Synthesis and Degree of Branching of Epoxy-Terminated Hyperbranched Polysiloxysilane

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Hyperbranched polysiloxysilane (HBPS) with terminal vinyl groups **P1** was synthesized by self-condensation reaction using platinum-catalyzed hydrosilylation of 1,1,3,5,5-pentamethyl-1,5-divinyltrisiloxane. A number-average molecular weight (M_n) was 5400 with a polydispersity index of 1.49. End-functionalization of the terminal vinyl groups was carried out by epoxidation with 3-chloroperoxybenzoic acid to afford epoxy-terminated HBPS **P2**. The polymers obtained were characterized by IR, ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy. The degree of branching of HBPS was estimated as 0.57 in comparison of ^{29}Si NMR spectra of **P2** and model compounds. The glass transition temperatures (T_g) of **P1** and **P2** were observed at $-97\,^\circ$C and $-77\,^\circ$C, respectively. The 10% weight loss temperatures (T_{10}) of **P1** and **P2** were over $440\,^\circ$C in nitrogen.
KEY WORDS: Hyperbranched Polymer / Polysiloxysilane / End-functionalization / Epoxidation / Degree of Branching /

Developing siloxane-based organic-inorganic hybrid polymers has attracted much attention in studies on interfaces of various organic/inorganic materials because of their unique properties such as adhesion, excellent thermal and oxidative stability, lubricity, high flexibility, and biocompatibility.[1,2] Although many and various types of the siloxane-based polymers have been developed,[2–5] hyperbranched polysiloxysilanes (HBPS) are of particular recent interest. HBPS can be prepared by a facile and reliable one-pot synthetic method from hydrosilylation of AB_x type siloxane-monomers having silicon hydride (SiH) groups and terminal carbon-carbon double bonds, where x determines the ideal number of branches per repeating unit, to afford a large number of terminal functional groups of SiH or unsaturated bonds.[6–10] Furthermore, the resulting terminal groups can be easily modified to various other functional groups that offer opportunities for tailoring the polymers to specific applications for which multiple functionalities may be advantageous.[7–10]

However, little attention has been given to study of the degree of branching for HBPS.[9] The key properties of hyperbranched polymers such as viscosity and solubility are generally often determined by not only molecular weights, the kind of or the number of terminal functional groups, but also the degree of branching.[11]

Herein, in order to evaluate the modification potential of the terminal functional groups and the degree of branching of HBPS, we report the synthesis of the epoxy-terminated HBPS *via* the hydrosilylation of 1,1,3,5,5-pentamethyl-1,5-divinyltrisiloxane as an AB_2 type monomer and subsequent epoxidation of the resulting vinyl-terminated HBPS. The degree of branching for the epoxy-terminated HBPS was investigated by comparing to the ^{29}Si NMR spectrum of model compounds.

EXPERIMENTAL

Measurements

NMR (^{1}H, 300 MHz; ^{13}C, 75 MHz; [29]Si, 59.4 MHz) spectra were obtained in CDCl₃ on a JEOL JNM-AL 300 NMR spectrometer. Chemical shifts are reported in ppm, relative to CHCl₃ (δ 7.24, ^{1}H), CDCl₃ (δ 77.0, ^{13}C), and tetramethylsilane (δ 0.0, [29]Si). Infrared (IR) spectra were recorded using a JASCO FT/IR 460 plus spectrometer. Gel permeation chromatography (GPC) measurements coupled with multi-angle laser light scattering (MALLS) detector (Wyatt Technology miniDawn tristar) using tetrahydrofuran (THF) as an eluent, were carried out using a JASCO HBPX 880Pu, two polystyrene-divinylbenzene columns (two Shodex GPC LF-804), and a Shodex RI-71 refractive index detector. The molecular weight characteristics of the polymers were calculated by polystyrene calibration curve constructed from 8 polystyrene standards. MALLS measurements were performed using ASTRA® 4.90 from Wyatt Technology, which acquired data from the 3 scattering angles detector (miniDAWN tirstar) and a refractive index detector. Differential scanning calorimetry (DSC) measurements were carried out using a Seiko DSC 6200 at a heating rate of $10\,^\circ$C min^{-1} in nitrogen. The glass transition temperature (T_g) was taken at the middle of the step transition in the second heating run. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Seiko TG/DTA 6200 at a heating rate of $10\,^\circ$C min^{-1} in nitrogen.

Materials

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(dvs)] solution in xylenes (Aldrich) was used as

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received. Aniline was dried over calcium hydride and distilled under reduced pressure. Triethylamine was dried over calcium hydride and distilled. Diethylether and toluene were dried and distilled over sodium metal and benzophenone ketyl under nitrogen. The other reagents and solvents were used as received.

1,1,3,5,5-Pentamethyl-1,5-divinyltrisiloxane (1). Diethylether (700 mL), aniline (8.38 g, 90 mmol), and water (1.48 g, 82 mmol) were charged into a three-necked flask equipped with a dropping funnel and a condenser. A solution of vinyldimethylchlorosilane (11.6 mL, 82 mmol) in diethylether (50 mL) was slowly added dropwise to the mixture at 0 °C with vigorous stirring. After the mixture was stirred at this temperature for 15 min, the precipitate of aniline hydrochloride was filtered off. After drying the resulting solution over $MgSO_4$, the solution was combined with triethylamine (7.51 g, 74 mmol) in a three-necked flask equipped with a dropping funnel and a condenser. A solution of dichloromethylsilane (3.5 mL, 34 mmol) in diethylether (50 mL) was slowly added dropwise to the solution at 0 °C with vigorous stirring. The precipitate of triethylamine hydrochloride was filtered off and then the solvent was removed under reduced pressure to give a colorless liquid. Distillation of the residue under reduced pressure afforded **1** as a colorless liquid (3.77 g, 45%). IR (KBr, ν): 2961, 2152, 1408, 1257, 1059, 957, 910. ^{1}H NMR (CDCl₃, δ): 0.11 (d, 3H, $J = 1.4$ Hz, SiCH₃), 0.17 (s, 12H, SiCH₃), 4.65 (q, 1H, $J = 1.4$ Hz, SiH), 5.73 (q, 1H, $J = 4.4$ Hz, 19.4 Hz, SiCH=CH_2), 5.94 (q, 1H, $J = 4.4$ Hz, 14.9 Hz, SiCH=CH_2), 6.11 (q, 1H, $J = 14.9$ Hz, 19.4 Hz, SiCH=CH₂). ^{13}C NMR (CDCl₃, δ): 0.1, 1.5, 132.0, 138.9. ^{29}Si NMR (CDCl₃, δ): −35.4, −2.1.

Vinyl-Terminated HBPS (P1). AB₂ type monomer **1** (18.49 g, 75 mmol) was charged into a two-necked flask. Pt(dvs) solution in xylenes (0.75 mL, 0.075 mmol) was added at 0 °C with vigorous stirring. The system was then allowed to warm to room temperature and stirred for 15 h. The polymer was dissolved in diethylether (30 mL) and precipitated into methanol (300 mL) three times. **P1** was obtained as a colorless viscous liquid (8.31 g, 47%). GPC based on polystyrene calibration: $M_n = 4140$, $M_w/M_n = 1.48$. GPC-MALLS: $M_n = 4810$, $M_w/M_n = 1.60$. IR (KBr, ν): 2958, 2910, 2874, 1596, 1407, 1256, 1135, 1047, 955. ^{1}H NMR (CDCl₃, δ): −0.07 [br, SiCH(CH₃)Si], −0.01–0.18 (m, SiCH₃), 0.37, 0.43 (br, SiCH₂-CH₂Si), 0.92–1.02 [m, SiCH (CH_3)Si], 5.71 (m, SiCH=CH_2), 5.91 (m, SiCH=CH_2), 6.13 (m, SiCH=CH₂). ^{13}C NMR (CDCl₃, δ): −1.1, −0.2, 0.2, 0.6, 1.6, 8.1, 8.9, 9.6, 11.8, 131.7, 139.4. ^{29}Si NMR (CDCl₃, δ): −22.1, −21.8, −21.1, −20.5, −19.9, −4.8, −4.6, −4.5, −3.3, 7.0, 7.4, 7.6, 7.9, 8.1.

Epoxy-Terminated HBPS (P2). **P1** (1.23 g), toluene (10 mL), and 3-chloroperoxybenzoic acid (1.73 g, 10 mmol) were charged into a two-necked flask. The mixture was stirred for 48 h. Then the generated precipitate was filtered off. The residue was dissolved in hexane (50 mL), and extracted with 4×200 mL of a saturated $NaHCO_3$ solution. The organic phase was then dried over $MgSO_4$. Removal of the solvent under high vacuum for 6 h afforded **P2** (0.96 g, 73%) as a colorless viscous liquid. GPC based on polystyrene calibration: $M_n = 3950$, $M_w/M_n = 1.45$. GPC-MALLS: $M_n = 4710$, $M_w/M_n = 1.52$. IR (KBr, ν):

2957, 2912, 2874, 1407, 1319, 1256, 1231, 1136, 1047. ^{1}H NMR (CDCl₃, δ): −0.09 [br, SiCH(CH₃)Si], −0.05–0.09 (m, SiCH₃), 0.40 (br, SiCH₂CH₂Si), 0.90–1.02 [m, SiCH-(CH_3)Si], 2.15 [m, SiCH(OCH_2)], 2.57 [m, SiCH(OCH_2)], 2.86 [m, SiCH(OCH₂)]. ^{13}C NMR (CDCl₃, δ): −1.8, −1.6, −1.4, −1.3, −1.1, −0.6, 0.1, 1.5, 7.8, 8.8, 9.4, 11.6, 11.7, 43.5, 44.3. ^{29}Si NMR (CDCl₃, δ): −21.7, −21.2, −20.3, −19.8, −19.0, −18.5, 1.4, 1.9, 7.8, 8.5.

Terminal Vinyl-Model Compound [2(T)], and Linear/Terminal Vinyl-Model Compound [3(L/T)]. **1** (2.47 g, 10 mmol), vinyltrimethylsilane (20.00 g, 200 mmol) and Pt(dvs) solution in xylenes (0.1 mL, 0.01 mmol) were charged into a three-necked flask. The mixture was stirred for 15 h. Removal of volatile materials under reduced pressure afforded the crude products. Preparative gel permeation chromatography of crude products with THF as an eluent gave **2(T)** (0.24 g, 8%) and **3(L/T)** (0.23 g, 4%).

2(T): IR (KBr, ν): 2957, 2909, 1596, 1407, 1256, 1136, 1050, 956. ^{1}H NMR (CDCl₃, δ): −0.05 (s, 9H, SiCH₃), 0.00 (s, 3H, SiCH₃), 0.14 (s, 12H, SiCH₃), 0.36 (m, 4H, SiCH₂CH₂Si), 5.71 (q, 2H, $J = 4.2$ Hz, 19.9 Hz, SiCH=CH_2), 5.91 (q, 2H, $J = 4.2$ Hz, 14.6 Hz, SiCH=CH_2), 6.11 (q, 2H, $J = 14.6$ Hz, 19.9 Hz, SiCH=CH₂). ^{13}C NMR (CDCl₃, δ): −2.3, −1.2, 0.3, 7.8, 9.5, 131.6, 139.4. ^{29}Si NMR (CDCl₃, δ): −19.8, −4.3, 3.2.

3(L/T): IR (KBr, ν): 2957, 2873, 1596, 1407, 1256, 1135, 1047, 955. ^{1}H NMR (CDCl₃, δ): −0.06–0.14 [m, SiCH(CH₃)Si, SiCH₃], 0.32–0.40 (m, SiCH₂CH₂Si), 0.99 [d, $J = 7.5$ Hz SiCH_3 (CH)Si], 5.70 (m, SiCH=CH_2), 5.91 (m, SiCH=CH_2), 6.12 (m, SiCH=CH₂). ^{13}C NMR (CDCl₃, δ): −2.3, −1.1, −0.5, 0.1, 0.3, 1.5, 7.9, 9.6, 11.8, 131.6, 139.5. ^{29}Si NMR (CDCl₃, δ): −21.0, −20.5, −19.9, −4.9, −4.5, −4.4, 3.1, 7.5, 8.1.

Dendritic Model Compound [4(D)]. **2(T)** (0.14 g, 0.42 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.93 g, 4.2 mmol), and Pt(dvs) solution in xylenes (0.01 mL, 0.001 mmol) were charged into a two-necked flask. The mixture was stirred for 15 h. Removal of volatile materials under reduced pressure afforded the crude products. Preparative gel permeation chromatography of crude products with THF as an eluent gave **4(D)** (0.24 g, 74%). IR (KBr, ν): 2957, 2909, 1406, 1256, 1136. ^{1}H NMR (CDCl₃, δ): 0.00–0.15 (m, 66H, SiCH₃), 0.38–0.50 (m, 12H, SiCH₂CH₂Si). ^{13}C NMR (CDCl₃, δ): −2.2, −1.2, −0.5, 1.9, 8.0, 8.9, 9.5, 9.6. ^{29}Si NMR (CDCl₃, δ): −21.3, −20.8, 3.1, 6.8, 7.9.

Linear Vinyl-Model Compound [5(L)]. **2(T)** (0.24 g, 0.70 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.15 g, 0.70 mmol), diethylether (1.0 mL), and Pt(dvs) solution in xylenes (0.01 mL, 0.001 mmol) were charged into a two-necked flask. The mixture was stirred for 15 h. Removal of volatile materials under reduced pressure afforded the crude products. Preparative gel permeation chromatography of crude products with THF as an eluent gave **5(L)** (0.28 g, 21%). IR (KBr, ν): 2957, 2909, 1596, 1407, 1256, 1136, 1051, 956. ^{1}H NMR (CDCl₃, δ): −0.06–0.29 (m, 45H, SiCH₃), 0.30–0.45 (m, 8H, SiCH₂CH₂Si), 5.71 (q, 1H, $J = 4.3$ Hz, 20.1 Hz, SiCH=CH_2), 5.91 (q, 1H, $J = 4.3$ Hz, 14.6 Hz, SiCH=CH_2), 6.10 (q, 1H,

$J = 14.6$ Hz, 20.1 Hz, SiCH=CH$_2$). ^{13}C NMR (CDCl$_3$, δ): -2.2, -1.2, -0.5, 0.3, 1.9, 7.9, 8.9, 9.4, 9.5, 131.6, 139.5. ^{29}Si NMR (CDCl$_3$, δ): -20.6, -20.4, -4.4, 3.2, 7.0, 8.2.

Terminal Epoxy-Model Compound [6(T)]. **2(T)** (0.18 g, 0.53 mmol), toluene (2 mL), and 3-chloroperoxybenzoic acid (0.37 g, 2.1 mmol) were charged into a two-necked flask. The mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in hexane (50 mL), and washed with 4×100 mL of a saturated NaHCO$_3$ solution. The organic phase was then dried over MgSO$_4$. Removal of the solvent under reduced pressure afforded **6(T)** (0.14 g, 68%) as a colorless liquid. IR (KBr, ν): 2956, 2912, 1406, 1319, 1257, 1232, 1136, 1052, 947. ^{1}H NMR (CDCl$_3$, δ): -0.08 (s, 9H, SiCH$_3$), 0.02 (s, 3H, SiCH$_3$), 0.11 (s, 12H, SiCH$_3$), 0.34 (br, 4H, SiCH$_2$CH$_2$Si), 2.13 [q, 1H, $J = 4.1$ Hz, 5.6 Hz, SiCH(OCH_2)], 2.55 [q, 1H, $J = 4.1$ Hz, 5.9 Hz, SiCH(OCH_2)], 2.84 [t, 1H, $J = 5.6$ Hz, 5.9 Hz, SiCH(CH$_2$)]. ^{13}C NMR (CDCl$_3$, δ): -2.4, -2.2, -1.8, -1.4, 7.7, 9.2, 43.4, 44.3. ^{29}Si NMR (CDCl$_3$, δ): -18.3, 1.8, 3.3.

Linear/Terminal Epoxy-Model Compound [7(L/T)]. **3(L/T)** (0.23 g, 0.38 mmol), toluene (2 mL), and 3-chloroperoxybenzoic acid (0.39 g, 2.3 mmol) were charged into a two-necked flask. The mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in hexane (50 mL), and washed with 4×100 mL of a saturated NaHCO$_3$ solution. The organic phase was then dried over MgSO$_4$. Removal of the solvent under reduced pressure afforded **7(L/T)** (0.15 g, 62%) as a colorless liquid. IR (KBr, ν): 2957, 2912, 1407, 1319, 1257, 1232, 1135, 1050, 947. ^{1}H NMR (CDCl$_3$, δ): -0.09–0.11 [m, SiCH(CH$_3$)Si, SiCH$_3$], 0.29–0.37 (m, SiCH$_2$CH$_2$Si), 0.97–1.01 [m, SiCH_3 (CH)Si], 2.12 [m, SiCH(OCH_2)], 2.54 [m, SiCH(OCH_2)], 2.84 [m, SiCH(OCH$_2$)]. ^{13}C NMR (CDCl$_3$, δ): -2.4, -1.9, -1.8, -1.7, -1.3, -0.6, 0.1, 1.3, 7.7, 7.8, 9.4, 11.5, 43.5, 44.3. ^{29}Si NMR (CDCl$_3$, δ): -20.1, -19.8, -19.1, -18.5, 1.0, 1.2, 1.8, 3.1, 7.5, 8.3.

Linear Epoxy-Model Compound [8(L)]. **5(L)** (0.06 g, 0.38 mmol), toluene (0.5 mL), and 3-chloroperoxybenzoic acid (0.038 g, 0.22 mmol) were charged into a two-necked flask. The mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in hexane (50 mL), and washed with 4×100 mL of a saturated NaHCO$_3$ water solution. The organic phase was then dried over MgSO$_4$. Removal of the solvent under reduced pressure afforded **8(L)** (0.04 g, 71%) as a colorless liquid. IR (KBr, ν): 2957, 2910, 1406, 1319, 1256, 1136, 1051, 947. ^{1}H NMR (CDCl$_3$, δ): -0.05–0.15 (m, 45H, SiCH$_3$), 0.29–0.45 (8H, SiCH$_2$CH$_2$Si), 2.15 [q, 1H, $J = 4.1$ Hz, 5.4 Hz, SiCH(OCH_2)], 2.52 [q, 1H, $J = 4.1$ Hz, 5.9 Hz, SiCH (OCH_2)], 2.81 [t, 1H, $J = 5.4$ Hz, 5.9 Hz, SiCH (OCH$_2$)]. ^{13}C NMR (CDCl$_3$, δ): -2.3, -1.5, -1.2, -0.5, 1.9, 7.8, 8.9, 9.4, 43.7, 44.4. ^{29}Si NMR (CDCl$_3$, δ): -20.8, -19.7, 1.3, 3.2, 7.0, 8.6.

RESULTS AND DISCUSSION

Monomer Synthesis

As the simplest AB$_x$ type monomer for preparation of the
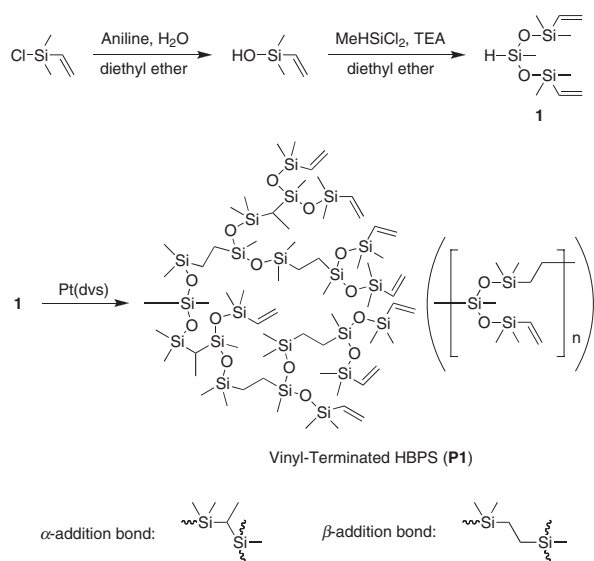
Scheme 1. Synthesis and polymerization of monomer **1**.

vinyl-terminated HBPS **P1**, AB$_2$ type monomer **1**, 1,1,3,5,5-pentamethyl-1,5-divinyltrisiloxane, was successfully prepared using the reactions outlined in Scheme 1. In the first step, hydrolysis of vinyldimethylchlorosilane was carried out to generate vinyldimethylsilanol. Condensation of the resulting vinyldimethylsilanol with dichloromethylsilane was performed in the presence of triethylamine to afford **1** in 45% yield. The structure of **1** was characterized by IR, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies. In the IR spectrum, peaks due to the Si-O stretching vibration were observed at 1059 cm^{-1}. The ^{1}H NMR spectrum clearly showed signals at 4.65 and 5.7–6.1 ppm due to the silicon hydride (Si-H) and vinyl groups, respectively. In the ^{13}C and ^{29}Si NMR spectra, four carbon signals and two silicon signals were observed. Analyses of these spectra confirmed that the desired monomer **1** was obtained without a side product.

Polymerization of 1

Hydrosilylation of **1** was carried out at room temperature for 15 h in the presence of 0.1 mol % of Pt(dvs) in bulk to give **P1** (Scheme 1). **P1** was isolated in 47% yield after precipitating three times from a diluted diethylether solution into methanol. GPC indicated a symmetrical and unimodal peak with a number average molecular weight (M_n) of 4140 and a polydispersity index of 1.48 (versus polystyrene standard in THF). GPC-MALLS measurement indicated that the absolute value of the number average molecular weight is 4810 with a polydispersity index of 1.60 (Table I). Consistent with dendritic topology, the relative molecular weight value by calculated by GPC against polystyrene standards is a little smaller than the absolute value measured by GPC-MALLS measurement. The IR spectrum showed strong siloxane and vinyl bands at 1047 and 955 cm^{-1}. No absorption corresponding to Si-H around at 2150 cm^{-1} was observed. In the ^{1}H NMR spectrum, characteristic peaks were found at 0.97 and 0.40 ppm, which were assigned to methyl and methylene groups of the α- and β-addition products, respectively

Table I. Molecular Weight of **P1** and **P2**

Polymer	GPC[a]		MALLS[b]	
	M_n	M_w/M_n	M_n	M_w/M_n
P1	4140	1.48	4810	1.60
P2	3950	1.45	4710	1.52

[a]Calculated by GPC against polystyrene standards. [b]Calculated by GPC-MALLS.
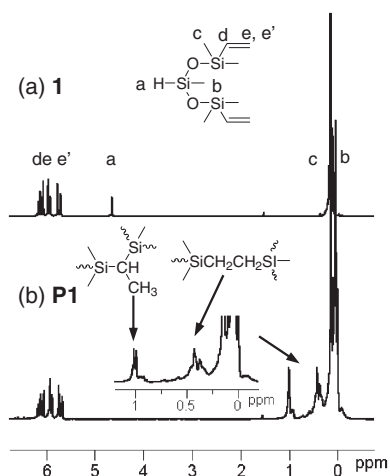
Figure 1. ^{1}H NMR spectra of **1** (a), and **P1** (b).

Figure 2. ^{13}C NMR spectra of **P1**: DEPT-135 (a), DEPT-90 (b), ^{13}C NMR (c).

Scheme 2. Epoxidation of **P1**.

Figure 3. ^{1}H NMR spectrum of **P2**.

(Figure 1). As shown in Figure 2, DEPT NMR spectrum revealed that the carbon signals of methyl and methine groups corresponding to the structure of α-addition product were observed at 8.1 and 11.8 ppm, respectively. The methylene carbon signals due to the structure of β-addition product were found at 8.9 and 9.6 ppm. The ^{29}Si NMR spectrum showed three multiplets at around −21.1, −4.3, and 7.6 ppm, which can be assigned to silicon atoms of -O-SiMe$_2$-CH$_2$-, -O-SiMe$_2$-CH=CH$_2$, -CH$_2$-SiMe(O-)$_2$ in **P1**, respectively. Relative integration of the signals of α- and β-addition products in the ^{1}H NMR spectrum indicates that the β-addition is present in 64% of the linkages. This value is in good agreement with that of polycarbosiloxane prepared by hydrosilylation of dimethyl-(dimethylvinylsiloxy)silane.[12] The vinyl groups attached to a silicon atom with low steric hindrance can allow the formation of α-addition product during the hydrosilylation reaction.

Epoxidation of P1

Epoxidation was used to evaluate the potential of the terminal vinyl group conversion. The epoxidation of the terminal vinyl groups of **P1** was performed with 3-chloroperoxybenzoic acid at room temperature for 48 h and afforded the epoxy-terminated HBPS **P2** (Scheme 2). The IR spectrum of **P2** indicated characteristic epoxy groups at 1231, 1319 cm^{-1}. ^{1}H NMR analysis showed the complete disappearance of the terminal vinyl groups and the appearance of the methylene and methine protons corresponding to the epoxy groups at 2.15, 2.57, and 2.86 ppm (Figure 3). In the ^{13}C NMR spectrum, characteristic signals were found at 43.5 and 44.3 ppm, which
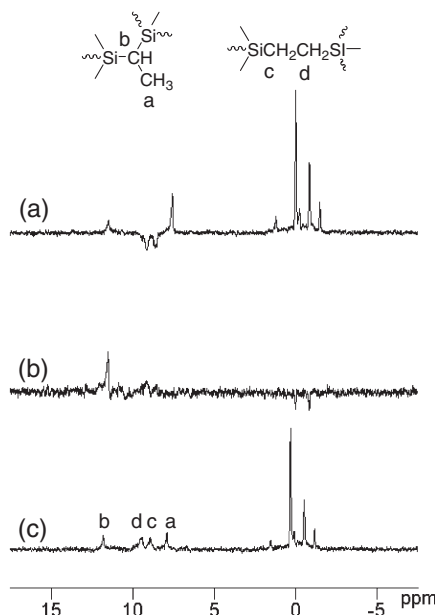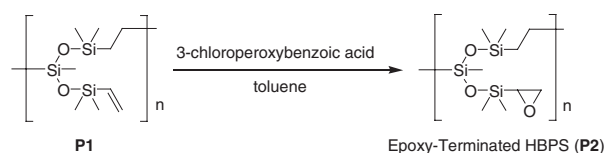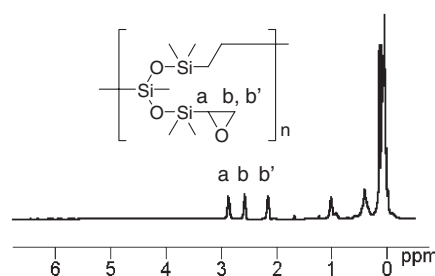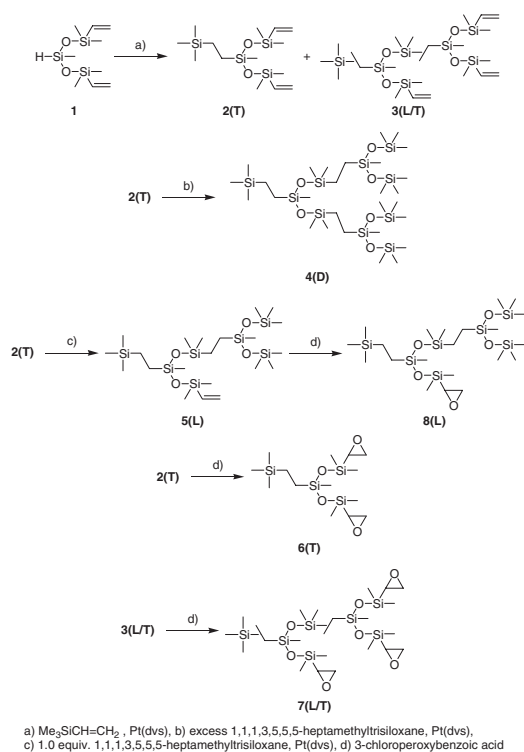
were assigned to the methylene and methine carbons of the epoxy group, respectively. All the signals were clearly assigned to **P2** in the spectra, indicating quantitative conversion of the terminal vinyl groups. The absolute values of the number average molecular weight (M_n) and polydispersity were 4710 and 1.52, respectively (Table I).
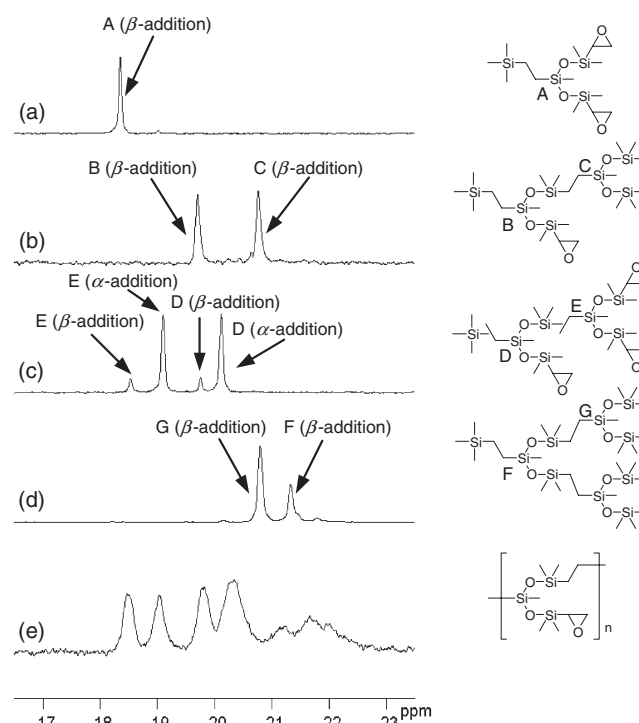
Degree of Branching (DB)

An important characteristic of hyperbranched polymers is degree of branching (DB) because properties such as solubility and viscosity strongly depend on the primary branching structure.[11] We initially attempted to determine the DB of **P1** from the ^{29}Si NMR signals, but it was difficult to estimate since the signals overlapped. Thus, the ^{29}Si NMR signals from

a) Me₃SiCH=CH₂ , Pt(dvs), b) excess 1,1,1,3,5,5,5-heptamethyltrisiloxane, Pt(dvs),
c) 1.0 equiv. 1,1,1,3,5,5,5-heptamethyltrisiloxane, Pt(dvs), d) 3-chloroperoxybenzoic acid

Scheme 3. Syntheses of the model compounds.

Figure 4. ^{29}Si NMR spectra of **6(T)** (a), **8(L)** (b), **7(L/T)** (c), **4(D)** (d), and **P2** (e).

P2 were used for the DB estimation of HBPS in this study. In the ^{29}Si NMR spectrum from **P2**, the four distinct silicon signals and a broad signal attributed to -SiMe(O-)$_2$ at -18.5, -19.0, -19.8, -20.3, and around -21.5 ppm were observed, respectively. These are due to α- and β-addition linear, terminal, and dendritic units.

In order to characterize these signals conclusively, several model compounds were prepared, which correspond to the linear (L), terminal (T), linear/terminal (L/T), and dendritic type (D) structures as shown in Scheme 3. The first synthetic step for the model compounds was hydrosilylation of monomer **1** performed with an excess amount of vinyltrimethylsilane to obtain compounds **2(T)** and **3(L/T)**. Dendritic model compound **4(D)** was synthesized by hydrosilylation of **2(T)** and an excess amount of 1,1,1,3,5,5,5-heptamethyltrisiloxane. In order to obtain the linear model compound, hydrosilylation of **2(T)** was carried out with 1.0 equivalent of 1,1,1,3,5,5,5-hepta-methytrisiloxane and an asymmetric compound with one terminal vinyl group **5(L)** was obtained. Subsequently, epox-idation of the vinyl groups of **2(T)**, **3(L/T)**, and **5(L)** was performed and afforded the terminal epoxy-model compound **6(T)**, the linear/terminal epoxy-model compound **7(L/T)** and the linear epoxy-model compound **8(L)**, respectively. ^{1}H NMR spectra of **4(D)**, **6(T)**, and **8(L)** indicated only β-addition products. In contrast, **7(L/T)** consisted of a mixture of α- and β-addition products, as characteristic proton signals were observed at 0.99 and 0.33 ppm in the ^{1}H NMR spectrum, which are consistent with methyl and methylene groups of α- and β-addition products.

The expanded ^{29}Si NMR spectra of these model compounds and **P2** are shown in Figure 4. The spectrum of **6(T)** had a single silicon signal corresponding to the terminal β-addition type -SiMe(O-)$_2$ at -18.3 ppm. In the spectrum of **8(L)**, two signals were observed at -19.7 and -20.8 ppm which were assigned to the linear and dendritic β-addition type -SiMe(O-)$_2$, respectively. In the case of **7(L/T)**, four silicon signals were observed at -18.5, -19.1, -19.8, and -20.1. The signals at -18.5 and -19.1 were assigned to the terminal β- and α-addition type -SiMe(O-)$_2$, while the signals at -19.8 and -20.1 were due to the linear β- and α-addition type -SiMe(O-)$_2$, respectively. In the spectrum of **4(D)**, the two signals of the β-addition type -SiMe(O-)$_2$ were observed at -20.8 and -21.3 ppm. Based on the characterization of the model compounds, the silicon signals of **P2** were assigned to the corresponding silicon atoms of the terminal β-addition unit (-18.5 ppm), the terminal α-addition unit (-19.0 ppm), the linear β-addition unit (-19.8 ppm), the linear α-addition unit (-20.3 ppm), and the dendritic unit (around -21.5 ppm). Chemical shifts of the silicon signals in the **P2** spectrum are good agreement with those of the model compounds.

Table II. Thermal properties of **P1** and **P2**

Polymer	$T_g(°C)^a$	$T_{10}(°C)^b$
P1	-97	499
P2	-77	440

^{a}Determined by DSC at heating rate of 10 °C/min on the second scan.
^{b}Determined by TGA at heating rate of 10 °C/min in N₂.

Table III. Solubility of **P1** and **P2**

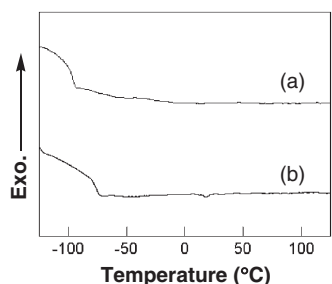| Polymer	Hexane	Toluene	Et$_2$O	CH$_2$Cl$_2$	CHCl$_3$	THF	Acetone	MeOH	DMF	DMAc
P1	++	++	++	++	++	++	−	−	−	−
P2	++	++	++	++	++	++	++	−	−	−

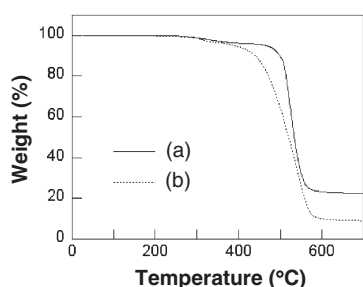**Figure 5.** DSC curves of **P1** (a), and **P2** (b).

Figure 6. TGA curves of **P1** (a), and **P2** (b).

The degree of branching of **P2** was determined following Frey's definition (1).[13] By the integrated intensities of the signals, DB of **P2** was calculated as 0.57 with the Frey's definition, which is a typical numerical value for hyperbranched polymers.

$$\text{Degree of Branching} = \frac{2[D]}{2[D] + [L]} \qquad (1)$$

Thermal Properties and Solubility of P1 and P2

The thermal behavior of **P1** and **P2** was examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In order to eliminate the effect of thermal history on sample transitions, the polymers were first heated to 100 °C and held at this temperature for 1 min, before cooling to −130 °C at a rate of 10 °C min^{-1}. As shown in Figure 5 and Table II, **P1** and **P2** exhibit glass transition temperatures (T_g) below at −70 °C due to the highly flexible siloxane skeleton and the branching structure as the primary structure. From the TGA curves, **P1** and **P2** also have good thermal stability as the 10% weight loss temperatures (T_{10}) are greater than 440 °C in nitrogen (Figure 6 and Table II). In the differential thermal analysis (DTA) curve of **P2**, an exothermic peak was observed at 315 °C. This is due to the crosslink reaction of the terminal epoxy groups.

P1 and **P2** exhibit excellent solubility in hexane, diethyl ether, tetrahydrofuran, dichloromethane and chloroform while they are insoluble in alcohols and aprotic polar solvents such as *N,N*-dimethylformamide and *N,N*-dimethylacetoamide (Table III).

CONCLUSION

We have studied synthesis of HBPS with terminal vinyl and epoxy groups to evaluate the potential for terminal group modification and the degree of branching. The vinyl-terminated HBPS was readily prepared by hydrosilylation of 1,1,3,5,5-pentamethyl-1,5-divinyltrisiloxane in the presence of Pt(dvs) in bulk. It was found that the resulting **P1** consists of a mixture of α- and β-addition products and the ratio is 36:64. The epoxy-terminated HBPS was obtained by epoxidation of the vinyl-terminated HBPS with 3-chloroperoxybenzoic acid. The degree of branching was estimated as 0.57 *via* a detail characterization of the ^{29}Si NMR spectra by model compounds. The large number of the vinyl and epoxy groups of HBPS can be modified to various functional groups that can offer unique organic and inorganic hybrid materials for surfaces and interfaces.

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