Synthesis, Structure, and Characteristics of Hyperbranched Polyterpene Alcohols

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ABSTRACT: A novel series of bio-based hyperbranched polymers, i.e., hyperbranched polyterpene alcohols, were prepared by the cationic ring-opening polymerizations of citronellol oxide (**1**) and nopol epoxide (**2**) using boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) as the catalyst. The polymerizations of **1** and **2** homogeneously proceeded without gelation to produce organic solvent-soluble polymers (**poly-1** and **poly-2**, respectively). The absolute weight-average molecular weights ($M_{w,MALLS}$), which were measured by a multiangle laser light scattering instrument (MALLS), were 3700−6200 g mol^{-1} for **poly-1** and 9000−20 000 g mol^{-1} for **poly-2**, which were ca. 1.4−4.8 times greater than the relative molecular weights ($M_{w,SEC}$) measured by size exclusion chromatography (SEC). The intrinsic viscosities ([η]) of these polymers were very low in the range of 8.5−10.1 mL g^{-1} for **poly-1** and 5.9−9.5 mL g^{-1} for **poly-2**. The Mark−Houwink−Sakurada exponent α was calculated to be 0.32−0.40 for **poly-1** and 0.25−0.35 for **poly-2**. These results of the MALLS, SEC, and viscosity measurements suggested that these polymers exist in a compact spherical conformation in solution.

Introduction

The spherical architectures of highly branched macromolecules, such as dendrimers and hyperbranched polymers, have attracted much attention from the viewpoint of nanotechnology because their numerous terminal units can be converted into various functional groups leading to novel nanomaterials.[1–30] The synthesis of dendrimers typically involves iterative procedures, which require purification after completion of each reaction cycle. Although they allow perfect control over the molecular weight and architecture, such multistep protocols are not very attractive for industrial use. In contrast, the synthetic method of making hyperbranched polymers is easier than that of dendrimers because they can be prepared through a one-step polymerization reaction of the AB_m-type monomers or A_2 and B_m monomers.[11,30] Although the control over the molecular weight and structural regularity are insufficient, the field of hyperbranched polymers has received increasing attention. Thus, various types of hyperbranched polymers have been synthesized, and their properties, such as the hydrodynamic volume, viscosity, and thermal properties, were compared with the linear analogues.[31–38]

Recently, the field of bio-based hyperbranched polymers, such as hyperbranched polysaccharide and hyperbranched polypeptide, has received increasing attention for exploring the potential of branched polymer architectures, i.e., the synthesis of a hyperbranched polyaminosaccharide by the acid-catalyzed polymerization of an oxazoline sugar having two hydroxyl groups,[39,40] the synthesis of highly branched polysaccharide by the thermal polycondensation of sugar derivatives,[41–43] the extraction and characterization of a natural hyperbranched β-D-glucan,[44–46] the synthesis of a hyperbranched poly-L-lysine with control of the degree of branching (DB) values,[47,48] the thermotropic ionic liquid crystal behavior of a cationic hyperbranched polypeptide and anionic surfactant,[49] etc. We have also proposed that the ring-opening multibranching polymerization of latent AB_m-type sugar derivatives should be a convenient method of synthesizing hyperbranched carbohydrate polymers as a novel spherical macromolecular architecture,[50–56] for example, the hyperbranched polysaccaharides from the cationic polymerization of 1,6-anhydro-α-D-hexopyranose,[50,53,54,56] the hyperbranched poly(2,5-anhydro-D-glucitol) from 1,2:5,6-dianhydro-D-mannitol,[51] and the hyperbranched polytetritols of 1,4-anhydroerythritol and 1,4-anhydro-L-threitol.[55]

Our continuing interest is to expand the family of bio-based hyperbranched polymers along with their characteristic properties due to their spherical and compact structure; thus, it is important to elucidate applicable monomers for the multibranching polymerization. We now report the synthesis of novel bio-based hyperbranched polymers, i.e., hyperbranched polyterpene alcohols (**poly-1** and **poly-2**), by the cationic ring-opening multibranching polymerization of citronellol oxide (**1**) and nopol epoxide (**2**) using boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$), as shown in Scheme 1. The structures of **poly-1** and **poly-2** are characterized using the results based on the NMR, light scattering, and MALDI-TOF-MS measurements. In addition, the solution viscosity and thermal property of **poly-1** and **poly-2** are discussed from the viewpoint of the physical properties of the hyperbranched polymer.

Experimental Section

Measurements. The ^{1}H (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded using a JEOL JNM-A400II instrument. The molecular weight values of the polymer samples were determined by size exclusion chromatography (SEC) in THF (1.0 mL min^{-1}) at 40 °C using an Agilent 1100 series instrumentation equipped with two Shodex KF-804L columns (linear, 8 mm × 300 mm; exclusion limit, 4×10^5), multiangle laser light scattering detector (MALLS) (Wyatt, DAWN 8), viscosity detector (Wyatt, Viscostar), and refractive index detector (Wyatt, Optilab rEX). The relative molecular weight ($M_{w,SEC}$) and the polydispersity ($M_{w,SEC}/M_{n,SEC}$) were calculated on the basis of a polystyrene calibration. The absolute molecular weights ($M_{w,SEC\text{-}MALLS}$), intrinsic viscosity ([η]), refractive index increment (dn/dc), and Mark−Houwink−Sakurada constants α and K were estimated by the software ASTRA 5.1.6.0 (Wyatt). The preparative SEC was performed in chloroform (3.0 mL min^{-1}) at 23 °C using a JAI LC-9201 equipped with a JAIGEL-3H polystyrene column (exclusion limit, 7×10^4) and a JAI RI-50S detector. The elemental analysis was performed using a MICRO

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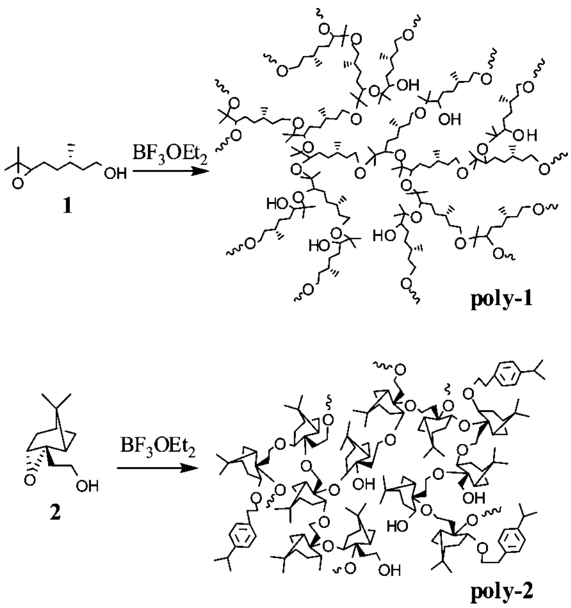
Scheme 1. Cationic Polymerizations of Citronellol Oxide (1) and Nopol Epoxide (2)



CORDER JM10 and Dionex DX-500 (Center of the Instrumental Analysis, Hokkaido University). The measurement of the decomposition temperature was performed using a BRUKERS TG-DTA2010. The measurement of the glass transition temperature and melting temperature were performed using a BRUKERS DSC3100. The measurement of the optical rotations was performed in $CHCl_3$ at 23 °C using a Jasco DIP-1000 digital polarimeter ($\lambda = 589$ nm). The FI-MASS spectroscopy measurement was performed using a JEOL JMS-SX102A mass spectrometer (GC-MS and NMR Laboratory, Graduate School of Agriculture, Hokkaido University). The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337 nm nitrogen laser (3 nm pulse width). Five hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflection mode and calibrated using insulin (TAKARA BIO, Inc.) as the internal standard. Samples for the MALDI-TOF-MS were prepared by mixing the polymer (10 mg mL^{-1}, 2 μL), a matrix (2,5-dihydroxybenzoic acid, 10 mg mL^{-1}, 20 μL), and a cationizing agent (sodium iodide, 10 mg mL^{-1}, 2 μL) in methanol.

Materials. (1*R*)-(−)-Nopol (>98.0%,), OXONE, and anhydrous dimethyl sulfoxide (dry DMSO, >99.9%, water content < 0.005%) were obtained from the Sigma-Aldrich Chem. Co. and used without further purification. (−)-β-Citronellol (>95.0%) and 18-crown-6 ether (>98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan), and used without further purification. Methyl iodide (>99.5%), potassium hydroxide (>85.5%), dichloromethane anhydrous (dry CH_2Cl_2, >99.5%; water content < 0.001%), tetrahydrofuran (THF, >99.0%), methanol (>99.5%), dichloromethane (CH_2Cl_2, >99.0%), hexane (>95.0%), ethyl acetate (EtOAc, >99.0%), sodium hydrogen carbonate ($NaHCO_3$, >99.0%), magnesium sulfate anhydrous ($MgSO_4$, >98.0%), and sodium thiosulfate ($Na_2S_2O_3$, >97.0%) were obtained from Kanto Chemical Co., Ltd. (Japan) and used without further purification. Boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$, 95.0%, Kanto Chemical Co., Ltd.) was distilled over CaH_2 under reduced pressure before use. Silica gel 60N (Kanto Chemical Co., Ltd.; spherical shape; particle size 40−50 μm; neutral) was used for the column chromatography. A hydrochloric acid methanoic solution (0.5 mol L^{-1}) was obtained from Wako Pure Chemical Industries, Ltd. (Japan). Amberlite IRA-96SB was purchased from the ORGANO Co. (Japan).

Synthesis of Citronellol Oxide (1). A solution containing (−)-β-citronellol (21.8 g, 139 mmol), $NaHCO_3$ (85 g), 18-crown-6 ether (1.80 g), H_2O (300 mL), acetone (600 mL), and CH_2Cl_2 (600 mL) were cooled at 0 °C, and the OXONE (170 g, 277 mmol) was carefully added to this solution in several portions. The mixture was vigorously stirred for 12 h and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$, 10% $Na_2S_2O_3$, and aqueous $NaHCO_3$ and dried with anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with hexanes/EtOAc (6/4 (v/v), R_f 0.3). The collected material was dried over CaH_2 and distilled under reduced pressure to give a colorless liquid **1** in a 70.9% yield; bp 72 °C (0.15 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.93 (d, CH_3 at C-3, 3H), 1.27 and 1.31 (s, 2 × CH_3 at C-7, 6H), 1.35−1.65 (m, CH_2 at C-2, 4, 5, and CH at C-3, 7H), 2.71 (m, CH at C-6, 1H), and 3.69 (m, CH_2 at C-1, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 18.80 (CH_3, C-9), 19.59 (CH_3, C-9), 19.79 (CH_3, C-9), 25.04 (CH_3, C-8, C-10), 26.37 (CH_2, C-5), 26.58 (CH_2, C-5), 29.36 (CH, C-3), 29.56 (CH, C-3), 33.84 (CH_2, C-4), 33.88 (CH_2, C-4), 39.72 (CH_2, C-2), 39.98 (CH_2, C-2), 58.43 (C, C-7), 58.53 (C, C-7), 61.14 (CH_2, C-1), 64.77 (CH, C-6), and 64.78 (CH, C-6). Anal. Calcd for $C_{10}H_{20}O_2$ (172.2): C, 69.72; H, 11.70. Found: C, 69.49; H, 11.96. FI-MS (*m/z*): 172 (M^+).

Synthesis of Nopol Epoxide (2). A solution containing (1*R*)-(−)-nopol (12.0 g, 72.2 mmol), $NaHCO_3$ (50 g), 18-crown-6 ether (720 mg), H_2O (250 mL), acetone (360 mL), and CH_2Cl_2 (360 mL) were cooled at 0 °C. To this solution was carefully added OXONE (50.0 g, 81.3 mmol) in several portions. The mixture was vigorously stirred for 12 h and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$, 10% $Na_2S_2O_3$, and aqueous $NaHCO_3$ and dried with anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with hexanes/EtOAc (7/3 (v/v), R_f 0.22). The collected material was dried over CaH_2 and distilled under reduced pressure to give a colorless liquid **2** in a 61.6% yield; bp 69 °C (0.2 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.93 (s, CH_3 at C-9, 3H), 1.30 (s, CH_3 at C-8, 3H), 1.62 (d, *endo*-CH_2 at C-7, 1H), 1.71−2.16 (m, CH_2 at C-4, 10, CH at C-1, 5, exo-7, 7H), 2.53 (t, OH), 3.36 (d, CH_2 at C-3, 2H), 3.70 ppm (t, CH_2 at C-11, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 20.31 (CH_3, C-9), 25.71 (CH_2, C-7), 26.81 (CH_2, C-4), 27.55 (CH_3, C-8), 36.30 (CH_2, C-10), 40.05 (CH, C-5), 40.75 (C, C-6), 44.54 (CH, C-1), 54.86 (CH, C-3), 58.94 (CH_2, C-11), and 63.58 (C, C-2).

Synthesis of 7-Methoxy-3(*S*),7-dimethyl-1,6-octanediol (3). $BF_3 \cdot OEt_2$ (1.10 mL, 8.71 mmol) was added to a solution of **1** (1.50 g, 8.71 mmol) in methanol (30 mL) at room temperature. After stirring for 2 h, methanol containing a small portion of an ammonia aqueous solution was added to quench the reaction. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (4/1 (v/v), R_f 0.35) to afford a colorless liquid **3**. Yield, 0.92 g (51.7%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.91 (dd, CH_3 at C-3, 3H), 1.10 and 1.12 (s, CH_3 at C-7, 6H) 1.21−1.75 (m, CH_2 at C-2, 4, and 5,CH at C-3, 7H), 3.22 (s, OCH_3, 3H), 3.40 (t, CH at C-6, 1H), and 3.57−3.70 (m, CH_2 at C-1, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 19.13 (CH_3), 19.16 (CH_3), 19.58 (CH_3), 19.88 (CH_3), 20.62 (CH_3), 28.25 (CH_2, C-5), 28.71 (CH_2, C-5), 29.12 (CH_2, C-3), 29.78 (CH, C-3), 33.85 (CH_2, C-4), 34.20 (CH_2, C-4), 39.61 (CH_2, C-2), 39.90 (CH_2,C-2), 49.01 (−OCH_3), 60.44 (CH_2, C-1), 76.60 (CH, C-6), and 77.15 (C, C-7). Anal. Calcd for $C_{11}H_{24}O_3$ (204.31): C, 64.67; H, 11.84. Found: C, 64.22; H, 11.90.

Synthesis of 1-Methoxy-3(*S*),7-dimethyl-6,7-epoxyoctane (4). Potassium hydroxide powder (0.65 g, 12 mmol) was added to 10 mL of dry DMSO. After the suspension was stirred for 5 min, **1** (0.77 g, 5.80 mmol) was added, followed by the addition of methyl iodide (0.72 mL, 12 mmol). The mixture was stirred for 4 h at room temperature, and then 20 mL of water was added to the solution. The solution was extracted with dichloromethane and washed with water (20 mL × 5). The organic phase was dried over potassium carbonate, and the solvent was evaporated. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (6/1 (v/v), R_f 0.23) to afford a colorless liquid **4**. Yield: 0.81 g (74.9%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.91 (d, CH_3 at C-3, 3H), 1.27 and 1.31 (s, CH_3 at C-7 a, 6H) 1.20−1.70 (m,

Table 1. Ring-Opening Cationic Polymerization of 1 Using $BF_3 \cdot OEt_2$[a]

entry	solvent	[**1**]/[cat.]	temp (°C)	time (h)	yield[b] (%)	$M_{w,SEC}$ ($M_{w,SEC}/M_{n,SEC}$)[c]	$M_{w,MALLS}$[d]	$[\eta]$[d] (mL g^{-1})	α[d]	K[d] (mL g^{-1})	$[\alpha]_D$[e] (deg)
1	CH_2Cl_2	10	23	160	50.7	2400 (1.7)	3700	8.5	0.32	0.67	−3.8
2	CH_2Cl_2	10	−30	120	56.6	2400 (1.6)	5300	8.9	0.32	0.64	−3.1
3	CH_2Cl_2	20	−10	120	40.6	3100 (1.8)	4500	9.6	0.36	0.52	−3.1
4	CH_2Cl_2	20	−30	120	61.9	3700 (2.0)	6200	10.1	0.40	0.36	−3.7
5	none	20	−10	120	22.5	2600 (1.4)	3700	9.1	0.33	0.65	−3.6

[a] Ar atmosphere, [**1**] = 3.0 mol L^{-1} in CH_2Cl_2. [b] Fractionated by preparative SEC in $CHCl_3$. [c] Determined by SEC in THF using polystyrene standards. [d] The weight-average molecular weight $M_{w,MALLS}$, intrinsic viscosity $[\eta]$, and Mark−Houwink−Sakurada constants α and K ($[\eta] = KM_{w,MALLS}^{\alpha}$) were determined by SEC in THF equipped with MALLS and viscosity detectors. [e] Measured at 23 °C in $CHCl_3$ (*c* 1.0).

Table 2. Ring-Opening Cationic Polymerization of 2 Using $BF_3 \cdot OEt_2$[a]

entry	[**2**]/[cat.]	temp (°C)	time (h)	yield[b] (%)	$M_{w,SEC}$ ($M_{w,SEC}/M_{n,SEC}$)[c]	$M_{w,MALLS}$[d]	$[\eta]$[d] (mL g^{-1})	α[d]	K[d] (mL g^{-1})	f_a[e] (%)
6	20	130	24	40.1	2900 (2.3)	14 000	5.9	0.25	0.55	0.32
7	80	130	24	13.7	6600 (4.7)	20 000	9.5	0.35	0.36	0.12
8	50	23	48	trace	2400 (2.1)	9 000	6.2	0.32	0.37	0.30

[a] Ar atmosphere; bulk polymerization. [b] Chloroform-soluble and methanol-insoluble part. [c] Determined by SEC in THF using polystyrene standards. [d] The weight-average molecular weight $M_{w,MALLS}$, intrinsic viscosity $[\eta]$, and Mark−Houwink−Sakurada constants α and K ($[\eta] = KM_{w,MALLS}^{\alpha}$) were determined by SEC in THF equipped with MALLS and viscosity detectors. [e] Ratio of vinyl and aromatic protons in total protons, which were estimated from ^1H NMR measurement.

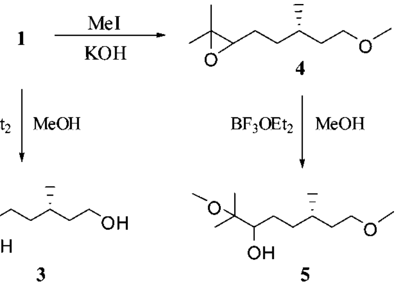
CH_2 at C-2, 4, and 5, CH at C-3, 7H), 2.70 (t, CH at C-6, 1H), 3.33 (s, OCH_3, 3H), and 3.40−3.42 (m, CH_2 at C-1, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 18.77 (CH_3, C-9), 19.57 (CH_3, C-9), 25.01 (CH_3, C-8, C-10), 26.48 (CH_2, C-5), 29.86 (CH, C-3), 33.76 (CH_2, C-4), 36.64 (CH_2, C-2), 58.31 (C, C-7), 58.68 (OCH_3), 64.67 (CH, C-6), and 71.06 (CH_2, C-1). Anal. Calcd for $C_{11}H_{22}O_2$ (186.29): C, 64.67; H, 11.84. Found: C, 63.72; H, 11.58.

Synthesis of 1,7-Dimethoxy-3(*S*),7-dimethyl-6-octanol (5). A 0.2 mol L^{-1} hydrochloric acid methanoic solution (30 mL) was added to a solution of **4** (0.82 g, 4.40 mmol) in methanol (30 mL) at room temperature. After stirring for 17 h, the reaction was quenched by column chromatography on Amberlite IRA-96SB. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (4/1 (v/v) R_f 0.14) to afford a colorless liquid **5**. Yield, 0.60 g (66.7%). ^1H NMR (400 MHz, $CDCl_3$, ppm): 0.91 (dd, CH_3 at C-3, 3H), 1.09 and 1.12 (s, CH_3 at C-7, 6H) 1.21−1.75 (m, CH_2 at C-2, 4, and 5,CH at C-3, 7H), 2.10 (s, OH), 3.22 (s, OCH_3, 3H), 3.28 (d, OCH_3, 3H), and 3.37−3.47 (m, CH_2 at C-1,CH at C-6, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 18.87 (CH_3), 18.89 (CH_3), 19.59 (CH_3), 19.88 (CH_3), 20.78 (CH_3), 28.71 (CH_2, C-5), 30.19 (CH, C-3), 34.36 (CH_2, C-4), 34.56 (CH_2, C-4), 36.48 (CH_2, C-2), 36.86 (CH_2, C-2), 49.09 ($-OCH_3$), 58.61 ($-OCH_3$), 71.16 (CH_2, C-1), 77.61 (CH, C-6), and 77.63 (C, C-7). Anal. Calcd for $C_{12}H_{26}O_3$ (218.33): C, 66.01; H, 12.00. Found: C, 66.05; H, 12.06.

Cationic Ring-Opening Polymerizations of 1. All procedures were performed under an argon atmosphere. A typical procedure for the polymerization (entry 4 in Table 1) is as follows: $BF_3 \cdot OEt_2$ (40.1 μL, [M]/[cat.] = 20) was added to a solution of **1** (1.09 g, 6.33 mmol) in dry CH_2Cl_2 (total volume = 2.11 mL, 3.0 mol L^{-1}) at −30 °C using a microsyringe. After 120 h, the polymerization was terminated by adding methanol containing a small portion of an ammonia aqueous solution. After evaporation of the solvent, the residue was redissolved in $CHCl_3$ (8 mL) and applied to the preparative SEC to remove the unreacted monomer **1** and other low molecular weight compounds (Figure S-1 in Supporting Information). The polymer solution in the range of 15−20.5 min as the elution time was concentrated and dried to in vacuo to give a viscous semisolid **poly-1** in a 61.9% yield; $M_{w,SEC}$ (THF) = 3700; $M_{w,SEC}/M_{n,SEC}$ (THF) = (2.0); $M_{w,SEC\text{-}MALLS}$ (THF) = 6,200; d*n*/d*c* (THF) = 0.089 mL g^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): 0.90 (br, s, C-9), 0.98−1.20 (br, m, C-8, C-10), 1.20−1.76 (br, m, C-2, C-3, C-4, C-5), 2.40−2.92 (br, m), 3.15−3.60 (br, m), and 3.60−3.95 (br, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 18.30 (CH_3), 19.25 (CH_3), 19.84 (CH_3), 19.87 (CH_3), 21.44 (CH_3), 28.33 (CH_2, C-5), 28.46 (CH_2, C-5), 28.70 (CH_2, C-5), 29.78 (CH, C-3), 30.20 (CH, C-3), 34.17 (CH_2, C-4), 34.52 (CH_2, C-4), 37.33 (CH_2, C-2), 37.67 (CH_2, C-2), 39.70 (CH_2, C-2), 39.99 (CH_2, C-2), 59.14 (CH_2, C-1), 60.71 (CH_2, C-1), 77.19 (CH, C-6), and 77.50 ppm (C, C-7).

Cationic Ring-Opening Polymerizations of 2. All procedures were performed under an argon atmosphere. A typical procedure for the polymerization (entry 6 in Table 2) is as follows: $BF_3 \cdot OEt_2$ (34.8 μL, [M]/[cat.] = 20) was added to **2** (1.00 g, 5.49 mmol) at 130 °C using a microsyringe. After 24 h, the polymerization was terminated by adding methanol containing a small portion of an ammonia aqueous solution. The solution was concentrated under reduced pressure and poured into a large amount of methanol (200 mL). The precipitated polymer was filtered off and dried in vacuo at 40 °C to give a white solid **poly-2** in a 40.1% yield; $M_{w,SEC}$ (THF) ($M_{w,SEC}/M_{n,SEC}$ = 2900 (2.3); $M_{w,SEC\text{-}MALLS}$ (THF) = 14 000; d*n*/d*c* (THF) = 0.127 mL g^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.28−4.40 (br, m), 4.44−5.70 (br, m), and 6.71−7.40 (br, m, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 10.56 (br), 11.95−52.03 (br, m), 57.47−74.03 (br, m), and 124.82−133.65 (br, m).

Scheme 2. Synthetic Route of 7-Methoxy-3(*S*),7-dimethyl-1,6-octanediol (3) and 1,7-Dimethoxy-3(*S*),7-dimethyl-6-octanol (5)



Results and Discussion

Polymerization of Citronellol Oxide (1). Citronellol oxide (**1**) was prepared by the epoxidation of (−)-β-citronellol, which is a terpene alcohol derivative naturally occurring in geraniums. The polymerizations of **1** were carried out using boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) in dichloromethane (CH_2Cl_2) at −30 to 23 °C. After the initiator was added to the monomer solution, the polymerization homogeneously proceeded without gelation, and the viscosity of the polymerization systems increased with the polymerization progress. The polymerization mixture was quenched by adding methanol including a small amount of ammonia−water, and the concentrated polymeric product was purified using preparative size exclusion chromatography (preparative SEC) to remove any unreacted monomers and other low molecular weight compounds. The resulting products were sticky semisolids, which were insoluble in water and highly soluble in a large variety of organic solvents, such as methanol, ethanol, diethyl ether, tetrahydrofuran, CH_2Cl_2, chloroform, and

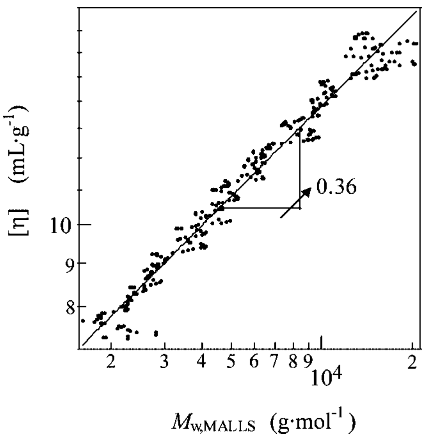


Figure 1. Double-logarithmic plots of [η] vs $M_{\mathrm{w,\ MALLS}}$ for **poly-1** (entry 3).

toluene. Table 1 lists the polymerization results. For the polymerization of **1** in CH_2Cl_2 as a solvent, the yields of the polymer (**poly-1**) were from ca. 40% to 62%, and the weight-average molecular weights ($M_{\mathrm{w,SEC}}$), which were measured by size exclusion chromatography (SEC) using tetrahydrofuran as the eluent, were from 2400 to 3700. The $M_{\mathrm{w,SEC}}$ values of **poly-1** increased with the decreasing polymerization temperature, e.g., when the [**1**]/[cat.] molar ratio of 20 was used at −30 °C for 120 h, **poly-1** having the highest $M_{\mathrm{w,SEC}}$ value (3700) was obtained in 62% yield (entry 4), while the $M_{\mathrm{w,SEC}}$ value of 3100 in 41% yield (entry 3) and 2400 in 51% yield (entry 1) were obtained at −10 and 23 °C, respectively. The polydispersities ($M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}}$) for the solution polymerization were found to be broad values in the range of 1.6−2.0. The specific rotations ($[\alpha]_D$, chloroform at 23 °C) of the obtained polymers were ca. −3° to −4°.

During the bulk polymerization of **1** (entry 5), the $M_{\mathrm{w,SEC}}$ value was 2600 in 22.5% yield, which exhibited a lower activity in contrast to the solution polymerization (entry 3). The $M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}}$ for the bulk polymerization was narrower (1.4) than those for the solution polymerizations.

In general, highly branched polymers, such as dendrimers, star polymers, and hyperbranched polymers, are known to have spherical conformations in a solution, and the $M_{\mathrm{w,SEC}}$ values were claimed to be too low because the hydrodynamic volumes of these polymers are smaller than the corresponding linear polymers used for the calibration. Therefore, the absolute weight-average molecular weight ($M_{\mathrm{w,MALLS}}$) of **poly-1** was also measured using SEC equipped with a multiangle laser light scattering instrument (MALLS) and was compared with the $M_{\mathrm{w,SEC}}$ value in Table 1. The $M_{\mathrm{w,MALLS}}$ values ranged from 3700 to 6200, which were ca. 1.4−2.2 those of the $M_{\mathrm{w,SEC}}$ values. The results suggest that **poly-1** has a compact form in solution because of their branched structure.

From the viscosity measurement using SEC in THF equipped with the viscosity detecter, the intrinsic viscosities ([η]) of **poly-1** were observed. The solution viscosities were very low in the range from 8.5 to 10.1 mL g^{-1}. The $M_{\mathrm{w,MALLS}}$ dependence of [η] for **poly-1** (entry 3) in THF is shown in Figure 1. On the basis of the results, the Mark−Houwink−Sakurada equations ($[\eta] = KM^{\alpha}$) for **poly-1** in the $M_{\mathrm{w,MALLS}}$ range from 2×10^3 to 2×10^4 were determined to be

$$[\eta] = 0.36{-}0.67 M_{\mathrm{w,MALLS}}{}^{0.32-0.40} \tag{1}$$

The exponent (α) is related to the shape of the macromolecules. In general, $\alpha = 0.5$ suggests that the polymer behaves as dense spheres, $\alpha = 0.6{-}0.8$ for a flexible chain and $\alpha > 1$ for an elongated rod, whereas it is well-known that the α value was less than 0.5 for the various hyperbranched polymers. Our experimental values of 0.32−0.40 were noticeably low, which are ascribed to the compact spherical structure in solution. Therefore, the SEC, MALLS, and viscosity measurement results suggested that **poly-1** was a branched spherical molecule, i.e., a hyperbranched polyterpene alcohol.

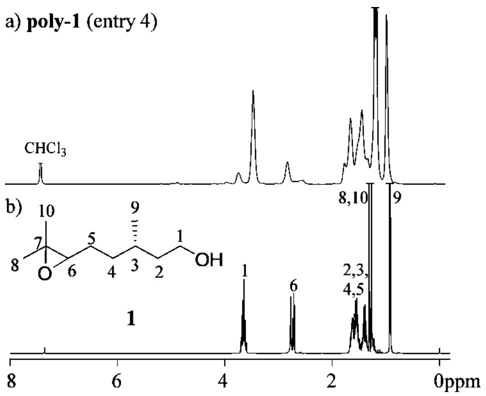


Figure 2. ^{1}H NMR spectra of (a) **poly-1** (entry 4) and (b) **1** in $CDCl_3$.

Polymerization of Nopol Oxide (2). The cationic ring-opening polymerization of nopol epoxide (**2**) as a terpene derivative was also carried out using $BF_3 \cdot OEt_2$. The typical results are summarized in Table 2. The bulk polymerization at high temperature (130 °C) homogeneously proceeded to produce a gel-free white solid, while a trace polymer was obtained when the bulk polymerization was carried out below 130 °C or CH_2Cl_2 was used as the solvent. The obtained polymers (**poly-2**) were insoluble in methanol and water but soluble in acetone, diethyl ether, EtOAc, THF, and chloroform. The $M_{\mathrm{w,MALLS}}$ values of **poly-2** were in the range of 9000−20 000, which were ca. 3.0−4.8 times greater than the $M_{\mathrm{w,SEC}}$ values of 2400−6600, indicating that **poly-2** had a compact spherical form in solution, as did **poly-1**. The $M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}}$ values were also broad in the range of 2.1−4.7. The [η] values were very low (5.9−9.5 mL g^{-1}), and the α values in the Mark−Houwink−Sakurada equation were in the range of 0.25−0.35, indicating **poly-2** is also a hyperbranched polymer.

Polymer Structure. In order to investigate the polymer structure, the ^{1}H and ^{13}C NMR measurements were carried out in $CDCl_3$. Parts a and b of Figure 2 show the ^{1}H NMR spectra of **poly-1** (entry 4) and monomer **1**, respectively. The ^{1}H NMR spectrum of **poly-1** (entry 4) consists of some broad peaks in the range of ca. 0.8−4.0 ppm, which is obviously different from the spectrum of **1**. Parts a and b of Figure 3 show the ^{13}C NMR spectra of **poly-1** (entry 3) and monomer **1**, respectively. In the ^{13}C NMR spectrum of **poly-1**, the characteristic absorption at 65 and 58 ppm due to the epoxy carbons of **1** completely disappeared, so that the polymer does not contain any epoxy groups. To investigate the polymer structure in detail, the signals of **poly-1** were compared with the signals of 7-methoxy-3(*S*),7-dimethyl-1,6-octanediol (**3**) and 1,7-dimethoxy-3(*S*),7-dimethyl-6-octanediol (**5**) as the model compounds (Figure 4, parts b and c, respectively). The signals, which are marked by the open circles in Figure 4a, are very similar to the chemical shifts of the C-2 carbon for **3** which corresponds to the model compound for the repeating units having a hydroxyl group at the C-1 position. Thus, these peaks of **poly-1** should be assigned to the C-2 carbons of the 7-linked terminal units (T_7) and 6,7-linked linear units (L_{67}), as shown in Figure 5. In a similar comparison with **5** corresponding to the model compound for the repeating units linked at the C-1 position, the signals marked by the closed cycle in Figure 4a were assigned to the C-2 carbons of the 1-linked terminal units (T_1), 1,7-linked linear units (L_{17}), and

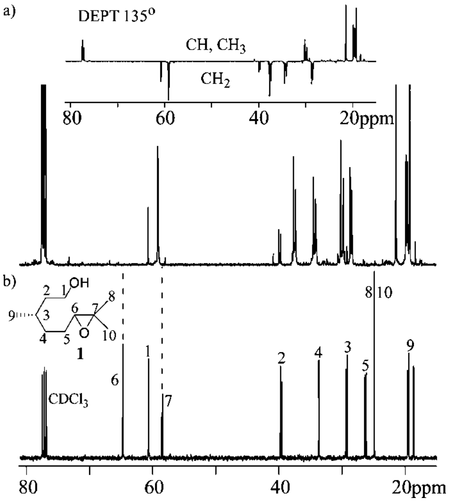


Figure 3. ^{13}C NMR spectra of (a) **poly-1** (entry 3) and (b) **1** in $CDCl_3$.

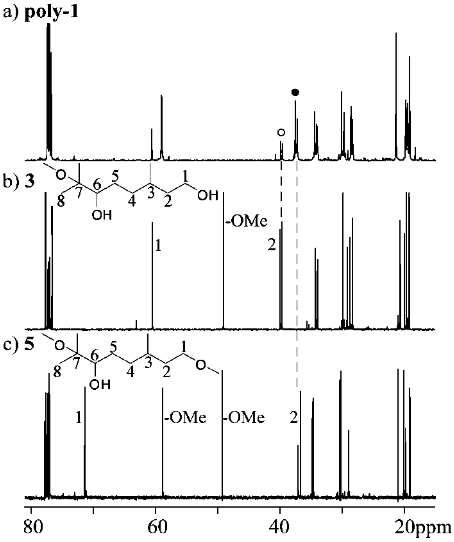


Figure 4. ^{13}C NMR spectra of (a) **poly-1** (entry 3), (b) **3**, and (c) **5** in $CDCl_3$.

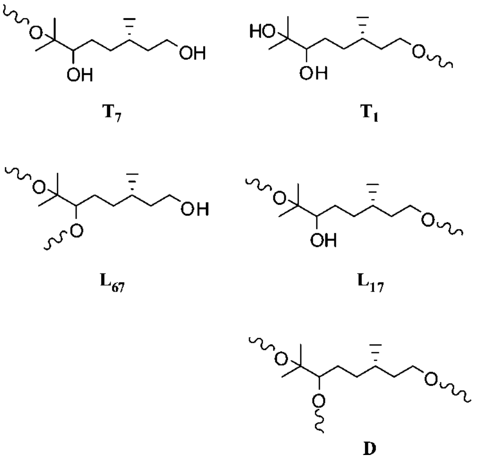


Figure 5. Possible repeating units in **poly-1**. T_1: 1-linked terminal unit; T_7: 7-linked terminal unit; L67: 6,7-linked linear unit; L_{17}: 1,7-linked linear unit; D: dendritic unit.

dendritic units (D). The area ratio of these peaks marked by the open and closed circles are ca. 18:82 (= T_7+L_{67}: T_1+L_{17}+D), which did not change according to the polymerization condition, meaning that **poly-1** consisted of ca. 18 mol % of T_7 and L_{67} repeating units and 82 mol % of T_1, L_{17}, and D repeating units.

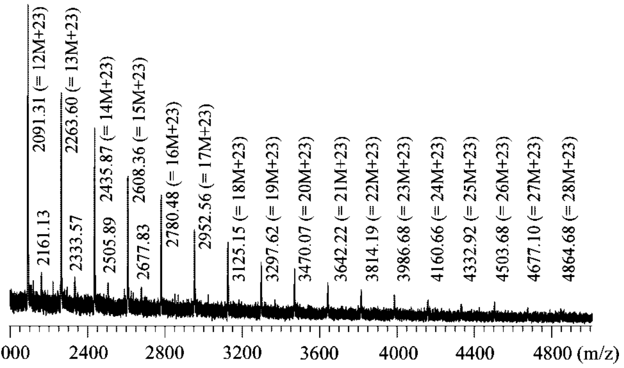


Figure 6. MALDI-TOF mass spectrum of **poly-1** (entry 5). Main signals appear at $m/z = n \times 172.26 + 23$ (Na). Samples were prepared by mixing the polymer (10 mg mL^{-1}, 2 μL), a matrix (2,5-dihydroxybenzoic acid, 10 mg mL^{-1}, 20 μL), and a cationizing agent (sodium iodide, 10 mg mL^{-1}, 2 μL) in methanol.

To confirm the polymer structure in detail, the matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurement of **poly-1** (entry 5) was performed using 2,5-dihydroxybenzoic acid as the matrix and sodium iodide as the cationizing agent. A typical spectrum is shown in Figure 6. In the mass spectrum, there are one series of peaks with a regular interval (ca. 172.26), and the absolute mass of each peak was equal to integer multiples of the molar mass of **1**, though the spectrum includes other series in which the molecular weight corresponds to $n \times 172.26 + 23$ (Na) + ca. 70, which probably correspond to the polymers bearing the end groups due to the cationic initiator BF_3. Therefore, these spectroscopic results suggested that the cationic polymerization of **1** proceeded through a ring-opening addition reaction without any side reactions such as the elimination of a water molecule.

Figure 7 and Figure S-2 (see Supporting Information) show the ^{1}H and ^{13}C NMR spectra of **poly-2** (entry 7) and monomer **2**, respectively. In the ^{13}C NMR spectrum of **poly-2**, the characteristic absorption at 54.9 ppm due to the epoxy carbon of **2** disappeared, indicating that the epoxy groups in **2** were consumed. The ^{1}H NMR spectrum of **poly-2** consists of a number of broad signals and includes the unexpected signals at 4.5−7.4 ppm assignable to the vinyl and aromatic protons. The corresponding peaks were also found in the ^{13}C NMR spectrum, indicating that the cationic polymerization of **2** should include the rearrangement reaction to produce the vinyl and aromatic groups. In fact, the reaction of **2** with acid leads to vinyl and aromatic compounds, as already reported (Scheme 3).[57] The

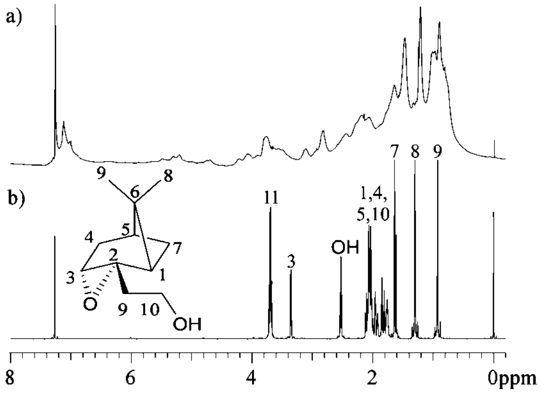


Figure 7. ^{1}H NMR spectra of (a) **poly-2** (entry 7) and (b) **2** in $CDCl_3$.

Scheme 3. Possible Rearrangement Reactions of Nopol Epoxide (2) To Produce the Vinyl and Aromatic Groups

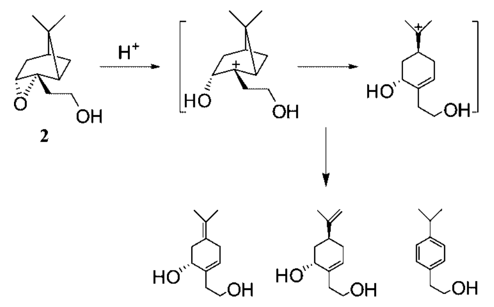


Table 3. Thermal Properties of Poly-1 and Poly-2

entry	$T_{d,10}$ (°C)[a]	T_g (°C)[b]	entry	$T_{d,10}$ (°C)[a]	T_g (°C)[b]
1	253.7	−8.0	5	271.0	−9.8
2	246.0	−13.6	6	290.2	118.2
3	273.2	−13.1	7	179.0	73.4
4	266.7	−5.2	8	244.5	93.3

[a] 10% weight loss temperature determined by TGA under a N_2 atmosphere. [b] Glass transition temperature determined by DSC on second heating scan (5 °C min^{-1}) under a N_2 atmosphere.

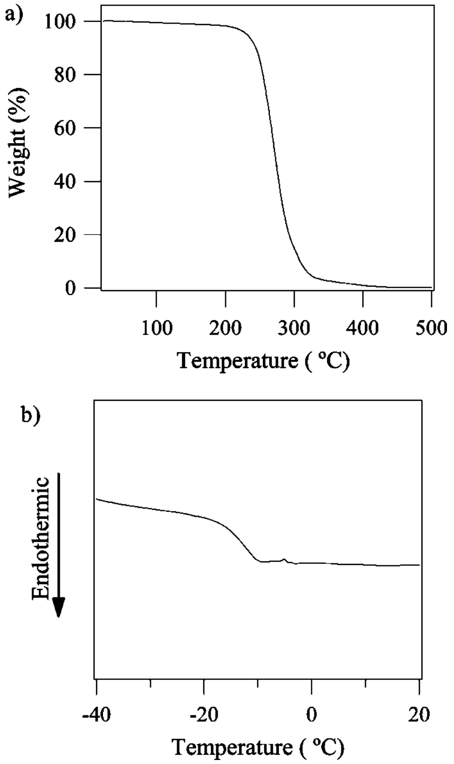
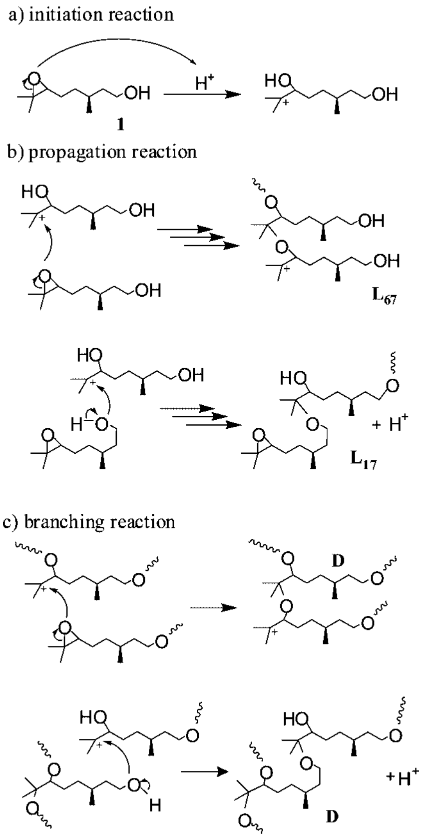


Figure 8. Thermal properties of **poly-1** (entry 2): (a) TGA and (b) DSC.

fraction of these protons in **poly-2** were ca. 32% for the [**2**]/[$BF_3 \cdot OEt_2$] value of 20 (entry 6) and ca. 12% for [**2**]/[$BF_3 \cdot OEt_2$] of 80 (entry 7), indicating that the increasing $BF_3 \cdot OEt_2$ leads to the increasing vinyl and aromatic groups.

Thermal Properties of Poly-1 and Poly-2. The thermal properties of **poly-1** were studied by thermal gravimetric analysis (TGA) and differential scanning carlorimetry (DSC). The 10% weight loss temperature ($T_{d,10}$) and the glass transition temperatures (T_g) are summarized in Table 3, and the typical results are shown in Figure 8a,b (entry 2). **Poly-1** is stable up to ca. 220 °C under a nitrogen atmosphere, and the $T_{d,10}$ values were recorded in the range from ca. 246 to 271 °C. From the differential scanning carlorimetry (DSC) study, low T_g values were recorded in the range of ca. −5 to −14 °C, while it was difficult to determine the melting transition temperatures, indicating that **poly-1** was amorphous.

Scheme 4. Proposed Mechanism for the Cationic Polymerization of Citronellol Oxide (1)



For **poly-2**, the T_g and $T_{d,10}$ values were increased by the amount of the vinyl and aromatic groups in **poly-2**, e.g., T_g of 118 °C and $T_{d,10}$ of 290 °C for entry 6 (32% of vinyl and aromatic groups), T_g of 93.3 °C and $T_{d,10}$ of 244.5 °C for entry 8 (30%), and T_g of 73.4 °C and $T_{d,10}$ of 179 °C for entry 7 (12%).

Polymerization Mechanism. Hyperbranched poly(citronellol oxide), **poly-1**, mainly consisted of five repeating units, i.e., T_1, T_7, L_{67}, L_{17}, and D repeating units, as shown in Figure 5. The proposed mechanism for the cationic polymerization of **1** is shown in Scheme 4. During the initiation reaction, the oxygen atom of the epoxy group of **1** was protonated, and the protonated **1** underwent ring opening to afford an intermediate carbocation derivative via an S_N1 mechanism (Scheme 4a). The ring-opening reaction generates a secondary hydroxyl group. During the propagation reaction, the carbocation derivative reacted with the oxygen atom of the epoxy group from another monomer, thus leading to the L_{67} repeating units, while the reaction of the carbocation derivative with the hydroxyl group in **1** produce L_{17} repeating units (Scheme 4b). The branched units D for **poly-1** should be produced by the proton-transfer reaction of the hydroxyl groups in the polymer with the carbocation end of the other polymer (Scheme 4c). The reaction of the epoxy groups in the macromonomer with the carbocation end of the other polymer also produces the D units. These reactions mentioned above simultaneously occurred in the polymerization systems and consequently produced hyperbranched poly(citronellol oxide), **poly-1**. Although the polymerization of **2** proceeded through a mechanism similar to that for **1**, the rearrangement reaction of **2** proceeded as a side reaction to produce the hyperbranched polymer with vinyl and aromatic groups, **poly-2**.

Conclusions

In this study, the synthesis of a novel bio-based hyperbranched polymer, i.e., hyperbranched polyterpene alcohols, is achieved by the cationic ring-opening polymerization of citronellol oxide (**1**) and nopol epoxide (**2**) using boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$). Although the cationic polymerization of **2** includes the rearrangement reaction to produce the vinyl and aromatic groups, the polymerizations of **1** and **2** smoothly proceeded to yield gel-free hyperbranched polymers (**poly-1** and **poly-2**). The $M_{w,MALLS}$ values ranged from 3700 to 6200 g mol^{-1} for **poly-1** and 9000 to 20 000 g mol^{-1} for **poly-2**, which were ca. 1.4−2.2 and 3.0−4.8 times greater than the $M_{w,SEC}$ values, respectively. The solution viscosities of these polymers were very low in the range of 8.5−10.1 mL g^{-1} for **poly-1** and 5.9−9.5 mL g^{-1} for **poly-2**. The Mark−Houwink exponents α were calculated to be 0.32−0.40 for **poly-1** and 0.25−0.35 for **poly-2**. The results of the SEC, MALLS, and viscosity measurements indicated that **poly-1** and **poly-2** exist in a compact spherical conformation in solution, i.e., hyperbranched polyterpene alcohols. The very low intrinsic viscosities and the high solubility of the hyperbranched polyterpene alcohols should allow its use as a biocompatible viscosity modifier.

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Supporting Information Available: SEC traces of **poly-1** (entry 4) before and after fractionation using preparative SEC in $CHCl_3$; ^{13}C NMR spectra of **poly-2** (entry 7) and **2** in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hawker, C. J.; Devonport, W. *ACS Symp. Ser.* **1996**, *624*, 186–196.
(2) Frechet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Chem.* **1996**, *A33*, 1399–1425.
(3) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681–1712.
(4) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1–56.
(5) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685–1698.
(6) Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, *143*, 1–34.
(7) Fischer, M.; Vogtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884–905.
(8) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505–2525.
(9) Vogtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog. Polym. Sci.* **2000**, *25*, 987.
(10) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453–571.
(11) Jikei, M.; Kakimoto, M.-A. *Prog. Polym. Sci.* **2001**, *26*, 1233–1285.
(12) Frey, H.; Haag, R. *Rev. Mol. Biotechnol.* **2002**, *90*, 257.
(13) Stiriba, S.-E.; Frey, H.; Haag, R. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1329.
(14) Pirrung, F. O. H.; Loen, E. M.; Noordam, A. *Macromol. Symp.* **2002**, *187*, 683–694.
(15) Turnbull, W. B.; Stoddart, J. F. *Rev. Mol. Biotechnol.* **2002**, *90*, 231–255.
(16) Frey, H.; Haag, R. *Rev. Mol. Biotechnol.* **2002**, *90*, 257–267.
(17) Tomalia, D. A.; Frechet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719–2728.
(18) Gitsov, I.; Lambrych, K. R. Dendrimers. Synthesis and Applications. In *Microspheres, Microcapsules & Liposomes*; Arshady, R., Ed.; Citus Books: London, 2002; Vol. *5*, pp 31−68.
(19) Hecht, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1047–1058.
(20) Ishizu, K.; Tsubaki, K.; Mori, A.; Uchida, S. *Prog. Polym. Sci.* **2003**, *28*, 27–54.
(21) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183–275.
(22) Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111–182.
(23) Mather, B. D.; Viswanathan, K.; Miller, K. M.; Long, T. E. *Prog. Polym. Sci.* **2006**, *31*, 487–531.
(24) Feng, X.; Taton, D.; Borsali, R.; Chaikof, E. L.; Gnanou, Y. *J. Am. Chem. Soc.* **2006**, *128*, 11551–11562.
(25) Hadjichristidis, N.; Iatrou., H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068–1132.
(26) Satoh, T.; Tamaki, M.; Kitajyo, Y.; Maeda, T.; Ishihara, H.; Imai, T.; Kaga, H.; Kakuchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 406–413.
(27) Hirao, A.; Sugiyama, K.; Yokoyama, H. *Prog. Polym. Sci.* **2007**, *32*, 1393–1438.
(28) Kitajyo, Y.; Imai, T.; Sakai, Y.; Tamaki, M.; Tani, H.; Takahashi, K.; Narumi, A.; Kaga, H.; Kaneko, N.; Satoh, T.; Kakuchi, T. *Polymer* **2007**, *48*, 1237–1244.
(29) Kitajyo, Y.; Nawa, Y.; Tamaki, M.; Tani, H.; Takahashi, K.; Kaga, H.; Satoh, T.; Kakuchi, T. *Polymer* **2007**, *48*, 4683–4690.
(30) Peleshanko, S.; Tsukruk, V. V. *Prog. Polym. Sci.*, in press.
(31) Wooley, K. L.; Frechet, J. M. J.; Hawker, C. J. *Polymer* **1994**, *35*, 4489–4495.
(32) Schipp, C.; Hill, M. J.; Barham, P. J.; Cloke, V. M.; Higgins, J. S.; Oiarzabalt, L. *Polymer* **1996**, *37*, 2291–2297.
(33) Hawker, C. J.; Malmstrom, E.; Frank, C. W.; Kampf, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 9903–9904.
(34) Weimer, M. W.; Frechet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955–970.
(35) Stiriba, S.-E.; Kautz, H.; Frey, H. *J. Am. Chem. Soc.* **2002**, *124*, 9698–9699.
(36) Kumar, K. R.; Brooks, D. E. *Macromol. Rapid Commun.* **2005**, *26*, 155–159.
(37) Samadi, F.; Eckelt, J.; Wolf, B. A.; Lopez-Villanueva, F.-J.; Frey, H. *Eur. Polym. J.* **2007**, *43*, 4236–4243.
(38) Kitajyo, Y.; Kinugawa, Y.; Tamaki, M.; Kaga, H.; Kaneko, N.; Satoh, T.; Kakuchi, T. *Macromolecules* **2007**, *40*, 9313–9321.
(39) Kadokawa, J.; Sato, M.; Karasu, M.; Tagaya, H.; Chiba, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2373–2376.
(40) Kadokawa, J.; Tagaya, H. *Polym. Adv. Technol.* **2002**, *11*, 122–126.
(41) Kanazawa, A.; Okumura, S.; Suzuki, M. *Org. Biomol. Chem.* **2005**, *3*, 1746–1750.
(42) Kanazawa, A.; Suzuki, M. *Polymer* **2006**, *47*, 176–183.
(43) Kanazawa, A.; Namiki, S.; Suzuki, M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3851–3860.
(44) Tao, Y.; Zhang, L. *Biopolymers* **2006**, *83*, 414–423.
(45) Tao, Y.; Zhang, L.; Cheung, P. C. K. *Carbohydr. Res.* **2006**, *341*, 2261–2269.
(46) Tao, Y.; Zhang, L.; Yan, F.; Wu, X. *Biomacromolecules* **2007**, *8*, 2321–2328.
(47) Scholl, M.; Nguyen, T. Q.; Bruchmann, B.; Klok, H.-A. *Macromolecules* **2007**, *40*, 5726–5734.
(48) Scholl, M.; Nguyen, T. Q.; Bruchmann, B.; Klok, H.-A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5494–5508.
(49) Canilho, N.; Scholl, M.; Klok, H.-A.; Mezzenga, R. *Macromolecules* **2007**, *40*, 8374–8383.
(50) Satoh, T.; Imai, T.; Ishihara, H.; Maeda, T.; Kitajyo, Y.; Narumi, A.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2003**, *36*, 6364–6370.
(51) Imai, T.; Satoh, T.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2003**, *36*, 6359–6363.
(52) Imai, T.; Satoh, T.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2004**, *37*, 3113–3119.
(53) Satoh, T.; Imai, T.; Kitajyo, Y.; Maeda, T.; Narumi, A.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromol. Symp.* **2004**, *217*, 39–46.
(54) Satoh, T.; Imai, T.; Ishihara, H.; Maeda, T.; Kitajyo, Y.; Sakai, Y.; Kaga, H.; Kaneko, N.; Ishii, F.; Kakuchi, T. *Macromolecules* **2005**, *38*, 4202–4210.
(55) Imai, T.; Nawa, Y.; Kitajyo, Y.; Satoh, T.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2005**, *38*, 1648–1654.
(56) Satoh, T.; Kakuchi, T. *Macromol. Biosci.* **2007**, *7*, 999–1009.
(57) Il'ina, I. V.; Volcho, K. P.; Korchagina, D. V.; Salakhutdinov, N. F.; Barkhash, V. A. *Russ. J. Org. Chem.* **2000**, *40*, 1483–1487.

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