Substituent Effect on Ring-Opening Polymerization of Regioselectively Acylated 1,4-Anhydro-α-D-glucopyranose Derivatives

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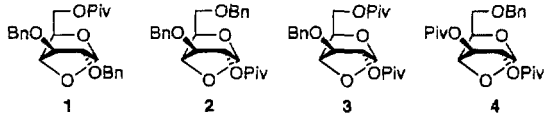
ABSTRACT: To investigate the substituent effects at the 2-*O*, 6-*O*, and 3-*O* positions on ring-opening polymerization, 1,4-anhydro-2,3-di-*O*-benzyl-6-*O*-pivaloyl-α-D-glucopyranose (**1**), 1,4-anhydro-3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-glucopyranose (**2**), 1,4-anhydro-3-*O*-benzyl-2,6-di-*O*-pivaloyl-α-D-glucopyranose (**3**), and 1,4-anhydro-6-*O*-benzyl-2,3-di-*O*-pivaloyl-α-D-glucopyranose (**4**) were selected as starting monomers and were polymerized under various reaction conditions. It was concluded from the results of monomers **1** and **2** reported previously and from those of monomers **3** and **4** in our present study that both the pivaloyl group at the 2-*O* position and the benzyl group at the 3-*O* position are indispensable for yielding stereoregular (1→5)-β-D-glucofuranan derivatives with high molecular weights and that a substituent group at the 6-*O* position hardly affects stereoregularity or polymerizability. The 1,4-anhydro-α-D-glucopyranose skeleton is not suitable for yielding a (1→4)-β-D-glucopyranan i.e., cellulose.

Introduction

Recently, we reported substituent effects on the highly stereoselective β-glycosylation in the syntheses of cello-oligosaccharides.[1−3] Utilizing such substituent effects in the ring-opening polymerization of 1,4-anhydro-3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-glucopyranose (**2**),we have



for the first time prepared stereoregular (1→5)-β-D-glucofuranan and have clarified that a pivaloyl group at the 2-*O* position is indispensable in order to produce the stereoregular skeleton (β-glucan).[4]

On the other hand, Ichikawa *et al.*[5] and Kobayashi *et al.*[6] reported the syntheses of (1→6)-β-D-galactooligosaccharides by applying the neighboring group participation of the 2-*O*-acyl group. However, there is no report investigating the influence of position for the acyl group and benzyl group in those anhydro-sugar skeletons except for the 2-*O* position.

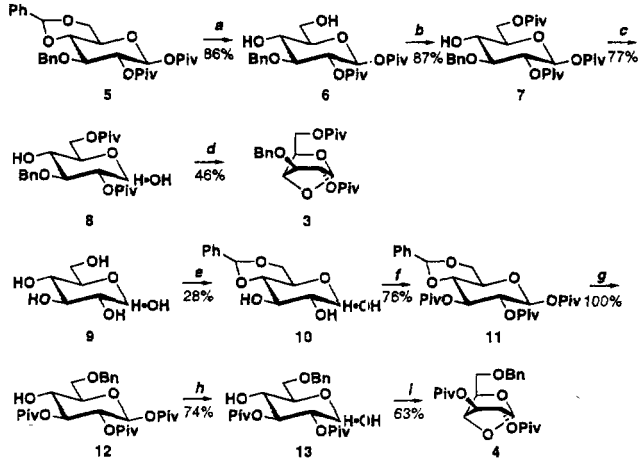
In this paper, we describe substituent effects at the 2-*O*, 3-*O*, and 6-*O* positions on ring-opening polymerization for obtaining cellulose by chemical synthesis.

Results and Discussion

Syntheses of the 1,4-Anhydro-α-D-glucopyranose Derivatives. In order to systematically study the effect of acyl groups on ring-opening polymerization, two 1,4-anhydro-α-D-glucopyranose derivatives, 1,4-anhydro-3-*O*-benzyl-2,6-di-*O*-pivaloyl-α-D-glucopyranose (**3**) and 1,4-anhydro-6-*O*-benzyl-2,3-di-*O*-pivaloyl-α-D-glucopyranose (**4**), were newly selected in addition to 1,4-anhydro-α-D-glucopyranose derivatives **1** and **2** whose polymerizations have been reported.[4,7] Those two compounds **3** and **4** were prepared according to synthetic routes shown in Scheme 1.

Polymerization of the Four Monomers. The results of polymerizations are summarized in Table 1.

Scheme 1. Synthetic Routes for Compounds 3 and 4



[a] p-TsOH / MeOH / r.t. / 3h, [b] PivCl / pyridine / r.t. / 3 h, [c] $NH_2NH_2{\cdot}H_2O$ / 1,4-dioxane / 50°C 15h,
[d] p-TsOH / benzene / reflux / 23h, [e] $C_6H_5CH(OMe)_2$ / DMF / 50°C / 15 mmHg / 40 min
[f] PivCl / pyridine / 80°C / 12h, [g] $NaBH_3CN$ / TMSCl / M.S.4A / CH_3CN / r.t. / 1.5h,
[h] $NH_2NH_2{\cdot}H_2O$ / THF / 50°C / 51h, [i] p-TsOH / benzene / reflux / 51h

All polymerizations were carried out under the same initiator concentration (5 mol %) and the same monomer concentration (50 g/100 mL). For comparing monomer concentration and temperature dependence among the four monomers, new experimental results (Table 1, experiment nos. 1−3, 5−7, 11−13) obtained from monomers **1** and **2** were added to those previously reported.[4] Each monomer was polymerized with phosphorus pentafluoride, boron trifluoride−diethyl etherate, and antimony pentachloride.

It was found that monomers **3** and **4** having two acyl groups had low polymerizability using phosphorus pentafluoride as initiator (Table 1, experiment nos. 14, 17, 20, and 23). There exist optimal initiators for the respective monomers to obtain polysaccharides with high degrees of polymerization (for example, Table 1, experiment nos. 1, 8, 15, and 24); that is, the selection of initiator is very important.

Determination of the Structure of the Polysaccharides. In general, there are four possible structural units in the poly(D-glucose) prepared by ring-opening

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Table 1. Polymerizations of 1,4-Anhydro-α-D-glucopyranose Derivatives[a]

exp no.	monomer	initiator	temp, °C	time, h	yield, %	$[\alpha]_D$, deg	$10^{-3}M_{GPC}$[e]	$\overline{DP_n}$
1	1	PF_5	−30	25	65[b]	+79.7	10.4	**24.3**
2	1	BF_3·Et_2O	−30	21	66[b]	+72.9	8.0	18.9
3	1	$SbCl_5$	−30	20	80[b]	+43.4	1.9	4.3
4	1	PF_5	0	20	82[b]	+88.9	9.3	21.8
5	1	PF_5	20	17	11[b]	+68.1	2.7	6.4
6	1	BF_3·Et_2O	20	20	56[b]	+58.1	5.1	12.1
7	1	$SbCl_5$	20	16	62[b]	+27.2	3.1	7.3
8	2	PF_5	−30	34	87[b]	−66.9	9.4	**22.0**[f]
9	2	BF_3·Et_2O	−30	60	78[b]	−69.3	7.5	17.6[f]
10	2	$SbCl_5$	−30	20	100[c]	−65.6	3.4	8.1[f]
11	2	PF_5	20	15	74[b]	−5.8	1.4	3.3
12	2	BF_3·Et_2O	20	20	86[b]	−19.0	4.7	11.0
13	2	$SbCl_5$	20	1	*ca.* 100[c]	−23.4	2.2	5.2[f]
14	3	PF_5	−30	239	trace			
15	3	BF_3·Et_2O	−30	136	42[b]	−59.3	10.0	**23.4**[f]
16	3	$SbCl_5$	−30	20	100[c]	−57.9	6.3	14.9[f]
17	3	PF_5	20	240	trace			
18	3	BF_3·Et_2O	20	18	100[c]	−15.7	3.2	7.6
19	3	$SbCl_5$	20	1.5	100[c]	−48.0	4.6	11.0[f]
20	4	PF_5	−30	26	trace			
21	4	BF_3·Et_2O	−30	17	7[d]		1.4	3.3
22	4	$SbCl_5$	−30	17	7[d]		2.0	4.8
23	4	PF_5	20	24	35[d]		1.9	4.4
24	4	BF_3·Et_2O	20	16	*ca.* 100[c]	−26.0	2.5	**6.2**
25	4	$SbCl_5$	20	16	7[d]		1.6	3.7

[a] Initiator concentration: 5 mol %. Solvent: CH_2Cl_2. Monomer/solvent: 50 g/100 mL. [b] Polymer was insoluble fraction in *n*-hexane. [c] No unreacted monomer was detected. [d] Polymer was separated from unreacted monomer by PTLC (EtOAc/*n*-hexane, v/v, 1:4). [e] Number-averaged molecular weight of polysaccharide was determined by gel permeation chromatography (GPC) using polystyrene standards. [f] Stereoregular (1→5)-β-D-glucofuranan derivative was given.

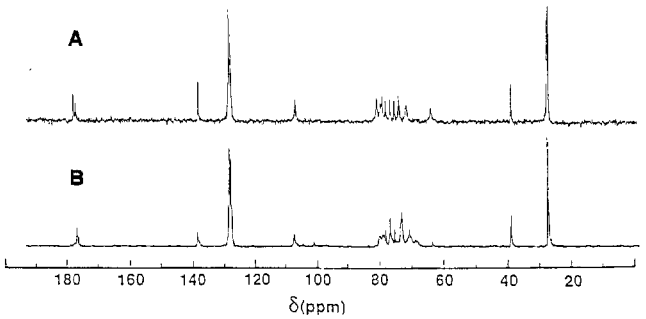

Figure 1. ^{13}C-NMR spectra of (A) poly(**3**) prepared by BF_3·Et_2O at −30 °C (Table 1, experiment no. 15) and (B) poly(**4**) prepared by BF_3·Et_2O at 20 °C (Table 1, experiment no. 24) ($CDCl_3$ as solvent).

polymerization of 1,4-anhydro-α-D-glucopyranose derivatives, namely, the (1→4)-β- ((1→4)-β-P) and (1→4)-α-D-glucopyranosidic ((1→4)-α-P) units and the (1→5)-β- ((1→5)-β-F) and (1→5)-α-D-glucofuranosidic ((1→5)-α-F) units.[4]

We reported that polymerization of **1** gave a non-stereoregular poly(**1**) mainly consisting of (1→5)-α-F units and that of **2** gave a stereoregular (1→5)-β-D-glucofuran derivative which had a single anomeric peak at 108.0 ppm in the ^{13}C-NMR spectrum.

The ^{13}C-NMR spectrum (Figure 1A) of poly(**3**) (Table 1, experiment no. 15) shows a single anomeric peak at 106.8 ppm, indicating a stereoregular poly(**3**). Taking into account the fact that D-glucans with high negative specific rotation generally have β-configuration, the poly(**3**) having $[\alpha]_D$ −59.3° is thought to be a stereoregular (1→5)-β-D-glucofuranan derivative or a stereoregular (1→4)-β-D-glucopyranan derivative. On the other hand, the C-1 peak of the cellotetraose derivative with the same protective group system (benzyl group at the 3-*O* position, and pivaloyl groups at the 2-*O* and 6-*O* positions) appears at 100.0 ppm.[2] Therefore, it was concluded that the stereoregular poly(**3**) is a 3-*O*-benzyl-2,6-di-*O*-pivaloyl-(1→5)-β-D-glucofuranan.

According to the same strategy as described above, the ^{13}C-NMR spectrum (Figure 1B) of poly(**4**) having $[\alpha]_D$ −26.0° (Table 1, experiment no. 24) shows two anomeric peaks at 107.5 (main) and 101.4 ppm (minor). In order to assign these peaks, poly(**4**) was converted into its actyl derivative. The anomeric peaks of acetylated poly(**4**) appeared at 106.3 (main) and 101.2 ppm (minor). Anomeric peaks of acetylated (1→4)-α-P, (1→5)-α-F, (1→4)-β-P, and (1→5)-β-F units appeared at 95.7, 100.4, 100.5, and 106.2 ppm, respectively.[4] Therefore the main anomeric peak at 107.5 ppm of poly(**4**) was assigned to (1→5)-β-F units, and a minor anomeric peak of poly(**4**) at 101.2 ppm may indicate (1→5)-α-F or (1→4)-β-P units.

Substituent Effect on the Molecular Weight of Polysaccharides. The molecular weights of poly(**1**)s, poly(**2**)s, and poly(**3**)s decrease with an increase of temperature, but those of poly(**4**)s were low under all conditions tried. The polymerizability of four monomers is in the order **1** ≅ **2** ≅ **3** ≫ **4**, as judged from the highest molecular weight obtained from these monomers (Table 1, experiment nos. 1, 8, 15, and 24) and from the yield of polymer at −30 °C.

Generally, the electron-donating benzyl group accelerates reactivity, but the electron-withdrawing acetyl groups retards both the glycosylations and polymerizations of anhydro-sugars. For example, Zachoval *et al.*[8] reported that 1,6-anhydro-β-D-glucopyranose triacetate was less reactive than 1,6-anhydro-β-D-glucopyranose tribenzyl ether.

Monomers **1** and **2** having two benzyl groups expectedly afforded polymer with high molecular weight, and monomer **4** having one benzyl group did not afford polymer under various reaction conditions (Table 1, experiment nos. 20−25), but unexpectedly, monomer **3** having only one benzyl group afforded polymer with

high molecular weight. Consequently, the present results indicate that the important factor for accelerating polymerizability is not only the number of the substituent benzyl groups but also the positions of the benzyl groups. The common substituent among monomers **1**–**3** is a benzyl group at the 3-*O* position: monomer **4** does not have a benzyl group at the 3-*O* position. Thus, the benzyl group at the 3-*O* position is indispensable for yielding glucan with a high molecular weight.

Comparing monomers **2** having a benzyl group at the 6-*O* position and **3** having a pivaloyl group at the 6-*O* position, there is little difference in molecular weight under optimum reaction conditions (Table 1, experiment nos. 8 and 15). Consequently, the benzyl group at the 6-*O* position did not have much effect on polymerizability.

Substituent Effect on the Stereoregularity of Polysaccharides. Substituent groups at O-2 greatly affect specific rotation, as shown in Table 1. All poly(**1**)s are dextrorotatory. The polymerization of **1** having a benzyl group at the 2-*O* position gave a nonstereoregular polymer mainly consisting of (1→5)-α-F units. On the other hand, all poly(**2**)s, poly(**3**)s, and poly(**4**)s are levorotatory. All these monomers have a pivaloyl group at the 2-*O* position. The polymerization of **2** gave a stereoregular (1→5)-β-D-glucofuranan derivative (Table 1; experiment nos. 8–10, and 13).[4] Polymerization of **3** also gave a stereoregular (1→5)-β-D-glucofuranan derivative (Table 1, experiment nos. 15, 16, and 19). Polymerization of **4** tended to give (1→5)-β-F units, but none of the conditions afforded a stereoregular poly(**4**), although monomer **4** has the same 2-*O*-pivaloyl group as monomers **2** and **3** have (Table 1, experiment nos. 20–25). Consequently, it turned out that the benzyl group at the 3-*O* position is indispensable for obtaining a stereoregular polysaccharide.

The reason for the indispensability is hereinafter described. It is predicted that the favorable complexation of Lewis acids with both a C_5- and a C_3-oxygen tends to occur and results in enhancement of polymerizability and stereoregularity, because the electron-donating 3-*O*-benzyl group raises the electron density of the C_3-oxygen and consequently elevates the coordination power with Lewis acids. The electron-withdrawing pivaloyl group at the 3-*O* position, on the contrary, weakens the coordination power of the Lewis acids so that the polymerizability and stereoregularity are lowered.

The fact that both polymerization of **2** having a benzyl group at the 6-*O* position and that of **3** having a pivaloyl group at the 6-*O* position gave stereoregular (1→5)-β-D-glucofuranan derivatives with almost the same $\overline{DP}_n$ under these optimum conditions (Table 1, experiment nos. 8 and 15) indicates that the substituent group at the 6-*O* position hardly affects either stereoregularity or polymerizability.

Conclusions

Substituent groups at the 6-*O* position did not remarkably affect stereoregularity or polymerizability, comparing results from monomers **3** and **2**. It was confirmed that the benzyl group at the 3-*O* position has a special function for yielding a stereoregular polysaccharide with high molecular weight in a ring-opening polymerization as found in stepwise synthesis of cellooligosaccharide[1] (results from monomers **4** and **2**). It was reconfirmed that the pivaloyl group at the 2-*O* position makes the polysaccharide take the β-configuration (results from monomers **3** and **1**). Polysaccharides with high molecular weights tend to have high stereoregularity, as shown in Table 1 (experiment nos. 8, 9, 15, and 16). Consequently, both the pivaloyl group at the 2-*O* position and the benzyl group at the 3-*O* position are indispensable for yielding stereoregular (1→5)-β-D-glucofuranan derivatives with high molecular weights.

Furthermore, polymerization of 1,4-anhydro-α-D-glucopyranose was found to always preferentially afford (1→5)-D-glucofuranose units, not (1→4)-β-glucopyranose units. These results agreed with the cases of the ring-opening polymerization of 2,7-dioxabicyclo[2.2.1]heptane[9] and that of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose.[10] Thus, it is also concluded that the 1,4-anhydro-α-D-glucopyranose skeleton is not suitable for yielding a (1→4)-β-D-glucopyranan, cellulose, molecule.

Experimental Section

General Methods. Anhydrous dichloromethane was distilled from P_2O_5. Preparative thin layer chromatography (PTLC) was performed on silica gel plates (Kieselgel 60 F_{254}, Merck). The standard workup procedure included diluting with ethyl acetate, washing with aqueous $NaHCO_3$ and brine, drying over Na_2SO_4, and evaporating *in vacuo*.

Synthesis of 1,4-Anhydro-α-D-glucopyranose Derivatives. 3-*O*-Benzyl-1,2-di-*O*-pivaloyl-β-D-glucopyranose (6). To a suspension of 3-*O*-benzyl-4,6-*O*-benzylidene-1,2-di-*O*-pivaloyl-β-D-glucopyranose (**5**)[7] (2.57 g, 4.89 mM) in methanol (20 mL) was added *p*-toluenesulfonic acid (420 mg, 2.45 mM) at room temperature. After 3 h, the suspension turned to a clear solution. Solid $NaHCO_3$ was added to the mixture. The solution was concentrated to a syrup. The syrup was worked up by the standard procedure. Compound **6** was crystallized from *n*-hexane (1.85 g, 86% yield), mp 100–102 °C, $[\alpha]_D$ −8.0° (*c* 0.95, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.23–1.14 (18 H, piv H), 3.50 (m, 1H, C_5–H), 3.34–3.90 (m, 2H, C_6–H), 3.65 (t, 1H, $J_{3,4}$ = 8, C_3–H), 3.76 (t, 1H, $J_{4,5}$ = 8, C_4–H), 4.64, 4.79 (d, 2H, J = 12, C*H*C_6H_5), 5.18 (t, 1H, $J_{2,3}$ = 8, C_2–H), 5.67 (d, 1H, $J_{1,2}$ = 8, C_1–H), 7.25–7.35 (5H, aromatic).

3-*O*-Benzyl-1,2,6-tri-*O*-pivaloyl-β-D-glucopyranose (7). To a solution of **6** (1.85 g, 4.22 mM) in pyridine (10 mL) was added pivaloyl chloride (0.78 mL, 6.34 mM) at room temperature. After 3 h, the reaction mixture was diluted with ethyl acetate and washed successively with a saturated sodium hydrogen carbonate solution, aqueous hydrochloric acid, and brine. The organic phase was dried over Na_2SO_4 and concentrated to dryness. 3-*O*-Benzyl-1,2,6-tri-*O*-pivaloyl-β-D-glucopyranose (**7**) was crystallized from *n*-hexane (1.92 g, 87% yield), mp 116–119 °C, $[\alpha]_D$ −11.5° (*c* 0.93, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.17–1.20 (27H, piv H), 3.50–3.65 (m, 3H, C_3–H, C_4–H, C_5–H), 4.27 (dd, 1H, J_{gem} = 12, $J_{5,6}$ = 1.9, C_6–H), 4.44 (dd, 1H, $J_{5,6'}$ = 4.5, $C_{6'}$–H), 4.70–4.74 (2H, C$H_2C_6H_5$), 5.14 (t, $J_{2,3}$ = 8, C_2–H), 5.62 (d, 1H, $J_{1,2}$ = 8, C_1–H), 7.28–7.35 (5H, aromatic).

3-*O*-Benzyl-2,6-di-*O*-pivaloyl-D-glucopyranose (8). To a solution of **7** (1.92 g, 3.68 mM) in 1,4-dioxane (22 mL) was added hydrazine hydrate (*ca.* 90%, 357 μL, 7.36 mM) at 50 °C. After 15 h, the reaction mixture was worked up by the standard method to give a colorless syrup. The product was purified by PTLC (1:2, v/v, ethyl acetate/*n*-hexane) to give colorless crystals of **8** (1.24 g, 77% yield), mp 45–50 °C, $[\alpha]_D$ +38.6° (*c* 1.09, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.16–1.28 (18H, piv H), 7.26–7.35 (5H, aromatic).

1,4-Anhydro-3-*O*-benzyl-2,6-di-*O*-pivaloyl-α-D-glucopyranose (3). To a solution of **8** (436.9 mg, 1.00 mM) in benzene (450 mL) was added *p*-toluenesulfonic acid (17 mg, 0.1 mM). The solution was stirred at reflux temperature for 23 h with a Dean-Stark trap. The reaction mixture was worked up by the standard procedure. Compound **3** was purified by PTLC (1:4, v/v, ethyl acetate/*n*-hexane) to afford colorless crystals (193.1 mg, 46% yield), mp 81–82 °C, $[\alpha]_D$

−0.2° (*c* 1.15, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.20 (18H, piv H), 3.97 (m, 1H, $J_{3,4}$ = 5, C_3−H), 4.09 (m, 1H, C_5−H), 4.45 (d, 1H, J_{gem} = 12, C_6−H), 4.59 (dd, 1H, $J_{5,6'}$ = 3.5, $C_{6'}$−H), 4.50, 4.67 (d, 1H, J = 12, C*H*C_6H_5, respectively), 4.68 (dd, 1H, $J_{4,5}$ = 3, C_4−H), 4.80 (d, 1H, $J_{2,3}$ = 2.5, C_2−H), 5.43 (s, 1H, $J_{1,2}$ = 0, C_1−H), 7.2−7.3 (5H, aromatic).

4,6-*O*-Benzylidene-D-glucopyranose (10). To a suspension of D-glucopyranose (**9**) (18 g, 100 mM) in *N*,*N*-dimethylformamide (18 mL) was added benzaldehyde dimethyl acetal (18 mL, 120 mM). The solution was kept at 50 °C under 15 mmHg for 40 min. Solid $NaHCO_3$ was added to the mixture. The solution was concentrated to a syrup. The reaction mixture was diluted with water and washed with dichloromethane. The water layer was concentrated to dryness, yielding compound **10** as a syrup which was crystallized from water, obtained by filtration, washed with water, and dried by heating (80 °C, 8 h) (7.5 g, 28% yield), mp 172−173 °C, $[\alpha]_D$ −3.3° (*c* 0.89, methanol). ^{1}H-NMR ($CDCl_3$): δ 5.55 (s, 1H, C*H*C_6H_5), 7.37−7.50 (5H, aromatic).

4,6-*O*-Benzylidene-1,2,3-tri-*O*-pivaloyl-β-D-glucopyranose (11). To a solution of **10** (7.5 g, 28 mM) in pyridine (20 mL) was added pivaloyl chloride (15.5 mL, 127 mM) at 80 °C. After 12 h, the reaction mixture was diluted with ethyl acetate and washed successively with a saturated sodium hydrogen carbonate solution, aqueous hydrochloric acid, and brine. The organic phase was dried over Na_2SO_4 and concentrated to dryness. Compound **11** was crystallized from *n*-hexane to afford colorless crystals (11.1 g, 76% yield), mp 152−153 °C, $[\alpha]_D$ −43.9° (*c* 3.03, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.12−1.19 (27H, piv H), 3.60−3.82 (m, 3H, C_4−H, C_6−H, $C_{6'}$−H), 4.41 (dd, 1H, J = 10.9, 6.4, C_5−H), 5.24 (dd, 1H, $J_{2,3}$ = 9, C_2−H), 5.42 (d, $J_{3,4}$ = 9.4, C_3−H), 5.52 (s, 1H, C*H*C_6H_5), 5.79 (d, 1H, $J_{1,2}$ = 8, C_1−H) 7.33−7.41 (5H, aromatic).

6-*O*-Benzyl-1,2,3-tri-*O*-pivaloyl-β-D-glucopyranose (12). To a solution of **11** (1.04 g, 2.0 mM) in acetonitrile (10 mL) were added powdered molecular sieves 4 Å (1.0 g) and $NaHCO_3$ (0.53 g, 8.0 mM). Trimethylchlorosilane (2.0 mL, 15.8 mM) was added dropwise over a period of 1.5 h to the reaction mixture. The reaction mixture was filtered using Celite 535, and the residue was washed with ethyl acetate. The combined filtrate and washings were worked up by the standard method to afford a yellow syrup. Compound **12** was purified on a silica gel column (Wacogel C-200) eluted with dichloromethane to give colorless crystals (1.04 g, ca. 100%), mp 85.4−88 °C, $[\alpha]_D$ −5.8° (*c* 1.44, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.10−1.19 (27H, piv H), 3.64−3.84 (m, 4H, C_4−H, C_5−H, C_6−H, $C_{6'}$−H), 4.61, 4.53 (d, d, 1H, J = 12, respectively, C$H_2$$C_6H_5$), 7.29−7.33 (5H, aromatic).

6-*O*-Benzyl-2,3-di-*O*-pivaloyl-D-glucopyranose (13). To a solution of **12** (303 mg, 0.580 mM) in THF (8 mL) was added hydrazine hydrate (ca. 90%, 112 μL, 2.32 mM) at 50 °C. After 51 h, the reaction mixture was worked up by the standard method to give a colorless syrup. Compound **13** was purified by PTLC (1:2, v/v, ethyl acetate/*n*-hexane) to afford a colorless syrup (189 mg, 74% yield), $[\alpha]_D$ +46.7° (*c* 1.05, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.19−1.20 (18H, piv H), 4.58 (2H, C$H_2$$C_6H_5$), 7.26−7.35 (5H, aromatic).

1,4-Anhydro-6-*O*-benzyl-2,3-di-*O*-pivaloyl-α-D-glucopyranose (4). To a solution of **13** (386 mg, 0.880 mM) in benzene (500 mL) was added *p*-toluenesulfonic acid (15.2 mg, 0.088 mM) at reflux temperature. The solution was stirred at reflux temperature for 51 h with a Dean-Stark trap. The reaction mixture was worked up by the standard procedure. Compound **4** was purified by PTLC (1:4, v/v, ethyl acetate/*n*-hexane) to give colorless crystals (234 mg, 63% yield), mp 42.4−43.9 °C, $[\alpha]_D$ −9.5° (*c* 1.34, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.12−1.20 (18H, piv H), 3.70 (dd, 1H, J_{gem} = 11, $J_{5,6}$ = 3.5, C_6−H), 3.82 (dd, 1H, $J_{5,6'}$ = 8, C_6−H) 4.19 (m, 1H, C_5−H), 4.54, 4.65 (d, d, 1H, respectively, C$H_2$$C_6H_5$), 4.74 (d, 1H, $J_{2,3}$ = 2.5, C_2−H), 4.81 (dd, 1H, $J_{4,5}$ = 3, C_4−H), 4.93 (m, 1H, $J_{3,4}$ = 5, C_3−H), 5.46 (s, 1H, $J_{1,2}$ = 0, C_1−H), 7.32 (5H, aromatic). ^{13}C-NMR: δ 103.3 (C-1).

Polymerization and Deprotection. Polymerizations were carried out under high vacuum at −30, 0, and +20 °C as described previously.[4]

Measurements. All melting points (mp) are uncorrected. ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded with a Bruker AC300 FT-NMR (300 MHz) spectrometer and a JEOL FX-90 FT-NMR (22.5 MHz), respectively, in chloroform-*d* with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in δ values (ppm) and Hz, respectively. Some chemical shift assignments were made using a decoupling method; others were made by analogy with values in the literature and by analogy with model compounds. Optical rotations were measured using a JASCO Dip-1000 digital polarimeter. Molecular weight distributions of the substituted polymer were analyzed by gel permeation chromatography (GPC) in tetrahydrofuran. Calibration curves were obtained by using polystyrene standards (Shodex). A Waters universal liquid chromatograph injector (model U6K), a Waters solvent delivery system (model 6000A), a Waters refractive index detector (series R-400), a Waters absorbance detector (model 440), and Shodex columns (KF802 and KF803) were used. The flow rate was 1.0 mL/min.

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