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Synthesis, Characterization, and Functionalization of Hyperbranched Poly(3,4-epoxycyclohexanemethanol)

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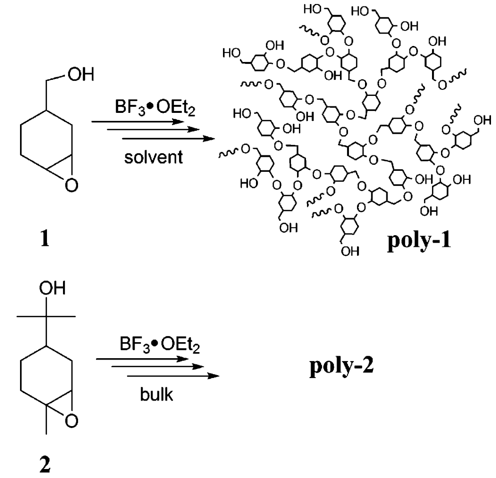
ABSTRACT: The cationic ring-opening polymerizations of an alicyclic epoxyalcohol, 3,4-epoxycyclohexanemethanol (**1**), were carried out using boron trifluoride diethyletherate ($BF_3 \cdot OEt_2$) as a catalyst. Polymerization of **1** heterogeneously proceeded to yield a gel-free polymer (**poly-1**). On the basis of the ^{13}C NMR measurement, **poly-1** was a hyperbranched polymer with numerous terminal units, and the degrees of branching (DBs) of **poly-1** were in the range from 0.36 to 0.42. The three-dimensional property of **poly-1** was investigated by comparison to the physical property of a linear poly(3,4-epoxycyclohexanemethanol) (**poly-3**). The viscosity and Mark−Houwink exponent α of **poly-1** were much lower than those of **poly-3**, suggesting that **poly-1** had a compact conformation in solution. In addition, the glass-transition temperature (T_g) of **poly-1** was ca. 105 °C, which was also lower than that of **poly-3**. A novel amphiphilic dendritic polymer (**poly-1ASP**) having a hydrophobic **poly-1** core and hydrophilic L-aspartic acid shell was synthesized. On the basis of the results of an encapsulation experiment, **poly-1ASP** possessed an encapsulation property for hydrophobic molecule (Reichardt's dye) in water.

Introduction

Three-dimensional macromolecular architectures have attracted much attention because they exhibit unusual physical properties, e.g., a higher solubility and lower viscosity in solution and the molten state, when compared to conventional linear polymers. In particular, hyperbranched polymers with an irregular branching structure, though they are conveniently prepared via the one-pot polymerization of the AB_x-type monomer, have characteristics similar to dendrimers as the perfectly branched monodispersed molecules. Therefore, the property and synthetic advantage of hyperbranched polymers provides the possibility of industrial use as a key material in nanotechnology.[1−8] Since Kim and Webster reported that hyperbranched polyphenylene was synthesized by the polycondensation of (3,5-dibromophenyl)boronic acid,[9,10] there have been various studies on the design and synthesis of hyperbranched polymers. For example, Matyjaszewski and co-workers synthesized a hyperbranched poly(acrylate) by the atom transfer radical polymerization of 2-(2-bromopropionyloxy)ethyl acrylate as an AB*-type monomer.[11−14] In addition, Fréchet,[15,16] Matyjaszewski,[17,18] and Ishizu[19−21] reported the synthesis of hyperbranched polystyrene by the self-condensing vinyl polymerization of the styrene derivatives and the lower intrinsic viscosity of the polymer relative to linear polystyrene.

Of the several synthetic methods of producing a hyperbranched polymer, a ring-opening multibranching polymerization (ROMBP) of epoxy alcohols is a versatile method for synthesizing hyperbranched polyethers due to the high reactivity and polymerizability of the epoxy group. For example, Penczek and Dworak et al. reported that glycidol, which is a commercially available and cheap epoxy alcohol, was polymerized by the cationic ring-opening polymerization to yield a water-soluble highly branched polyglycerol.[22,23] Frey et al. reported the controlled synthesis of a hyperbranched polyglycerol by the anionic ring-opening polymerization of glycidol using slow-monomer addition techniques.[24] Recently, we also proposed that the ROMBP of epoxy alcohol monomers was a facile method for synthesizing the family of hyperbranched carbohydrate polymers, e.g., a hyperbranched poly(2,5-anhydro-D-glucitol),[25] and hyperbranched polytetritols.[26] Epoxy alcohols are easily prepared by reactions, such as the oxidation of alkenyl alcohol; thus, it is important to polymerize a series of epoxy alcohols

Scheme 1



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and elucidate the characteristic properties. A paper concerning the polymerizations of various alicyclic epoxyalcohols, which are highly reactive monomers with a highly strained epoxycyclohexane system,[27] has been published by Crivello et al.[28] However, characterization of the branching structure, solution property, and thermal property of the obtained polymer along with their three-dimensional structure have not yet been reported.

We now report the cationic ring-opening polymerization of several alicyclic epoxyalcohols, 3,4-epoxycyclohexanemethanol (**1**) and α-terpineol epoxide (**2**), using boron trifluoride diethyletherate ($BF_3{\cdot}OEt_2$) as a catalyst leading to hydrophobic hyperbranched polymers (**poly-1** and **poly-2**), as shown in Scheme 1. The three-dimensional property of **poly-1** was elucidated in conjunction with its branching structure, viscosity, and thermal property and compared to a corresponding linear analog, poly(3,4-epoxycyclohexanemethanol) (**poly-3**). In addition, a novel water-soluble amphiphilic polymer with hydrophobic **poly-1** as a core (**poly-1ASP**) was synthesized via the carbamation reaction of **poly-1** with *N*-carbonyl L-aspartic acid diethyl ester followed by de-esterification using potassium trimethylsilanolate. The molecular encapsulation property of **poly-1ASP** was examined using a water-insoluble guest molecule, Reichardt's dye (RCD), to investigate the performance of **poly-1ASP** as the molecular nanocarrier.

Experimental Section

Materials. 3,4-Epoxycyclohexanemethanol (**1**) and α-terpineol epoxide (**2**) were synthesized from 3-cyclohexene-1-methanol (98%, Sigma-Aldrich) and α-terpineol (>99.0%, Wako Pure Chemical Industries, Ltd.), respectively, according to a similar method by Pedro et al.[29] *N*-Carbonyl L-aspartic acid diethyl ester was synthesized from L-aspartic acid according to a previous study.[30] 3,4-Epoxy-1-methoxymethylcyclohexane was synthesized from **1** according to a similar method by Crivello et al.[28] *tert*-Butyldimethylchlorosilane (>97%, Tokyo Kasei Kogyo Co., Ltd.), imidazole (>98%, Kanto Chemical Co., Ltd.), and tetrabutylammonium fluoride (TBAF) (1.0 $mol{\cdot}L^{-1}$ tetrahydrofuran solution, Sigma-Aldrich) were used as received. Boron trifluoride diethyletherate ($BF_3{\cdot}OEt_2$) was purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan) and distilled over CaH_2 under reduced pressure. Pyridine (>99.0%, Kanto Chemical Co., Ltd.) was distilled over CaH_2 just before use. Reichardt's dye (dye content = 90%), potassium trimethylsilanolate (90%), and dimethyl sulfoxide anhydrous (dry DMSO) (>99.9%, water content, <0.005%) were purchased from Sigma-Aldrich and used as received. Silica gel 60N (Kanto Chemical Co., Ltd.; spherical shape; particle size, 40−50 μm; neutral) was used for column chromatography. Methyl iodide (>99.5%), potassium hydroxide (>85.5%), dry dichloromethane (dry CH_2Cl_2) (>99.5%; water content, <0.001%), tetrahydrofuran (THF) (>99.0%), toluene (>99.0%), methanol (>99.5%), acetone (>99.0%), dichloromethane (CH_2Cl_2) (> 99.0%), hexane (>95.0%), ethyl acetate (>99.0%), and *N*,*N*-dimethylformamide (DMF) (>99.0%) were obtained from Kanto Chemical Co., Ltd., and used without further purification.

Instrumentation. The ^1H NMR and ^{13}C NMR spectra were recorded using a JEOL JNM-A400II instrument. Quantitative ^{13}C NMR spectra were obtained using a 15% (wt/vol) sample in methanol-d_4 (CD_3OD) at 25 °C, 45° pulse angle, inverse gated decoupling with a 7.0 s delay, 5000 scans, and the solvent peak (δ = 49.00 ppm) as the internal reference. Preparative SEC for the chloroform-soluble polymers was performed in chloroform (3.5 $mL{\cdot}min^{-1}$) at 23 °C using a JAI LC-9201 equipped with a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7×10^4) and a JAI RI-50s refractive index detector. The preparative SEC for the water-soluble polymers was performed in water (14 $mL{\cdot}min^{-1}$) at 23 °C using a JAI LC-928 equipped with a JAI JAIGEL-W253−40 column (40 mm × 500 mm; exclusion limit, 5×10^4) and a JAI RI-50s refractive index detector.

The molecular weight value and viscosity of **poly-1** were determined by size exclusion chromatography (SEC) in THF (1.0 $mL{\cdot}min^{-1}$) at 40 °C using an Agilent 1100 series instrumentation equipped with two Shodex KF-804L columns (linear, 8 mm × 300 mm; bead size, 7 μm; exclusion limit, 4×10^5), a DAWN 8 multiangle laser light scattering (MALLS) detector (Wyatt Technology, Santa Barbara, CA), a Viscostar viscosity detector (Wyatt Technology), and an Optilab rEX refractive index detector (Wyatt Technology). The absolute molecular weights ($M_{w,SEC-MALLS}$s) and intrinsic viscosities ([η]s) were estimated by the software ASTRA 5.1.6.0 (Wyatt Technology). The apparent molecular weights ($M_{w,SEC}$s) and the polydispersities (M_w/M_ns) were calculated on the basis of a polystyrene calibration. The molecular weight values and viscosities of **poly-1** and **poly-3** were measured by SEC in DMF containing 0.01 M LiBr (0.4 $mL{\cdot}min^{-1}$) at 40 °C using a Agilent 1100 series instrumentation equipped with a Shodex KD-806M column (linear, 8 mm × 300 mm; bead size, 10 μm; exclusion limit, 2×10^7), a DAWN HELEOS MALLS detector (Wyatt Technology), a Viscostar viscosity detector, and an Optilab rEX refractive index detector (Shoko Research Center, Shoko Co., Ltd., Tokyo). The $M_{w,SEC-MALLS}$s and [η]s were estimated by the software ASTRA 5.3.1 (Wyatt Technology). Field-ionization mass spectroscopy (FI-MS) of the low molecular weight compounds was performed using a JEOL JMS AX-500 mass spectrometer (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Elemental analysis was performed using a Yanako MT-6 CHN corder (Center for Instrumental Analysis, Hokkaido University).

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 reflector 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 $mg{\cdot}mL^{-1}$, 2 μL), a matrix (2,5-dihydroxybenzoic acid, 10 $mg{\cdot}mL^{-1}$, 20 μL), and a cationizing agent (sodium trifluoroacetate, 10 $mg{\cdot}mL^{-1}$, 2 μL) in methanol.

UV−vis spectra were measured at 23 °C in water with a 10-mm path length using a Jasco V-550 spectrometer with a deuterium lamp as the light source for the UV range (190−350 nm) and a halogen lamp for the visible range (330−900 nm).

Cationic Ring-Opening Polymerizations of 1 and 2. All procedures were performed under an argon atmosphere. A typical procedure for the polymerization (run 3) is as follows: $BF_3{\cdot}OEt_2$ (12.5 μL, [M]/[cat.] = 80) was added to a solution of **1** (1.00 g, 7.82 mmol) in dry CH_2Cl_2 (total volume = 2.60 mL, 3.0 $mol{\cdot}L^{-1}$) at −5 °C using a microsyringe. After 2 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 ethyl acetate (300 mL). The precipitated polymer was filtered off and dried in vacuo at 40 °C to give a white solid **poly-1**. Yield: 0.439 g (44.0%). $M_{w,SEC}$ (THF) (M_w/M_n) = 3700 (1.72). $M_{w,SEC-MALLS}$ (THF) = 9000. d*n*/d*c* (THF) = 0.1194 $mL{\cdot}g^{-1}$. $M_{w,SEC-MALLS}$ (DMF) = 9500. d*n*/d*c* (DMF) = 0.089 $mL{\cdot}g^{-1}$. ^1H NMR (400 MHz, CD_3OD): δ 3.95−2.92 (br, H-3, H-4, CH_2O, 4H), 2.42−0.77 (br, H-1, H-2, H-5, H-6, 7H). ^{13}C NMR (100 MHz, CD_3OD): δ 79.92−75.60 (CH), 74.71 (CH_2), 70.42−68.64 (CH), 68.46−67.35 (CH_2), 35.47 (3-bonded terminal unit ($\boldsymbol{T_a}$) and 3,4-bonded linear unit ($\boldsymbol{L_a}$), CH), 35.07 (4-bonded terminal unit ($\boldsymbol{T_b}$), CH), 33.61 (CH), 33.17 (1,3-bonded linear unit and 1,4-bonded linear unit ($\boldsymbol{L_b}$), CH_2), 32.78 ($\boldsymbol{T_b}$, CH_2), 32.23−30.39 (br, $\boldsymbol{L_a}$, CH_2), 30.17 (CH_2), 29.78 (CH_2), 29.33 ($\boldsymbol{D}$, CH_2), 28.75 ($\boldsymbol{T_a}$, CH_2), 28.61 ($\boldsymbol{T_a}$, $\boldsymbol{L_b}$, CH_2), 27.76−26.31 ($\boldsymbol{L_a}$, CH_2), 24.98 ($\boldsymbol{D}$, CH_2), 24.57 ($\boldsymbol{T_b}$, $\boldsymbol{L_a}$, $\boldsymbol{L_b}$, $\boldsymbol{D}$, CH_2), 24.07 ($\boldsymbol{T_a}$, CH_2).

The degrees of branching (DBs) of **poly-1** prepared from **1** as an AB_2-type monomer were calculated using Frey's equation (eq 1).[31]

$$\mathrm{DB} = \frac{2\boldsymbol{T}}{\boldsymbol{T}+\boldsymbol{L}+\boldsymbol{D}}\left(= \frac{2(\boldsymbol{T_a}+\boldsymbol{T_b})}{\boldsymbol{T_a}+\boldsymbol{T_b}+\boldsymbol{L_a}+\boldsymbol{L_b}+\boldsymbol{D}}\right) \qquad (1)$$

In the ^{13}C NMR spectra of **poly-1** (Figure 1 and S1), the signals at 35.07 and 24.07 ppm were assigned as the C-1 carbon of $\boldsymbol{T}_\mathbf{b}$ and the C-6 carbon of $\boldsymbol{T}_\mathbf{a}$, according to the comparison with the chemical shifts of the model compounds **4b** and **4a**, respectively (Figure S1). In addition, the signals at 35.94−23.67 ppm were also assigned to the C-1, C-2, C-5, and C-6 carbons based on the total units in **poly-1**. Thus, the quantitative ^{13}C NMR spectra of **poly-1** were recorded and the ($\boldsymbol{T}_\mathbf{a} + \boldsymbol{T}_\mathbf{b}$)/($\boldsymbol{T}_\mathbf{a} + \boldsymbol{T}_\mathbf{a} + \boldsymbol{L}_\mathbf{a} + \boldsymbol{L}_\mathbf{b} + \boldsymbol{D}$) values in eq 1 were estimated from the integral ratio of the signals for the terminal units to that for the total units, as shown in eq 2.

$$\frac{\boldsymbol{T_a}+\boldsymbol{T_b}}{\boldsymbol{T_a}+\boldsymbol{T_b}+\boldsymbol{L_a}+\boldsymbol{L_b}+\boldsymbol{D}} = \frac{\text{(the signals for } \boldsymbol{T_b} \text{ and } \boldsymbol{T_a} \text{ at 35.07 and 24.07 ppm)}}{\text{(the signals for total units at 35.94−23.67 ppm)} \times \dfrac{1}{4}} \qquad (2)$$

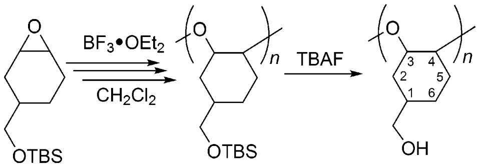
The ($\boldsymbol{T}_\mathbf{a} + \boldsymbol{T}_\mathbf{b}$)/($\boldsymbol{T}_\mathbf{a} + \boldsymbol{T}_\mathbf{a} + \boldsymbol{L}_\mathbf{a} + \boldsymbol{L}_\mathbf{b} + \boldsymbol{D}$) value of **poly-1** (run 3) was 0.20. Therefore, the DB value of the polymer was 0.40.

4-Hydroxy-3-methoxy Cyclohexanemethanol (4a) and 3-Hydroxy-4-methoxy Cyclohexanemethanol (4b). $BF_3{\cdot}OEt_2$ (0.76 mL, 0.2 mol·L^{-1}) was added to a solution of 1 (0.82 g, 6.4 mmol) in methanol (29 mL) at room temperature. After stirring for 20 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 acetone/dichloromethane (1/1, v/v; $R_f = 0.35$) to afford a mixture of 4a and 4b as a colorless liquid. Yield: 0.56 g (54.6%). ^{1}H NMR for 4a (400 MHz, CD_3OD): δ 3.66−3.59 (m, H-4, 1H), 3.29 (d, J = 2.0 Hz, CH_2O, 2H), 3.26 (s, CH_3, 3H), 3.23−3.15 (m, H-3, 1H), 1.85−1.18 (m, H-1, H-2, H-5, H-6, 7H). ^{13}C NMR for 4a (100 MHz, CD_3OD): δ 80.51 (C-3), 69.38 (C-4), 67.36 (CH_2O), 56.81 (CH_3), 35.45 (C-1), 28.82 (C-2), 28.53 (C-5), 24.09 (C-6). ^{1}H NMR for 4b (400 MHz, CD_3OD): δ 3.74−3.67 (m, H-3, 1H), 3.29 (d, J = 2.0 Hz, CH_2O, 2H), 3.26 (s, CH_3, 3H), 3.13−3.06 (m, H-4, 1H), 1.85−1.18 (m, H-1, H-2, H-5, H-6, 7H). ^{13}C NMR for 4b (100 MHz, CD_3OD): δ 81.41 (C-4), 68.58 (C-3), 67.36 (CH_2O), 56.91 (CH_3), 35.16 (C-1), 32.78 (C-2), 24.60 (C-5), 24.34 (C-6). Anal. Calcd for $C_8H_{16}O_3{\cdot}2/9H_2O$ (164.2): C, 58.51; H, 10.09. Found: C, 58.55; H, 10.10. FI-MS: m/z (relative intensity): 160 (M$^+$, 100), 161 (MH$^+$, 51.5).

4-Hydroxy-3-methoxy-1-methoxymethyl Cyclohexane (5a) and 3-Hydroxy-4-methoxy-1-methoxymethyl Cyclohexane (5b). $BF_3{\cdot}OEt_2$ (0.76 mL, 0.2 mol·L^{-1}) was added to a solution of 3,4-epoxy-1-methoxymethylcyclohexane (0.99 g, 6.96 mmol) in methanol (29 mL) at room temperature. After stirring for 5 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 hexane/ethyl acetate (2/3, v/v; $R_f = 0.31$) to afford a mixture of 5a and 5b as a colorless liquid. Yield: 0.70 g (57.7%). ^{1}H NMR for 5a (400 MHz, CD_3OD): δ 3.74−3.69 (m, H-4, 1H), 3.35 (s, CH_2-OCH_3, 3H), 3.30 (s, CH_3, 3H), 3.29−3.25 (m, H-3, 1H), 3.24−3.20 (m, CH_2O, 2H), 2.04−1.21 (m, H-1, H-2, H-5, H-6, 7H). ^{13}C NMR for 5a (100 MHz, CD_3OD): δ 80.53 (C-3), 78.46 (CH_2O), 69.35 (C-4), 59.00 (CH_3), 56.81 (CH_3), 32.76 (C-1), 28.57 (C-2 and C-5), 24.39 (C-6). ^{1}H NMR for 5b (400 MHz, CD_3OD): δ 3.81−3.76 (m, H-3, 1H), 3.35 (s, CH_2OCH_3, 3H), 3.30 (s, CH_3, 3H), 3.24−3.20 (m, CH_2O, 2H), 3.20−3.16 (m, H-4, 1H), 2.04−1.21 (m, H-1, H-2, H-5, H-6, 7H). ^{13}C NMR for 5b (100 MHz, CD_3OD): δ 81.43 (C-4), 78.46 (CH_2O), 68.65 (C-3), 59.00 (CH_3), 56.92 (CH_3), 33.04 (C-2), 32.76 (C-1), 29.11 (C-5), 24.67 (C-6). Anal. Calcd for $C_9H_{18}O_3{\cdot}2/11H_2O$ (177.5): C, 60.89; H, 10.43. Found: C, 60.87; H, 10.47. FI-MS: m/z (relative intensity): 174 (M$^+$, 100), 175 (MH$^+$, 24.9).

3,4-Dimethoxy-1-methoxymethyl Cyclohexane (6). Potassium hydroxide powder (2.2 g, 38 mmol) was added to 20 mL of dry DMSO. After the suspension was stirred for 5 min, **4** (0.77 g, 4.8 mmol) was added, followed by addition of methyl iodide (0.60 mL, 9.6 mmol). The mixture was stirred for 4 h at room temperature, and then 200 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 (7/3, v/v; $R_f = 0.39$) to afford a colorless liquid **6**. Yield: 0.65 g (71.8%). ^{1}H NMR (400 MHz, CD_3OD): δ 3.43−3.39 (m, H-3, 1H), 3.37−3.32 (m, H-4, 1H) including the peaks at 3.34 (s, CH_3, 3H) and 3.33 (s, CH_3, 3H), 3.29 (s, CH_3, 3H), 3.17 (d, J = 7.0 Hz, CH_2O, 2H), 1.91−1.19 (m, H-1, H-2, H-5, H-6, 7H). ^{13}C NMR (100 MHz, CD_3OD): δ 79.05 (CH_2O), 78.16 (C-4), 78.03 (C-3), 59.00 (CH_3), 56.82 (CH_3), 56.70 (CH_3), 32.68 (C-1), 29.23 (C-2), 24.95 (C-6), 24.31 (C-5). Anal. Calcd for $C_{10}H_{20}O_3$ (188.3): C, 63.80; H, 10.71. Found: C, 63.63; H, 10.71. FI-MS: m/z (relative intensity): 188 (M$^+$, 100), 189 (MH$^+$, 12.4).

Scheme 2



3

poly-3

1-*tert*-Butyldimethylsilyloxymethyl-3,4-epoxycyclohexane (3). *tert*-Butyldimethylchlorosilane (3.90 g, 25.8 mmol) was added to a solution of **1** (3.17 g, 23.4 mmol) and imidazole (3.60 g, 51.6 mmol) in DMF (20 mL) under an argon atmosphere. After the solution was stirred for 6 h at room temperature, the solvent was evaporated to dryness and the residue diluted with ethyl acetate. The solution was washed with water, and the organic phase was dried with $MgSO_4$. After the solvent was removed in vacuo, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (9/1, v/v; $R_f = 0.37$) and distilled under reduced pressure to afford a colorless liquid **3** containing a mixture of isomers. Yield: 2.75 g (46.9%). Bp: 78 °C (0.25 mmHg). ^{1}H NMR (400 MHz, CD_3OD): δ 3.42−3.31 (m, CH_2O, 2H), 3.18−3.09 (m, epoxy, 2H), 2.18−0.90 (m, CH and CH_2 × 3, 7H), 0.86 (s, CH_3 × 3, 9H), 0.00 (s, SiCH_3 × 2, 6H). ^{13}C NMR (100 MHz, CD_3OD): δ 67.88 (CH_2), 67.41 (CH_2), 53.00 (CH), 52.73 (CH), 51.91 (CH), 51.47 (CH), 35.41 (CH), 32.41 (CH), 27.98 (CH_2), 27.17 (CH_2), 25.89 (CH_3 × 3), 24.75 (CH_2), 23.62 (CH_2), 23.13 (CH_2), 18.28 (C), −5.44 (CH_3 × 2). Anal. Calcd for $C_{13}H_{26}O_2Si$ (242.4): C, 64.41; H, 10.81. Found: C, 64.14; H, 10.92. FI-MS: m/z (relative intensity): 242 (M$^+$, 100), 243 (MH$^+$, 42.2).

Poly(3,4-epoxycyclohexanemethanol) (poly-3). All procedures were performed under an argon atmosphere (Scheme 2). $BF_3{\cdot}OEt_2$ (20.5 μL, [M]/[cat.] = 40) was added to a solution of **2** (1.56 g, 6.41 mmol) in dry-CH_2Cl_2 (total volume = 2.50 mL, 2.6 mol·L^{-1}) at −40 °C using a microsyringe. After 40 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 the original product was fractionated into two parts, i.e., the main part and the oligomer part, using preparative SEC (eluent chloroform). The main product fraction was evaporated and then dried in vacuo to give a white solid. Yield: 0.517 g (33.3%).

TBAF (1.0 mol·L^{-1} THF solution; 4.2 mL, 4.2 mmol) was added to a solution of the resulting polymer (0.504 g, 2.08 mmol) in THF (20 mL) at room temperature. After 20 h, the solution was evaporated to dryness and the residue purified by reprecipitation with methanol/ethyl acetate. The precipitate was filtered off and dried in vacuo at 40 °C to give a white solid **poly-3**. Yield: 0.202 g (75.8%). $M_{\mathrm{w,SEC-MALLS}}$ (DMF) (M_w/M_n) = 16 000 (1.30). dn/dc (DMF) = 0.068 mL·g^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ 3.68−2.88 (m, H-3, H-4, CH_2OH, 4H), 1.91−0.90 (m, H-1, H-2, H-5,

Table 1. Cationic Ring-opening Polymerization of 1 and 2 Using $BF_3 \cdot OEt_2$[a]

run	monomer	solvent	[M]/[cat.]	temp. (°C)	time (h)	yield (%)[b]	$M_{w,SEC}$ (M_w/M_n)[c]	$M_{w,SEC-MALLS}$[d]	DB[e]
1	**1**	PC[f]	40	23	48	11.8	1800 (1.36)	6300	0.36
2	**1**	CH_2Cl_2	40	23	48	35.3	3300 (1.49)	8100	0.42
3	**1**	CH_2Cl_2	80	−5	2	44.0	3700 (1.72)	9000	0.40
4	**1**	CH_2Cl_2	80	23	2	43.6	3800 (1.81)	10 300	0.41
5	**1**	none	40	23	24	19.4	3200 (1.82)	10 200	0.42
6	**1**	none	40	100	24	25.7	4700 (2.11)	21 600	0.38
7	**2**	none	20	100	98	trace	<1000		
8	**2**	none	20	130	64	trace	<1000		

[a] Ar atmosphere; [M] = 3.0 mol L^{-1}. [b] Methanol-soluble and ethyl acetate-insoluble parts. [c] Determined by SEC in THF using polystyrene calibration. [d] Determined by SEC-MALLS in THF. [e] Degree of branching determined by quantitative ^{13}C NMR spectra in CD_3OD. [f] Propylene carbonate.

H-6 7H). ^{13}C NMR (100 MHz, CD_3OD): δ 75.79 (C-3 and C-4), 68.25 (CH_2OH), 35.54 (C-1), 31.13−30.91 (C-2), 27.16−26.77 (C-5), 24.58 (C-6).

Synthesis of Carbamated Hyperbranched Poly(3,4-epoxycyclohexanemethanol) (Poly-1ASP). *N*-Carbonyl L-aspartic acid diethyl ester (0.38 g, 1.8 mmol) was added to a solution of **poly-1** (run 4, $M_{w,SEC-MALLS}$ = 10 300; 0.10 g, 0.75 unit mmol) in dry pyridine (10 mL) at 100 °C. After 24 h, the reaction mixture was cooled to room temperature and methanol (5 mL) added to quench the remaining isocyanate. The solvent was evaporated under reduced pressure, and azeotropic distillation with toluene (three times) was performed to remove any residual pyridine. The crude product was subjected to preparative SEC (eluent chloroform) to remove any low molecular weight parts. The solvent was evaporated to give a white solid. Yield: 0.14 g. ^1H NMR (400 MHz, $CDCl_3$): δ 5.75 (N*H*), 4.51 (NHC*H*, 1H), 4.20−4.02 (m, CH_2CH_3 × 2, 4H), 3.98−3.02 (m, **poly-1** scaffold, 4H), 2.99−2.69 (m, $CH_2C{=}O$, 2H), 2.10−0.72 (br, m, **poly-1** scaffold, 7H) including the peaks at 1.25−1.08 (m, CH_3 × 2, 6H). The degree of substitution (DS) value of the obtained polymer was 22% (eq.S1 in Supporting Information). The calculated molecular weight ($M_{w,cal}$) of the obtained polymer was 14 100 (eq.S2 in Supporting Information).

Potassium trimethylsilanolate (0.26 g, 2.0 mmol) was added to a solution of the obtained polymer (0.13 g) in THF (20 mL) at room temperature. After stirring for 17 h, the white precipitate was collected by filtration and washed with THF. The crude product was subjected to preparative SEC (eluent water) to remove any impurities. The solution was lyophilized to give a white fluffy solid **poly-1ASP**. Yield: 0.10 g. ^1H NMR (400 MHz, D_2O): δ 4.35 (NHC*H*, 1H), 4.08−3.04 (m, **poly-1** scaffold, 4H), 2.80 ($CHCH_2C{=}O$, 2H), 2.43−0.82 (m, **poly-1** scaffold, 7H). DS = 22% (eq.S3 in Supporting Information). $M_{w,cal}$ = 14 500 (eq.S4 in Supporting Information).

Synthesis of Carbamated Linear Poly(3,4-epoxycyclohexanemethanol) (Poly-3ASP). A carbamated linear poly(3,4-epoxycyclohexanemethanol) (**poly-3ASP**) was synthesized using the same synthetic procedure as that used for **poly-1ASP**. ^1H NMR (400 MHz, D_2O): δ 4.37 (NHC*H*, 1H), 4.07−3.22 (m, **poly-3** scaffold, 4H), 2.80 ($CHCH_2C{=}O$, 2H), 2.43−0.86 (m, **poly-3** scaffold, 7H). The DS value of **poly-3ASP** was 31% (eq.S5 in Supporting Information). $M_{w,cal}$ = 25 100 (eq.S6 in Supporting Information).

Encapsulation of Reichardt's Dye Using Poly-1ASP. A typical procedure for the solid/liquid phase transfer is as follows: Reichardt's dye (RCD) (11 mg, 20 mmol) was added to ion-exchanged water (9 mL), and the suspension was sonicated for 1 h at room temperature. **Poly-1ASP** (1.9 mg, 0.13 mmol) was solved in the aqueous suspension of RCD, and then the suspension was placed in a water bath shaker at 37 °C. After 24 h, any undissolved dye was removed by filtration using 0.45 μm membrane filters. The colored filtrate was characterized by its UV−vis spectra. UV−vis (water, 10 mm cell): λ_{max} (abs) = 562 nm (0.30). The $E_T(30)$ value of the **poly-1ASP** aqueous solution was 50.9 kcal·mol^{-1}, calculated using eq 3.[32]

$$E_T(30)\ (\text{kcal}\cdot\text{mol}^{-1}) = 28\,591/\lambda_{max}\ (\text{nm}) = 50.9\ \text{kcal}\cdot\text{mol}^{-1} \qquad (3)$$

The encapsulated amount of RCD per **poly-1ASP** ([RCD]/[**poly-1ASP**]) was 1.2, which was approximately estimated using the extinction coefficient ($\epsilon_{max} = 3.78 \times 10^3$ mol^{-1}·L·cm^{-1}) of RCD in 1-propanol (λ_{max} = 566 nm).

Results and Discussion

Polymerization. The cationic ring-opening polymerizations of 3,4-epoxycyclohexanemethanol (**1**) and α-terpineol epoxide (**2**) were carried out using boron trifluoride diethyletherate ($BF_3 \cdot OEt_2$) as a catalyst under an argon atmosphere. The polymerization product of **1** was a gel-free polymer as a white solid (**poly-1**), which was soluble in methanol, tetrahydrofuran (THF), tetrahydropyran, and *N*,*N*-dimethylformamide (DMF) but insoluble in water, acetone, chloroform, toluene, and ethyl acetate. Table 1 lists the polymerization results of **1**. The weight-average molecular weight values ($M_{w,SEC-MALLS}$) of **poly-1**, which were measured by size-exclusion chromatography using a multiangle laser light scattering detector (SEC-MALLS), increased with the increasing polymerization temperature; when the [M]/[cat.] molar ratio of 80 was used for 2 h, the $M_{w,SEC-MALLS}$ value was 9000 at −5 °C (run 3) and 10 300 at 23 °C (run 4). The $M_{w,SEC-MALLS}$ value of **poly-1** also increased with the increasing [M]/[cat.] molar ratio (runs 2 and 4). The polymer yields were in the range of 11.8−44.0%, which varied by the type of polymerization solvent, i.e., dichloromethane was a better solvent than propylene carbonate. Furthermore, the $M_{w,SEC-MALLS}$ values of **poly-1** obtained by bulk polymerization (runs 5 and 6) were relatively greater than those of **poly-1** obtained by the solution polymerization (runs 1−4). The weight-average molecular weight ($M_{w,SEC}$) values of **poly-1**, estimated by SEC coupled with a refractive index detector on the basis of a polystyrene calibration, were lower than the $M_{w,SEC-MALLS}$ values, i.e., the $M_{w,SEC-MALLS}$ values (6300−21 600) were ca. 2.4−4.6 times greater than the $M_{w,SEC}$ values (1800−4700). These results are commonly found in the SEC measurement of highly branched polymers due to their compact molecular form in solution.

On the contrary, the polymerization products of **2** were viscous oils consisting of the oligomer, and a high-molecular weight product was not obtained at all (runs 7 and 8 in Table 1). The polymerizability difference between **1** and **2** mainly causes the number of substituents into the epoxy group of these monomers, i.e., the trisubstituted epoxy group of monomer **2** was less reactive toward nucleophilic attack by the next monomer due to their higher steric hindrance than that of monomer **1** as a disubstituted epoxide.[27]

Polymer Structure. As already discussed, the $M_{w,SEC}$ values of **poly-1** were significantly lower than the $M_{w,SEC-MALLS}$ values. This result suggested that **poly-1** had a highly branched structure. Thus, the ^{13}C NMR measurements of **poly-1** were carried out in CD_3OD to investigate the polymer structure. Figure 1 shows the ^{13}C NMR spectra of **poly-1** and a linear analog, poly(3,4-epoxycyclohexanemethanol) (**poly-3**). There

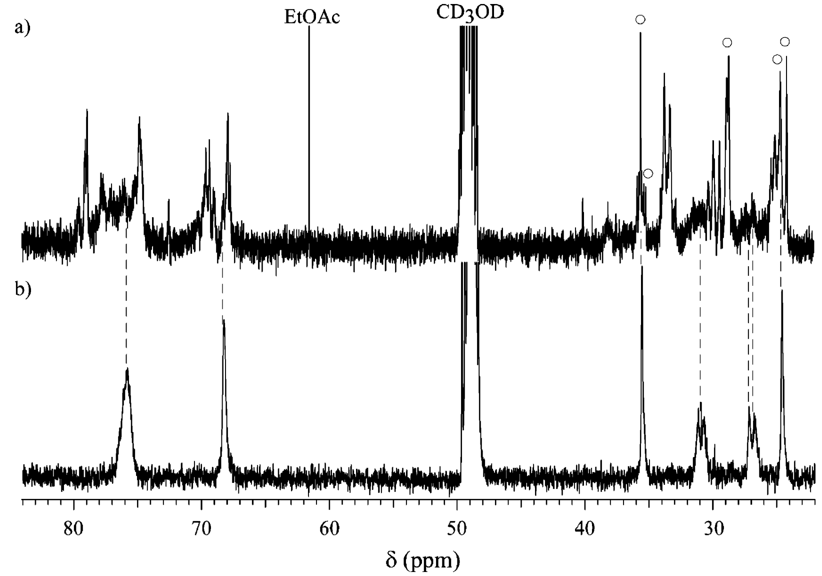


Figure 1. ^{13}C NMR spectra of (a) **poly-1** (run 4) and (b) **poly-3** in CD_3OD (○, peaks corresponding to terminal units ($\boldsymbol{T}_a$, $\boldsymbol{T}_b$)).

Chart 1

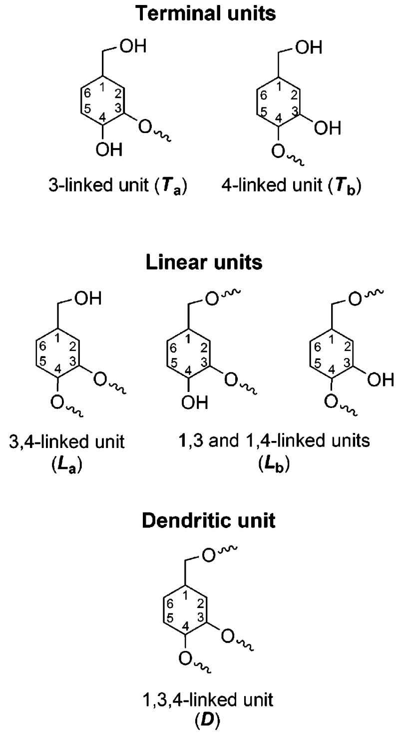
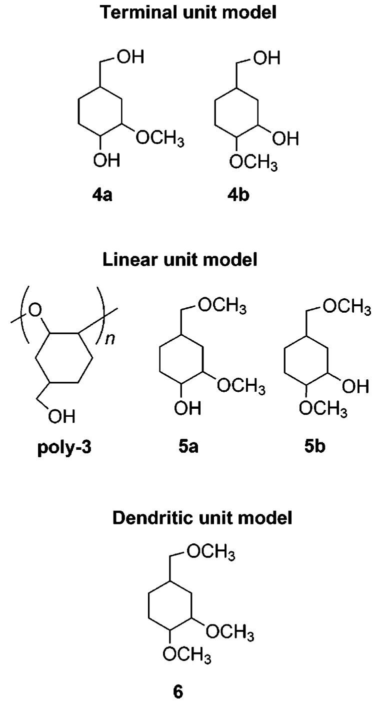


Chart 2



are many signals in the spectrum of **poly-1** along with the signals corresponding to the repeating units of **poly-3**, indicating that **poly-1** contained various polymer sequences. In Figure 1a, since the signals due to the epoxy carbons at 54.06−52.66 ppm had completely disappeared, it is expected that the epoxy groups in the polymerization system were perfectly consumed by the ring-opening reaction due to the proton-transfer reaction. On the basis of these results, the obtained polymer **poly-1** should consist of six kinds of repeating units, which are the 3-linked and 4-linked terminal units ($\boldsymbol{T}_a$ and $\boldsymbol{T}_b$), the 3,4-linked linear unit ($\boldsymbol{L}_a$), the 1,3-linked and 1,4-linked linear unit ($\boldsymbol{L}_b$), and the 1,3,4-linked dendritic unit (***D***) as shown in Chart 1. To confirm the branching structure, the chemical shifts for the carbons of **poly-1** were compared to those of the model compounds, which were 4-hydroxy-3-methoxy cyclohexanemethanol (**4a**) as $\boldsymbol{T}_a$, 3-hydroxy-4-methoxy cyclohexanemethanol (**4b**) as $\boldsymbol{T}_b$, **poly-3** as $\boldsymbol{L}_a$, 4-hydroxy-3-methoxy-1-methoxymethyl cyclohexane (**5a**) and 3-hydroxy-4-methoxy-1-methoxymethyl cyclohexane (**5b**) as $\boldsymbol{L}_b$, and 3,4-dimethoxy-1-methoxymethyl cyclohexane (**6**) as ***D*** (Chart 2). In the ^{13}C NMR spectrum of **poly-1**, the major signals marked by the open circles at 35.47, 35.07, 28.61, 24.57, and 24.07 ppm were assigned to the carbons of $\boldsymbol{T}_a$ and $\boldsymbol{T}_b$. Furthermore, most of the other signals in Figure 1a were also assigned to the carbons of $\boldsymbol{L}_b$ and ***D*** (Figure S1 in Supporting Information). These results indicated that **poly-1** was a hyperbranched polymer possessing numerous terminal and branching units.

In addition, to confirm the polymer structure in detail, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements of **poly-1** were performed using 2,5-dihydroxybenzoic acid as the matrix and sodium trifluoroacetate as the cationizing agent (Figure 2). In

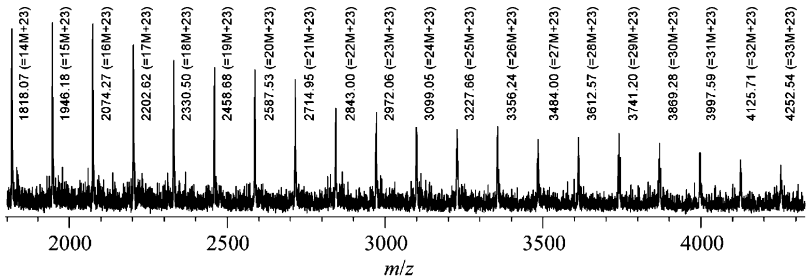
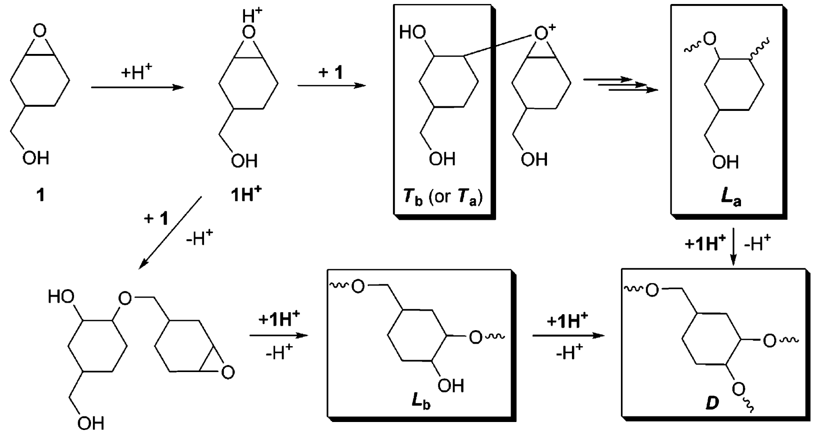


Figure 2. Expanded MALDI-TOF-MS spectrum of **poly-1** (run 4).

Scheme 3. Proposed Mechanism for Ring-Opening Multibranching Polymerization (ROMBP) of 1



the mass spectrum, there is only one series of peaks with a regular interval (ca. 128.2) and the absolute mass of each peak was equal to integer multiples of the molar mass of **1**. Therefore, these spectroscopic results suggested that the cationic polymerization of **1** proceeded through a ring-opening addition reaction without any side reactions such as elimination of a water molecule.[33]

Monomer **1** has one epoxy and one hydroxyl group in a molecule; thus, **1** should be classified as a latent AB_2-type monomer. The degrees of branching (DBs) of the AB_2-type monomer were calculated from the equation using a molar ratio of terminal units in **poly-1**, i.e., $DB = 2(\boldsymbol{T}_a + \boldsymbol{T}_b)/(\boldsymbol{T}_a + \boldsymbol{T}_a + \boldsymbol{L}_a + \boldsymbol{L}_b + \boldsymbol{D})$, as shown in the Experimental Section (eq 2). In order to estimate the DB values, the quantitative ^{13}C NMR measurements of **poly-1** were performed in CD_3OD, and then the $(\boldsymbol{T}_a + \boldsymbol{T}_b)/(\boldsymbol{T}_a + \boldsymbol{T}_a + \boldsymbol{L}_a + \boldsymbol{L}_b + \boldsymbol{D})$ values were calculated using the integral ratios of the signals for $(\boldsymbol{T}_a + \boldsymbol{T}_b)$ at 24.07 and 35.07 ppm to those for $(\boldsymbol{T}_a + \boldsymbol{T}_a + \boldsymbol{L}_a + \boldsymbol{L}_b + \boldsymbol{D})$ at 35.47−24.07 ppm (eq 1 in the Experimental Section). The DB values of **poly-1** were in the range of 0.36−0.42 (Table 1), which slightly varied by the polymerization conditions, such as solvent (run 1) and temperature (run 6). These values were lower than the statistical value (ca. 0.5) for the polymerization of the AB_2-type monomer.[31] The low DB values of **poly-1** should be due to the different reactivity between the primary hydroxyl group of **1** and the secondary hydroxyl group formed during the polymerization.

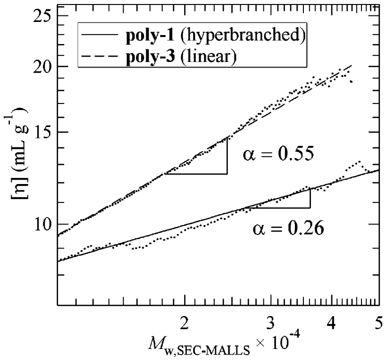


Figure 3. Mark−Houwink plots in DMF at 25 °C of **poly-1** (run 6) and **poly-3**.

Polymerization Mechanism. From the results of the ^{13}C NMR and MALDI-TOF-MS measurements, **poly-1** mainly consists of six kinds of repeating units as shown in Chart 1. Therefore, polymerization should proceed through a ring-opening multibranching polymerization (ROMBP) mechanism similar to the cationic ring-opening polymerization of glycidol reported by Kubisa and Penczek et al.[22,23] Scheme 3 is the proposed mechanism for the polymerization of **1**. The epoxy oxygen of **1** was quickly protonated by the generated protons in the polymerization medium, and the protonated **1** (**$1H^+$**) undergoes nucleophilic attack by the epoxy oxygen of another monomer, leading to $\boldsymbol{T}_b$ (or $\boldsymbol{T}_a$) and $\boldsymbol{L}_a$. On the other hand, when the remaining hydroxyl groups of **1** or the polymer chain were reacted with the activated epoxy group, $\boldsymbol{L}_b$ and $\boldsymbol{D}$ were formed along with regeneration of a proton. These reactions simultaneously occurred during the polymerization to produce a hyperbranched poly(3,4-epoxycyclohexanemethanol), **poly-1**.

Physical Property. Dendritic macromolecules, such as a dendrimer, star polymer, and hyperbranched polymer, have a spherical conformation with a low physical entanglement. Therefore, the physical properties of dendritic macromolecules are quite different from those of linear and lower branched polymers.[1] To clarify the three-dimensional property of **poly-1**, we compared the physical properties of **poly-1** with those of the linear **poly-3**.

In general, the relationship between the intrinsic viscosity and the molecular weight of polymer can be described by the Mark−Houwink−Sakurada equation of $[\eta] = KM^{\alpha}$. In particular, the Mark−Houwink exponent α is known as a target for the conformation of a polymer in solution, e.g., conventional

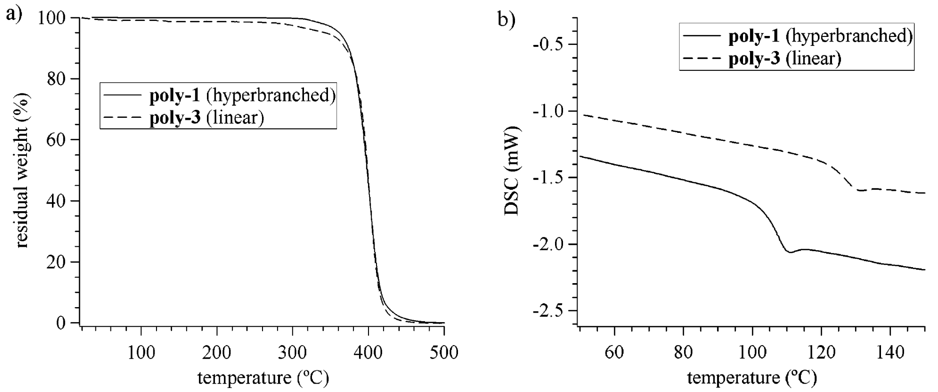


Figure 4. Thermogravimetric analysis (TGA, a) and differential scanning calorimetry (DSC, b) of **poly-1** (run 3) and **poly-3** under a nitrogen atmosphere.

Table 2. Viscosity and Hydrodynamic Radius of poly-1 and poly-3

			measured in THF[a]				measured in DMF[b]			
sample	$M_{w,SEC-MALLS}$	DB	$[\eta]$ (dL g^{-1})	$K \times 10^{3\,c}$ (dL g^{-1})	α^d	R_h (nm)	$[\eta]$ (dL g^{-1})	$K \times 10^{3\,c}$ (dL g^{-1})	α^d	R_h (nm)
run 3	9000[a]	0.40	0.071	10.4	0.22	2.1	0.106	6.2	0.32	2.4
run 4	10 300[a]	0.41	0.072	9.2	0.22	2.1	0.108	8.2	0.28	2.5
run 6	21 600[a]	0.38	0.075	10.0	0.21	2.6	0.100	7.6	0.26	3.6
poly-3	16 000[b]	0	nd[e]	nd[e]	nd[e]	nd[e]	0.112	0.58	0.55	3.0

[a] Determined by SEC-MALLS with a viscosity detector in THF at 25 °C. [b] Determined by SEC-MALLS with a viscosity detector in DMF containing 0.01 M LiBr at 25 °C. [c] Mark−Houwink constant K ($[\eta] = KM^{\alpha}$). [d] Mark−Houwink exponent α ($[\eta] = KM^{\alpha}$). [e] Not determined because of their insolubility in THF.

linear polymers with a randomly coiled form possess α values between 0.5 and 1.0. Thus, the intrinsic viscosities ($[\eta]$) of **poly-1** and **poly-3** were estimated using SEC-MALLS coupled with a viscosity detector, and then the α values were determined by the value of the slope for the double-logarithmic plots of $[\eta]-M_{w,SEC-MALLS}$ as shown in Figure 3. The results of the viscosity and hydrodynamic radius (R_h) measurements for **poly-1** and **poly-3** are summarized in Table 2. The α values of **poly-1** were in the range from 0.21 to 0.32, which were much lower than those of the polymers with a random coil structure. These values changed depending on the type of solvent, e.g., the α values of **poly-1** in DMF (0.26−0.32) were slightly greater than those in THF (0.21−0.22), indicating that the conformation of **poly-1** in DMF was slightly expanded when compared to that in THF. The explanation was also supported by the difference in the R_h values for **poly-1**, i.e., 2.4−3.6 nm in DMF and 2.1−2.6 nm in THF. Additionally, the α value of **poly-3** in DMF was 0.55, which was comparable to that of the random coil polymer and significantly greater than that of **poly-1**. These results suggested that the low viscosity of **poly-1** originated from their compact molecular form, i.e., globular shape with less physical entanglement based on the highly branched structure.

The thermal properties of **poly-1** and **poly-3** were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. Figure 4 and Table 3 show the results of the thermal analysis. For the polymer obtained by the solution polymerization (runs 1−4), the 10% weight-loss temperature (T_{d10}) of **poly-1** was ca. 374 °C, which was comparable to that of **poly-3** (372 °C). On the other hand, the glass-transition temperature (T_g) of **poly-1** was observed at ca. 105 °C, which was 20 °C lower than that of **poly-3** (125 °C). This fact suggested that the free volume of **poly-1** with many end groups was greater than that of **poly-3**. In addition, T_{d10} and T_g of the polymer obtained by the bulk polymerization (runs 5 and 6) were a little lower than those of the others. It should be considered that the structure difference of the polymer, e.g., polymer sequence and branching manner, affected their thermal property.

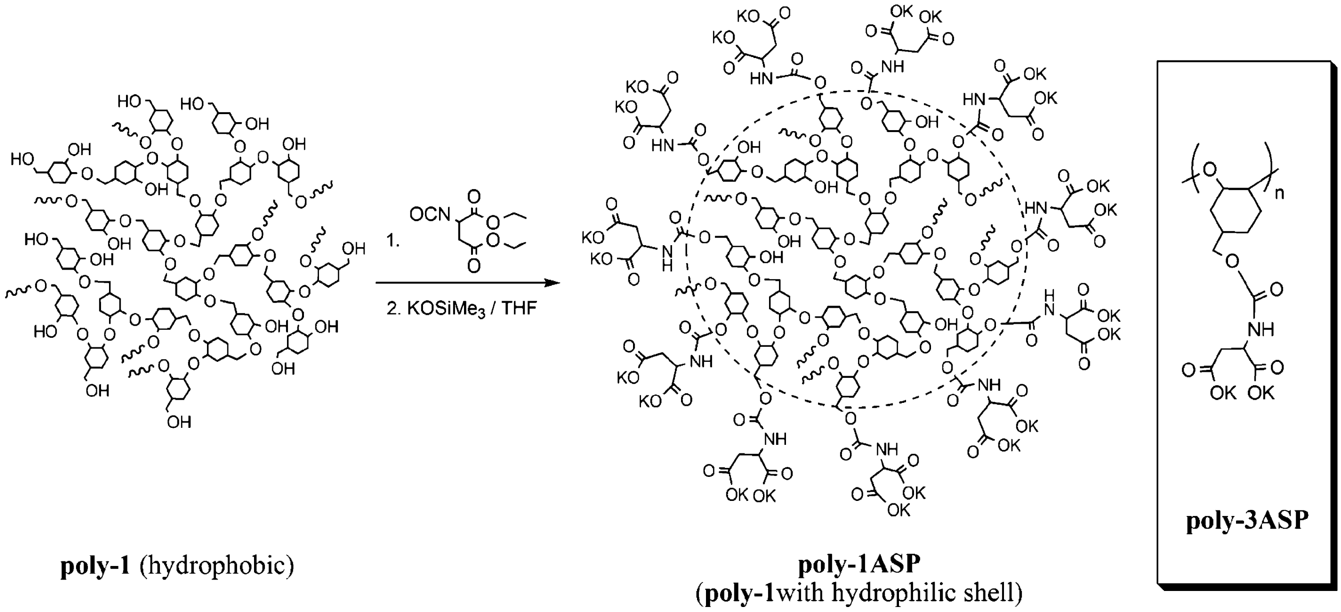
Table 3. Thermal Analysis of poly-1 and poly-3 under a Nitrogen Atmosphere

sample	$M_{w,SEC-MALLS}$	T_{d10} (°C)[a]	T_g (°C)[b]
run 1	6300[c]	381	97
run 2	8100[c]	374	105
run 3	9000[c]	370	105
run 4	10 300[c]	374	105
run 5	10 200[c]	343	85
run 6	21 600[c]	343	103
poly-3	16 000[d]	372	125

[a] Measured by TGA at a heating rate of 10 °C·min^{-1}. [b] Measured by DSC in the second heating scan at a rate of 10 °C·min^{-1}. [c] Determined by SEC-MALLS in THF. [d] Determined by SEC-MALLS in DMF.

Molecular Encapsulation Property of Amphiphilic Dendritic Polymer with Poly-1 as a Core. In the recent applied research of dendritic polymers, encapsulation of hydrophobic molecules in water using amphiphilic dendritic polymers is one of the greatest challenges because its property should be directly linked to practical use in biological applications such as drug delivery.[34−37] However, there are only a few reports of a water-soluble nanocarrier using a hyperbranched aliphatic polyether.[38,39] Therefore, in order to investigate the potential of **poly-1** as a dendritic host toward a hydrophobic guest molecule, we produced a novel amphiphilic dendritic polymer (**poly-1ASP**) with **poly-1** as a hydrophobic dendritic core, and its encapsulation property toward a hydrophobic dye was elucidated in water. **Poly-1ASP** was prepared by the carbamation reaction of **poly-1** (run 4) using *N*-carbonyl L-aspartic acid diethyl ester followed by de-esterification using potassium trimethylsilanolate, as shown in Scheme 4. On the basis of the results of the ^{1}H NMR spectral assignments, the obtained polymer was identified as **poly-1ASP** with a 22% degree of substitution (DS) (Figure S3 and eq.S3 in Supporting Information). The calculated weight-average molecular weight ($M_{w,cal}$) value of **poly-1ASP**, which was estimated by the calculation based on the $M_{w,SEC-MALLS}$ value of **poly-1** and the DS value, was 14 500 (eq.S4 in Supporting Information). **Poly-1ASP** was readily soluble in

Scheme 4. Syntheses of Poly-1ASP and Poly-3ASP



water and insoluble in other organic solvents, which remarkably differed from the solubility of **poly-1**.

Since **poly-1ASP** was completely soluble in water, we examined the encapsulation characteristics for the hydrophobic dye. To evaluate the microenvironment of **poly-1ASP** in an aqueous solution, we chose Reichardt's dye (RCD) as a hydrophobic dye, which is often used as a solvatochromic probe to test the polarity of the inside of polymeric micelles or dendrimers.[40−43] **Poly-1ASP** was added to an aqueous suspension of RCD, and the mixture was shaken for 24 h at 37 °C. The UV−vis spectra of RCD in the respective solutions are shown in Figure 5. The absorption peak, which was derived from the intermolecular charge-transfer $\pi-\pi^*$ absorption of RCD, appeared at 562 nm for the **poly-1ASP** aqueous solution, whereas no peak appeared for the control in the absence of **poly-1ASP**, indicating that RCD was solubilized in water by **poly-1ASP**. In addition, the calculated $E_T(30)$ polarity value for RCD in the **poly-1ASP** aqueous solution using eq 3 was 50.9 kcal·mol^{-1} (see Experimental Section), which was fairly close to that in 1-propanol (50.7 kcal·mol^{-1}).[32] This means that the RCD in the **poly-1ASP** aqueous solution existed with a polarity similar to 1-propanol, i.e., the hydrophobic core of **poly-1ASP**. The RCD encapsulation amount per the core of **poly-1ASP** ([RCD]/[**poly-1ASP**]), which was approximately determined by the extinction coefficient of RCD in 1-propanol, was 1.2. On the other hand, the linear polymer **poly-3ASP**, which was prepared from **poly-3** using the same synthetic method as for **poly-1ASP**, showed an encapsulation property lower than **poly-1ASP**, i.e., the [RCD]/[**poly-3ASP**] value was 0.10. These results concluded that the dendritic topology of **poly-1ASP** along with their amphiphilicity could be effectively used for encapsulation of RCD.

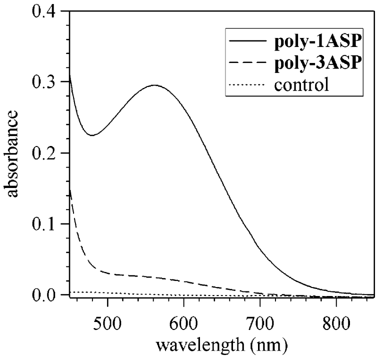


Figure 5. UV−vis spectra of RCD in water at room temperature (λ_{max} = 562 nm; polymer concentration = 0.06 mmol·L^{-1}).

On the basis of these experimental results, **poly-1** with a hyperbranched structure is a polymer useful as a dendritic host for a hydrophobic guest molecule. More detailed and rigorous studies are now in progress to investigate the unimolecular micelle property and encapsulation mechanism of **poly-1ASP** in aqueous solution.

Conclusions

In this study, we performed the cationic ring-opening polymerization of 3,4-epoxycyclohexanemethanol (**1**) and α-terpineol epoxide (**2**) using boron trifluoride diethyletherate ($BF_3 \cdot OEt_2$) as a catalyst that produced a hydrophobic hyperbranched polymer. Although polymerization of **2** was a failure, polymerization of **1** proceeded smoothly to yield a gel-free polymer (**poly-1**). For the ^{13}C NMR measurement, it was clarified that **poly-1** was a hyperbranched polymer with numerous terminal units, and the degrees of branching (DBs) of **poly-1** were in the range from 0.36 to 0.42. The Mark−Houwink exponent α of **poly-1** was less than 0.5, suggesting that the viscosity of **poly-1** was very low due to their spherical conformation with less physical entanglement in solution. In addition, the glass-transition temperature (T_g) of **poly-1** was ca. 105 °C, which was lower than that of the corresponding linear polymer (**poly-3**). An amphiphilic dendritic polymer (**poly-1ASP**) with the **poly-1** core and L-aspartic acid shell was synthesized, and its encapsulation property of Reichardt's dye (RCD) as a hydrophobic molecule was examined. For the comparative study of the linear polymer (**poly-3ASP**) with **poly-1ASP**, **poly-1ASP** was capable of encapsulating RCD and the property was derived from its dendritic topology and amphiphilicity. Thus, hyperbranched poly(alicyclic epoxyalcohol)s were found to be a good candidate as a dendritic core molecule of a nanocapsule with the ability to solubilize hydrophobic drugs.

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Supporting Information Available: Detailed peak assignment for the ^{13}C NMR spectrum of **poly-1** along with a comparison of the chemical shifts of various model compounds; calculations of the DS and the $M_{w,cal}$ values of **poly-1ASP** and **poly-3ASP**. This material is available free of charge via the Internet at http://pubs.acs.org.

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