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Regioselectively Modified Stereoregular Polysaccharides XIV. Synthesis of a *C*-Methylated Linear Dextran 3-*C*-Methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan

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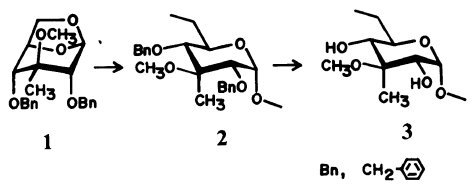
ABSTRACT: The synthesis and polymerization of 1,6-anhydro-2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-β-D-glucopyranose (**1**) followed by debenzylation of the polymer were carried out. Stereospecific homopolymerization of **1** and its copolymerization with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose proceeded in the presence of phosphorus pentafluoride (PF_5) as an initiator in dichloromethane at −60°C. Subsequent debenzylation gave a stereoregular homopolysaccharide 3-*C*-methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan (**3**) and also a stereoregular copolysaccharide consisting of 3-*C*-methyl-3-*O*-methyl- and unsubstituted (1→6)-α-D-glucopyranose units. Under conditions using less initiator for a longer time, the monomer **1** afforded a stereoirregular oligomeric product consisting of mixed α- and β-configurational units.

KEY WORDS Anhydro Sugar / Ring-Opening Polymerization / Synthetic Polysaccharide / *C*-Methyl Polysaccharide /

Branched-chain monosaccharides occur widely in nature as components of glycosides and polysaccharides in a variety of plants, fungi, and bacteria.[1,2] This class of monosaccharides carry methyl, hydroxymethyl, or formyl branches on a straight carbon skeleton by replacing either a hydrogen atom or a hydroxyl group. Discovery of their antibiotic activity promoted synthetic studies of branched monosaccharides.[3] Synthesis of a well-defined polysaccharide composed of alkyl-branched monosaccharide unit is of interest in this respect.

In this paper, a modified linear dextran, 3-*C*-methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan (**3**) was synthesized according to Scheme 1: ring-opening polymerization of 1,6-anhydro-2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-β-D-glucopyranose (**1**) and subsequent debenzylation of the resulting 2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan (**2**). In the polysaccharide **3**, one methyl substituent is attached to the C-3 carbon of each repeating pyranose ring directly and another methyl substituent is attached to the O-3 oxygen by an ether bond.

Ring-opening polymerization of anhydrosugar derivatives is a useful synthetic method to lead to structurally well-defined polysaccharides.[4-6] The present monomer and polymeric unit are unique with respect to tetrasubstituted structure. The polymerization reactivity of **1** and its polymer structure are



Scheme 1. Synthesis of 3-*C*-methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan (**3**).

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compared with those of trisubstituted analogues.[7-10]

EXPERIMENTAL

General Methods

200-MHz ^{1}H and 50-MHz ^{13}C NMR spectra were obtained on a Japan Electro-Optic Laboratory JNM-FX-200 Fourier transform NMR spectrometer for solutions in deuteriochloroform and Me_2SO-d_6 with tetramethylsilane as the internal reference. For deprotected polysaccharides, measurements were made on solution in D_2O with acetone as a reference (2.07 ppm in ^{1}H NMR and 39.4 ppm in ^{13}C NMR). Optical rotations were determined with a JASCO DIP 181 digital polarimeter using a jacketed 1-dm cell. Viscosities were measured in Ubbelohde viscometers at 25°C. Gel permeation chromatography was carried out using a Shodex GPC-A-80M column (8-mm i.d. × 1000 mm) on a Hitachi 634A high speed liquid chromatograph (solvent, chloroform; polystyrene standard). Microanalysis was made on a Perkin-Elmer 240C elemental analyzer. TLC was performed on Merck silica gel $60F_{254}$ precoated plates.

*1,6-Anhydro-2,4-di-O-benzyl-β-*D*-ribo-hexopyranos-3-ulose* (**5**)

A solution of 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose (**4**) (7.87 g, 23 mmol) in benzene (320 ml) was added to a refluxed suspension of pyridinium chlorochromate[11] (11.2 g, 51 mmol) in benzene (40 ml) with vigorously stirring. TLC (hexane–ethyl acetate, 2 : 1, v/v) showed conversion of **4** to **5** in 70 min. The hot reaction mixture was filtered through Celite, and the reaction vessel and Celite were washed with hot benzene. The combined filtrates were concentrated *in vacuo*, passed through silica gel column (eluent, ethyl acetate), and then evaporated. A crystalline product was obtained in a yield of 7.57 g (96%). It was recrystallized from ethanol. mp 81—82°C. $[\alpha]_D^{25}$ −18.9° (c = 1, in chloroform). *Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.58%; H, 5.92%. Found: C, 70.57%; H, 5.94%.

^{1}H NMR ($CDCl_3$): 7.29 (m, 10H, C_6H_5), 5.55 (d, 1H, $J_{1,2}$ 1.7, H-1), ~4.7 (m, 1H, H-5), 4.72 and 4.49 (d × 2, 1H × 2, J 12.1, $CH_2\phi$), 4.71 and 4.46 (d × 2, 1H × 2, J 11.9, $CH_2\phi$), 3.72 (d × d, 1H, $J_{5,6exo}$ 5.4, $J_{6endo,6exo}$ 8.1, H-6_{exo}), 3.60 (d × d, 1H, $J_{5,6endo}$ 1.2, $J_{6endo,6exo}$ 8.1, H-6_{endo}), and 3.52 ppm (m, 2H, H-2 and H-4). ^{13}C NMR ($CDCl_3$): 201.0 (C-3), 136.7 (aromatic C-1), 128.3 (aromatic C), 101.5 (C-1), 80.0 and 79.0 (C-2 and C-4), 76.0 (C-5), 72.2 and 71.6 ($CH_2\phi$), and 65.4 ppm (C-6). IR (in CCl_4): 1740 cm^{-1} ($\nu_{C=O}$).

*1,6-Anhydro-2,4-di-O-benzyl-3-C-methyl-β-*D*-glucopyranose* (**6**)

An ethereal solution (170 ml) of methylmagnesium iodide (produced from 37 ml of methyl iodide and 7.3 g of magnesium turning) was cooled at 0°C and a solution of **5** (5.14 g, 15 mmol) in THF (30 ml) was added dropwise. The reaction mixture was stirred at 0°C for 70 min, and treated with methanol (150 ml) and then with 10% hydrochloric acid (100 ml). After extraction with chloroform, the combined chloroform extracts were concentrated to dryness. The residue was chromatographed on silica gel (ethyl acetate) to give **6** in a yield of 4.93 g (93%) as a syrup. $[\alpha]_D^{25}$ −56.7 (c = 1, in chloroform). *Anal.* Calcd for $C_{21}H_{24}O_5$: C, 70.77%; H, 6.79%. Found: C, 70.78%; H, 6.59%.

^{1}H NMR ($CDCl_3$): 7.35 (m, 10H, C_6H_5), 5.34 (d, 1H, $J_{1,2}$ 2.0, H-1), 4.9—4.6 (m, 4H, $CH_2\phi$), 4.50 (d, 1H, $J_{5,6exo}$ 5.4, H-5), 3.76 (s, 1H, OH), 3.66 (d, 1H, $J_{6endo,6exo}$ 8.0, H-6_{endo}), 3.58 (d × d, 1H, $J_{6endo,6exo}$ 8.0, $J_{5,6exo}$ 5.4, H-6_{exo}), 3.15 (d, 1H, $J_{4,5}$ 1.7, H-4), 3.12 (d, 1H, $J_{1,2}$ 2.0, H-2), and 1.38 ppm (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 137.7 (aromatic C-1), 128.3, 128.0, and 127.8 (aromatic C), 100.7 (C-1), 80.8 and 79.4 (C-2 and C-4), 74.3 (C-5), 74.2 and 73.4 ($CH_2\phi$), 67.8 (C-3), 64.6 (C-6), and 28.5 ppm (C-CH_3). IR (in CCl_4): 3550 cm^{-1} (ν_{O-H}).

*1,6-Anhydro-2,4-di-O-benzyl-3-C-methyl-3-O-methyl-β-*D*-glucopyranose* (**1**)

Potassium hydride in dispersion in mineral oil[12] (32.2%, 4.3 g, 0.034 mol) was washed with dry pentane and dispersed in THF (15 ml). The flask was attached to a gas measuring buret through drying reagent. A solution of **6** (4.51 g, 0.013 mol) in THF was added dropwise and the solution was stirred until gas evolution was complete. Methyl iodide (4 ml, 0.064 mol) was added dropwise for 15 min; the mixture was stirred for 55 min at room temperature, treated with 5 ml of *tert*-butanol (5 ml), and extracted with chloroform. The chloroform layer was washed with water, dried on anhydrous magnesium sulfate, and concentrated *in vacuo*. Chromatography of the residue (hexane–ethyl acetate, 2 : 1) gave **1** as a syrup (4.08 g, 87%). $[\alpha]_D^{25}$ −60.9° ($c=1$, in chloroform). *Anal.* Calcd for $C_{22}H_{26}O_5$: C, 71.33%; H, 7.08%. Found: C, 71.26%; H, 7.03%.

^{1}H NMR ($CDCl_3$): 7.45—7.25 (m, 10H, C_6H_5), 5.44 (d, 1H, $J_{1,2}$ 1.7, H-1), 4.90—4.68 (m, 4H, $CH_2\phi$), 4.64 (m, 1H, H-5), 3.61—3.59 (m, 2H, 6_{endo} and 6_{exo}), 3.34 (d, 1H, $J_{4,5}$ 1.7, H-4), 3.31 (s, 3H, OCH_3), 3.24 (d, 1H, $J_{1,2}$ 1.7, H-2), and 1.40 ppm (s, 3H, CCH_3). ^{13}C NMR ($CDCl_3$): 138.5 (aromatic C-1), 128.0, 127.8, 127.7, and 127.2 (aromatic C), 101.5 (C-1), 80.0 and 79.5 (C-2 and C-4), 74.7 (C-5), 73.5 (C-3), 73.3 and 72.0 ($CH_2\phi$), 65.4 (C-6), 49.9 (OCH_3), and 25.2 ppm (C-CH_3).

Polymerization

A comonomer 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**7**) was synthesized and purified according to the previously described method.[7-10] *p*-Chlorobenzenediazonium hexafluorophosphate and dichloromethane were purified as usual.

Monomers **1** and **7** were throughly dried in anhydrous dichloromethane in a polymerization vessel under high vacuum. Polymerization was carried out with phosphorus pentafluoride at −60°C and terminated with a cold mixture of methanol and petroleum ether. The product was purified by precipitation of a chloroform solution into methanol–petroleum ether four times, and then isolated by freeze-drying from benzene.

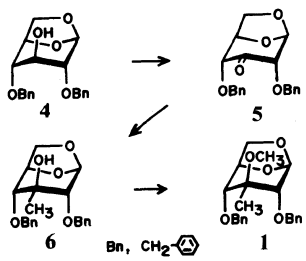
Debenzylation

The polymer was debenzylated using sodium in liquid ammonia by a published method.[7-10]

RESULTS AND DISCUSSION

*Synthesis of 1,6-Anhydro-2,4-di-O-benzyl-3-C-methyl-3-O-methyl-β-*D*-glucopyranose* (**1**)

Compound **1** was synthesized from 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose (**4**) *via* three step reactions as shown in Scheme 2. Each reaction proceeded rigio- and stereospecifically. Oxidation of the secondary hydroxyl group of **4** was accomplished by refluxing a benzene solution of **4** in the presence of pyridinium chlorochromate. It proceeded without epimerization and a pure crystalline compound 1,6-anhydro-2,4-di-*O*-benzyl-β-D-*ribo*-hexopyranos-3-ulose (**5**) was isolated in 96% yield. The carbonyl group of ulose **5** was alkylated with methylmagnesium iodide in diethyl ether at 0°C and only one product was obtained in 93% yield. The *C*-methylation proceeded stereospecifically, and the product was 1,6-anhydro-2,4-di-*O*-benzyl-3-*C*-methyl-β-D-glucopyranose (**6**), the one with a methyl group of the equatorial configuration and a hydroxyl group of the axial configuration. *O*-



Scheme 2. Synthesis of 1,6-anhydro-2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-β-D-glucopyranose (**1**).

Table I. Polymerization of 1,6-Anhydro-2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-β-D-glucopyranose (**1**)[a]

Exptl. No.	Monomer		PF_5	Time	Yield	$[\alpha]_D^{25}$,[b]	$[\eta]$[c]	$10^{-3}M_n$[d]
	mmol	mol l^{-1}	mol%	h	%	deg		
T3	1.74	1.3	11.5	2	39.1[e]	+110.8	0.08	19
T4	3.44[f]	0.86	4.4	3	67.0[g]	+108.8	0.15	23
T5	3.62	0.98	5.5	17	88.1	+48.8	—	—
					16[h]	+76.0	—	4.1
					84[i]	+43.5	—	1.6

[a] Solv., dichloromethane; temp, −60°C.
[b] In chloroform.
[c] In chloroform at 25°C. Calculation was made using the concentration expressed in g/100 ml.
[d] GPC (polystyrene standard).
[e] *Anal.* Calcd for $(C_{22}H_{26}O_5)_n$: C, 71.33%; H, 7.08%. Found: C, 71.22%; H, 7.06%.
[f] Copolymerization with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**7**); mole fraction of **1** in feed, 0.50.
[g] Mole fraction of **1** in copolymer, 0.49.
[h] Methanol-insoluble fraction, precipitated by fractionation with chloroform–methanol.
[i] Methanol-soluble fraction: unprecipitated by fractionation with chloroform–methanol.

Table II. Debenzylation

Exptl. No.	Polymer	NH_3	Toluene/DME[a]	Time	Yield	$[\alpha]_D^{25}$,[b]	$[\eta]$[c]
	g	ml	ml/ml	min	%	deg	
T3-D	0.20	20	11/3	150	55	—	—
T4-D	0.51	50	15/5	135	88	160	0.13
T5-D	0.66[d]	50	15/5	120	~100	—	—

[a] DME, 1,2-dimethoxyethane.
[b] In Me_2SO.
[c] In Me_2SO; 25°C. Calculation was made using the concentration expressed in g/100 ml.
[d] The methanol-soluble fraction was used.

Methylation of the tertiary hydroxyl group of **6** was performed by reacting **6** with potassium hydride and then with methyl iodide and a syrupy compound **1** was obtained in 87% yield.

Polymerization and Debenzylation

The polymerization was carried out under high vacuum at −60°C using phosphorus pentafluoride as the initiator in anhydrous dichloromethane. The resulting polymer was debenzylated by the conventional method using sodium in liquid ammonia. The results of polymerization and debenzylation are summarized in Tables I and II.

Stereoregular Polysaccharide 3-C-Methyl-3-O-methyl-(1→6)-α-D-glucopyranan (**3**)

Experiment T3 was the homopolymerization of **1** using a relatively large amount of PF_5 initiator. The polymerization solution became viscous in 2 h and a white powdery polymer was isolated in 39.1% yield. It was soluble in benzene, toluene, dichloromethane, chloroform, carbon tetrachloride, diethyl ether, tetrahydrofuran (THF), acetone, ethyl acetate, pyridine, dimethylformamide (DMF), and Me_2SO. Debenzylation of the polymer

proceeded smoothly. The debenzylation product was partially soluble in Me_2SO and insoluble in water, DMF, and pyridine. Its optical rotation and intrinsic viscosity could not be determined owing to poor solubility.

Figures 1 and 2 show the ^{13}C NMR spectra of the homopolymer **2** and its debenzylated product **3**, respectively. Several peaks due to the benzyl substituents have disappeared in Figure 2; complete debenzylation proceeded. In each anomeric carbon region, there appeared only one signal assignable to the α-anomeric C-1 carbon (97.48 ppm of **2** and 98.04 ppm of **3**). The α-stereoregularity was also evidenced from the positively high optical rotation of **2** and from the H-1 proton signal with a relatively low-field chemical shift (4.66 ppm) and small coupling constant (doublet, $J_{1,2}=4.0$ Hz) of **3**.

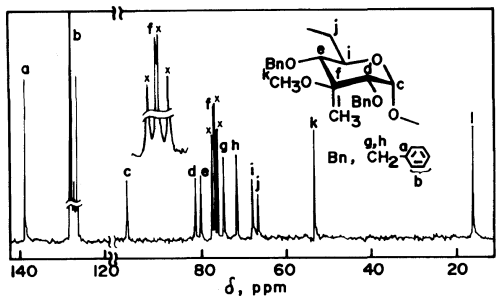


Figure 1. 50-MHz ^{13}C NMR spectrum of 2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan (**2**) in $CDCl_3$ (concentration, 7%) at room temperature.

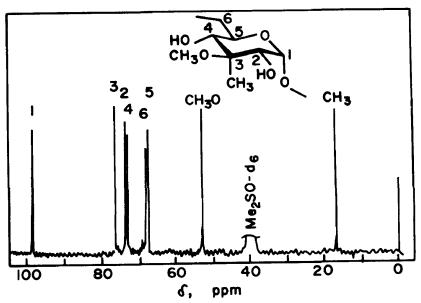


Figure 2. 50-MHz ^{13}C NMR spectrum of 3-*C*-methyl-3-*O*-methyl-(1→6)-α-D-glucopyranan (**3**) in Me_2SO-d_6 (concentration, 6%) at 80°C.

The D-gluco configurations of the present substances were assigned on the basis of the chemical shifts of the 3-*C*-methyl carbon. It is known[13-15] that equatorial methyl resonances in methyl-branched monosaccharides shift downfield by 4—10 ppm relative to the corresponding axial ones due to the latters' steric compression effect. The 3-*C*-methyl signals of the 1,6-anhydropyranose derivatives appeared at 28.47 (**6**) and 25.15 ppm (**1**), whereas those of the polysaccharides at 16.88 (**2**) and 16.86 ppm (**3**). The interconversion between the equatorial and axial bonds on the pyranose ring is caused by the stereospecific ring-opening polymerization, since the $^1C_4$ conformation of a 1,6-anhydro pyranose ring is converted into a $^4C_1$ conformation of the (1→6)-pyranan ring structure. It was reasonably concluded that the 3-*C*-methyl group in **6** and **1** is equatorially oriented and that in **2** and **3** is axially oriented: this series of compounds belong to the class of the D-gluco configuration.

A Stereoregular Copolysaccharide Consisting of 3-C-Methyl-3-O-methyl- and Unsubstituted (1→6)-α-D-Glucopyranan Units

Experiments T4 in Table I was the copolymerization of **1** with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**7**) in a 0.50:0.50 molar composition. Both the intrinsic viscosity and molecular weight of the product were higher than those of homopolymer T3. Debenzylation yielded a copolysaccharide soluble in water, Me_2SO, DMF, and pyridine. High α-anomeric stereoregularity was suggested by NMR spectra and optical rotation.

In the ^1H NMR spectrum of the debenzylated copolymer, there appeared two separated α-anomeric H-1 signals of almost the same intensity: one at 4.65 ppm assignable to the 3-*C*-methyl unit and one at 4.70 ppm to the non-substituted unit. From the area ratio of these signals to the 3-*C*-methyl resonance at 1.30 ppm, the mole fraction of the **1** unit in the copolymer was evaluated to be 0.49. The

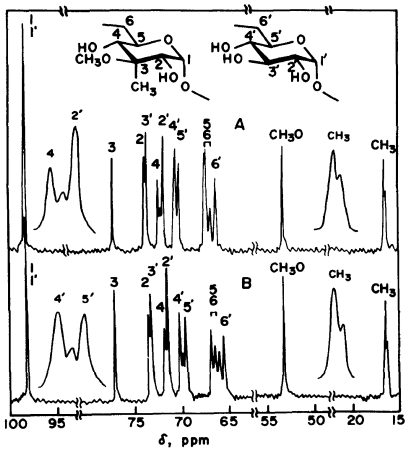


Figure 3. 50-MHz ^{13}C NMR spectra of the copolymer consisting of 3-*C*-methyl-3-*O*-methyl- and unsubstituted (1→6)-α-D-glucopyranose residues in D_2O (concentration, 10%) at (A) 80°C and (B) 38°C (internal standard, acetone).

monomer reactivity of **1** seemed comparable to that of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose.

Figure 3 shows the ^{13}C NMR spectra of the debenzylated copolymer taken in D_2O at 80°C (A) and 38°C (B). The primed numbers indicate the assignment of the non-substituted sugar unit and the non-primed numbers that of the modified sugar unit. There were observed several small signals which were distinct from those of the corresponding homopolymers and were variable with measured temperature and solvent. These signal splittings were due to the dyad sequences of the two components along the polymer chain. Such signals splittings due to dyad sequences were not detected in the spectra of partially 3-*O*-methylated, 3-*O*-octadecylated, and 3-deoxygenated (1→6)-α-D-glucopyranans. It is reasonable to assume that the axially substituted *C*-methyl group afforded a large non-bonded steric interaction against the polymer chain.

A Stereoirregular Polysaccharide Consisting of 3-C-Methyl-3-O-methyl-(1→6)-α- and β-D-glucopyranose Units

When the homopolymerization of **1** was carried out with less initiator (expt. T5), it took 17 h until the polymerization solution became viscous and the product was of low molecular weight and stereoirregular. It was partially soluble in methanol and fractionated with the solvent.

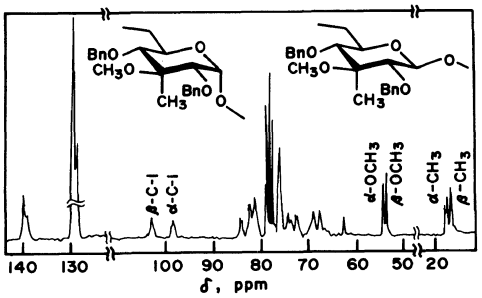


Figure 4. 50-MHz ^{13}C NMR spectrum of 2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-(1→6)-α- and β-D-glucopyranan (polymer T5, unfractionated) in $CDCl_3$ (concentration, 14%) at room temperature.

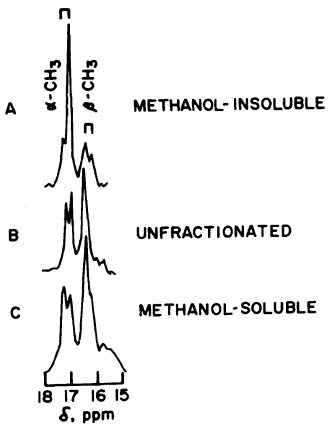


Figure 5. Extended *C*-methyl signals of 2,4-di-*O*-benzyl-3-*C*-methyl-3-*O*-methyl-(1→6)-α- and β-D-glucopyranan (polymer T5) in $CDCl_3$ at room temperature. A, methanol-insoluble fraction; B, unfractionated polymer; C, methanol-soluble fraction.

The ^{13}C NMR spectrum of the unfractionated polymer is shown in Figure 4. The signals at 97.3 (α-C-1), 53.5 (α-3-*O*-CH_3), and 16.9 ppm (α-3-*C*-CH_3) had almost the same chemical shifts as the corresponding ones of the homopolymer T3. There appeared additional signals assignable to the β-anomeric

unit at 101.7 (β-C-1), 52.9 (β-3-*O*-CH_3), and 16.3 ppm (β-3-*C*-CH_3). β-Anomer content was estimated to be 0.58 for the unfractionated polymer, 0.30 for the methanol-insoluble fraction, and 0.71 for the methanol-soluble one. The optical rotation of each fraction was much lower than that of the stereoregular homopolymer, and an approximately linear relationship was observed between the optical rotation and β-anomer content.

Figure 5 shows that each *C*-methyl signal of the α- and β-form is split into two peaks (α-3-*C*-CH_3, 17.1 and 16.9; β-3-*C*-CH_3, 16.3 and 16.0 ppm) and their intensity changes with the α-/β-anomer ratio. We assumed that the signal splittings were due to the α- and β-anomeric dyad sequences.

It is noteworthy that β-anomer content was higher than those of trisubstituted analogous polymers obtained under similar conditions.[7-10] The higher β-anomer content and lowered molecular weight of the polymer can be explained by the steric effect of substituents as follows. The methyl group attached directly to the pyranose ring, together with the methoxy group, brings about a severe strain on the bicyclic acetal structure and also on the polymer backbone. Non-bonded 1,3-diaxial interaction between the axially oriented *C*-methyl group and the α-anomeric oxygen atom in position 1, especially, imposes a much greater strain on the polymer backbone. Conversion to the more stable β-configurational unit accompanying degradation of the polymer chain occurred more readily during prolonged polymerization.

Recently, Okada *et al.*[16,17] reported that ring-opening polymerization of deoxy-anhydro sugar derivatives possessing an equatorial benzyloxy group in position 3 under proper reaction conditions gave polysaccharide derivatives exclusively consisting of the (1→6)-β-anomeric linkage. We assume that too much crowding in monomer **1** and polymer **2** with the two substituents in position 3 enhanced the degradation of the polymer chain.

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