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Regioselectively Modified Stereoregular Polysaccharides X. Equilibrium Polymerization of 1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-β-D-*threo*-hexopyranose

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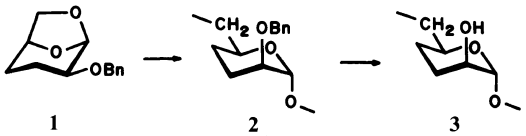
ABSTRACT: A synthetic linear polysaccharide having one axial hydroxyl group in position 2 in each repeating unit, 3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**3**), was synthesized by cationic ring-opening polymerization of 1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-β-D-*threo*-hexopyranose (**1**), followed by debenzylation. The polymerization of **1** using phosphorus pentafluoride as initiator at temperatures ranging from −60 to 0°C gave the stereoregular polymer with an α-anomeric configuration, 2-*O*-benzyl-3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**2**). The apparent polymerization rate and copolymerization reactivity of **1** were high, but the polymer yield was relatively low owing to the high equilibrium monomer concentration of **1** ($[M]_e = 0.31$—$0.54\ mol\ l^{-1}$ at −60°C). It is suggested that the free energy change in polymerization is negative but small because the benzyloxy group oriented equatorially in the monomer is converted to the axially oriented one in the course of polymerization. Debenzylation of **2** with sodium metal in liquid ammonia afforded a white powdery polysaccharide identified as **3**. On the basis of the ^{13}C NMR spectrum of the optically active polysaccharide **3** consisting of D-enantiomer unit, an unambiguous assignment was made on diad tacticities of D,L-enantiomeric units in the racemic polymer reported previously.

KEY WORDS Anhydrosugar / Ring-Opening Polymerization / Equilibrium Polymerization / Synthetic Polysaccharide /

The ring-opening polymerization of anhydrosugar derivatives has proved to be a useful method for synthesizing structurally well-defined polysaccharides.[1-3] Compounds having a variety of parent sugars, substituents, and ring sizes have been employed as monomers. We reported the polymerization of 2,4-di-*O*-benzylated 1,6-anhydro glucoses having different substituents in position 3.[4-6] Debenzylation of the resulting polymers led to regiospecifically modified linear dextrans.

The present paper is concerned with the polymerization of 1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-β-D-*threo*-hexopyranose (**1**) and the debenzylation of the resulting polymer **2** (Scheme 1). The compound **1** is a dideoxy derivative substituted with an equatorial benzyloxy group in position 2, and a stereoregular polysaccharide having only one axially oriented hydroxyl group, 3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**3**), was synthesized.



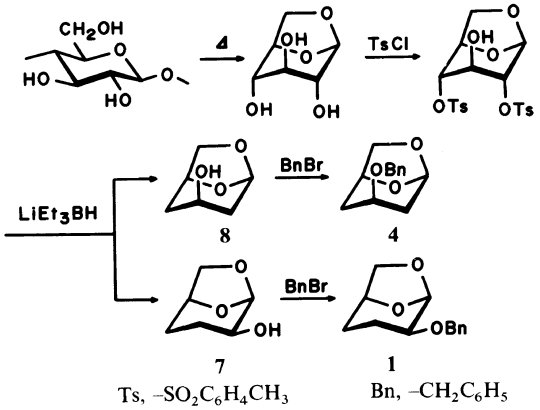
1 2 3

Bn, $-CH_2C_6H_5$

Scheme 1. Synthesis of 3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**3**).

In the previous paper, we reported the polymerization of an isomer 1,6-anhydro-3-*O*-benzyl-2,4-dideoxy-β-D-*threo*-hexopyranose (**4**) whose benzyloxy substituent is axially ori-

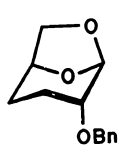
ented in position 3.[7] These optically active monomers **1** and **4** were prepared *via* the reduction of 1,6-anhydro-2,4-di-*O*-*p*-toluenesulfonyl-*β*-D-glucopyranose, an intermediate obtained from microcrystalline cellulose as the starting material (Scheme 2). On the other



Scheme 2. Synthesis of 1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-*β*-D-*threo*-hexopyranose (**1**).

hand, DL-isomer of **1** (1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-*β*-DL-*threo*-hexopyranose) and its axially substituted DL-isomer (1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-*β*-DL-*erythro*-hexopyranose) were also prepared and polymerized.[8,9] These optically inactive DL-isomers obtained from a non-carbohydrate source (an acrolein dimer) are termed DL-**1** and DL-**5**, respectively, in this paper.

The polymerization of **1** proceeded rapidly, but the conversion remained relatively low. The polymerization reactivity and resulting polymer structure are discussed in connection with the position and orientation of benzyloxy substituent as well as the chirality of the parent bicyclic acetal ring, and compared with those of the isomers **4**, DL-**1**, DL-**5**, and also 1,6-anhydro-2,3,4-tri-*O*-benzyl-*β*-D-glucopyranose (**6**).



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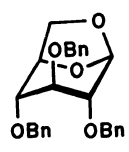

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EXPERIMENTAL

*1,6-Anhydro-2-O-benzyl-3,4-dideoxy-β-*D*-threo-hexopyranose* (**1**)

The monomer **1** was synthesized *via* four step reactions from microcrystalline cellulose as shown in Scheme 2. 1,6-Anhydro-2,4-di-*O*-*p*-toluenesulfonyl-*β*-D-glucopyranose was treated with lithium triethylborohydride in tetrahydrofuran according to the method described by Kelly *et al.*[7,10] An isomeric mixture consisting of 1,6-anhydro-3,4-dideoxy-*β*-D-*threo*-hexopyranose (**7**) and 1,6-anhydro-2,4-dideoxy-*β*-D-*threo*-hexopyranose (**8**) was obtained and chromatographed over silica gel (eluent, ethyl acetate–triethylamine, 20 : 1, v/v) to separate the former isomer in a 14% yield and the latter in a 73% yield.

To a solution of **7** (1.7 g) in tetrahydrofuran (25 ml) were added 0.6 g of sodium hydride, 0.25 g of tetrabutylammonium iodide, and 1.7 ml of benzyl bromide. The solution was stirred at room temperature for 2 h. After another portion of sodium hydride (1.8 g) was added, the stirring was continued at 50°C for 2 h. The reaction was quenched by the addition of excess water, and the product was extracted with chloroform and purified by silica gel column chromatography to give a viscous liquid (1.8 g, 61%). $[\alpha]_D^{25}$ −39.4° (*c*, 1.0 in chloroform). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89%; H, 7.32%. Found: C, 70.89%; H, 7.31%. ^{13}C NMR data ($CDCl_3$, TMS), *δ* 138.2, phenyl (*ipso*); 128.3, phenyl (*ortho*); 127.6, phenyl (meta and para); 100.9, C-1; 75.6, C-2; 73.0, C-5; 70.6, CH_2 (benzyl); 68.3, C-6; 27.8, C-4; 22.8, C-3.

Polymerization

Polymerization of **1** was carried out with high vacuum techniques as described.[4-7] It was terminated with a small amount of pyridine, and a large excess of methanol was added to precipitate a white powdery polymer. The polymer was purified by reprecipitation from a chloroform solution into methanol three times

and a methanol–insoluble polymer was isolated. The supernatant methanol solution was collected and concentrated to recover a mixture of methanol–soluble oligomer and unreacted monomer. The amount of the oligomer was estimated by GPC analysis.

Depolymerization

Depolymerization was carried out in a high vacuum reaction vessel. Polymer **2** was dried in vacuum for several days and dissolved in dichloromethane. The solution was frozen and degassed; the break-seal was broken; the initiator was transferred to the polymer solution vessel cooled in a liquid nitrogen bath. The vessel was sealed and kept at $-60°C$ in a thermostated refrigerator with occasional shaking. A small amount of pyridine was added to terminate the reaction. The resulting solution was dissolved in chloroform and washed with water, and the organic layer was concentrated. The conversion was determined from the anomeric H-1 absorptions of the monomeric and polymeric components in ^1H NMR spectra.

Debenzylation

The benzyl group of polymer **2** was removed by treating **2** with sodium in liquid ammonia. The debenzylation and work-up procedures were similar to those described previously.[7]

Characterization

^1H and ^{13}C NMR spectra were recorded on a Japan Electron Optics Laboratory JNM-FX-200 Fourier transform NMR spectrometer operating at 200 and 50 MHz, respectively. Optical rotations were determined at 25°C on a Japan Spectroscopic Co. DIP-181 digital polarimeter using a water-jacketed 1-dm cell. Gel-permeation chromatography was carried out on a Hitachi 634A high performance liquid chromatograph with a Shodex GPCA-80M column (8 mmϕ × 1000 mm; polystyrene standard; solvent, chloroform).

RESULTS AND DISCUSSION

*Polymerization of 1,6-Anhydro-2-O-benzyl-3,4-dideoxy-β-*D*-threo-hexopyranose* (**1**)

Polymerization was carried out under high vacuum in anhydrous dichloromethane in the presence of phosphorus pentafluoride (PF_5) and boron trifluoride diethyl etherate as the initiators. The polymerization using PF_5 initiator proceeded rapidly and a methanol–insoluble white powdery polymer was isolated. Table I summarizes the polymerization conditions and yield of the methanol–insoluble polymer and methanol–soluble oligomer, together with characterization results of the methanol–insoluble polymer.

Figure 1 shows the ^{13}C NMR spectrum of a polymer obtained at $-60°C$. There appeared only a set of ten sharp signals assignable to the stereoregular 2-*O*-benzyl-3,4-dideoxy-(1→6)-α-*threo*-hexopyranan structural unit (**2**). ^{13}C NMR ($CDCl_3$), δ 138.5, phenyl (*ipso*); 128.0, phenyl (*ortho*); 127.2, phenyl (meta and para); 97.4, C-1; 72.3, C-2; 70.5, CH_2 (benzyl); 69.4, C-6; 67.6, C-5; 22.8, C-3; 22.0, C-4. The specific rotations of these polymers were positive and high, which is also suggestive of α-stereoregularity. No β-configurational unit was detected even in the spectra of the polymers prepared at -40 and 0°C, although the specific optical rotation decreased with rise in polymerization temperature.

The polymer was soluble in a wide variety of solvents including benzene, chloroform, carbon tetrachloride, tetrahydrofuran, and dimethylformamide. The melting point determined on a heating block with the aid of a magnifying glass was 56—74°C, and the molecular weight was below 3.1×10^4.

Optically inactive DL-polymer (DL-**2**) with high α-stereoregularity was prepared from racemic monomer DL-**1** using antimony pentachloride, antimony pentafluoride and trifluoromethanesulfonic acid as the initiators at $-60°C$.[8] The molecular weight of the present polymer **2** was slightly higher than those of DL-

Table I. Polymerization of 1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-β-D-*threo*-hexopyranose (**1**)[a]

Exptl. No.	$[M]_0$	Initiator		Temp	Time	Yield, %		$[\alpha]_D$[b,d]	$\bar{M}_n$[b,e]	mp[b,f]
	$mol\,l^{-1}$	mol% to **1**		°C	min	Polymer[b]	Oligomer[c]	deg	$\times 10^{-3}$	°C
I-49	1.0	PF_5	2.5	0	60	3.7	18	—	3.6	—
I-51	1.0	PF_5	2.5	−40	60	14	6.5	+80.3	7.3	—
I-57	1.0	PF_5	2.5	−60	30	30	~0	+91.7	31	58—74
I-45	1.0	PF_5	2.5	−60	180	40[h]	—	+94.6	18	59—73
I-50	1.0	PF_5	2.5	−60	(2)[g]	27	8.6	+94.4	7.9	56—72
I-52	2.0	PF_5	2.5	−60	180	69	4.0	+94.9	12	—
I-61	2.0	BF_3OEt_2	2.7	−60	(1)[g]	trace	~0	—	—	—

[a] **1**, 2.0 mmol; solvent, dichloromethane.
[b] Methanol–insoluble polymer.
[c] Methanol–soluble oligomeric products.
[d] In chloroform at 25°C.
[e] By GPC; polystyrene standard.
[f] Determined by optical observation on a heating block with the aid of a magnifying glass.
[g] Day.
[h] Elementary analysis, Calcd for $(C_{13}H_{16}O_3)_n$: C, 70.89%; H, 7.32%. Found: C, 70.91%; H, 7.25%.

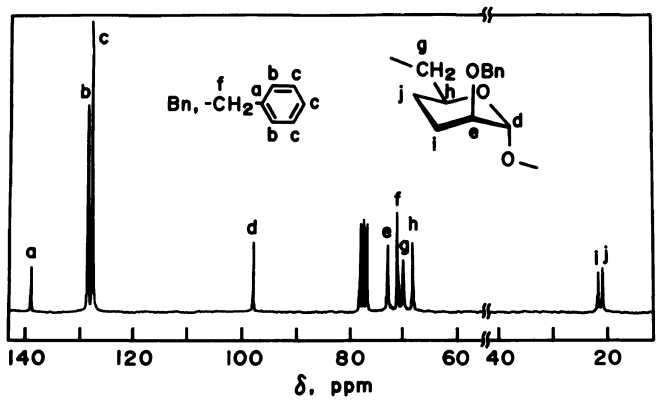

Figure 1. 50 MHz ^{13}C NMR spectrum of 2-*O*-benzyl-3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**2**). Solv., $CDCl_3$; concentration, 3%; Me_4Si, standard.

2, while the solubility and melting point were almost the same.

Polymerization Reactivity of 1,6-Anhydro-2-O-benzyl-3,4-dideoxy-β-D-threo-hexopyranose (**1**)

The monomer **1** was not polymerized by boron trifluoride diethyl etherate. This supports the reported diagnostic character of the weak Lewis acid BF_3OEt_2 for the polymerization of 1,6-anhydrosugar derivatives; it is an effective initiator for **4**[7] and other monomers[11-13] deoxygenated at the C-2 position, but uneffective for DL-**5**[9] and others[14] having a benzyloxy substituent at this position.

Copolymerization between **1** and 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**6**) was carried out to obtain information on the polymerization reactivity of **1**. The copolymerization of 0.50 : 0.50 molar feed afforded a copolymer composed of 0.78 **1** and 0.22 **6** (initiator, 2.5 mol% of PF_5; the total monomer

concentration, 2.0 mol l^{-1}; temp, −60°C; time, 8 min; yield, 12%). Splitting of some signals was observed in the ^{13}C NMR of the product, indicating the presence of crossover diad sequences between **1** and **6** units. Data on the polymerization of an equimolar mixture of **4** and **6** and of DL-**1** and DL-**5** are available[7,8] to confirm that the copolymerization reactivity is qualitatively in the order of **4** > **1**(DL-**1**) > DL-**5** > **6**.

It has been shown that the apparent polymerization rate and copolymerization reactivity of **1** are relatively high. Nevertheless, the polymer yield was rather low, compared to those in polymerization of other 1,6-anhydrosugar derivatives. Axially 3-*O*-benzylated isomer **4** gave an almost quantitative yield of polymer (97%) under the reaction conditions identical to those for the experimental No. I-57 whose conversion was 30%. The polymer yield in polymerization of **1** was highest at 69% when the polymerization (exptl. No. I-52) was carried out in a high monomer concentration ($[M]_0 = 2.0$ mol l^{-1}) at −60°C, and it decreased at lower monomer concentration ($[M]_0 = 1.0$ mol l^{-1}) and elevated temperature. Experimental Nos. I-45 and I-50 showed that prolonged polymerization did not increase polymer yield but caused formation of oligomeric products and reduction of the molecular weight of the polymer. These data suggest that the monomer **1** has a high equilibrium monomer concentration; the polymerization using PF_5 initiator progressed quickly until the monomer concentration was reached and then cleavage of the resulting polymer chains occurred simultaneously.

Polymerization of the racemic monomer DL-**1** using antimony pentachloride, antimony pentafluoride and trifluoromethanesulfonic acid as the initiators was reported[8] (monomer, 5 mmol; solvent, dichloromethane, 1.0 ml; initiator, 0.25 mmol; temp, −60°C; time, 2 day; high vacuum technique was not applied). The initial monomer concentration of DL-**1** was much higher than that of the present polymerization system and hence, a high polymer yield (84%) was attained (initiator, $SbCl_5$). Under conditions of such a high monomer concentration, the polymerization of **1** using a stronger Lewis acid PF_5 initiator by high vacuum technique occurred too rapidly to be controlled. The reaction started before the initiator was mixed thoroughly with the monomer solution, and hence, the reaction sites were localized so much that the reaction did not progress sufficiently (data not shown).

The equilibrium monomer concentration was determined in the course of both polymerization and depolymerization. The residual monomer concentration ($[M]_r$) at −60°C estimated in exptl. No. I-52 was 0.54 mol l^{-1} and that estimated in depolymerization of polymer **2** was 0.31 mol l^{-1} (Table II). Therefore, the equilibrium monomer concentration ($[M]_e$) of **1** is in the range of 0.31—0.54 mol l^{-1} (at −60°C). This equilibrium monomer concentration was higher than those of other anhydrosugar derivatives: 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**6**) (0.0064 mol l^{-1}) and 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (0.029—0.042 mol l^{-1}).[15]

The high equilibrium monomer concentration, that is, a small negative free energy change in polymerization, is attributable to the spatial arrangement of the benzyloxy substituent in the monomer **1** and polymeric unit **2**. Figure 2 compares non-bonded interaction energies of related 1,6-anhydrosugars and corresponding (1→6)-α-D-glycopyranan units. The term (X_a, Y_a) is the interaction energy between 1,3-diaxially oriented *X* and *Y* atoms, and the term (X_1, Y_2) is the energy between two vicinal, gauche *X* and *Y* atoms. The values proposed by Angyal[16] and also those of hydroxy group as substitutes for benzyloxy group are used in the calculation. The sum of the interaction energies of **1** is the smallest among the three monomers, and that of **2** is the largest among the three polymeric units. The difference in nonbonded interactions be-

Table II. Depolymerization of 2-*O*-benzyl-3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**2**)[a]

Exptl. No.	Polymer	$[P]_0$[b]	PF_5	Time	Convn.[c]	$[M]_r$[d]
	g (mmol)	mol l^{-1}	mol%	day	%	mol l^{-1}
I-62	0.22 (1.0)	1.4	9.9	2	22	0.30
I-63	0.14 (0.65)	0.65	15	6	47	0.31

[a] Solvent, dichloromethane; temp, −60°C.
[b] Initial concentration of **1** unit.
[c] Estimated by ^{1}H NMR spectroscopy.
[d] Concentration of monomer **1** formed by depolymerization.

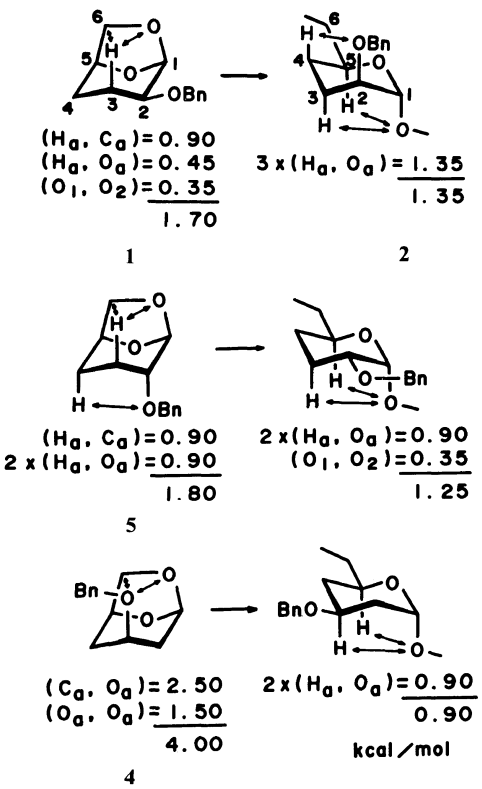

Figure 2. Non-bonded interaction energies of 1,6-anhydrosugar derivatives and corresponding (1→6)-α-D-hexopyranan units.

tween the polymeric units and monomer is in the order of **4**>**5**>**1**, which is assumed to reflect thermodynamic polymerizability.

It should be pointed out that the α-stereoregularity of the polymer **2** is high and no resonance due to β-structural unit was detectable even in the ^{13}C NMR spectra of the depolymerization product as well as the prolonged-polymerization product. This finding suggests that α-structural unit along the polymer sequence of **2** once produced was hardly inverted to a β-structural one. This is in contrast to the polymerization of **4** in which the content of β-structural unit in the polymer increased at a later stage of polymerization.[7] Inversion of α to β-structure is assumed to proceed through an acetal-exchange reaction involving the polymer chain and oxonium ion in the growing chain end.[17] The attack of oxonium ion on the acetal C-1 carbon in polymer **2** would be sterically hindered by the axially-oriented benzyloxy group in position 2.

Optically Active 3,4-Dideoxy-(1→6)-α-D-threo-hexopyranan (**3**)

Polymer **2** was debenzylated with sodium in liquid ammonia and the reaction mixture was worked up according to the conventional procedure. The polymer was isolated as a white powder from both the aqueous solution and precipitate of the work-up mixture in a quantitative total yield. The polymer obtained from the aqueous solution was soluble in dimethyl sulfoxide and partially soluble in water and methanol. This soluble polymer was a stereoregular polysaccharide of low molecular weight ($\bar{M}_n$, 2.6×10^3), as indicated by the presence of ^{13}C NMR signals of the terminal residues as well as the stereoregular main chain units. The polymer obtained from the precipi-

Table III. Debenzylation of 2-*O*-benzyl-3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**2**)

Exptl. No.	**2**	Na	Liq. NH_3	Toluene	DME[a]	Time	Yield	$[\alpha]_D$[b]	$\bar{M}_n$[c] $\times 10^{-3}$
	g	g	ml	ml	ml	min	%	deg	
ID-52	0.22	0.20	50	25	15	165	40[d] ~60[e]	+139.8 —	2.6 —

[a] 1,2-Dimethoxyethane.
[b] In dimethyl sulfoxide at 25°C.
[c] Estimated by ^1H NMR spectroscopy.
[d] Obtained from the aqueous solution of the work-up mixture.
[e] Obtained from the precipitate of the work-up mixture.

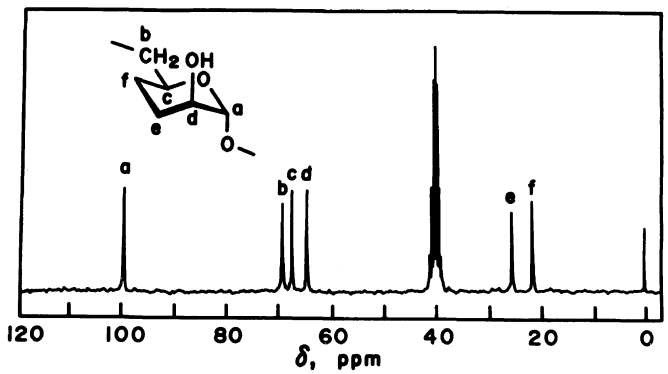

Figure 3. 50 MHz ^{13}C NMR spectrum of 3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**3**). Solv., Me_2SO-d_6; concentration, 3%; Me_4Si, standard.

tate was partially soluble in dimethyl sulfoxide and insoluble in water as well as other common organic solvents. This less-soluble polymer had a melting point at 149—160°C (the melting point of optically inactive polymer DL-**2** was reported to be 136—150°C[8]). Elemental analytical data agreed with the calculated values (Calcd for $(C_6H_{10}O_3)_n$: C, 55.37%; H, 7.74%. Found; C, 55.37%; H, 7.77%).

Figure 3 shows the ^{13}C NMR spectrum of the less soluble polymer. There appeared six sharp signals due to the stereoregular 3,4-dideoxy-(1→6)-α-D-*threo*-hexopyranan (**3**). ^{13}C NMR (Me_2SO-d_6), δ 99.01, C-1; 68.67, C-6; 67.04, C-5; 64.19, C-2; 25.31, C-3; 21.40, C-4. These chemical shifts can be compared with those of a completely deoxygenated skeletal polymer 2,3,4-trideoxy-(1→6)-α-L-*glycero*-hexopyranan (measured in $CDCl_3$ as solvent).[12] The hydroxyl substitution in place of the axial hydrogen atom in position 2 of each pyranose unit caused a 34.8 ppm downfield shift for the C-2 resonance, and 7.3 and 2.5 ppm downfield shifts for the adjacent C-3 and C-1, respectively. The C-4 resonance showed a 5.9 ppm upfield shift attributable to steric compression caused by the axial hydroxyl group in position 2.

Diad Tacticity of D,L-*Enantiomeric Units in Racemic Polymers* DL-**2** *and* DL-**3**

In the ^{13}C NMR spectrum of the optically inactive polysaccharide (DL-**3**), each signal of C-1 and C-5 carbon had a shoulder in the lower field side.[8] These signal splittings are due to the diad tacticities of the D,L-enantiomer units along the polymer chain. The optically active polymer **3** consisting exclusively of D-

enantiomer unit enabled unambiguous assignment of these signal pairs to the diad tacticities. As predicted, the main peaks of the signal pairs (C-1, 98.82; C-5, 66.97) were due to the respective carbons of isotactic diads (D–D and L–L consecutive units) and the lower field shoulders (C-1, 99.54; C-5, 67.59) to those of the syndiotactic diads (D–L and L–D crossover units). These assignments were also confirmed by comparing the ^{13}C NMR spectra of benzylated polymers **2** and DL-**2**, although the signal splittings of optically inactive polymer DL-**2** were less clearly discernible than those of DL-**3**.

The isotactic diad fraction of polymer DL-**3** estimated from relative peak intensity was 0.70.[8] In the polymerization of DL-**1**, the enantiomer whose chirality is the same as that of a growing terminal unit tended to be incorporated into a polymer chain preferentially. Similar preference of an isotactic diad sequence was also observed in the polymerization of 6,8-dioxabicyclo[3.2.1]octane and its derivatives.[13,18–20] This enantiomer selection is explained by the growing chain end control mechanism, as proved by the D,L-copolymerization of enantiomerically unbalanced 6,8-dioxabicyclo[3.2.1]octane[13] and by the asymmetric selective copolymerization of racemic 4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]octane with **6**.[21]

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