

## Synthesis, End-Functionalization and Characterization of Hyperbranched Polysiloxysilanes from AB<sub>3</sub> Type Monomer

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**Abstract:** Hyperbranched polysiloxysilanes (HBPSs), with a variety of terminal functional groups (vinyl, epoxy, carboxyl and hydroxyl), were synthesized by the self-polymerization of an AB<sub>3</sub> type monomer of tris(dimethylvinylsiloxy) silane, with subsequent end-functionalizations, such as epoxidation and radical addition reaction, respectively. The ratio of the  $\alpha$ - and  $\beta$ -addition linkages in the HBPS polymerized by hydrosilylation of the AB<sub>3</sub> monomer was found to be approximately 1 to 3. The thermal stability and solubility were affected by the terminal functional groups.

**Keywords:** hyperbranched polymer, polysiloxysilane, hydrosilylation, end-functionalization.

### Introduction

Hyperbranched polymers possess a randomly branching structure as well as a number of terminal functional groups. They are generally prepared by self-polymerization of AB<sub>x</sub> type monomers. This class of polymers has become of increasing interest as new functionalized polymers whose properties should differ significantly from those of linear polymers and a potential alternative for the perfectly branched dendrimers that have to be constructed by taking an usually tedious and stepwise approach.<sup>1,2</sup>

Polysiloxanes and their derivatives have unique properties such as low glass transition temperature ( $T_g$ ), high decomposition temperature, water repulsion, and good dielectric property.<sup>3,4</sup> They offer intriguing possibilities for the materials especially as coatings, adhesives, and surfactants because of their good affinity between organic and inorganic materials. Recently, we found that hyperbranched polysiloxysilanes (HBPSs) possess strong affinity with metal oxide surface and the immobilized silica bead with the HBPS derivative can be applied as a column packing material for temperature-responsive high-performance liquid chromatography (HPLC).<sup>5</sup> Furthermore, we have successfully applied the HBPS to an aluminum solid electrolytic capacitor to improve adhesion for the interface of aluminum oxide and conductive polymer of poly(3,4-ethylenedioxythiophene) (PEDOT).<sup>6</sup>

In our previous studies, we used HBPS prepared from AB<sub>2</sub> type monomer of 1,1,3,5,5-pentamethyl-1,5-divinyl-trisiloxane

(A: Si-H, B: vinyl). Increasing Si-O content in the HBPS and adding a variety of terminal functional groups may improve the affinity to various inorganic materials. Although Rubinsztajn *et al.* have reported the synthesis of HBPS with highly Si-O content by the polymerization of AB<sub>3</sub> type monomer such as vinyltris(dimethylsiloxy)silane and tris(dimethylvinylsiloxy)silane, the detail structural characterization and various end-functionalization have not been conducted.<sup>7</sup>

In this study, we report a successful synthesis of HBPS terminated by the vinyl functional group from AB<sub>3</sub> type monomer of tris(dimethylvinylsiloxy)silane and end-functionalization of the HBPS obtained from the vinyl to epoxy, carboxyl, and hydroxy groups.

### Experimental

**Measurements.** NMR (<sup>1</sup>H, 300 MHz; <sup>13</sup>C, 75 MHz; <sup>29</sup>Si, 59.4 MHz) spectra were obtained in CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> on a JEOL JNM-AL 300 NMR spectrometer. Chemical shifts are reported in ppm, relative to CHCl<sub>3</sub> ( $\delta$  7.24, <sup>1</sup>H), CDCl<sub>3</sub> ( $\delta$  77.0, <sup>13</sup>C), and tetramethylsilane ( $\delta$  0.0, <sup>29</sup>Si). Infrared (IR) spectra were recorded using a JASCO FT/IR 460 plus spectrometer. Gel permeation chromatography (GPC) measurements using THF as an eluent, were carried out by using a JASCO HBPX 880Pu, two polystyrenedivinylbenzene columns (Shodex GPC 803L and Shodex GPC804L), and a Shodex RI-71 refractive index detector. Thermogravimetric analyses (TGA) were carried out using a Seiko TGA 6200 thermogravimetric analyzer at a heating rate of 10 °C min<sup>-1</sup> in nitrogen. Differential scanning calorimetry (DSC) measurements were carried

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out using a Seiko DSC 6200 at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in nitrogen. The glass transition temperature ( $T_g$ ) was taken at the middle of the step transition in the second heating run.

**Materials.** Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt(dvs)) solution in xylenes (Aldrich) was used as received. 2-Mercaptoacetic acid was purified by distillation under reduced pressure. Toluene was dried and distilled over sodium metal and benzophenone ketyl under nitrogen. The other reagents and solvents were used as received.

**Tris(dimethylvinylsiloxy)silane (1).** Diethylether (1.6 L), triethylamine (121.43 g, 1.2 mol), and water (10.81 g, 0.6 mol) were charged into a separable three-necked flask equipped with a dropping funnel, a condenser and mechanical stirrer. Chlorodimethylvinylsilane (72.39 g, 0.6 mol) was slowly added dropwise to the solution mixture at  $0^{\circ}\text{C}$  with vigorous stirring. The mixture was stirred for 30 min at this temperature, then trichlorosilane (27.09 g, 0.2 mol) was added slowly to the mixture at  $0^{\circ}\text{C}$  and the solution was further stirred overnight at room temperature. Then the precipitate of triethylamine hydrochloride was filtered off and the solution was washed with 0.3 M HCl and saturated NaCl solution, and dried with  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. Distillation of the residue under reduced pressure afforded **1** as a colorless liquid (42.67 g, 63%). b.p.  $51^{\circ}\text{C}/0.4\text{ mmHg}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.18 (s, 18H,  $\text{SiCH}_3$ ), 4.23 (s, 1H,  $\text{SiH}$ ), 5.74 (q, 3H,  $J=4.20\text{ Hz}$ , 20.1 Hz,  $\text{Si-CH=CH}_2$ ), 5.93 (q, 3H,  $J=4.20\text{ Hz}$ , 14.7 Hz,  $\text{Si-CH=CH}_2$ ), 6.11 (q, 3H,  $J=14.7\text{ Hz}$ , 20.1 Hz,  $\text{Si-CH=CH}_2$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.2, 132.1, 138.7.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.1, -3.7. IR (KBr,  $\nu$ ): 786, 813, 1067, 1255, 1406, 1595, 2207, 2961.

**Vinyl-terminated HBPS (P1).**  $\text{AB}_3$  type monomer **1** (19.96 g, 60 mmol) was charged into a two-necked flask. Pt (dvs) solution in xylenes (0.6 mL, 0.060 mmol) was added at  $0^{\circ}\text{C}$  with vigorous stirring. The system was then allowed to warm to room temperature and stirred for 24 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 (17.34 g, 61%).  $M_n=5,500$ ,  $M_w/M_n=1.64$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -0.05 (br,  $\text{Si-CH(CH}_3\text{)-Si}$ ), 0.05 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{CH}_2\text{-Si}$ ,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 0.15 (br,  $\text{Si(CH}_3\text{)-CH=CH}_2$ ), 0.36 (m,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 0.49 (m,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 1.04 (m,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 5.71 (br,  $\text{Si-CH=CH}_2$ ), 5.90 (br,  $\text{Si-CH=CH}_2$ ), 6.11 (br,  $\text{Si-CH=CH}_2$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -0.7, 0.3, 5.7, 8.3, 8.8, 9.6, 131.7, 139.2.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.1, -3.7, 8.7. IR (KBr,  $\nu$ ): 784, 837, 1054, 1254, 1595, 2959.

**Epoxy-terminated HBPS (P2).** **P1** (3.99 g, 12 mmol), toluene (48 mL), and 3-chloroperoxybenzoic acid (8.28 g, 48 mmol) were charged into a two-necked flask. The mixture was stirred for 48 h at room temperature. Then the generated precipitate was filtered off. The residue was dissolved into hexane (300 mL), and filtered off to remove excess amount

of 3-chloroperoxybenzoic acid. Then the solution was extracted with  $4 \times 200\text{ mL}$  of saturated solution of  $\text{Na}_2\text{CO}_3$ . The organic layer was then dried over  $\text{MgSO}_4$ . Removal of the solvent under high vacuum for 6 h afforded **P2** (3.46 g, 79%) as yellowish viscous liquid.  $M_n=4,900$ ,  $M_w/M_n=1.69$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.07 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 0.15 (br,  $\text{Si(CH}_3\text{)-epoxy}$ ), 0.39 (m,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 0.46 (m,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 1.06 (m,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 2.15, 2.56, 2.85 (br,  $\text{Si-epoxy}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -2.0, -0.8, 5.4, 8.1, 8.4, 9.4, 43.2, 44.1.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.3, 2.3, 8.74. IR (KBr,  $\nu$ ): 789, 836, 1057, 1231, 1254, 2959.

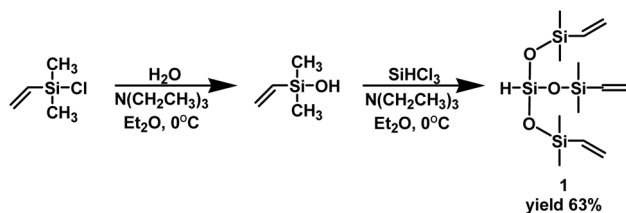
**Carboxyl-terminated HBPS (P3).** **P1** (3.99 g, 12 mmol), AIBN (0.20 g, 1.2 mmol), 2-mercaptoacetic acid (3.32 g, 36 mmol) and toluene (5 mL) were charged into a round-bottom flask. The mixture was stirred for 4 h at  $80^{\circ}\text{C}$ . Then toluene and excess amount of 2-mercaptoacetic acid was removed by evaporation from the mixture. The residue was dissolved in THF and purified by repeated precipitation from the solution into water. The precipitated viscous fluid was dissolved in THF and dried with  $\text{MgSO}_4$ . Removal of the solvent afforded **P4** (2.76 g, 45%) as a colorless viscous liquid.  $M_n=10,100$ ,  $M_w/M_n=2.51$ .  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 0.05 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 0.09 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-S}$ ), 0.35 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 0.43 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 0.86 (m,  $\text{Si-CH}_2\text{-CH}_2\text{-S}$ ), 1.01 (m,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 2.63 (m,  $\text{Si-CH}_2\text{-CH}_2\text{-S}$ ), 3.17 (br,  $\text{S-CH}_2\text{-COOH}$ ), 12.29 (br,  $\text{COOH}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) -0.8, 0.1, 5.4, 8.2, 8.4, 9.4, 18.0, 26.7, 34.0, 171.6. IR (KBr,  $\nu$ ): 782, 838, 1054, 1253, 1420, 1708, 2956.

**Hydroxyl-terminated HBPS (P4).** A 100 mL round-bottom flask was charged with **P1** (3.99 g, 12 mmol), AIBN (0.20 g, 1.2 mmol), 2-mercaptoethanol (2.81 g, 36 mmol) and toluene (5 mL), and stirred for 4 h at  $80^{\circ}\text{C}$ . Then toluene and excess amount of 2-mercaptoethanol was removed by evaporation from the mixture. The residue was dissolved in THF and the solution was poured into water. The precipitated viscous fluid was dissolved in THF and dried with  $\text{MgSO}_4$ . After colorless viscous liquid. Yield: 1.62 g (29%).  $M_n=8,400$ ,  $M_w/M_n=1.87$ .  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 0.04 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 0.09 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-S}$ ), 0.34 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 0.41 (br,  $\text{Si(CH}_3\text{)-CH}_2\text{-CH}_2\text{-Si}$ ), 0.83 (m,  $\text{Si-CH}_2\text{-CH}_2\text{-S}$ ), 1.01 (m,  $\text{Si(CH}_3\text{)-CH(CH}_3\text{)-Si}$ ), 2.49 (m,  $\text{Si-CH}_2\text{-CH}_2\text{-S}$ ), 2.53 (m,  $\text{S-CH}_2\text{-CH}_2\text{-OH}$ ), 3.48 (br,  $\text{S-CH}_2\text{-CH}_2\text{-OH}$ ), 4.73 (br,  $\text{OH}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) -0.8, 0.1, 5.3, 8.0, 8.3, 9.3, 18.6, 26.2, 33.8, 60.8. IR (KBr,  $\nu$ ): 763, 783, 838, 1052, 1410, 2955, 3365.

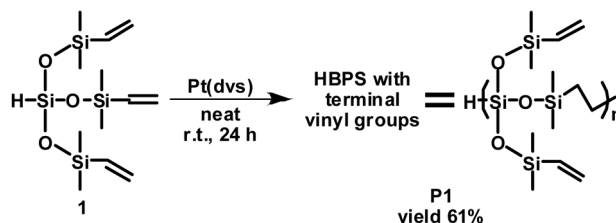
## Results and Discussion

**Monomer Synthesis.**  $\text{AB}_3$  type monomer of tris(dimethylvinylsiloxy)silane (**1**) was prepared by one-pot synthesis

Scheme I



Scheme II



method according to Scheme I. At first, hydrolysis of chlorodimethylvinylsilane was carried out by using stoichiometric water in diethylether to give dimethylvinylsilanol. Trichlorosilane was then added to the solution in the presence of triethylamine to afford **1**. The yield of **1** after distillation was 63%, which was 13% higher than that of the reference data.<sup>7</sup> Dimethylvinylchlorosilane and trichlorosilane were easily and efficiently hydrolyzed via a one-pot method to prepare the AB<sub>3</sub> type monomer.

The structure of **1** was characterized by IR, <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopies. In the IR spectrum, two remarkable characteristic peaks due to the stretching vibrations of Si-O and vinyl group at 1067 and 1595 cm<sup>-1</sup> were observed respectively. The <sup>1</sup>H NMR spectrum clearly showed signal at 4.23 ppm due to the silicon hydride (Si-H). The signals of

vinyl group were observed around 5.7–6.1 ppm. The <sup>13</sup>C NMR spectrum showed three carbon signals at 0.2, 132.1, and 138.7 ppm which are consistent with methyl group connected to silicon and vinyl group, respectively. In the <sup>29</sup>Si NMR spectrum, two silicon signals at -64.7 and -3.7 ppm were clearly assigned to hydrosilyl and dimethylsilyl groups, respectively. Analyses of the all spectra confirmed that the desired monomer **1** was obtained without a side product.

**Polymer Synthesis.** Hydrosilylation reaction of **1** was carried out at room temperature for 24 h in the presence of 0.1 mol% of Pt(dvs) in bulk to give **P1** (Scheme II). **P1** was isolated in 61% yield after reprecipitation three times from the diluted diethyl ether solution into methanol. Gel permeation chromatography (GPC) showed a symmetrical and unimodal peak. **P1** has a number average of molecular

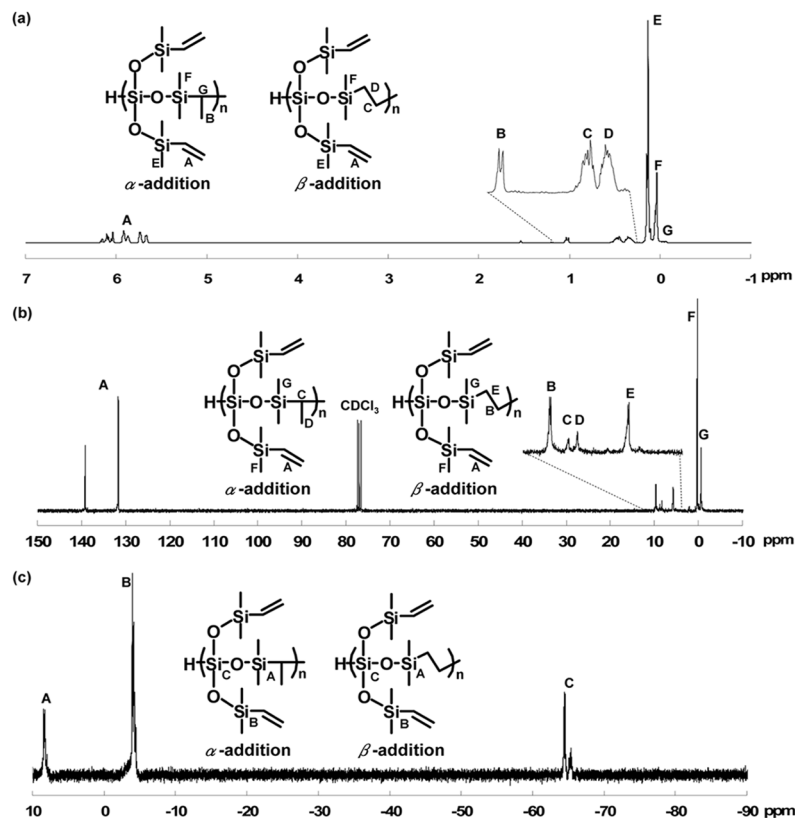
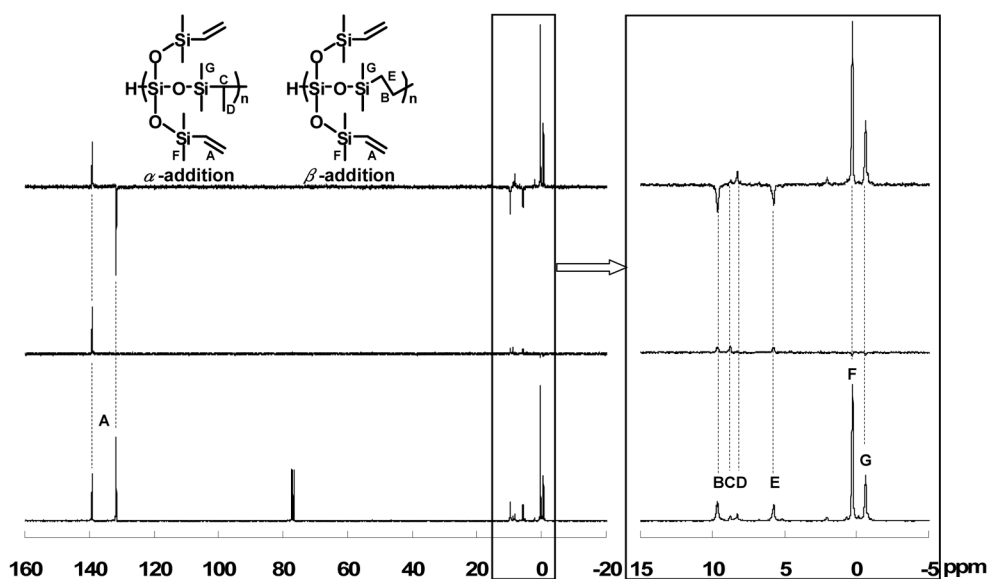


Figure 1. (a) <sup>1</sup>H, (b) <sup>13</sup>C, and (c) <sup>29</sup>Si NMR spectra of **P1**.

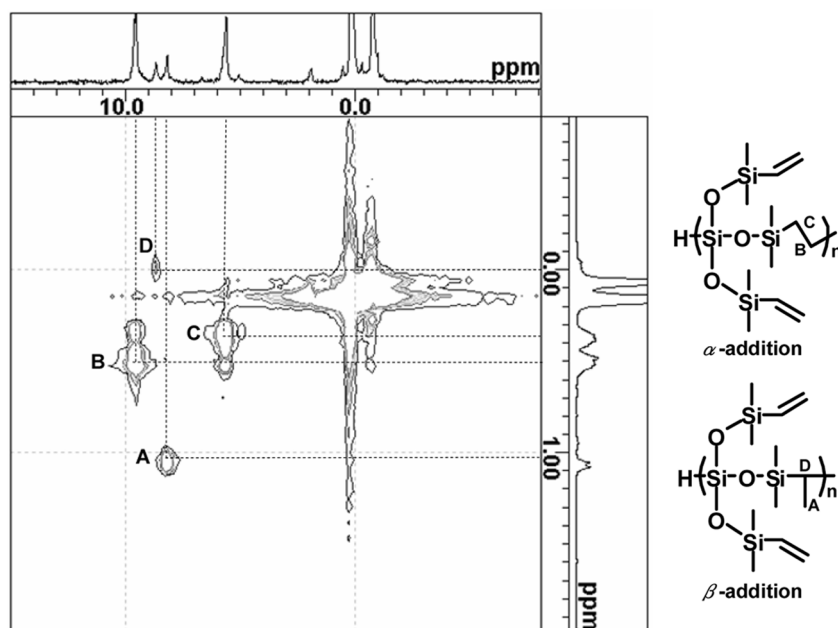
weights  $M_n$  of 5,500 with a polydispersity index of 1.64 (versus polystyrene standard in tetrahydrofuran). Since the HBPS is considerably more flexible than polystyrene, the molecular weights obtained by GPC are only rough estimations.

In order to characterize the structure of **P1**, IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT 90 and 135, C-H COSY, and  $^{29}\text{Si}$  NMR measurements were carried out. The IR spectrum showed strong siloxane band at  $1054\text{ cm}^{-1}$  and vinyl band at  $1595\text{ cm}^{-1}$ . No peaks corresponding to Si-H around at  $2210\text{ cm}^{-1}$  was observed. In the  $^1\text{H}$  NMR spectrum, two characteristic peaks were found

at 1.04 and -0.05 ppm, which are assigned to methyl and methine groups due to the  $\alpha$ -addition product, respectively (Figure 1(a)). The proton signals at 0.49 and 0.36 ppm came from the methylene groups of the  $\beta$ -addition product. The  $^{13}\text{C}$  NMR (Figure 1(b)), DEPT 90, and 135 (Figure 2), and C-H COSY (Figure 3) spectra revealed the assignments of all carbon signals corresponding to the  $\alpha$ - and  $\beta$ -addition products. The carbon signals of methyl and methine groups corresponding to the structure of  $\alpha$ -addition product were observed at 8.3 and 8.8 ppm, respectively. The methylene

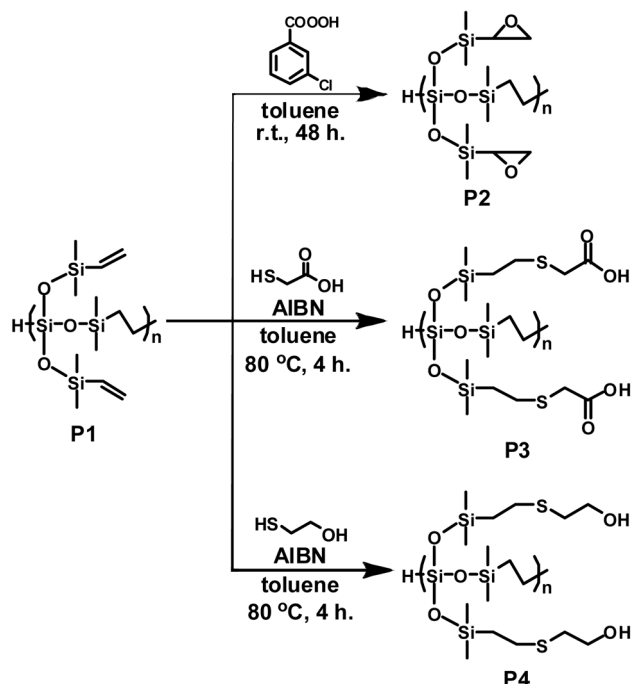


**Figure 2.**  $^{13}\text{C}$  NMR spectra of **P1**: (a)  $^{13}\text{C}$  NMR, (b) DEPT-90, and (c) DEPT-135.



**Figure 3.** H-C COSY NMR spectrum of **P1**.

Scheme III



carbon signals due to the structure of  $\beta$ -addition product were found at 5.7 and 9.6 ppm. The  $^{29}\text{Si}$  NMR spectrum showed the three signals at around -64.1, -3.7, and 8.7 ppm, which can be reasonably assigned to silicon atoms of  $-\text{CH}_2-\text{Si}(\text{O}-)_3$ ,  $-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}_2-$ , and  $-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$  in **P1**, respectively. In the  $^1\text{H}$  NMR spectrum, relative integration of the signals corresponding to  $\alpha$ - and  $\beta$ -addition products indicated that the  $\beta$ -addition is present in 74% of the linkages.

#### End-Functionalization of Vinyl Terminated HBPS.

The epoxidation of the terminal vinyl groups of **P1** performed with 3-chloroperoxybenzoic acid at room temperature for 48 h afforded the epoxy-terminated HBPS (**P2**) (Scheme III). The IR spectrum of **P2** indicated characteristic epoxy groups at 1231, 1319  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR analysis showed the complete disappearance of the terminal vinyl groups and the newly appearance of the methylene and methine protons corresponding to the epoxy groups at 2.15, 2.56, and 2.85 ppm (Figure 4(b)). The  $^{13}\text{C}$  NMR spectrum showed characteristic signals at 43.2 and 44.1 ppm, which are assigned to methylene and methane carbons of epoxy groups, respectively. All the signals were clearly assigned in the spectra, indicating quantitative conversion of the terminal vinyl groups. The number average of molecular weight

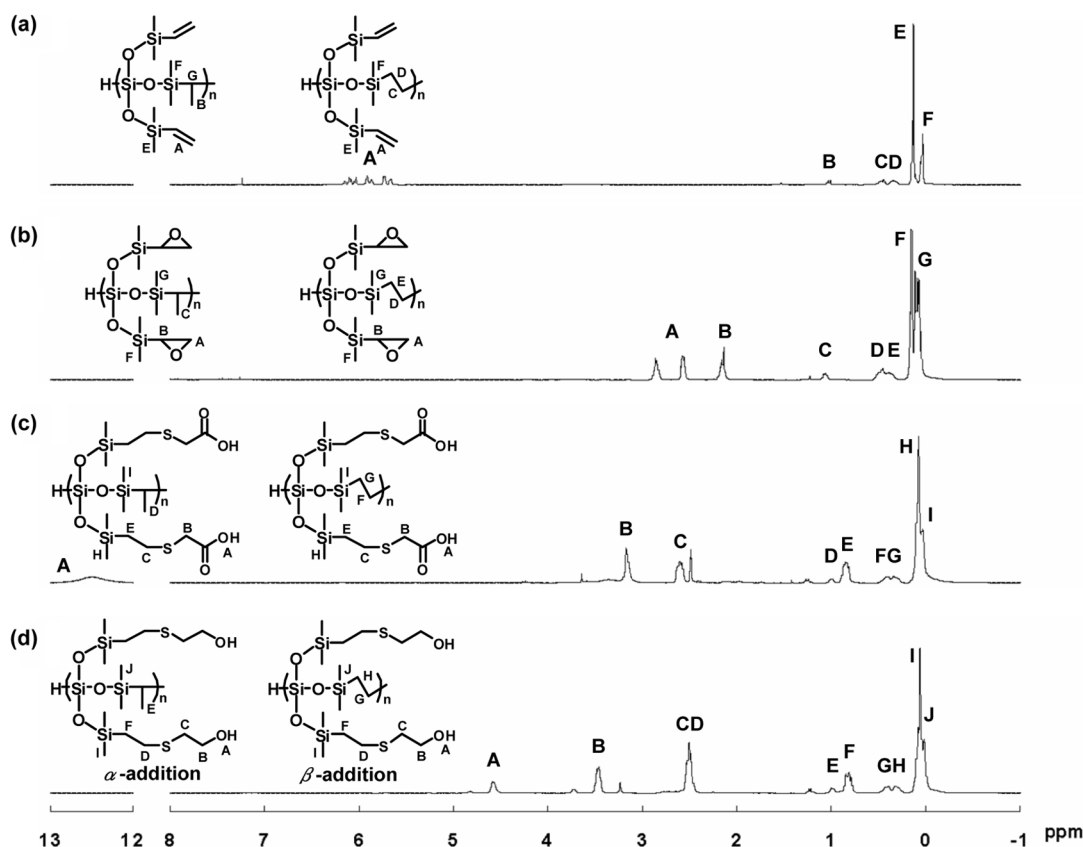


Figure 4.  $^1\text{H}$ -NMR spectra of (a) **P1** in  $\text{CDCl}_3$ , (b) **P2** in  $\text{CDCl}_3$ , (c) **P3** in  $\text{DMSO}-d_6$ , and (d) **P4** in  $\text{DMSO}-d_6$ .

**Table I. Molecular Weights and Thermal Behaviors of P1-4**

Polymer	$M_n^a$	PDI <sup>a</sup>	$T_d^b$ (°C)	$T_{ds}^b$ (°C)	Char Yield <sup>c</sup> (%)	$T_g^d$ (°C)
<b>P1</b>	5,490	1.64	257	430	55	-103
<b>P2</b>	4,890	1.68	275	486	38	-89
<b>P3</b>	10,100	2.28	165	213	24	-35
<b>P4</b>	8,420	1.89	190	241	25	-59

<sup>a</sup>Determined by GPC in THF relative to polystyrene with RI. <sup>b</sup>Determined by TGA (heating rate: 10 °C/min). <sup>c</sup>Determined by TGA at 700 °C (heating rate: 10 °C/min). <sup>d</sup>Determined by DSC (heating rate: 10 °C/min).

$M_n$  and polydispersity were 4,900 and 1.69, respectively.

The carboxylation and hydroxylation of the terminal vinyl groups of **P1** were carried out by radical addition of 2-mercaptoacetic acid and 2-mercaptoethanol to the vinyl groups in the presence of AIBN, respectively (Scheme III). The reactions were proceeded quantitatively under mild conditions. In the <sup>1</sup>H NMR spectra, the signals corresponding to the terminal vinyl groups were completely disappeared and the new signals corresponding to the methylene protons of the 2-carboxylethyl and 2-hydroxyethyl groups of **P3** and **P4** appeared respectively (Figures 4(c) and 4(d)). Analyses of the all spectra supported the successful endfunctionalization of the terminal vinyl group of **P1** without any side reactions.

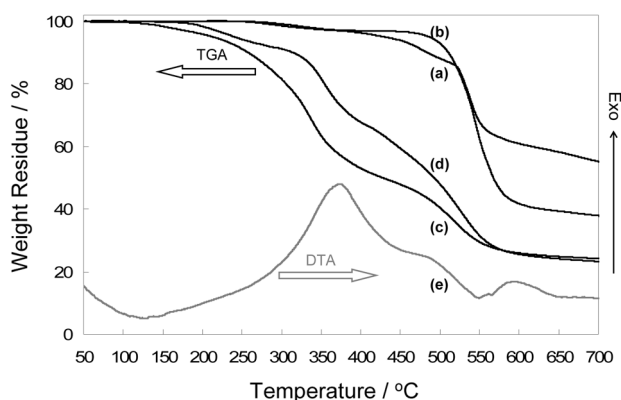
**Characterization of HBPSs.** The thermal behavior of **P1-4** was examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table I). In order to

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<sup>-1</sup>. **P1** and **P2** exhibit a very low glass transition temperature ( $T_g$ ) below -80 °C due to the highly flexible siloxane skeleton and the branching structure. The differential thermal analysis (DTA) curve of **P2** showed the exothermic peak at 315 °C (Figure 5(e)). Due to the crosslink reaction of the terminal epoxy groups. The  $T_g$ s of **P3** and **P4** are significantly higher than that of **P1**, presumably because of the strong intra- and intermolecular interactions by the terminal polar functional groups. The TGA curves of **P1** and **P2** showed a good thermal stability. The 5% weight loss temperatures ( $T_{ds}$ ) were over 430 °C in nitrogen. On the other hand, the weight losses of **P3** and **P4** started relatively at lower temperatures (less than 190 °C) because of the thermal decomposition of the terminal polar functional groups (Figures 5(a)-(d)).

**P1** and **P2** exhibited excellent solubility in hexane, diethyl ether, tetrahydrofuran, dichloromethane and chloroform while they were not soluble in alcohols and aprotic polar solvents such as dimethylformamide and *N,N*-dimethylacetamide. **P3** and **P4** showed poor solubility in hexane and toluene due to the polar terminal groups, but they were dissolved well in alcohols (Table II).

## Conclusions

In summary, a series of HBPS with a variety of terminal functional groups was successfully synthesized by the self-polymerization of AB<sub>3</sub> type monomer of tris(dimethylvinyl-siloxy)silane and the subsequent endfunctionalizations. The ratio of  $\alpha$ - and  $\beta$ -addition linkages in the HBPS polymerized



**Figure 5.** TGA curves of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, and (e) DTA curve of **P2**.

**Table II. Solubility of P1-4**

Polymer	Hexane	Toluene	CHCl <sub>3</sub>	Et <sub>2</sub> O	EtAc	THF	Acetone	CH <sub>3</sub> CN	EtOH	MeOH	H <sub>2</sub> O
<b>P1</b>	++	++	++	++	++	++	++	-	-	-	-
<b>P2</b>	+	++	++	++	++	++	++	++	++	+	-
<b>P3</b>	-	-	+	++	++	++	++	-	++	++	-
<b>P4</b>	-	-	+	+	+	++	++	+	++	++	-

++: soluble, +: partially soluble, -: insoluble.

by hydrosilylation of the AB<sub>3</sub> monomer was found to be approximately 1 to 3. End-functionalizations of the HBPS terminated by the vinyl functional group were afforded the desired epoxy, carboxyl, and hydroxy groups via epoxidation and radical addition reaction. The thermal stability and solubility were affected by the terminal functional groups.

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