Synthesis of Hyperbranched 2,5-Anhydro-D-glucitol by Proton-Transfer Cyclopolymerization of 1,2:5,6-Dianhydro-D-mannitol

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ABSTRACT: The cyclopolymerization of 1,2:5,6-dianhydro-D-mannitol (**1**) was carried out using BF_3•OEt_2 and *t*-BuOK. Although the anionic polymerization tended to form gels, the cationic polymerization proceeded through the proton-transfer reaction mechanism to produce hyperbranched carbohydrate polymers (**2**) mainly consisting of 2,5-anhydro-D-glucitol units. The weight-average molecular weight ($M_{w,SLS}$) values of **2** measured by static light scattering (SLS) varied in the range of 2.08×10^5−26.9×10^5, which were significantly higher than the weight-average molecular weight ($M_{w,SEC}$) values by size exclusion chromatography (SEC). The degree of branching (DB), estimated by the ^{13}C NMR measurements, was ca. 0.44−0.46. The α value of the Mark−Houwink equation, which was determined by the viscosity measurements, was ca. 0.3. The hyperbranched polymers **2** were nanoscale particle with the radii of gyration (R_g) of 67.4−132.0 nm.

Introduction

The design, synthesis, and properties of three-dimensional macromolecular architectures, such as hyperbranched and star-shaped polymers, dendrimers, etc., have been interestingly developed in terms of functional materials for nanoscale applications. Hyperbranched polymers can be synthesized by a one-pot reaction, which is an attractive characteristic in comparison with the synthesis of other three-dimensional macromolecules from the viewpoint of synthetic methodology. Thus, there are many synthetic methods leading to various kinds of hyperbranched polymers, e.g., the ring-opening polymerization of an AB_2 type monomer such as epoxy alcohols. Frey et al. reported that a hyperbranched aliphatic polyether was prepared by the multibranching ring-opening polymerization of glycidol using an anionic initiator.[1] In addition, Frechet et al. reported that the polymerization of an aromatic diepoxy alcohol proceeded through the proton-transfer reaction to produce the hyperbranched poly(hydroxy ether).[2]

Although diepoxy compounds are generally used as cross-linking agents for adhesives and coatings, we have developed the cyclopolymerization of suitably designed diepoxides leading to various well-defined polymers with functional properties, such as molecular recognition ability. In particular, our continuous efforts have allowed us to produce novel carbohydrate polymers by the cyclopolymerization of a dianhydro sugar, such as 1,2:5,6-dianhydrohexitol and 1,2:4,5-dianhydropentitol; e.g., the cationic and anionic polymerizations of 1,2:5,6-dianhydro-3,4-di-*O*-alkyl-D-mannitol proceeded through a cyclopolymerization mechanism to produce the regio- and stereoselective polymer, (1→6)-2,5-anhydro-3,4-di-*O*-alkyl-D-glucitol.[3] Thus, of great interest is to expand the limit and scope of the cyclopolymerization method in connection with the structure of the resulting polymers. In this study, we focused on the ring-opening polymerization of diepoxy diol through a proton-transfer cyclopolymerization mechanism, leading to a hyperbranched polymer, which should be a new class of cyclopolymerization together with a novel type of hyperbranched carbohydrate polymer. We now report the polymerization of 1,2:5,6-dianhydro-D-mannitol (**1**) using anionic and cationic initiators, as shown in Scheme 1. The proton-transfer cyclopolymerization mechanism is discussed by determining the structure of the resulting polymers, such as the cyclic constitutional units and degree of branching. In addition, the three-dimensional property of the hyperbranched poly(2,5-anhydro-D-glucitol) (**2**) is characterized on the basis of static laser light scattering and viscosity measurements, which is compared with the linear polymer of (1→6)-2,5-anhydro-D-glucitol (**3**).

Scheme 1

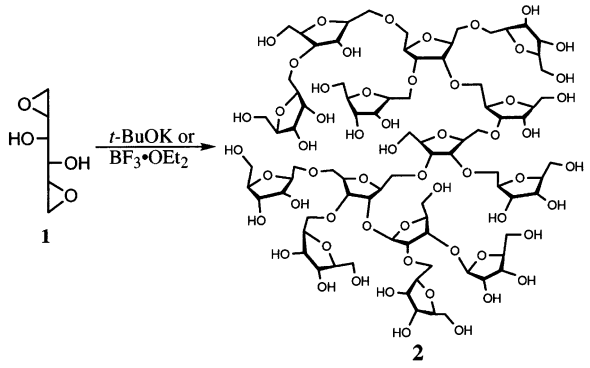

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Table 1. Polymerization of 1,2:5,6-Diahhydro-D-mannitol (1) Using *t*-BuOK and BF_3·OEt_2

no.	initiator	solvent	[M]	[M]/[I]	temp, °C	time, h	yield, %	$M_{w,SEC}$ (M_w/M_n)[a]	$M_{w,SLS} \times 10^{-4}$ [b]	$[\eta] \times 10^2$ [c]	DB[d]
1	*t*-BuOK	THF	1.0	20	23	200	85.4 (72.3)[e]	1600 (5.07)	132.0		
2			0.5	50	0	200	8.04	1210 (2.29)			
3	BF_3·OEt_2	CH_2Cl_2	0.5	100	0	100	30.5	1120 (1.28)	20.8	1.91	0.46
4			0.5	100	0	200	41.8	1880 (2.23)	30.8	2.16	0.46
5			0.5	100	0	240	50.4	2680 (3.03)	39.0	2.38	0.46
6			0.5	100	0	300	72.7	2740 (4.64)	98.4	3.07	0.46
7			0.5	100	23	100	47.9	3590 (3.55)	269.3	4.04	0.44
8			1.0	100	0	100	40.4	3200 (2.88)	231.9	3.89	0.46

[a] Determined by SEC in 0.2 M aqueous $NaNO_3$ solution using PEG as standards. [b] Determined by SLS in 0.2 M aqueous $NaNO_3$ solution. [c] Using Canon-Fenske viscometer in 0.2 M aqueous $NaNO_3$ solution. [d] Determined by ^{13}C NMR spectra. [e] Water-insoluble part.

Experimental Section

Measurements. The ^1H and ^{13}C NMR spectra 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, 45° pulse angle, inverse gated decoupling with a 7.0 s delay, 6000 scans, and acetone as the internal reference. Size exclusion chromatography (SEC) was performed at 40 °C in aqueous sodium nitrate ($NaNO_3$) solution (0.2 mol L^{-1}) using a TOSOH HPLC system equipped with two TSK gel $GMPW_{XL}$ columns. The weight-average molecular weights ($M_{w,SEC}$) and the molecular weight distribution (M_w/M_n) of the polymer samples were calculated on the basis of poly(ethylene glycol) calibration. A static laser light scattering (SLS) measurement was performed at 40 °C in aqueous $NaNO_3$ solution (0.2 mol L^{-1}) using an Otsuka Electronics DLS-7000 light scattering spectrometer. 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 40 °C using a Canon-Fenske viscometer.

Materials. D-Mannitol, dry tetrahydrofuran (THF), dry dichloromethane (CH_2Cl_2), and potassium *tert*-butoxide (*t*-BuOK) in THF solution (1.0 mol L^{-1}) were purchased from Kanto Chemical Co. and were used without further purifications. Borontrifluoride etherate (BF_3·OEt_2) was purified by distillation of a commercial product (Kanto Chemical Co.). 1,2:5,6-Dianhydro-D-mannitol (**1**) was synthesized from 1,6-di-*O*-(*p*-toluenesulfonyl)-D-mannitol[4] using a procedure similar to that reported by Golding.[5] (1→6)-2,5-Anhydro-D-glucitol (**3**) was synthesized according to the previous method.[3n]

Anionic Polymerization. To a solution of **1** (0.50 g, 3.42 mmol) in dry THF was added *t*-BuOK (0.17 mmol) in THF solution at 23 °C using a microsyringe under a nitrogen atmosphere. After 100 h, the reaction mixture was poured into a large amount of water containing a few drops of acetic acid. The solvent was evaporated, and the residue was purified using a permeable membrane in water. After the permeation, the residue was freeze-dried in vacuo to produce the polymer in 85.4% (water-soluble part 13.1% and insoluble part 72.3%) yield. The $M_{w,SEC}$, M_w/M_n, and $M_{w,SLS}$ were 1600, 5.07, and 1.32×10^6, respectively. ^1H NMR (400 MHz, D_2O): δ (ppm) 4.48−3.50 (br), 3.31−3.15 (CH, epoxy proton, br), 2.97−2.85 (CH_2, epoxy proton, br). ^{13}C NMR (100 MHz, D_2O): δ (ppm) 86.7−73.1 (CH, m), 73.0−71.8 (CH_2, m), 71.7−71.4 (CH, m), 71.3−70.3 (CH_2, m), 70.3−66.2 (CH, m), 63.8−60.0 (CH_2, m), 57.7−54.7 (CH, m), 53.5−52.8 (CH, m), 50.5−50.4 (CH, m), 47.4, (CH, m), 46.3−45.7 ppm (CH_2, m).

Cationic Polymerization. To a solution of **1** (0.50 g, 3.42 mmol) in dry CH_2Cl_2 was added BF_3·OEt_2 (3.42×10^{-2} mmol) at 0 °C using a microsyringe under a nitrogen atmosphere. After 100 h, the reaction mixture was poured into a large amount of water containing a drop of aqueous ammonia. The solvent was evaporated, and the residue was purified using a permeable membrane in the water. After the permeation, the residue was freeze-dried in vacuo to give the polymer in 30.5% yield. The $M_{w,SEC}$ and M_w/M_n were 1120 and 1.28, respectively, and the $M_{w,SLS}$ was 2.08×10^5. ^1H NMR (400 Hz, D_2O): δ (ppm) 4.41−3.37 (m). ^{13}C NMR (100 Hz, D_2O): δ (ppm) 87.9−87.8 (CH, m), 86.0 (CH, linear unit), 83.9 (CH), 83.7 (CH, terminal unit), 82.5 (CH, linear unit), 81.8 (CH, terminal unit), 81.2 (CH, linear unit), 80.7−80.2 (CH, m), 79.6−78.5 (CH, linear and terminal unit), 77.5 (CH, terminal unit), 77.1−74.3 (CH, m), 74.0 (CH_2, linear unit), 71.9−71.5 (CH_2, terminal and linear), 71.3−70.2 (CH_2, m), 69.3 (CH, m), 68.7−68.5 (CH_2, m), 67.0−65.0 (CH_2, m), 61.3 (CH_2, 1,3,4-bonded-semi-dendritic unit and (1→3)-bonded-linear unit), 60.6 (CH_2, terminal unit), 60.4 (CH_2, (1→4)-bonded-linear unit).

Degree of Branching. The degree of branching (DB) of the polymer **2** prepared from the AB_3 monomer was determined from the ratio of the terminal unit by Frey's equation.[6] In the ^{13}C NMR spectrum of **2**, the C1 and C6 methylene carbon peaks for the repeating 2,5-anhydro D-glucitol units were observed at 74.0−60.3 ppm, including the peaks at 64.0−60.3 ppm due to the C6 methylene carbon bonded hydroxy group. Compared with the chemical shift of the model compounds, the peak at 61.3, 60.6, and 60.5−60.3 ppm was attributed to the C6 methylene carbon for the semidendritic and (1→4)-bonded linear units, the terminal units, and the (1→3)-bonded linear units, respectively (Supporting Information). The ratio of terminal units, i.e.

$$\frac{T}{D + sD + L + T}$$

was estimated from the area ratio of the methylene carbon peaks as

$$\frac{\text{the integrated ratio of C6 methylene peak for terminal unit}}{{}^1/_2(\text{the integrated ratio of entire C1 and C6 methylene peak in } \mathbf{2})}$$

Results and Discussion

Polymerization and Polymer Structure. The anionic and cationic polymerizations of 1,2:5,6-dianhydro-D-mannitol (**1**) were carried out using potassium *tert*-butoxide (*t*-BuOK) in tetrahydrofuran (THF) and boron trifluoride etherate (BF_3·OEt_2) in dichloromethane (CH_2Cl_2), respectively. After the initiators were added to the monomer solution, the polymerization systems immediately became heterogeneous. Table 1 lists the polymerization results. For the anionic polymerization, the polymer yield was the relatively high value of 85.4% for the polymerization temperature of 23 °C, while it was as low as 8.0% at 0 °C. However, the polymer obtained at 23 °C was mostly insoluble along with a small amount of the water-soluble polymer, which was quite different from the anionic cyclopolymerization of 1,2:5,6-dianhydro-3,4-di-*O*-alkyl-D-mannitol, leading to gel-free polymers.[3f,h−j,l,n] In the ^1H NMR spectrum of the polymer prepared by the anionic polymerization, the signal was broad and the characteristic absorption due to the epoxy protons was observed. Although the extent of the cyclization (f_c) of the water-soluble polymer was 0.91, the polymer gradually became insoluble after

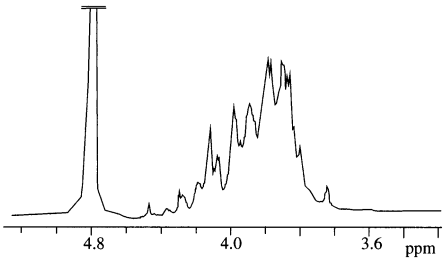


Figure 1. ^{1}H NMR spectrum of **2** (no. 3).

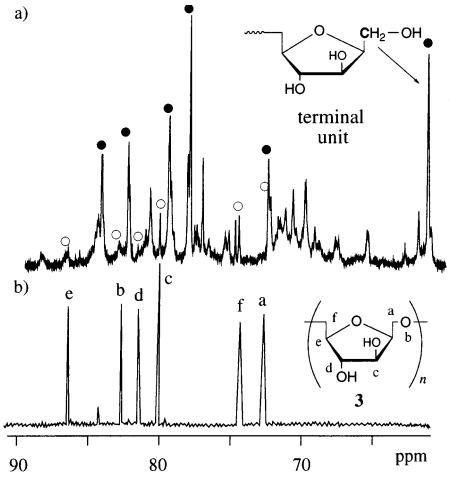


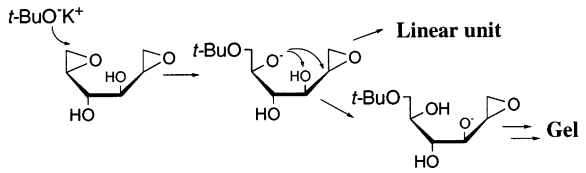
Figure 2. ^{13}C NMR spectra of (a) **2** (no. 3) and (b) (1→6)-2,5-anhydro-D-glucitol.

storage for a few days. The weight-average molecular weight ($M_{w,SEC}$) values measured by size exclusion chromatography (SEC) were 1210 and 1600.

On the other hand, polymers obtained from the cationic polymerization were soluble in methanol and water, which was very similar to the solubility of the linear polymer of (1→6)-2,5-anhydro-D-glucitol (**3**). The characteristic absorption at 2.6−3.6 ppm due to the epoxy proton of **1** completely disappeared in the ^{1}H NMR spectrum of the polymer prepared, as shown in Figure 1, so that the polymerization proceeded according to a cyclopolymerization mechanism leading to the polymers essentially consisting of cyclic repeating units; i.e., the f_c was 1.0 for every polymer. The $M_{w,SEC}$ values were varied in the range from 1120 to 3590. For the polymerization with a monomer concentration ([M]) of 0.5 mol L^{-1} at 0 °C, the $M_{w,SEC}$ values increased with the increasing polymerization time. The weight-average molecular weight ($M_{w,SLS}$) values measured by the static light scattering (SLS) were greater than the $M_{w,SEC}$ ones for all of the polymers prepared by the anionic and cationic polymerizations.

Figure 2 shows the ^{13}C NMR spectra of the cationic polymer and the linear polymer of (1→6)-2,5-anhydro-D-glucitol (**3**). In the ^{13}C NMR spectrum of the cationic polymer, the six major signals marked with closed circles were observed together with many small signals. The major signals marked by the closed circles at 60.6, 77.5, 78.9, and 81.8 ppm were very close to those of the C1, C2, C3, and C4 for 2,5-anhydro-D-glucitol,[7] which was the model compound for the terminal unit of **2**. The six small signals marked the open circles were consistent with those for (1→6)-bonded 2,5-anhydro-D-glucitol (**3**). Thus, the rest of the signals should be due to the multibonded 2,5-anhydro-D-glucitol units (Supporting Information). These results indicated that the cationic polymer should be a branched structure having many terminal units, i.e., a hyperbranched polymer mainly consisting of 2,5-anhydro-D-glucitol units.

Scheme 2



Branching Degree and Polymerization Mechanism. Although monomer **1** has two epoxy and two hydroxy groups in a molecule, one of the two epoxy groups is consumed during the intramolecular cyclization on the cyclopolymerization so that **1** is virtually a monomer possessing one epoxy and two hydroxy groups. Thus, **1** can be classified as a latent AB_3 type monomer. Frey et al. reported that the degree of branching (DB) of the hyperbranched polymer prepared from an AB_3 monomer was calculated from the number of dendritic units (D), the number of semidendritic units (sD), and the number of linear units (L), using eq 1.[6]

$$\mathrm{DB} = \frac{2D + sD}{\frac{2}{3}(3D + 2sD + L)} \tag{1}$$

The number of terminal units (T) for N molecules was obtained from eq 2.[6]

$$T = 2D + sD + N \tag{2}$$

Since the resulting polymers were hyperbranched molecules with high molecular weights, N in eq 1 can be negligible, i.e., $T \gg N$.[6,8,9]

$$T = 2D + sD \tag{3}$$

Thus, DB was calculated, as shown in eq 4.

$$\mathrm{DB} = \frac{2D + sD}{\frac{2}{3}(3D + 2sD + L)} = \frac{T}{\frac{2}{3}(D + sD + L + 2D + sD)} = \frac{3}{2}\left(\frac{T}{D + sD + L + T}\right) \tag{4}$$

From the area ratio of the methylene carbon signals in the ^{13}C NMR spectrum of **2**, the ratio of the terminal unit (= $T/(D + sD + L + T)$) was estimated to be 0.29−0.31. Therefore, the DB of **2** was calculated as 0.44−0.46, as shown in Table 1. Because DB denotes the suitability of a hyperbranching reaction to create a dendritic structure, the values of DB are 0 and 1 for a linear polymer and a dendrimer, respectively.[10] The DB value for the cyclopolymerization of **1** was approximately consistent with the theoretical value of 0.45 for the random polycondensation of an AB_3 type monomer.[6]

Scheme 2 shows an anionic polymerization mechanism. During the polymerization, the intramolecular proton transfer occurred from the hydroxy group to the alkoxide, which was generated by the ring opening of the epoxide group, to afford an insoluble gel. On the other hand, the cationic polymerization of **1** proceeded through the cyclopolymerization mechanism to give the polymers consisting of 2,5-anhydro-D-glucitol units. Scheme 3 represents the proposed mechanism for the

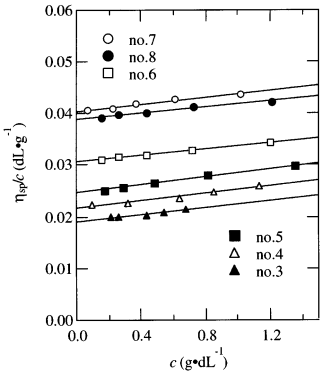


Figure 3. Viscosity vs concentration plots for **2**.

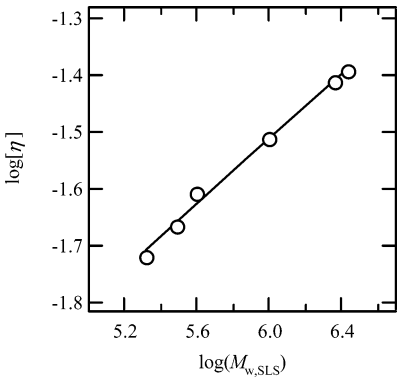
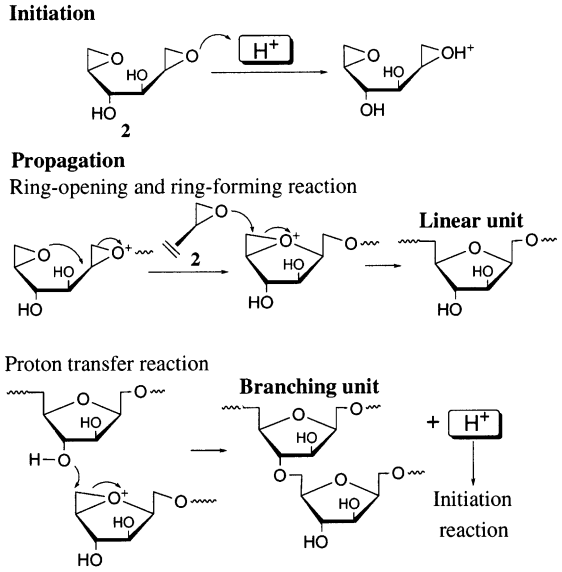


Figure 4. Logarithmic plots of [η]−$M_{w,SLS}$ for **2**.

Scheme 3



cationic cyclopolymerization. In the propagation step, the repeating units of 2,5-anhydro-D-glucitol should be formed by the alternative reaction of the intermolecular propagation and the intramolecular cyclization through β- and α-scissions of two epoxy groups in **1**, respectively. The branches of the polymer should be produced by the proton transfer from the hydroxy groups in the polymer chains to the oxonium cations.

Three-Dimensional Property. For the polymers obtained from the cationic polymerization, the hyperbranched 2,5-anhydro-D-glucitol (**2**), the $M_{w,SLS}$ values (2.08×10^5−26.9×10^5) were ca. 150−750 times greater than the $M_{w,SEC}$ values (1120−3590). In contrast, for the linear polymer of (1→6)-2,5-anhydro-D-glucitol (**3**), the $M_{w,SLS}$ value of 1.50×10^4 was somewhat greater than the $M_{w,SEC}$ value of 1700. The difference between the $M_{w,SLS}$ and $M_{w,SEC}$ values for **2** was significantly greater than that for **3**, indicating that the hyperbranched polymers of **2** had a more spherical form in solution in comparison to the linear polymer of **3**.[8,11]

In addition, the three-dimensional property is characterized on the basis of the viscosity study. Figure 3 shows the relation between the viscosity and the concentration of **2**. A linear dependence between the reduced viscosity and the concentration was observed, indicating that no aggregation of **2** occurred in the range of the measured polymer concentrations. The intrinsic viscosity ([η]) value increased with the increasing $M_{w,SLS}$ value, as listed in Table 1. The relation between the [η] and the $M_{w,SLS}$ is generally described by the Mark−Houwink equation [η] = KM^{α}. The α value was found to be 0.286, which was obtained from the slope of the logarithmic plots of [η] vs $M_{w,SLS}$ (Mark−Houwink plots), as shown in Figure 4. It is well-known that the α value was less than 0.5 for the various hyperbranched polymers, so that **2** had a spherical shape in solution.[8] Finally, we estimated the size of the hyperbranched polymer, **2**, on the basis of the SLS measurement, i.e., the radii of gyration (R_g) was in the range 67.4−132.0 nm, which increased with the increasing $M_{w,SLS}$ value.

Conclusions

The cyclopolymerization of 1,2:5,6-dianhydro-D-mannitol (**1**) was carried out using BF_3·OEt_2 and *t*-BuOK. Although the anionic polymerization tended to form gels, the cationic polymerization proceeded through a proton-transfer reaction mechanism to produce a hyperbranched carbohydrate polymer (**2**) mainly consisting of 2,5-anhydro-D-glucitol units. From the three-dimensional property characterized by the measurement of the static light scattering and the viscosity study, **2** was a nanoscale particle. This is the first report of the synthesis of a hyperbranched polymer via the cyclopolymerization mechanism.

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Supporting Information Available: Possible units of the hyperbranched carbohydrate polymer (**2**) and the structures and chemical shifts of the model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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