

Steric Control in the Polymerization of 1,6-Anhydro- β -D-glucopyranose Derivatives

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Abstract: Poly- α -(1 \rightarrow 6')-anhydro-2,3,4-tri-*O*-benzyl-D-glucopyranose is produced at highest degrees of polymerization and stereoregularity by treatment of the corresponding 1,6-anhydro sugar derivative with low concentrations (2.5 mol %) of phosphorus pentafluoride in methylene chloride at -78° . The use of other solvents or additives or higher concentrations of catalyst or *in situ* generation of the catalyst from silver salts tends to result in the formation of lower molecular weight polymers with minor amounts of configurational imperfections. A few other fluorine-containing Lewis acids or cations with fluorine-containing gegenions produce essentially stereoregular polymers. The use of higher temperatures or gegenions that do not contain fluorine results in production of polymers of random configuration. Loss of stereospecificity apparently results from the use of conditions which convert the propagating site from trialkyloxonium ion into a glycosyl carbonium ion. In the case of esters, the cations are probably stabilized by C-2 ester participation. The anhydro sugar triacetate and its cation are less reactive than the anhydro sugar ethers and their cations. Therefore, the esters are polymerizable only at higher temperatures and produce low molecular weight random polymers.

In 1961 Korshak and coworkers¹ reported the formation of a crystallizable polymer from 1,6-anhydro-2,3,4-tri-*O*-methyl- β -D-glucopyranose (trimethyllevoglucosan). Hutten² in Bredereck's laboratory, at about the same time, developed a method of preparing nonstereoregular polymers from both ethers and esters of the same anhydro sugar. The two groups made use of cationic initiators under widely different conditions and it is of interest to learn, therefore, what experimental factors control the stereoregularity of propagation and the frequency of chain termination processes.

Considerable progress had been made on this problem already. Tu³ in this laboratory established that the polymeric trimethyl ether prepared under Korshak's conditions (BF_3 etherate, toluene solvent, room temperature) was of relatively low molecular weight and of high stereoregularity. Ruckel⁴⁻⁶ modified the conditions of polymerization (PF_5 , methylene chloride solvent, -78°) to obtain polymers of high molecular weight and high stereoregularity from three different ethers of levoglucosan. He also prepared the parent polysaccharide poly- α -(1 \rightarrow 6)-anhydro-D-glucopyranose by debenzoylation of the tribenzyl ether. Enzymic analysis of this material by Reese and Parrish⁷ led these men to estimate that the configuration at C-1 was 100% α , and 98% of the polymer was linked α -1 \rightarrow 6. The polymer is also oxidized by periodate with the consumption of theoretical amounts of oxidant and formation of theoretical amounts of formic acid.⁸ Ruckel

found in addition that the use of Korshak's conditions failed to result in polymerization of levoglucosan esters. Further work at this laboratory⁸ has shown that ethers of other 1,6-anhydro aldoses can also be polymerized to give α -(1 \rightarrow 6')-linked polysaccharides, so a systematic investigation of the polymerization of these compounds takes on added significance.

The reaction conditions used by Hutten on levoglucosan esters and ethers differ widely from those used by Korshak and by this laboratory. Hutten's conditions include the use of a nitromethane solvent at 0° and a complex initiator system consisting of tetraacetylglucosyl halide or an acyl halide, and silver perchlorate. Reaction of the two catalyst components results in the generation of a carbonium ion perchlorate, the precipitation of silver halide, and propagation of a polymer of low molecular weight and random configuration. Compared to our preparative method for high molecular weight stereoregular polymers, his reaction conditions include a higher temperature, a different solvent, generation of a "free" carbonium ion as initiator, a different gegenion, precipitation, and presence of a foreign solid substance. Some of these experimental differences undoubtedly result in a greater carbonium ion character in the propagating species⁹ in Hutten's case and a lower stereospecificity. The preceding article demonstrates which are the most significant variables in producing polymers of high stereoregularity and viscosity.

Let us consider first simple variations in the experimental conditions used in phosphorus pentafluoride catalyzed polymerization of tribenzyllevoglucosan in methylene chloride. At -78° , the stereoregularity and the molecular weight of the product increases as the catalyst to monomer ratio is decreased. Intrinsic viscosities of 0.77 and specific rotations of $[\alpha]^{25}_D$ 113.5 $^\circ$ have been obtained at 2.5 mol % of catalyst. The specific rotation decreases 2-3% by increasing the catalyst to monomer ratio to 20 mol %, and viscosities

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

Notebook ref	Solvent, ml/g of monomer	Catalyst	Mol % catalyst	Temp, °C	Convrn, %	$[\alpha]^{25}_D$, ^b deg	$[\eta]$, ^c dl/g
112*	CH ₂ Cl ₂	PF ₅	1.0	-78	0.1
116*	CH ₂ Cl ₂	PF ₅	2.5	-78	98.6	113.5	0.77
121*	CH ₂ Cl ₂	PF ₅	5.0	-78	99.0	113.2	0.71
117*	CH ₂ Cl ₂	PF ₅	7.5	-78	96.8	112.5	0.52
114*	CH ₂ Cl ₂	PF ₅	10.0	-78	96.8	112.3	0.54
122*	CH ₂ Cl ₂	PF ₅	12.5	-78	96.0	112.0	0.42
35	CH ₂ Cl ₂	PF ₅	20.0	-78	92.3	109.5	0.36
115*	CH ₂ Cl ₂	PF ₅	40.0	-78	85.6	101.1	0.16
52	CH ₂ Cl ₂	PF ₅	20.0	0	50.0	62.4	0.04
47	CH ₃ NO ₂	PF ₅	20.0	0	38.0	60.1	0.05
27	Toluene	SbF ₅	20.0	0	15.5	62.3	0.04
38	CH ₂ Cl ₂	SbF ₅	20.0	-78	31.3	105.7	0.10
45	CH ₂ Cl ₂	SbCl ₅	20.0	-78	59.7	83.4	0.06
44	CH ₂ Cl ₂	TiCl ₄	20.0	-78	2.0
39	SO ₂	PF ₅	20.0	-78	83.5	105.7	0.10
46	SO ₂	PF ₅	20.0	-78	78.3	102.8	0.09
55	CH ₂ Cl ₂	PF ₅ -H ₂ O, 2:1	20.0	-78	92.0	108.4	0.28
124*	CH ₂ Cl ₂	PF ₅ -CH ₃ COOCH ₃ , 1:1	20.0	-78	60.2	105.7	0.37
19	CH ₃ NO ₂	(C ₆ H ₅) ₃ C ⁺ -SbCl ₆ ⁻	20.0	0	37.3	67.0	0.04
36	CH ₂ Cl ₂	PF ₅ -CH ₃ COF, 1:1	20.0	-78	74.9	109.5	0.10
37	CH ₂ Cl ₂	PF ₅ -CH ₃ COF, 1:1	20.0	-78	62.8	109.4	0.11
123*	CH ₂ Cl ₂	PF ₅ -CH ₃ COF, 1:1	2.5	-78	96.0	110.6	0.54
53	CH ₂ Cl ₂	AgPF ₆ -CH ₃ COCl, 1:1	20.0	-78	59.0	101.0	0.06
4	CH ₃ NO ₂	(C ₆ H ₅) ₃ C ⁺ -SbCl ₆ ⁻	6.0	0	10.0	59.0	...
54	CH ₂ Cl ₂	AgPF ₆ -(CH ₃) ₃ C ₆ H ₅ CH ₂ Cl	20.0	-78	31.0	70.2	0.04
66	CH ₂ Cl ₂	AgPF ₆ -TAcGCl ^d	20.0	-78	0
15	CH ₃ NO ₂	SbF ₅ -CH ₃ COCl, 1:1	14.0	0	55.0	61.0	0.05
133	CH ₂ Cl ₂	BF ₃ ·OEt ₂	20.0	-78

^a 1.0 g of monomer was polymerized in 3.0 ml of solvent for 100 hr except for experiments indicated by asterisks which were 0.5 g of monomer in 1.5 ml of CH₂Cl₂. ^b Determined in chloroform, ^c 1 g/100 ml. ^d Determined in chloroform at 25°. ^e TAcGCl = tetraacetylglucosyl chloride.

are approximately halved ($[\eta]^{25}_{CHCl_3}$ 0.36). An increase to 40 mol % ratio produces even larger changes. Similar changes over a narrower range are apparent in Ruckel's data, and have been observed by Frechet.⁸ Since the catalyst is generated by pyrolysis of a diazonium salt and transferred through the gas phase, the actual percentage of active initiator obtained under particular conditions may depend upon the completeness of catalyst decomposition and transfer and may be sensitive to minor changes in technique or equipment design. Other decomposition products may also act as terminators or chain transfer agents and may pass into the reaction vessel in varying amounts. However, polymers of this degree of stereoregularity and viscosity have been obtained by three investigators in this laboratory (*cf.* Table I, expt 112, 114, 115, 116, 117, 121, and 35). Since the relationship between catalyst concentration and stereoregularity was not understood until late in this research, most other variables were investigated at an initiator-monomer ratio of 20 mol %.

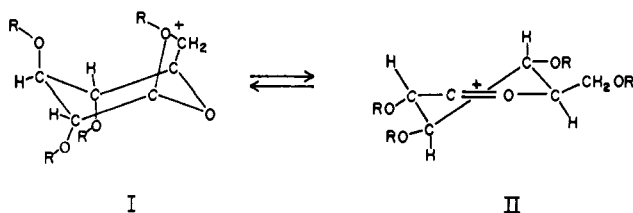
The particular Lewis acid and reaction temperature employed also influence the propagation and termination processes. When the same monomer is treated with 20 mol % phosphorus pentafluoride at 0°, a low polymer, $[\eta]$ 0.04, of low rotation ($[\alpha]$ 62.4°) is formed, in contrast to the high viscosity highly stereoregular polymer obtained at -78° (expt 35, 52, and 47, Table I). Virtually the same difference in regularity and viscosity was obtained with antimony pentafluoride at -78 and 0°, but the maximum viscosity of the polymer was lower in a limited number of experiments (expt 27 and 38, Table I) than that obtained

with phosphorous pentafluoride. Ruckel had previously shown a similar temperature effect by polymerizing levoglucosan trimethyl ether with phosphorus pentafluoride at +17 and -78° and obtaining a less regular polymer at the higher temperature. The significance of the observation was, however, not emphasized. In contrast, the reaction of the trimethyl ether with boron trifluoride etherate produced a stereoregular low molecular weight polymer at room temperature (Korshak's conditions) and did not cause polymerization at all at -78°⁵ (expt 133, Table I). Clearly the phosphorus and antimony pentafluorides act as rather powerful Lewis acids, causing stereoregular polymerization at very low temperatures and inducing carbonium ion character in the propagating site at higher temperatures, with concomitant loss in stereoregularity. Boron trifluoride etherate acts as a much weaker acid, inducing no carbonium ion character even at room temperature, and it is not sufficiently reactive to cause polymerization at low temperature (expt 133, Table I).

More specifically, this interpretation implies the presence of and probably an equilibrium between the oxonium (I) and carbonium (II) ions, the former (I) reacting stereospecifically at one rate, kp_1 , to produce α linkages, the latter nonstereospecifically to produce both α and β linkages at another composite rate, kp_2 . It is not known whether the proportion of α links produced from a species like II is a function of temperature or not. However, since α -D-glucosides are usually thermodynamically preferred, the rate of propagation ($kp_2\alpha$) to form α linkages from carbonium ion II may represent an increasing proportion of kp_2 as the

temperature is decreased.

We doubt, however, that such a change can be accepted as a complete explanation of the stereospecificity of this reaction. Whenever very high stereospecificity has been observed in polymerization processes of olefins, dienes, acrylates, or vinyl ethers, it has been the result of powerful coordination or shielding effects. Steric control by freezing out a less favored reaction course has been much less effective. We feel, therefore, that the assumption of both ionic species is



required. Trialkyloxonium ions are known to be highly reactive alkylating species^{10,11} and it is not surprising that they should be reactive at low temperatures. The fact that attack on C-1 can occur from only one direction is sufficient reason to expect a high degree of steric control from them. Conversion of the trialkyloxonium ion I to carbonium ion II would allow relaxation of the strained conformation of the anhydro sugar, and it is not unexpected at higher temperatures.

We have tested a number of Lewis acids and other initiators under a variety of conditions but we have obtained stereoregular polymers only in systems that generate fluorine-containing gegenions such as BF_4^- , SbF_6^- , or PF_6^- . Antimony pentachloride generates a polymer at -78° in methylene chloride, but its molecular weight is low and its anomeric configuration mixed (expt 45, Table I). Titanium tetrachloride is almost inactive under these conditions (expt 44, Table I). If indeed the presence of fluorine in the gegenion is a necessary condition for the production of stereoregular polymers, its role is not understood and it has not been explained previously in our mechanistic interpretation. Apparently the relatively concentrated negative charge on fluorine stabilizes the positively charged oxonium ion which is formed first and inhibits its rearrangement to a more stable glycosyl carbonium ion.

Solvent character frequently affects the course of other stereoregular polymerizations markedly. However, at -78° PF_5 generated a polymer in sulfur dioxide that was almost as pure in α configuration as that produced in methylene chloride (expt 35, 39, and 46, Table I). In view of the difference in chemical character and dielectric constant of these solvents (ϵ 9 vs. 14) it seems probable that solvent effects *per se* are relatively minor.¹² The polymerization is also relatively insensitive to water and other chemicals that might compete for the Lewis acid. When 0.5 mol of water or 1 mol of methyl acetate/mol of phosphorus pentafluoride was added to the system, the stereoregularity and the

viscosity of the polymer were decreased only slightly (cf. expt 35, 55, and 124, Table I).

Of the nonstereospecific polymers produced from the tribenzyl ether at 0° with a number of different initiators and solvents (expt 19, 27, 47, and 52, Table I) there is relatively little difference in either the specific rotation or viscosity ($[\alpha]^{25}_D$ 60.1–67.0°, $[\eta]$ 0.04–0.06). Presumably the propagating center and its gegenion are sufficiently separated that the gegenion exerts little influence on the course of the reaction under these conditions.

The preceding has clarified the role of initiator, solvent, and temperature in the Lewis acid catalyzed polymerization of levoglucosan tribenzyl ether. It is also useful to compare various methods of generating a propagating center with phosphorus hexafluoride gegenion. The method used by Ruckel was the direct treatment of monomer solution with phosphorus pentafluoride. This technique involves a complex initiation process⁵ and viscosity changes are observable only after a few hours. A second method we have tested is to allow phosphorus pentafluoride to react with acetyl fluoride in the presence of monomer. The acetyl carbonium ion hexafluorophosphate is apparently generated immediately and polymerization begins very rapidly. Viscosity changes are observable within minutes of the time that the solution is mixed and reaches reaction temperature. Although both experiments gave polymers of high optical rotation (cf. expt 35, 36, and 37, Table I) the use of acetyl fluoride never gave the highest stereoregularity (cf. 116 and 123, Table I). In addition, acetyl fluoride apparently acted as a weak chain transfer agent and in the quantity used caused the production of a lower molecular weight polymer. A third method of initiation used was to allow silver hexafluorophosphate to react with acetyl chloride in the presence of monomer. Both compounds are soluble in methylene chloride at -78° and carbonium ion generation can be accomplished in homogeneous solution. The initiation step should, therefore, be identical with the former case and the only difference is in the precipitation of silver chloride from the solution. The polymer produced in this case is significantly different from the former ones, being measurably lower in stereoregularity and quite low in molecular weight (cf. expt 35, 36, and 53, Table I). This initiation technique is a modification of that used by Hutten and Bredereck and it is clear that the method should be avoided if stereoregular high molecular weight polymers are desired.

Much less reactive carbonium ions can also be used to initiate polymerization. Both triphenylmethyl and pentamethylbenzyl carbonium ions are moderately active at -78° . (Since we used them with an anion which does not give steric control they did not give stereoregular polymers (expt 4 and 54, Table I)). In contrast, the tetraacetylglucosyl carbonium ion, which Hutten first used to cause polymerization of levoglucosan ethers and esters at 0° , failed to initiate polymerization at -78° of either the tribenzyl ether or triacetate. Undoubtedly the sluggishness of this carbonium ion is due to the additional resonance stabilization of an orthoacetoxonium ion formed by neighboring group participation of the C-2 acetoxy group.

(10) P. H. Plesch, Ed., "The Chemistry of Cationic Polymerization," Pergamon Press, New York, N. Y., 1963, p 439.

(11) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience Publishers, New York, N. Y., 1967.

(12) NOTE ADDED IN PROOF. We have now found more pronounced solvent effects at higher temperatures with BF_3 etherate.

Table II. Polymerization of 1,6-Anhydro-2,3,4-tri-*O*-acetyl- β -D-glucopyranose^a

Notebook ref	Solvent, ml/g of monomer	Catalyst	Mol % catalyst	Temp, °C	Convrnsn, %	$[\alpha]^{20D}$, ^b deg	$[\eta]$, ^c dl/g
1	CH ₃ NO ₂ , 3.0	AgClO ₄ -TAcGBr ^d	6.0	0	70.0	178.0	0.05
24	CH ₂ Cl ₂ , 7.0	AgClO ₄ -(C ₆ H ₅) ₃ CCl	20.0	0	0
25	CH ₃ NO ₂ , 7.0	AgClO-(C ₆ H ₅) ₃ CCl	20.0	0	0
43	CH ₃ NO ₂ , 3.0	AgClO ₄ -(CH ₃) ₃ C ₆ CH ₂ -Cl	20.0	0	6.0	144.1	...
11	CH ₃ NO ₂ , 8.0	AgClO ₄ -CH ₃ COCl	6.0	0	54.0	152.2	0.04
5	CH ₃ NO ₂ , 9.0	AgBF ₄ -TAcGBr ^d	6.0	0	Trace
12	CH ₃ NO ₂ , 8.0	AgBF ₄ -CH ₃ COCl	6.0	0	21.0	138.8	0.03
29	CH ₂ Cl ₂ , 3.0	AgSbF ₆ -CH ₃ COCl	10.0	-25	0
30	CH ₃ NO ₂ , 2.0	AgSbF ₆ -TAcGBr ^d	20.0	0	45.0	141.0	0.04
31	CH ₂ Cl ₂ , 2.5	AgSbF ₆ -TAcGBr ^d	20.0	0	20.0	112.0	0.04
48	CH ₃ NO ₂ , 3.0	AgPF ₆ -TAcGCl ^d	20.0	0	25.2	164.0	0.04
49	CH ₃ NO ₂ , 3.0	AgPF ₆ -TAcGCl ^d	20.0	-25	2.9	164.5	...
67	CH ₂ Cl ₂ , 3.0	PF ₅	20.0	0	23.2	157.6	0.04
41	CH ₂ Cl ₂ , 3.0	PF ₅	20.0	-78	0
61	CH ₂ Cl ₂ , 3.0	PF ₅ -H ₂ O, 1:1	20.0	-78	0
42	CH ₂ Cl ₂ , 3.0	PF ₅ -CH ₃ COF, 1:1	20.0	-78	0
32	CH ₂ Cl ₂ , 3.0	PF ₅ -CH ₃ COCl, 1:1	20.0	-78	0
20	CH ₃ NO ₂ , 3.0	SbCl ₅	20.0	0	0
10	CH ₃ NO ₂ , 10.0	SbCl ₅ -CH ₃ COCl, 1:1	16.6	0	0
33	CH ₂ Cl ₂ , 3.0	SbF ₅	20.0	-78	0

^a 1 g of monomer was polymerized in a corresponding volume of solvent for 100 hr. ^b Determined in chloroform, ^c 1.0 g/100 ml. ^d Determined in chloroform at 25°. ^e Tetraacetylglucosyl.

Table III. Copolymerization of 1,6-Anhydro-2,3,4-tri-*O*-benzyl- β -D-glucose and 1,6-Anhydro-2,3,4-tri-*O*-acetyl-D-glucose^a

Notebook ref	Mole ratio TAcG:TBG in monomer mixture	Temp, °C	Convrnsn, %	$[\alpha]^{20D}$, ^c deg	Mole ratio TAcG:TBG in polymer	$[\eta]$, ^d dl/g
68	1:1 ^e	0	34.2	29.2	10.1:1	0.04
51	1:1 ^f	-78	37.5 ^b	109.0	53:1	0.14

^a 1.0 g of monomer mixture was polymerized in 3.0 ml of methylene chloride for 100 hr. ^b 75% conversion with respect to the TBG concentration. ^c Determined in chloroform, ^d 1.0 g/100 ml. ^e Compare with runs 67 and 52. ^f Compare with runs 41 and 35.

This observation gives some insight into the polymerization of levoglucosan esters. A series of over 20 exploratory experiments (Table II) has shown that the esters of levoglucosan are far less satisfactory monomers for polymerization. Ruckel has pointed out that the acetate does not polymerize at low temperature with phosphorus pentafluoride catalyst. At 0° we find meager polymerization with PF₅ and initiation does not occur to any significant degree with antimony pentafluoride or antimony pentachloride at either -78° or 0°. In contrast, generation of a carbonium ion at 0° in the presence of the acetate does produce polymer in varying amounts. A wide variety of systems modeled on Hutten's technique (silver salts and active halides) can be used to generate the carbonium ion. The results, however, tend to be erratic, conversions low, and the specific rotations vary unpredictably and widely ($[\alpha]_D + 112$ -178°).

Preferential coordination of Lewis acids with carbonyl groups may inhibit initiation as suggested by Ruckel. However, even when carbonium ions are used as initiators, the propagation process is also sluggish. The trialkyloxonium ion formed is undoubtedly stabilized by neighboring C-2 acetate group interaction as discussed for the tetraacetylglucosyl carbonium ion. This is not, however, the entire explanation for the poor polymerizability of the monomer. It can be shown by a simple copolymerization experiment that not only is the carbonium ion derived from triacetyllevoglucosan less

reactive than that of tribenzyllevoglucosan but also the monomer is substantially less susceptible to attack. When an equimolar mixture of the two monomers is treated with phosphorus pentafluoride at 0 and -78°, polymerization occurs in both cases to form nearly pure tribenzyllevoglucosan polymer (expt 51 and 68, Table III). If the reactivity of the two monomers were equal and only that of the propagating ions different, a random copolymer should have been produced at a temperature at which both homopolymerize (*i.e.*, 0°).¹³ On the other hand, as soon as any levoglucosan triacetate was incorporated into the growing chain at -78°, polymerization would stop because an unreactive end group would be formed (*cf.* expt 68, 51, 67, 41, 52, and 35, Tables I, II, and III). It is therefore clear that the levoglucosan esters owe their poor polymerizability to the unreactive nature of both the monomer and the corresponding oxonium ion.

The tribenzoate and the trinitrate of levoglucosan are too insoluble at low temperatures in useful solvents to be of interest. However, the trinitrate polymerizes at 0° in sulfur dioxide with 20 mol % phosphorus pentafluoride and produces polymer of specific rotation $[\alpha]^{20D} + 43.6$ ° (*c* 1, ethyl acetate). These monomers have not, however, been investigated in detail.

In summary, it is possible to polymerize tribenzyllevoglucosan stereospecifically α and to control the

(13) A more rigorous analysis would, of course, involve two propagation and two cross-propagation constants.

molecular weight within wide limits by an appropriate choice of solvent, cationic initiator, temperature, and chain transfer agent. It is also possible to introduce a variable proportion of β linkages into the polymer by manipulation of the same reaction conditions. It appears that the use of conditions which result in large proportions of β linkages (probably 40–50%) convert the propagating site into a "free" carbonium ion and it appears probable that these polymers have a random distribution of α and β linkages. Under these conditions termination or transfer processes are also severe and only low molecular weight random polymers are produced. Nothing, however, is known at the present time regarding the distribution of the few β linkages in those polymers which approach stereoregularity. They may be concentrated in a particular molecular weight fraction, or as stereoblock structures or near chain ends, or as random flaws in a nearly stereospecific chain. Enzymic analysis of these materials would give a more detailed understanding of the polymerization process.

Experimental Section

Preparation of Starting Material. 1,6-Anhydro-2,3,4-tri-*O*-benzyl- β -D-glucopyranose. This monomer was obtained in 75% yield from 1,6-anhydro-2,3,4-tri-*O*-acetyl- β -D-glucopyranose by employing a modification of the method of Zemplén, Csürös, and Angyal,¹⁴ mp 89.5–90.5°, $[\alpha]^{25}_D - 30.5^\circ$ (*c* 2.3, CHCl₃).

1,6-Anhydro-2,3,4-tri-*O*-acetyl- β -D-glucopyranose. The monomer was prepared from levoglucosan by acetylation with acetic anhydride in pyridine solution at room temperature,¹⁵ mp 109.5–110.5°, $[\alpha]^{25}_D - 50.8^\circ$.

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(15) I. A. Wolff, *J. Am. Chem. Soc.*, **67**, 1623 (1945).

Tetraacetyl- β -D-glucopyranosyl Bromide. This compound was prepared from pentaacetyl- β -D-glucopyranose by direct bromination in acetic anhydride solution in the presence of perchloric acid as a catalyst,¹⁶ yield 85%, mp 87°.

Antimony pentafluoride and antimony pentachloride, products of Peninsular Chemresearch Inc., Fla., were distilled three times in a vacuum system before use. Silver salts used in this work were products of Ozark-Manoning Co., Oklahoma, and were used without further purification.

Polymerizations and Recovery of the Polymers. The high vacuum polymerization technique used in this work was described in detail by Ruckel and Schuerch.⁵ Methylene chloride was dried over calcium hydride; for drying of nitromethane Linde Molecular Sieves A5 were used. Solid components were introduced directly into the polymerization tube under a stream of nitrogen; liquid catalysts were distilled into the polymerization tube from calibrated micro breakseals. Complex catalysts from silver salts and halogen compounds were usually prepared *in situ* in the presence of monomer. Trityl hexachloroantimonate was prepared externally as described in the literature¹⁷ and added to the system as a solid. Tetraacetyl- β -D-glycosyl hexachloroantimonate was prepared by mixing of equimolecular solutions of tetraacetyl- β -D-glucosyl chloride and antimony pentachloride in carbon tetrachloride. The yellow precipitate was removed by filtration, washed with carbon tetrachloride, and dried under high vacuum. All operations were performed in a drybox.

Polymerizations were stopped by addition of an excess of methanol; the mixture was diluted with chloroform and neutralized with 10% excess of sodium bicarbonate solution. The organic layer was washed with distilled water until neutral and dried over sodium sulfate. The polymer was reprecipitated twice from solvent naphtha and freeze dried from benzene.

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