Synthesis, Branched Structure, and Solution Property of Hyperbranched D-Glucan and D-Galactan

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ABSTRACT: The ring-opening multibranching polymerizations of 1,6-anhydro-β-D-glucopyranose (**1**) and 1,6-anhydro-β-D-galactopyranose (**2**) have been studied in order to synthesize hyperbranched polysaccharides. The solution polymerization in propylene carbonate and the bulk polymerization of **1** and **2** using a thermally induced cationic initiator proceeded through a ring-opening reaction and a proton transfer reaction to afford highly water-soluble polysaccharides, i.e., **poly-1** and **poly-2**, respectively. For the polymers from **1** and **2** with the same polymerization conditions, the $M_{w,SLS}$ and yield of **poly-1** were higher than those of **poly-2**. Here, **poly-1** and **poly-2** were characterized as hyperbranched polysaccharides consisting of α- and β-linked D-hexopyranosyl and D-hexofuranosyl repeating units, hyperbranched D-glucan and D-galactan, respectively. In addition, **poly-1** and **poly-2** had ca. 30−40 mol % nonreducing D-hexopyranosyl and D-hexofuranosyl terminal units, and the degree of branching was ca. 0.38 for **poly-1** and 0.44−0.60 for **poly-2**. The respective viscosities of **poly-1** and **poly-2** in aqueous $NaNO_3$(0.2 mol·L^{-1}) solution were very low with the intrinsic viscosity values of 0.023−0.042 dL·g^{-1}. The steady shear flow of **poly-1** in aqueous solution exhibited a Newtonian behavior with steady shear viscosities independent of the shear rate, even at high concentrations. The results indicated that the characteristics of the viscosities were attributed to the spherical structure of the hyperbranched polysaccharide in aqueous solution.

Introduction

Spherical macromolecular architectures with their surfaces covered with sugars are of increasing interest due to their unique structures along with specific properties, such as the multivalent or cluster effect on carbohydrate-protein interactions. For the spherical polymer with many terminal sugar residues, there are a few types of glycodendrimers, e.g., dendrimers prepared from the reaction of the dendrimer surface with mono- and disaccharides,[1−7] and dendrimers prepared through the convergent method using semidendritic branched oligosaccharides.[8−10]

Although the synthesis of such glycodendrimer types were accomplished, dendrimers essentially consisting of sugar units, i.e., dendritic polysaccharides, have not been prepared due to the complicated and time-consuming synthetic process involving numerous protection, deprotection, and purification procedures until now. Thus, of great interest is to synthesize and characterize spherical polysaccharides, such as dendritic, star-shaped, and hyperbranched polysaccharides, from the viewpoint of material science.

Hyperbranched polysaccharides from the polymerization of AB_m-type monomers can be prepared more easily than dendritic polysaccharides. Previously, Schuerch et al. and other groups reported highly branched polysaccharides prepared by the acid-catalyzed ring-opening polymerization of 1,6-anhydrohexopyranose,[11−13] though the branching structure was insufficiently characterized as well as the solution properties. For the pioneer research for hyperbranched polysaccharides, Kadokawa et al. reported the synthesis of a hyperbranched polyaminosaccharide by the acid-catalyzed polymerization of an oxazoline sugar having two hydroxyl groups as an AB_2-type monomer.[14,15] Recently, we proposed that the ring-opening multibranching polymerization of latent AB_m-type monomers should be a convenient method of synthesizing hyperbranched carbohydrate polymers as a novel spherical macromolecular architecture, for example, the hyperbranched D-mannan from the cationic polymerization of 1,6-anhydro-β-D-mannopyranose,[16] the hyperbranched poly(2,5-anhydro-D-glucitol) from 1,2:5,6-dianhydro-D-mannitol,[17] and the hyperbranched polytetritols of 1,4-anhydroerythritol and 1,4-anhydro-L-threitol.[18]

For our synthetic strategy of hyperbranched carbohydrate polymers, it is important to elucidate the effect of the structure of the sugar monomers on the ring-opening multibranching polymerization tendency and to clarify the relationship between the structure and solution property of the hyperbranched carbohydrate polymers. In this article, we report the ring-opening multibranching polymerization of 1,6-anhydro-β-D-glucopyranose (**1**) and 1,6-anhydro-β-D-galactopyranose (**2**) as latent AB_4-type monomers using a thermally induced cationic initiator, as shown in Scheme 1, leading to hyperbranched D-glucan (**poly-1**) and D-galactan (**poly-2**), respectively. The characteristics of the polymerization and the polymer structure involving repeating units

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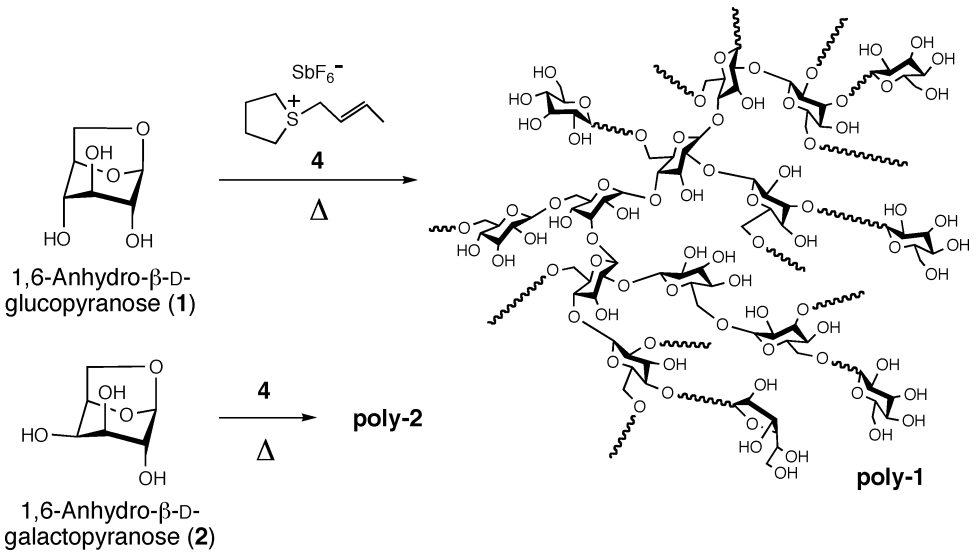
Scheme 1



and branching degrees were compared with those for the polymerization of 1,6-anhydro-*β*-D-mannopyranose (**3**).[16] In addition, the solution characteristics, such as the viscosity and steady shear flow property, of **poly-1** and **poly-2** in aqueous solution are discussed from the viewpoint of the physical properties of the hyperbranched macromolecule.

Experimental Section

Materials. 1,6-Anhydro-*β*-D-glucopyranose (**1**) was prepared by the microwave pyrolysis of cellulosic materials.[19,20] 1,6-Anhydro-*β*-D-galactopyranose (**2**) was synthesized from D-(+)-galactose using a procedure similar to that reported by Sözmen.[21] **1** and **2** were recrystallized twice from dry methanol and dried in a vacuum oven at 50 °C for 2 days. (*S*-2-Butenyl)-tetramethylenesulfonium hexafluoroantimonate (**4**) in propylene carbonate solution (66 wt %) was a gift from Asahi Denka Kogyo K.K. and was used without further purification. D-(+)-Galactose (>97.0%), methyl α-D-glucopyranoside (>98.0%), (**5a**) methyl *β*-D-glucopyranoside (>98.0%), (**5b**) and methyl *β*-D-galactopyranoside (>98.0%) (**8b**) were purchased from Tokyo Kasei Kogyo Co., Ltd. Methyl α-D-galactopyranoside (**8a**) was purchased from Junsei Chemical Co., Ltd. Anhydrous propylene carbonate (99.7%) was purchased from Sigma-Aldrich Co. (1→6)-α-D-glucopyranan (**7a**) and (1→6)-α-D-galactopyranan (**10a**) were synthesized by the cationic polymerization of 1,6-anhydro-2,3,4-tri-*O*-allyl-*β*-D-glucopyranose and 1,6-anhydro-2,3,4-tri-*O*-allyl-*β*-D-galactopyranose using $BF_3 \cdot OEt_2$, respectively, followed by deallylation, according to a procedure reported in our previous paper.[22] The $[\alpha]_D$ values of **7a** and **10a** were +153.4 and +125.7°, respectively (*c* 1.0 in H_2O at 25 °C). **10a**: ^{13}C NMR (100 MHz, D_2O, acetone as the internal reference) *δ* (ppm) 98.73 (C-1), 70.13 (C-5), 69.87 (C-3), 69.26 (C-2), 68.92 (C-4), 67.06 (C-6).

Measurements. The ^1H (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded using a JEOL JNM-A400II instrument. The quantitative ^{13}C NMR spectra were obtained using a 20% (w/v) sample in deuterium oxide (D_2O) at 25 °C and 45° pulse angle, inverse gated decoupling with a 7.0 s delay, 6000 scans, and acetone as the internal reference. A static laser light scattering (SLS) measurement was performed in aqueous $NaNO_3$ solution (0.2 mol·L^{-1}) at 23 °C using an Otsuka Electronics CALLS-1000 light scattering spectrometer (λ = 632.8 nm). The refractive index increment (d*n*/d*c*) was measured in aqueous $NaNO_3$ solution (0.2 mol·L^{-1}) using an Otsuka Electronics DRM-1021 double-beam differential refractometer. The intrinsic viscosity ([*η*]) was determined in aqueous $NaNO_3$ solution (0.2 mol·L^{-1}) at 23 °C using a Canon-Fenske viscometer, after the sample solution was filtered. The specific rotations were measured using a Jasco DIP-1000 digital polarimeter.

Typical Procedure for Thermally Induced Cationic Polymerization. Solution Polymerization of 1. All procedures were performed under an argon atmosphere. To a solution of **1** (1.87 g, 11.5 mmol) in anhydrous propylene carbonate (2.90 mL) was added a solution of **4** in propylene carbonate (4.10 μL, 1.64 × 10^{-2} mmol) at 150 °C using a microsyringe. After 40 min, the reaction mixture was poured into a large amount of methanol. The residue was purified by reprecipitation with water and methanol to obtain the polymer in a 60.0% yield. The $M_{w,SLS}$ value was 3.30 × 10^4 (d*n*/d*c* = 0.140). $[\alpha]_D$ +99.5° (*c* 1.00, H_2O, 23 °C). ^1H NMR (400 MHz, D_2O); *δ* (ppm) 5.75−5.10 (H-1, m), 4.97 (α-H-1, br. s), 4.53 (*β*-H-1, br. s), 4.40−3.10 (H-2, H-3, H-4, H-5, H-6, m). ^{13}C NMR (100 MHz, D_2O); *δ* (ppm) 105.40−95.20 (C-1, m) including the peaks at 103.48 (*β*-C-1, glucopyranosyl unit), 103.30, 100.28, 99.74 (α-C-1, glucopyranosyl unit) and 98.47 ppm (α-C-1, (1→6)-linked glucopyranosyl unit), 84.73, 82.77, 80.41, 79.20, 77.52, 76.53 (*β*-C-2, glucopyranosyl unit), 76.31 (*β*-C-3, glucopyranosyl unit), 75.17, 74.90, 73.77 (*β*-C-4, glucopyranosyl unit), 73.57 (α-C-2, glucopyranosyl unit), 72.45 (α-C-3, glucopyranosyl unit), 72.16 (α-C-4, glucopyranosyl unit), 70.89, 70.63, 70.16 (α,*β*-C-5, glucopyranosyl unit), 68.81, 66.10 (α-C-6, (1→6)-linked glucopyranosyl unit), 64.27, 63.82, 61.41 ppm (*β*-C-6, glucopyranosyl terminal unit), and 61.17 ppm (α-C-6, glucopyranosyl terminal unit).

Bulk Polymerization of 1. All procedures were performed under an argon atmosphere. To a melted solution of **1** (5.13 g, 31.6 mmol) was added a solution of **4** in propylene carbonate (22.3 μL, 8.95 × 10^{-2} mmol) at 210 °C using a microsyringe. After an appropriate time, the reaction mixture was poured into a large amount of methanol. The residue was purified by reprecipitation with water and methanol to obtain the polymer in a 59.0% yield. The $M_{w,SEC}$ and $M_{w,SEC}/M_{n,SEC}$ values were 4300 and 1.45, respectively, and the $M_{w,SLS}$ value was 4.90 × 10^4 (d*n*/d*c* = 0.143). $[\alpha]_D$ +87.0° (*c* 1.00, H_2O, 23 °C). ^1H NMR (400 MHz, D_2O): *δ* (ppm) 5.75−5.10 (H-1, m), 4.97 (α-H-1, br. s), 4.53 (*β*-H-1, br. s), 4.40−3.10 (H-2, H-3, H-4, H-5, H-6, m). ^{13}C NMR (100 MHz, D_2O): *δ* (ppm) 108.72 (*β*-C-1, glucofuranosyl unit), 103.48−98.47 (C-1, m) including the peaks at 103.51 (*β*-C-1, glucopyranosyl unit), 100.44, 99.68 (α-C-1, glucopyranosyl unit), and 98.46 ppm (α-C-1, (1→6)-linked glucopyranosyl unit), 80.36, (*β*-C-2, glucofuranosyl unit), 79.25, 77.63 (*β*-C-2, glucofuranosyl unit), 76.50 (*β*-C-2, glucopyranosyl unit), 76.28 (*β*-C-3, glucopyranosyl unit), 75.38, 74.80, 73.76 (α-C-2, glucopyranosyl unit and *β*-C-4, glucopyranosyl unit), 72.42 (α-C-3, glucopyranosyl unit), 72.13 (α-C-4, glucopyranosyl unit), 70.15 (α,*β*-C-5, glucopyranosyl unit), 68.71, 66.05 (α-C-6, (1→6)-linked glucopyranosyl unit), 64.39 (*β*-C-6, glucofuranosyl terminal unit), 63.50 (α-C-6, glucofuranosyl terminal unit), 61.20 (*β*-C-6, glucopyranosyl terminal unit), and 61.17 ppm (α-C-6, glucopyranosyl terminal unit).

Solution Polymerization of 2. All procedures were performed under an argon atmosphere. To a solution of **2** (1.73 g, 10.7 mmol) in anhydrous propylene carbonate (1.70 mL) was added a solution of **4** in propylene carbonate (5.80 μL, 1.54 mmol) at 150 °C using microsyringe. After 40 min, the reaction mixture was poured into a large amount of methanol. The residue was purified by reprecipitation with water and methanol to obtain the polymer in a 63.1% yield. The $M_{w,SLS}$ value was 2.69×10^4 ($dn/dc = 0.135$). $[\alpha]_D$ +86.2° (*c* 1.00, H_2O, 23 °C). ^{1}H NMR (400 MHz, D_2O): δ (ppm) 5.46−5.27 (H-1 m), 5.26−5.10 (H-1, m, galactofuranosyl unit), 5.10−4.91 (α-H-1, m, galactopyranosyl unit), 4.44 (β-H-1, galactopyranosyl unit), 4.37−3.37 (H-2, H-3, H-4, H-5, H-6, m). ^{13}C NMR (100 MHz): δ (ppm) 109.74 (β-C-1, galactofuranosyl unit), 108.35 (β-C-1, (1→5)-linked galactofuranosyl unit), 104.81 (β-C-1, galactopyranosyl unit), 103.92 (α-C-1, galactofuranosyl unit), 101.17 (α-C-1, galactopyranosyl unit), 99.13 (α-C-1, (1→6)-linked galactopyranosyl unit), 84.20−83.00 (α,β-C-4, br. s, galactofuranosyl unit), 82.20−81.20 (β-C-2, m, galactofuranosyl unit), 81.20−78.10 (m), 78.10−76.10 (α,β-C-3 and α-C-2, m, galactofuranosyl unit), 75.72 (β-C-5, galactopyranosyl unit), 74.59−74.34 (m), 73.20 (β-C-3, galactopyranosyl unit), 71.44 (α-C-5 and β-C-2, galactopyranosyl units and β-C-5, galactofuranosyl unit), 70.00 (α-C-5, (1→6)-linked galactopyranosyl unit), 69.81 (α-C-3, (1→6)-linked galactopyranosyl unit and α-C-4, galactopyranosyl unit), 69.20 (β-C-4, galactopyranosyl unit α-C-2, (1→6)-linked galactopyranosyl unit), 68.81 (α-C-3, galactopyranosyl unit and α-C-4, (1→6)-linked galactopyranosyl unit), 67.34 (α-C-6, br, (1→6)-linked galactopyranosyl unit), 63.87, 63.32 (β-C-6, galactofuranosyl terminal unit), 62.93, 61.77 (α-C-6, galactopyranosyl terminal unit). 61.60 (β-C-6, galactopyranosyl terminal unit).

Methylation Analysis. Methylation of the polysaccharide was carried out according to the method described by Tomoda et al.[23] The resulting polysaccharides were soluble in chloroform, methanol, and dimethyl sulfoxide and insoluble in water. The methylated polysaccharides were converted to partially methylated D-glucitol acetates (PMGlA) and partially methylated d-galactitol acetates (PMGaA), as described by Kennedy et al.[24] The samples were analyzed by gas chromatography (GC) using a Shimadzu GC-17A chromatograph equipped with a BPX 70 capillary column (70% bis(cyanopropyl)poly(silphenylenesiloxane), 30 m × 0.25 mm, 0.25 μm film thickness, SGE) and a flame-ionization detector. The oven was heated to 190 °C as the initial temperature, then heated at a rate of 1.0 °C/min to a final temperature of 250 °C, and maintained there for 10 min. The injection and detector temperatures were 260 °C. The PMGlA and PMGaA were identified by gas chromatography and mass spectrometry (GC-MS) analyses using a JEOL JMS-AX-500 equipped with a BPX 70 capillary column and electron impact ionization at 70 eV (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University), and also by their retention times relative to *myo*-inositol hexaacetate as described by Bacic et al.[25] For the quantitative PMGlA and PMGaA analysis using GC, the relative molar response factors were estimated from theoretical calculations.[26] The calculated response factors were 0.70 for di-*O*-acetyl-tetra-*O*-methyl-D-hexitol, 0.74 for the 1,2,5-, 1,3,5-, and 1,4,5-tri-*O*-acetyl-tri-*O*-methyl-D-hexitols, 0.75 for the 1,5,6- and 1,4,6-tri-*O*-acetyl-tri-*O*-methyl-D-hexitols, 0.79 for the 1,2,3,5-, 1,3,4,5-, and 1,2,4,5-tetra-*O*-acetyl-di-*O*-methyl-D-hexitols, 0.80 for the 1,2,5,6-, 1,3,5,6-, and 1,4,5,6-tetra-*O*-acetyl-di-*O*-methyl-D-hexitols, 0.84 for penta-*O*-acetyl-*O*-methyl-D-hexitol, and 0.89 for hexa-*O*-acetyl-D-hexitol.

Degree of Branching. The degrees of branching (DB) of the polysaccharide prepared from the latent cyclic AB_4-type monomers **1** and **2** were calculated from the number of terminal units (T), linear units (L), semi-dendritic units (sD_1 and sD_2), and dendritic units (D) by Frey's equation (eq 1).[27]

$$DB = \frac{3D + 2sD_2 + sD_1}{0.75\,(4D + 3sD_2 + 2sD_1 + L)} \qquad (1)$$

Table 1. Ring-Opening Multibranching Polymerization of 1,6-Anhydro-β-D-glucopyranose (1) and 1,6-Anhydro-β-D-galactopyranose (2) Using (*S*-2-Butenyl)tetramethylenesulfonium Hexafluoroantimonate (4)[a]

run no.	**M**	[**M**], mol·L^{-1}	[**M**]/[**4**]	time, min	temp, °C	yield,[b] %	$M_{w,SLS}$[c] $\times 10^{-3}$
1	**1**	4.0	700	40	150	60.0	33.0
2		6.4	350	20	130	35.9	24.5
3		6.4	700	40	130	49.1	62.0
4		6.4	700	40	150	73.8	70.6
5		bulk	180	<1	210	59.0	49.0
6	**2**	3.2	350	20	130	17.2	12.9
7		6.4	350	20	130	30.7	22.3
8		6.4	700	20	130	21.2	16.2
9		6.4	700	40	150	63.1	26.9
10		bulk	350	<1	220	35.8	111

[a] Solvent, propylene carbonate. [b] Water-soluble and methanol-insoluble parts. [c] Determined by static laser light scattering (SLS) in aqueous $NaNO_3$ solution (0.2 mol·L^{-1}).

The numbers of each unit were determined by the methylation analysis of the polysaccharide and the correction using the molar response factors.[26]

Steady Shear Rheometry. The hyperbranched D-glucan solutions were prepared by mixing the dry hyperbranched D-glucan ($M_{w,SLS}$ of 52 400) and deionized water for several hours. The concentrations (weight percent) of the solutions used in this study ranged from 30% to 60%. The steady shear flows of the aqueous hyperbranched D-glucan solutions were performed using a Brookfield cone and plate rotational viscometer at various concentrations. The cone diameter was 24 mm, and the cone angle was 1.565°. Measurements were performed over a shear rate range from 1.15 to 382 s^{-1}. The testing temperature was 25 °C, which was controlled using a constant-temperature bath.

Results and Discussion

Polymerization. The ring-opening multibranching polymerizations of 1,6-anhydro-β-D-glucopyranose (**1**) and 1,6-anhydro-β-D-galactopyranose (**2**) were carried out using (*S*-2-butenyl)tetramethylenesulfonium hexafluoroantimonate (**4**) as a thermally induced cationic initiator which was suitable for the polymerization above 120 °C. The typical results are summarized in Table 1. When propylene carbonate was used as an aprotic polar solvent with high boiling point, the polymerizations of **1** and **2** homogeneously proceeded for ca. 5 min, and then the reaction systems suddenly became heterogeneous, while the bulk polymerizations of **1** and **2** immediately proceeded to produce brown cakes. These polymerization behaviors were very similar to the polymerization systems with 1,6-anhydro-β-D-mannopyranose (**3**).[16] The resulting polysaccharides (**poly-1** and **poly-2**), which were isolated by reprecipitation using water and methanol, were gel-free white solids that were soluble in water, dimethyl sulfoxide, and dimethylformamide, slightly soluble in pyridine, and insoluble in toluene, chloroform, acetone, and methanol. The weight-average molecular weights ($M_{w,SLS}$) of **poly-1** and **poly-2**, measured by static laser light scattering (SLS), corresponded to the absolute molecular weight values, because no aggregation of **poly-1** and **poly-2** occurred in the range of the polymer concentrations measured for SLS (this is described in the solution viscosity result section). For the solution polymerization of **1** and **2** in propylene carbonate, the $M_{w,SLS}$ and yields of **poly-1** and **poly-2** gradually increased with the increasing monomer concentration ([**M**]) in a manner similar to **poly-3**;[16] for the polymerization of **1** for 40

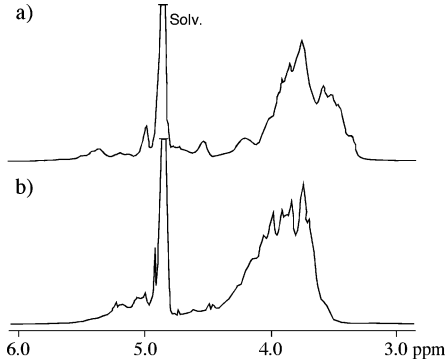


Figure 1. ^{1}H NMR spectra (D_2O) of polymers prepared from (a) 1,6-anhydro-β-D-glucopyranose (**1**) (run 1) and (b) 1,6-anhydro-β-D-galactopyranose (**2**) (run 9).

min at 150 °C, the $M_{w,SLS}$ values were 3.30×10^4 in 60.0% yield for 4.0 mol·L^{-1} of [**1**] (run 1) and 7.06×10^4 in 73.8% yield for 6.4 mol·L^{-1} of [**1**] (run 4), while for the polymerization of **2** for 20 min at 130 °C, the $M_{w,SLS}$ values were 1.29×10^4 in 17.2% yield for 3.2 mol·L^{-1} of [**2**] (run 6), and 2.23×10^4 in 30.7% yield for 6.4 mol·L^{-1} of [**2**] (run 7). The extension of the polymerization time and the increasing polymerization temperature also led to an increase in the $M_{w,SLS}$ and polymer yield, for example, the polymerization with the parameters of [**M**]/[**4**] = 700 and [**M**] = 6.4 mol·L^{-1} was carried out at 150 °C for 40 min to give the highest molecular weight and polymer yield values such as the $M_{w,SLS}$ of 7.06×10^4 and the yield of 74% for **1** (run 4) and 2.69×10^4 and the yield of 63.1% for **2** (run 9). For all the polymerizations under the same conditions, the $M_{w,SLS}$ and yield of **poly-1** were higher than those of **poly-2**. On the other hand, the polymerizability of **1** and **2** in propylene carbonate was lower than that of **3**; for the polymerization with the conditions of [**3**]/[**4**] = 700 and [**3**] = 6.4 mol·L^{-1} at 150 °C for 40 min, the $M_{w,SLS}$ and yield were 6.37×10^5 and 63.0%, respectively.[16] The $M_{w,SLS}$ values of **poly-1** varied in the range from 2.45×10^4 to 7.06×10^4, which corresponded to the average degrees of polymerization (DP) from ca. 150 to 440, while those of **poly-2** were in the range from 1.29×10^4 to 2.69×10^4 (DP = ca. 80 to 170). The polysaccharides obtained by the bulk polymerization were light brown solids with the $M_{w,SLS}$ values of 4.90×10^4 and 59.0% yield for **1** (run 5) and the $M_{w,SLS}$ values of 1.11×10^5 and 35.8% yield for **2** (run 10).

Polymer Structure. Figure 1 shows the ^{1}H NMR spectra of **poly-1** (run 1) and **poly-2** (run 9). Both spectra consisted of broad signals, meaning that **poly-1** and **poly-2** should be constructed using a variety of repeating units. The spectrum of **poly-1** showed the characteristic resonances at 5.75−5.10, 4.97, and 4.53 ppm due to the H-1 protons and 4.40−3.10 ppm due to the H-2 − H-6 protons, while **poly-2**, 5.46−4.44 are due to the H-1 protons, and 4.37−3.37 ppm are due to the H-2 − H-6 protons.

To investigate the polymer structure, the ^{13}C NMR measurements of **poly-1** and **poly-2** were carried out in D_2O. Figure 2 shows the ^{13}C NMR spectra of **poly-1** prepared by the solution (run 1) and bulk (run 5) polymerizations. Both spectra consisted of a number of split and broad signals, which were constructed by the different sequences of the D-glucopyranosyl units. The assignment of the signals was carried out by a comparison with the chemical shifts of methyl α-D-glucopyranoside (**5a**), methyl β-D-glucopyranoside (**5b**), methyl

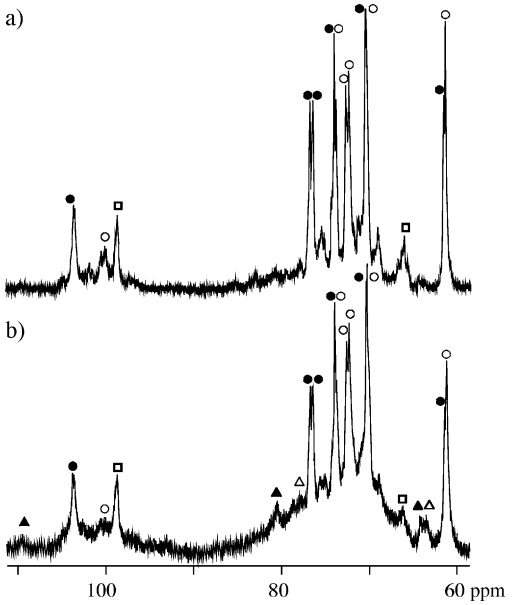


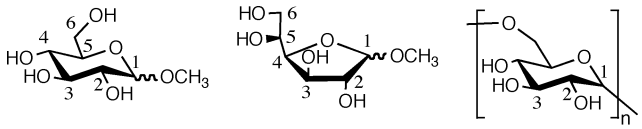
Figure 2. ^{13}C NMR spectra of polymers ((a) run 1 and (b) run 5) prepared by the solution and bulk polymerizations of 1,6-anhydro-β-D-glucopyranose (**1**), respectively.

Table 2. ^{13}C Chemical Shifts (δ/ppm) of 5a, 5b, 6a, 6b, and 7a in D_2O

C	**5a**[a]	**5b**[a]	**6a**[28]	**6b**[28]	**7a**[22]
1	100.3	104.3	104.0	110.0	98.1
2	74.2	77.0	77.7	80.6	71.8
3	72.6	77.0	76.6	75.8	73.8
4	72.3	74.2	78.8	82.3	69.9
5	70.7	70.8	70.7	70.7	70.6
6	61.7	61.9	64.2	64.7	65.9
OCH_3	56.1	58.2	57.0	56.3	-

[a] Acetone was used as internal reference.

Chart 1



5a : α-form
5b : β-form

6a : α-form
6b : β-form

7a

α-D-glucofuranoside (**6a**),[28] methyl β-D-glucofuranoside (**6b**),[28] and (1→6)-α-D-glucopyranan (**7a**)[22] as the model compounds shown in Table 2. The major signals, which are marked by the open and closed circles in Figure 2, are very similar to the chemical shifts of the carbons for **5a** and **5b**, corresponding to the model compounds of the α- and β-D-glucopyranosyl terminals in **poly-1**, respectively. Thus, these peaks should be assigned to the carbons of the nonreducing D-glucopyranosyl terminals in **poly-1**. This result indicated that **poly-1** was a highly branched polysaccharide having numerous terminal units, which is the characteristic of a hyperbranched polymer. By comparison of parts a and b of Figure 2, a distinct difference between the two spectra was found, i.e., the signals in Figure 2b were broader than those in Figure 2a. The results mean that **poly-1** obtained by the bulk polymerization had a more complicated structure than that by the solution polymerization. In fact, Figure 2b exhibited the presence of the nonreducing D-glucofuranosyl terminals in **poly-1**. The peaks, shown by the open and closed triangles, fairly agreed with the chemical shifts of the carbons for **6a**

Table 3. Linkage Analysis of Hyperbranched Glucan (Poly-1) Obtained by Ring-Opening Multibranching Polymerization of 1,6-Anhydro-β-D-glucopyranose (1) Using (*S*-2-Butenyl)tetramethylenesulfonium Hexafluoroantimonate (4)[a]

unit	D-glucitol acetate[b]	type of linkage[c]	run 1	run 2	run 3	run 4	run 5
T	2,3,4,6- and 2,3,5,6-*O*-Me_4	T-*p*-glu and T-*f*-glu	33.6	35.8	36.4	38.5	41.8
		T-*p*-glu/T-*f* -glu[d]	95/5	94/6	96/4	94/6	84/16
L	2,3,4-*O*-Me_3	(1−6)-*p*-glu	25.0	19.6	21.2	24.8	22.0
	2,3,6-*O*-Me_3	(1−4)-*p*-glu	9.5	10.4	7.7	7.0	8.0
	2,4,6-*O*-Me_3	(1−3)-*p*-glu	5.0	5.7	5.8	4.8	4.5
	3,4,6-*O*-Me_3	(1−2)-*p*-glu	6.2	7.3	8.1	4.7	4.7
	total		45.7	43.0	42.8	41.3	39.2
sD_1	2,3-*O*-Me_2	(1−4−6)-*p*-glu	4.7	5.7	3.9	3.6	7.0
	2,4-*O*-Me_2	(1−3−6)-*p*-glu	6.2	5.3	5.5	4.4	4.7
	2,6-*O*-Me_2	(1−3−4)-*p*-glu	0.7	0.5	0.5	1.1	0.8
	3,4-*O*-Me_2	(1−2−6)-*p*-glu	3.8	5.1	6.0	4.1	3.2
	3,6-*O*-Me_2	(1−2−4)-*p*-glu	0.6	0.6	0.6	1.3	0.4
	4,6-*O*-Me_2	(1−2−3)-*p*-glu	0.5	0.4	0.5	1.3	0.3
	total		16.5	17.6	17.0	15.8	16.4
sD_2	2-*O*-Me	(1−3−4−6)-*p*-glu	1.0	0.9	1.2	2.0	1.2
	3-*O*-Me	(1−2−4−6)-*p*-glu	0.6	0.8	1.1	1.5	0.5
	4-*O*-Me	(1−2−3−6)-*p*-glu	0.9	0.8	1.2	0.7	0.6
	6-*O*-Me	(1−2−3−4)-*p*-glu	-	-	-	-	-
	total		2.5	2.5	3.5	4.2	2.3
D	hexa-acetates	(1−2−3−4−6)-*p*-glu	1.7	1.1	0.3	0.2	0.3
	degree of Branching[e]		0.38	0.38	0.38	0.38	0.37
	$[\alpha]_D$[f]		+99.5	+90.6	+87.5	+101.2	+87.0

[a] Estimated by the methylation analysis of polysaccharide and the correction by molar response-factors.[26] The values were normalized by mol %. [b] 2,3,5,6-*O*-Me_4 means 1,4-di-*O*-acetyl-2,3,5,6-tetra-*O*-methyl-D-glucitol, etc. [c] T-*p*-Glu and T-*f*-glu mean a nonreducing terminal D-glucopyranosyl and a D-glucofuranosyl residue, respectively. (1−4)-*p*-Glu means a (1→4)-linked D-glucopyranosyl residue, etc. [d] Estimated by quantitative ^{13}C NMR measurement (mol %/mol %). [e] Calculated by Frey's equation (eq 1).[27] [f] Measured in H_2O at 23 °C (*c* 1.00).

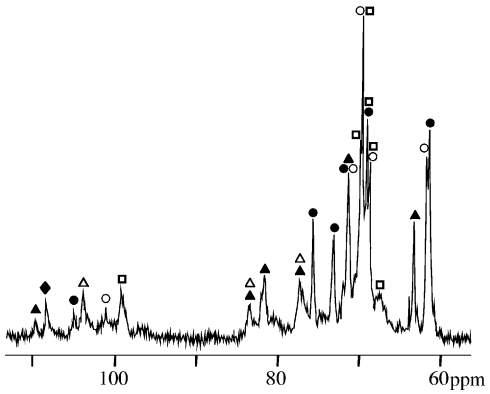


Figure 3. ^{13}C NMR spectra of polymer (run 9) prepared from 1,6-anhydro-β-D-galactopyranose (**2**).

and **6b**, corresponding to the model compounds of the α- and β-D-glucofuranosyl terminals, respectively. The ratio of the glucopyranosyl terminals to the glucofuranosyl ones in **poly-1**, which was calculated using the quantitative ^{13}C NMR measurements, varied by the polymerization method, as summarized in Table 3; 94−96 mol % of the glucopyranosyl terminals and 4−6 mol % of the glucofuranosyl terminals for the solution polymerizations (runs 1−4), and 84 mol % and 16 mol % for the bulk polymerization (run 5). Parts a and b of Figure 2 were also compared with the ^{13}C NMR spectrum of the stereoregular polysaccharide **7a**, which was synthesized by the cationic polymerization of 1,6-anhydro-2,3,4-tri-*O*-allyl-β-D-glucopyranose using $BF_3{\cdot}OEt_2$ followed by deallylation.[22] The signals at 98.47 and 66.10 ppm, which were marked by the open square in Figure 2a, were assigned to the C-1 and C-6 carbons for **7a**, respectively, indicating that **poly-1** included the (1→6)-α-D-linked glucopyranosyl units.

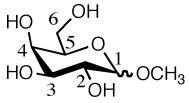
The ^{13}C NMR spectrum of **poly-2** (run 9) is shown in Figure 3. The assignment of the signals was also carried out using methyl α-D-galactopyranoside (**8a**), methyl

Table 4. ^{13}C Chemical Shifts of (δ/ppm) 8a, 8b, 9a, 9b, 10a, 10b, and 11b in D_2O

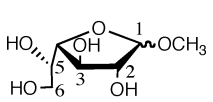
C	**8a**[a]	**8b**[a]	**9a**[28]	**9b**[28]	**10a**[a]	**11b**[29]
1	100.0	104.4	103.8	109.9	98.7	108.0
2	70.1	71.3	78.2	81.3	69.3	82.4
3	68.8	73.4	76.2	78.4	69.9	77.5
4	69.8	69.3	83.1	84.7	68.9	82.4
5	71.3	75.7	74.5	71.7	70.1	76.6
6	61.8	61.6	64.1	63.6	67.1	62.1
OCH_3	55.6	57.8	57.2	55.6		

[a] Acetone was used as internal reference.

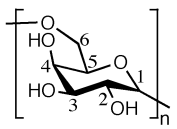
Chart 2



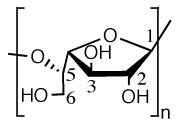
8a : α-form
8b : β-form



9a : α-form
9b : β-form



10a



11b

β-D-galactopyranoside (**8b**), methyl α-D-galactofuranoside (**9a**),[28] methyl β-D-galactofuranoside (**9b**),[28] (1→6)-α-D-galactopyranan (**10a**), and (1→5)-β-D-galactofuranan (**11b**)[29] as the model compounds shown in Table 4. From the comparison with the chemical shifts of model compounds **8a** and **8b**, the major signals, which were marked by the open and closed circles, were assigned to the carbons due to the nonreducing α- and β-D-galactopyranosyl terminal units, respectively. On the other hand, the signals marked by the open and closed triangles were very close to the chemical shifts of **9a**

Table 5. Linkage Analysis of Hyperbranched Galactan (Poly-2) Obtained by Ring-Opening Multibranching Polymerization of 1,6-Anhydro-β-D-galactopyranose (2) Using (*S*-2-Butenyl)tetramethylenesulfonium Hexafluoroantimonate (4)[a]

unit	D-galactitol acetate[b]	type of linkage[c]	run 6	run 7	run 8	run 9	run 10
T	2,3,4,6- and 2,3,5,6-*O*-Me_4	*T*-*p*-gal and T-*f*-gal	33.1	31.9	29.6	32.1	41.3
		T-*p*-gal/T-*f*-gal [d]	72/28	84/16	88/12	68/32	53/47
L	2,3,4-*O*-Me_3	(1−6)-*p*-gal	20.9	18.5	28.7	20.7	11.0
	2,3,5-*O*-Me_3	(1−6)-*f*-gal	4.2	3.1	4.1	3.0	4.8
	2,3,6-*O*-Me_3	(1−4)-*p*-gal and (1−5)-*f*-gal	1.4	2.6	2.1	2.4	1.9
	2,4,6-*O*-Me_3	(1−3)-*p*-gal	5.7	8.0	5.4	7.2	4.8
	2,5,6-*O*-Me_3	(1−3)-*f*-gal	1.1	1.1	0.5	0.9	1.9
	3,4,6-*O*-Me_3	(1−2)-*p*-gal	4.1	5.0	3.2	3.7	1.9
	total		37.4	38.3	44.0	37.9	26.3
sD_1	2,3-*O*-Me_2	(1−4−6)-*p*-gal	3.6	3.7	3.5	3.6	5.6
	2,4-*O*-Me_2 and 3,5-*O*-Me_2	(1−3−6)-*p*-gal and (1−2−6)-*f*-gal	7.1	8.5	6.2	7.3	3.6
	2,5-*O*-Me_2	(1−3−6)-*f*-gal	1.4	1.1	1.3	2.4	1.6
	2,6-*O*-Me_2	(1−3−4)-*p*-gal	1.6	1.5	2.1	2.2	2.9
	3,4-*O*-Me_2	(1−2−6)-*p*-gal	4.4	4.2	4.1	3.5	2.5
	3,6-*O*-Me_2	(1−2−4)-*p*-gal	0.8	0.6	1.2	1.2	1.1
	4,6-*O*-Me_2	(1−2−3)-*p*-gal	1.4	1.8	1.3	1.3	1.1
	total		20.3	21.4	19.7	21.5	18.4
sD_2	2-*O*-Me and 5-*O*-Me	(1−3−4−6)-*p*-gal and (1−2−3−6)-*f*-gal	3.4	3.3	2.0	3.5	6.8
	3-*O*-Me and 4-*O*-Me	(1−2−4−6)-*p*-gal and (1−2−3−6)-*p*-gal	4.0	3.7	2.7	3.0	4.1
	6-*O*-Me	(1−2−3−4)-*p*-gal	0.4	0.7	1.1	0.9	1.3
	total		7.8	7.7	5.8	7.4	12.2
D	hexa-acetates	(1−2−3−4−6)-*p*-gal	1.4	0.7	0.9	1.1	1.8
	degree of Branching [e]		0.50	0.48	0.43	0.49	0.60
	$[\alpha]_D$[f]		+82.4	+95.8	+92.2	+86.2	+40.5

[a] Estimated by the methylation analysis of polysaccharide and the correction by molar response-factors.[26] The values were normalized by mol %. [b] 2,3,5,6-*O*-Me_4 means 1,4-di-*O*-acetyl-2,3,5,6-tetra-*O*-methyl-D-galactitol, etc. [c] T-*p*-Gal and T-*f*-gal mean a nonreducing terminal D-galactopyranosyl and a D-galactofuranosyl residue, respectively. (1−4)-*p*-Gal and (1−5)-*f*-gal mean a (1→4)-linked D-galactopyranosyl and a (1→5)-linked galactofuranosyl residue, respectively, etc. [d] Estimated by quantitative ^{13}C NMR measurement (mol %/mol %). [e] Calculated by Frey's equation (eq 1).[27] [f] Measured in H_2O at 23 °C (*c* 1.00).

and **9b**, respectively, indicating that **poly-2** contained the nonreducing α- and β-D-galactofuranosyl terminal units. These results indicated that **poly-2** consisted of numerous D-galactopyranosyl and D-galactofuranosyl terminal units, analogous to **poly-1** and **poly-3**. The ratio of the D-galactopyranosyl terminal units to the D-galactofuranosyl ones in **poly-2** is summarized in Table 5. The ratio varied by the polymerization conditions and the galactofuranosyl terminals increased with the decreasing monomer concentration and the increasing monomer conversion; 53−88 mol % of the D-galactopyranosyl terminal units and 12−47 mol % of the D-galactofuranosyl ones for **poly-2**. In particular, the bulk polymerization produced a higher content of the D-galactofuranosyl terminal units than the solution polymerization in propylene carbonate, analogous to the bulk polymerizations of **1** and **3**. For the polysaccharide obtained by the same polymerization conditions, the content of the D-hexofuranosyl terminal units was also varied by the monomer structure and increased in the order **1** < **3** < **2**.

The peaks at 96−110 ppm due to the C-1 carbons in Figure 3 indicated the presence of both α- and β-D-linkages in **poly-2**. The peaks at 99.13 and 108.35 ppm, which were marked by the open square and closed diamonds, respectively, were assigned to the C-1 carbons for the (1→6)-α-D-linked galactopyranosyl units and the (1→5)-β-D-linked galactofuranosyl units, respectively, as compared with the chemical shifts of **10a**, and **11b** as the model compounds.

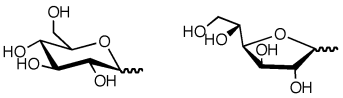
To confirm the branching and linkage manner of **poly-1** and **poly-2** in detail, a methylation analysis was carried out according to the procedure reported in a previous paper.[16] These results are summarized in Tables 3 and 5. From the gas chromatography results of the obtained partially methylated hexitol acetates, 16 different peaks corresponding to the seventeen kinds of repeating units as shown in Chart 3 were detected for **poly-1**, while 18 peaks corresponding to 23 kinds of repeating units, as shown in Chart 4, were detected for **poly-2**. These peaks were classified into five categories of terminal units (T), linear units (L) with two linkages, two semi-dendritic units (*s*D_1 and *s*D_2, respectively,) with three and four linkages, and perfect dendritic units (D) with five linkages. The main components in **poly-1** and **poly-2** were the *T* and L units and the ratio of each unit varied by the polymerization conditions, 33.6−41.8 mol % of T, 39.2−45.7 mol % of L, 15.8−17.6 mol % of *s*D_1, 2.3−4.2 of *s*D_2, and 0.2−1.7 of D for **poly-1**, while 29.6−41.3 mol % of T, 26.3−44.0 mol % of L, 18.4−21.5 mol % of *s*D_1, 5.8−12.2 of *s*D_2, and 0.7−1.8 of D for **poly-2**. In addition, the hyperbranched polysaccharides prepared by the bulk polymerization particularly included the high content of the nonreducing D-hexofuranosyl terminal units. The data corresponded to the results of the ^{13}C NMR measurement of **poly-1** and **poly-2**.

In addition, the methylation analysis provided information about the reactivity of the three hydroxyl groups in monomers **1** and **2**. For the solution polymerization of **1**, the C-3 hydroxyl groups were less reactive than the C-2 and C-4 hydroxyl groups, i.e., the reactivity increased in the order of C-3 < C-4 = C-2. On the other hand, the C-3 hydroxyl groups were more reactive than the C-2 and C-4 hydroxyl groups for the solution polymerization of **2**, i.e., the reactivity increased in the order of C-4 < C-2 < C-3. The bulk polymerizations of **1** and **2** showed the different reactivity of the hydroxyl groups, i.e., the reactivity increased in the order of C-2 = C-3 < C-4 for **1**, while C-4 < C-2 < C-3 for **2**.

The specific rotations ($[\alpha]_D$) in H_2O varied from +87.0 to +101.2° for **poly-1** and from +40.5 to +95.8° for **poly-2**, as listed in Tables 3 and 5. The increasing hexofura-

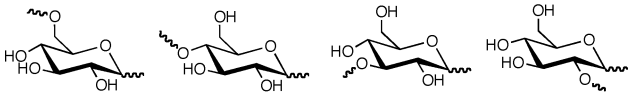
Chart 3

Terminal units (T)



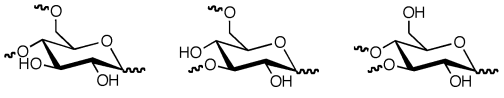
T-*p*-Glu T-*f*-Glu

Linear units (L)

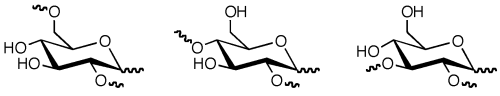


(1-6)-*p*-Glu (1-4)-*p*-Glu (1-3)-*p*-Glu (1-2)-*p*-Glu

Semi-dendritic units with three linkages (sD_1)

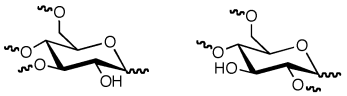


(1-4-6)-*p*-Glu (1-3-6)-*p*-Glu (1-3-4)-*p*-Glu

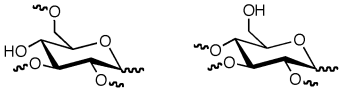


(1-2-6)-*p*-Glu (1-2-4)-*p*-Glu (1-2-3)-*p*-Glu

Semi-dendritic units with four linkages (sD_2)

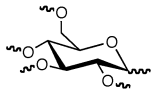


(1-3-4-6)-*p*-Glu (1-2-4-6)-*p*-Glu



(1-2-3-6)-*p*-Glu (1-2-3-4)-*p*-Glu

Perfect dendritic unit (D)



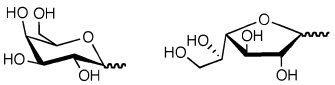
(1-2-3-4-6)-*p*-Glu

nosyl units in **poly-1** and **poly-2** obviously led to the decreasing specific rotation values. These values were lower than those of the corresponding linear polysaccharides; the $[\alpha]_D$ value (*c* 1.0 in H_2O at 25 °C) was from +153.4° for (1→6)-α-D-glucopyranan (**7a**)[22] and +125.7° for (1→6)-α-D-galactopyranan (**10a**), meaning that the resulting hyperbranched polysaccharides should contain α- and *β*-D-linkages between the sugar units.

The formation of the hyperbranched polysaccharides of **poly-1** and **poly-2** proceeded through a mechanism with the ring-opening reaction of the 1,6-anhydro moieties and the proton-transfer reaction, as well as the formation of **poly-3**.[16] In the polymerization system, a part of the 1,6-anhydro-*β*-D-hexopyranose derivative is converted to a 1,4-anhydro-*β*(or α)-D-hexofuranose derivative (**12**) to produce the D-hexofuranosyl repeating units, as shown in Scheme 2. These reactions simultaneously occurred in the polymerization system and, consequently, formed the spherical hyperbranched polysaccharide.

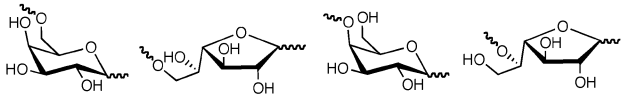
Chart 4

Terminal units (T)

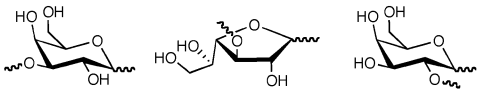


T-*p*-Gal T-*f*-Gal

Linear units (L)

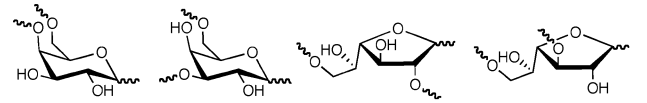


(1-6)-*p*-Gal (1-6)-*f*-Gal (1-4)-*p*-Gal (1-5)-*f*-Gal

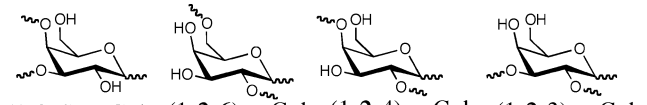


(1-3)-*p*-Gal (1-3)-*f*-Gal (1-2)-*p*-Gal

Semi-dendritic units with three linkages (sD_1)

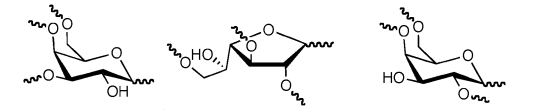


(1-4-6)-*p*-Gal (1-3-6)-*p*-Gal (1-4-6)-*f*-Gal (1-3-6)-*f*-Gal

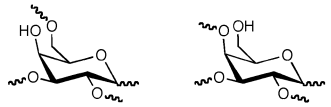


(1-3-4)-*p*-Gal (1-2-6)-*p*-Gal (1-2-4)-*p*-Gal (1-2-3)-*p*-Gal

Semi-dendritic units with four linkages (sD_2)

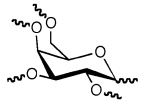


(1-3-4-6)-*p*-Gal (1-2-3-6)-*f*-Gal (1-2-4-6)-*p*-Gal



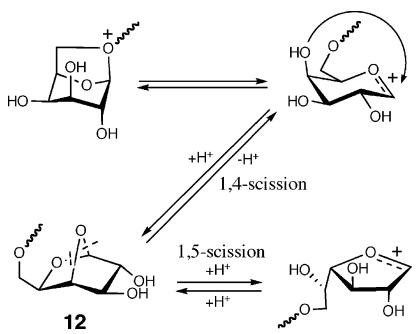
(1-2-3-6)-*p*-Gal (1-2-3-4)-*p*-Gal

Perfect dendritic unit (D)



(1-2-3-4-6)-*p*-Gal

Scheme 2



Degree of Branching. Monomers **1** and **2** have one anhydro moiety capable of ring-opening and three

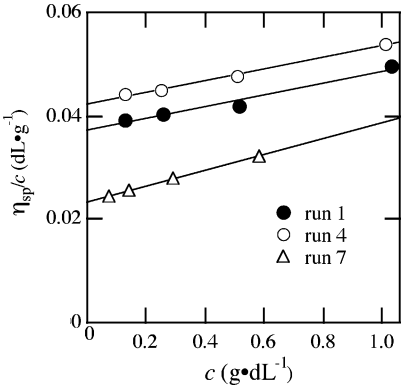


Figure 4. Reduced viscosity (η_{sp}/c) as a function of concentration (c) for **poly-1** and **poly-2** in aqueous $NaNO_3$ solution (0.2 mol·L^{-1}) at 23 °C. Intrinsic viscosities [η]: 0.037 dL·g^{-1} for run 1, 0.042 dL·g^{-1} for run 4, and 0.023 dL·g^{-1} for run 7.

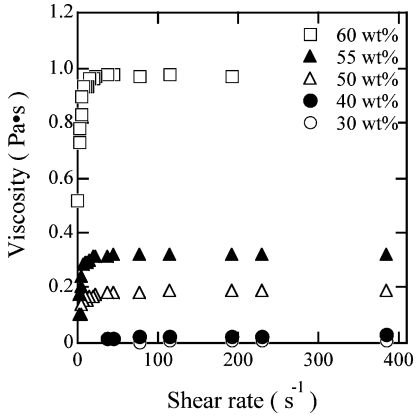


Figure 5. Steady shear viscosity as a function of shear rate for **poly-1** ($M_{w,SLS}$ of 52 400) in aqueous solution at 25 °C.

hydroxyl groups in a molecule; therefore, they should be classified as a latent AB_4-type monomer, even though the reactivity of the three hydroxyl groups was expected to be different from each other. The degrees of branching (DBs) for **poly-1** and **poly-2** were calculated from the number of T, L, sD_1, sD_2, and D units using Frey's equation (eq 1 in Experimental Section).[27] The calculated DB values are summarized in Tables 3 and 5. The DB values were ca. 0.38 for **poly-1** and varied in the range from 0.43 to 0.60 for **poly-2**, while those for **poly-3** were from 0.38 to 0.44. It is noteworthy that the DB values for **poly-2** were greater than the theoretical value of 0.42 for the polymerization of the AB_4-type monomers. Particularly, **poly-2** obtained from the bulk polymerization gave the highest DB values of 0.60. The DBs for **poly-2** increased with the increasing galactofuranosyl units, indicating that the formation of the 1,4-anhydro-β-D-galactopyranose derivative (**12**) should led to the slow monomer addition condition in the system.[27] As a result, the thermally induced cationic polymerization of 1,6-anhydro-β-D-hexopyranose with **4** is a facile synthetic strategy for a hyperbranched polysaccharide with a high DB value.

Viscosity of Solution. Figure 4 shows the reduced viscosity (η_{sp}/c) of the hyperbranched polysaccharides in aqueous $NaNO_3$ solution (0.2 mol·L^{-1}) as a function of concentration (c) at 23 °C. The respective values of η_{sp}/c for **poly-1** and **poly-2** solutions linearly increased with the increase of the concentration. The linear dependence of the concentration on the reduced viscosity means that no aggregation of **poly-1** and **poly-2** occurred over the wide range of the measured polymer concentration.[30] Although the hyperbranched polysaccharides have high molecular weights, their viscosities were very low, as compared to the viscosity value for the linear polysaccharide; the intrinsic viscosities ([η]) of **poly-1** and **poly-2** were in the range from 0.023 to 0.042 dL·g^{-1} for the $M_{w,SLS}$ value of 2.23×10^4 to 7.06×10^4, while the [η] value for the linear polysaccharide of (1→6)-α-D-glucopyranan (M_n of 4.28×10^4) was 0.37 dL·g^{-1} in aqueous solution at 25 °C.[31]

In the steady shear flow measurement in the aqueous **poly-1** solution, Figure 5 shows the typical plots of the steady shear viscosity as a function of the shear rate for several concentrations. All the aqueous **poly-1** solutions ranging in shear rate from 10 to 382 s^{-1} exhibited a Newtonian behavior with steady shear viscosities independent of the shear rate, even at the high concentrations, though the increase in the shear viscosity for the shear rate of <10 s^{-1} is obscure.

These experiment results in the viscosity and steady shear flow measurements of the hyperbranched polysaccharides indicated that the very low viscosity and the Newtonian behaviors were attributed to the spherical structure of the hyperbranched polysaccharides without any physical entanglements. More detailed and rigorous studies are currently in progress to investigate the specific molecular characterization of the hyperbranched polysaccharide in aqueous solution.

Conclusions

The thermally induced cationic polymerization of 1,6-anhydro-β-D-hexopyranose with (*S*-2-butenyl)tetramethylenesulfonium hexafluoroantimonate (**4**) was a facile synthetic strategy for a hyperbranched polysaccharide with a high degree of branching (DB) values. The polymerization of 1,6-anhydro-β-D-glucopyranose (**1**) produced the hyperbranched D-glucan (**poly-1**) consisting of 17 kinds of the D-glucopyranosyl and D-glucofuranosyl repeating units, while the polymerization of 1,6-anhydro-β-D-galactopyranose (**2**) gave hyperbranched D-galactan (**poly-2**) consisting of 23 kinds of D-galactopyranosyl and D-galactofuranosyl repeating units. The resulting hyperbranched polysaccharides also had ca. 30−40 mol % of nonreducing D-hexopyranosyl and D-hexofuranosyl terminal units. The DB value estimated by the methylation analysis was ca. 0.38 for **poly-1** and 0.43−0.60 for **poly-2**. The intrinsic viscosities of **poly-1** and **poly-2** in aqueous $NaNO_3$(0.2 mol·L^{-1}) at 23 °C were very low in the range of 0.023 to 0.042 dL·g^{-1}. In addition, the aqueous **poly-1** solution exhibited a Newtonian behavior with steady shear viscosities independent of the shear rate. The structural analysis and the characteristics of the viscosities indicated that **poly-1** and **poly-2** have spherical structures without any physical entanglements in aqueous solution. The very low intrinsic viscosities and the lack of entanglements of the hyperbranched polysaccharide should allow its use as the biocompatible and biodegradable viscosity modifier.

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