), C-2 (δ 72.2), C-3 (δ 83.2), C-4 (δ 71.7), C-5 (δ 73.7), and C-6 (δ 62.2))[19] corresponded closely to the spectrum recorded for synthetic stereoregular (100% α-linkages) D-glucopyranan (C-1 (δ 99.7), C-2 (δ 70.9), C-3 (δ 83.0), C-4 (δ 69.6), C-5 (δ 72.0), and C-6 (δ 60.4)). The small peak at δ 73.5 was assigned to C-3 of the nonreducing end groups by comparison with the ^{13}C spectrum of 3-*O*-α-D-glucopyranosyl-D-glucopyranose.[19] No peaks were evident in the region from δ 97 to δ 91, the region where C-1 of a reducing end group would resonate, suggesting that the $\overline{DP}_n$ of the synthetic stereoregular glucopyranan may be as high as 40 to 50. The differences between the reported and observed chemical shifts could result from difference in pD, solvent, temperature, and concentration. Usually not all resonances are equally sensitive to experimental conditions.

The reported ^{13}C NMR signals of a (1→3)-β-D-glucopyranan from *L. digitata* (pD 7, 50 mg/mL, 32 °C, D_2O; C-1 (δ 103.81), C-2 (δ 74.4), C-3 (δ 85.5), C-4 (δ 69.3), C-5 (δ 76.8), and C-6 (δ 61.9))[19] were used to identify peaks due to (1→3)-β-linkages of nonstereoregular synthetic D-glucopyranans (C-1 (δ 103.9), C-2 (δ 72.1), C-3 (δ 85.8), C-4 (δ 68.2), C-5 (δ 76.3), and C-6 (δ 60.7)). The signals due to α-linkages of nonstereoregular glucopyranans (C-1 (δ 100.0), C-2 (δ 71.0), C-3 (δ 83.0), C-4 (δ 69.5), C-5 (δ 72.1), and C-6 (δ 60.3)) were nearly identical with the corresponding resonances of stereoregular α-D-glucopyranans.

No resonances arising from aromatic residues were found in the ^{13}C spectra of the synthetic glucopyranans, indicating that debenzylation or debromobenzylation was complete.

The stereoregularity of the unsubstituted polymers was estimated by ^{13}C NMR by comparing the areas of the anomeric resonances at δ 103.9 (β) and δ 100.0 (α). The specific rotation of the unsubstituted polymers varied linearly with the estimated stereoregularity. The stereoregular α-D-glucopyranans generated by silver triflate and triflic anhydride had specific rotations of +259° (*c* 0.5, 1 N NaOH) and +252° (*c* 0.5, 1 N NaOH), respectively. These values of specific rotation are similar to values reported for naturally occurring (1→3)-α-D-glucopyranans (+220° to +257°).[1] The extrapolated value of specific rotation for a (1→3)-β-D-glucopyranan was +6.2°. For comparison, the specific rotation of pachyman was reported as +21.5° (*c* 1.0, 10% NaOH).[15] The accuracy of the extrapolated value is limited by the lack of data for glucopyranans with less than 70% α-linkages.

The solubility of the unsubstituted glucopyranans depended on their stereoregularity. Stereoregular (1→3)-α-D-glucopyranans were nearly insoluble in water and cold dimethyl sulfoxide, while less stereoregular glucopyranans were slightly soluble in water and soluble in dimethyl sulfoxide. All of the synthetic glucopyranans were soluble in 1 N NaOH. However, the presence of free reducing end groups, from chain-transfer or chain-cleavage reactions, made the glucopyranans unstable in basic media, as evidenced by the gradual decrease in their optical rotation with time. Reduction of the reducing end groups with $NaBH_4$ improved the stability of the glucopyranans.

In summary, it is possible to synthesize (1→3)-D-glucopyranan derivatives with various stereoregularities and molecular weights by the appropriate choice of polymerization conditions. The use of *p*-bromobenzylated monomer, triflic anhydride or silver triflate as initiator, and nonpolar solvent favors stereoregular polymerization. Linear (1→3)-D-glucopyranans can be synthesized by debenzylation or debromobenzylation of substituted polymers.

Experimental Section

Materials. Monomers **1**–**3** were synthesized in small quantitites (~1 g), sufficient for a few polymerizations, by a previously reported method.[8] Each monomer was purified repeatedly by liquid chromatography. Monomer **1** was crystallized several times from ethyl acetate–hexanes and then dried under high vacuum: mp 76–77 °C, $[\alpha]^{23}_D$ +64.7° (*c* 1.36, $CHCl_3$). Since **2** and **3** did not crystallize, they were dried, immediately before polymerization, by distilling benzene from a monomer solution several times on a high-vacuum line: compound **2**, $[\alpha]^{23}_D$ +59.2° (*c* 0.95, $CHCl_3$); compound **3**, $[\alpha]^{23}_D$ +56.1° (*c* 1.23, $CHCl_3$).

Dichloromethane, benzene, and toluene were purified by extracting with concentrated sulfuric acid, dried by refluxing over calcium hydride, distilled, and then kept over calcium hydride under high vacuum.

Phosphorus pentafluoride was generated in situ by pyrolysis of *p*-chlorobenzenediazonium hexafluorophosphate crystallized from water or ethanol and dried on a high-vacuum line. Antimony pentachloride and trifluoromethanesulfonic anhydride were distilled twice on a high-vacuum line, a center fraction collected each time, and finally distilled in vacuo, into calibrated capillary tubes connected to a break-seal.

Silver trifluoromethanesulfonate (Willowbrook Labs) was recrystallized from benzene. Triphenylchloromethane (Aldrich, reagent grade) was recrystallized from benzene–acetyl chloride and washed with petroleum ether according to the method of Vogel:[20] mp 111–112 °C, lit.[20] mp 111–112 °C. Triphenylcarbenium perchlorate was synthesized from triphenylcarbinol and perchloric acid by a reported procedure:[21] mp 145 °C, lit.[21] mp 144 °C. Tris(4-bromophenyl)amminium hexachloroantimonate (Aldrich, reagent grade) was used without further purification. All solid catalysts were dried under high vacuum immediately before use.

Polymerization. All polymerizations were carried out under high vacuum.[22] All solvents and some initiators were transferred under high vacuum. Solid initiators were added under positive nitrogen pressure. Polymerizations were terminated at the polymerization temperature by adding cold methanol. The precipitated polymers were dissolved in chloroform and precipitated into petroleum ether 3 times. The petroleum ether insoluble fractions were dissolved in benzene, filtered, and then freeze-dried.

Preparation of (1→3)-D-Glucopyranans. Selected polymers were debenzylated or debromobenzylated by a modification of Ruckel's technique.[23] A solution of benzylated polymer (150 mg) in toluene (5 mL) was added to a solution of sodium (96 mg) in liquid ammonia (40 mL) at −33 °C. After 1.5 h solid ammonium chloride was added until the blue color disappeared. The ammonia was evaporated and water was added. The aqueous layer was washed twice with dichloromethane.

Attempts to debromobenzylate isolated polymers under the same conditions were unsuccessful. Debromobenzylation was accomplished similarly by addition of a solution of polymer (140 mg) in toluene (5 mL) to liquid ammonia (40 mL) containing lithium (20 mg) at −78 °C and reaction for 3 h.

All glucopyranans were dialyzed from distilled water by using a UM-5 membrane (Amicon, nominal M_r = 500) until ion-free, and isolated as fluffy white powders by freeze-drying from distilled water, yield ~90%.

Hydrolysis of (1→3)-D-Glucopyranans and Identification of Sugars. (1→3)-D-glucopyranan (2–4 mg) was placed in a 25-mL round-bottomed flask equipped with a reflux condenser. Trifluoroacetic acid (2 N, 3 mL) was added, and the mixture refluxed for 1 h according to a reported method.[24] The solution was evaporated to dryness, and the residue redissolved in water (10 mL). Evaporation was repeated 3 times. The hydrolysate was subjected to paper chromatography (Whatman No. 1 paper) using ethyl acetate/pyridine/water (8/2/1) as the mobile phase. After 24 h the chromatograph was developed by using sodium hydroxide (5%) in 95% ethanol and silver nitrate (5% in acetone) as spray reagents. Only glucose was present, no allose (R_g 1.26) or nonhydrolyzable disaccharide was detected. Liquid chromatography using a carbohydrate column (Waters) with acetonitrile–water (85:15) as eluant confirmed these results.

Characterization of Polymers. The ^{13}C NMR spectra were recorded in the Fourier-transform-proton-noise-decoupled mode with a Varian XL-100-15 spectrometer. The ^{13}C NMR spectra of substituted glucopyranans were measured at ambient temperature in chloroform-*d* or benzene-d_6 with tetramethylsilane (Me_4Si) as the internal standard. The chemical shifts are expressed in ppm downfield of the internal Me_4Si absorption. The ^{13}C spectra of unsubstituted glucopyranans were recorded at 70 °C in dimethyl-d_6 sulfoxide, which also served as internal standard. Chemical shifts are expressed in ppm relative to the central absorption of dimethyl-d_6 sulfoxide (δ 39.5). A 60° pulse, 6151-Hz spectral width, 0.666-s acquisition time, and 8192 data points were used for all ^{13}C NMR spectra.

Optical rotations were determined in chloroform for benzylated or bromobenzylated polymers and in 1 N NaOH for free polysaccharides at 23 °C in a Perkin-Elmer Model 141 polarimeter with a jacketed 1-dm cell. Optical rotations for free polysaccharides were measured after allowing approximately 1 h for complete dissolution.

Molecular weight distributions of the substituted polymers were analyzed by gel permeation chromatography in tetrahydrofuran. A Glenco septumless injector (Model SV-3), a Glenco pump (Model HPLPS-1), a Waters differential refractometer (Model R-401), and five 30-cm-long stainless steel columns packed with micro-styragel (Waters, 1×10^5, 1×10^4, 1×10^3, 5×10^2, and 1×10^2 Å) were used. The flow rate was 2.0 mL/min. Calibration curves were obtained by using polystyrene standards (Waters). Viscosities were measured in chloroform with a Cannon-Ubbelohde viscometer at 25 °C. The absolute number-average molecular weights of the substituted polymers were determined in chloroform at 25 °C with a Mechrolab Model 301 vapor-phase osmometer.

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Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose and 1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose

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ABSTRACT: Ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (ABGLU) (=1,5-anhydro-2,3,6-tri-*O*-benzyl-β-D-glucofuranose) by phosphorus pentafluoride catalyst gave new stereoregular polysaccharide derivatives, 2,3,6-tri-*O*-benzyl-(1→5)-α-D-glucofuranans with $[\alpha]_D$ value of +82° and number-average molecular weights of 8.5×10^3 ($\overline{DP}_n = 20$). Natural cellulose and amylose, (1→4)-β-D-glucopyranan and (1→4)-α-D-glucopyranan, respectively, were used to determine the structure of the synthetic glucan by means of ^{13}C NMR spectroscopy and optical rotation. Cationic catalysts other than phosphorus pentafluoride provided poly(ABGLUs) with mixed structures depending on the polymerization conditions. The ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose (ABGAL) (=1,5-anhydro-2,3,6-tri-*O*-benzyl-α-D-galactofuranose) yielded polymers with mixed structures consisting, under all polymerization conditions employed, mainly of (1→5)-β-D-galactofuranosidic units. The structure of poly(ABGALs) was influenced by relatively minor changes in polymerization conditions. The mechanism of the ring-opening polymerization of ABGLU and ABGAL is discussed.

In addition to the successful synthesis of dextran-type polysaccharides from several D-aldohexoses,[1,2] a cellulose-type polysaccharide, (1→4)-β-D-ribopyranan, has been prepared with D-ribose as the starting monosaccharide.[3] Although it has been revealed that the ring-opening polymerization of 1,6-anhydro sugars is an excellent method for obtaining stereoregular (1→6)-α-D-glycopyranans, the application of the same method to 1,4-anhydro sugars has not always provided a cellulose-type polysaccharide, i.e., a (1→4)-β-D-glycopyranan. Previously, 1,4-anhydro-α-D-

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