# Synthesis and characterization of hyperbranched polymer consisting of silsesquioxane derivatives

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Hyperbranched polysiloxanes were synthesized by polyhydrosilylation of silsesquioxane derivatives and vinyl derivatives in the presence of Karstedt's catalyst. The hyperbranched polymers (HBPs) with  $M_n$ =5.2×10<sup>3</sup>-9.8×10<sup>4</sup> were soluble in common solvents and exhibited good thermal stability. HBPs based on double-decker-shaped silsesquioxane showed a large thermal–optical coefficient compared with the corresponding linear polymer. The refractive index values of the polymers obtained tended to decrease with the increasing structure size of the co-monomers. *Polymer Journal* (2010) **42**, 799–803; doi:10.1038/pj.2010.79

Keywords: hyperbranched polymer; low refractive index; silsesquioxane

## INTRODUCTION

The refractive index is a very important property of polymers for photonic applications, in which highly fluorinated polymers such as Teflon and CYTOP are well known and widely used in optical communication networks because of their low refractive value and high thermal stability, typically ascribed to the fluorine atoms.<sup>1</sup> To obtain low refractive index polymers, theoretically, there are two approaches based upon the Lorentz–Lorenz equation (Equation 1).<sup>2</sup> This equation is described by the relationship between the refractive index  $(n_D)$ , molecular volume (V) and molecular refraction (R).

$$n_{\rm D} = \sqrt{\frac{1 + 2[R]/V}{1 - [R]/V}} \tag{1}$$

According to the Lorentz–Lorenz equation, a low [R] and large V give a low refractive index value. The molecular refraction ([R]) appears to be sum of the atom refraction, and so if the polymers consist of a low atom refraction, it shows a low refractive index. The density of polymers is also an important factor, as well as the molecular refraction. Both the lowest atom refraction of fluorine and the cyclic structure of the polymers give the low refractive index values of Teflon and CYTOP. Most of the low refractive index polymers are based on fluorinated polymers. However, these fluorinated polymers produce fluorocarbons during their combustion. From an environmental perspective, the production of such chemicals is undesirable, and so we expect the usage of fluorinated compounds to be limited in the near future. Designing low refractive index materials without fluorine atoms is an important and challenging research topic. We previously found that the ladder-type cyclic polymer (calixresorcinarene-polymer) showed a small refractive index value (1.489) compared with the corresponding novolac polymer (1.517).<sup>3</sup> This result indicates that polymers with many cavities in the ladder-type skeleton might be a help to achieve the low refractive index value.

Hyperbranched polymers (HBPs) with high  $T_g$  are also good candidates for low density polymers because of their three-dimensional globular architectures with highly branched structures.<sup>4</sup> For example, we have observed and reported for the first time that the HBPs show no birefringence because their highly branched globular structure prevents their polymer orientation.<sup>5</sup>

Polyhedral oligomeric silsesquioxane (POSS) derivatives are very attractive for organic–inorganic hybrid materials because they show high thermal stability and transparency.<sup>6</sup> The incorporation of POSS into some polymer structures provides high performance materials that combine the hybrid properties.<sup>7,8</sup> Recently, double-decker-shaped silsesquioxane (DDSQ) has been of great interest because it possesses precisely two reactive groups with nanometer-sized cage structure.<sup>9–11</sup>

Designing a novel low refractive index polymer based on a new concept will be very important to future science and technology. Herein, we describe a novel approach for low refractive index materials using hyperbranched polysiloxane derivatives. We also focus on this unique nanometer-sized cage structure to achieve a low refractive index material combined with a hyperbranched structure (Scheme 1).

# EXPERIMENTAL PROCEDURE

# Materials

Toluene (Wako, Osaka, Japan) was distilled over sodium before use. Unless otherwise stated, reagents were purchased from commercial suppliers and used without any further purification.

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Scheme 1 A<sub>2</sub> and A<sub>3</sub> monomers.

#### Measurements

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra (500 and 600 MHz) were obtained using JEOL JNM-ECA-600 and JEOL JNM-ECA-500 spectrometers (JEOL Ltd, Tokyo, Japan) using chloroform-*d* (CDCl<sub>3</sub>) as the solvent. The chemical shift references were as follows: chloroform-*h*, 7.26 p.p.m. Typical 1-Dimensional Free Induction Decay (1D FID) was subjected to exponential multiplication with an exponent of 0.1 Hz (for <sup>1</sup>H).

Infrared (IR) spectra were obtained using a Nicolet Avatar 380 Fourier transform IR instrument (Thermo Scientific K. K., Kanagawa, Japan). A few drops of the compound in  $\rm CH_2\rm Cl_2$  or  $\rm CHCl_3$  were applied to the surface of KRS (Kristalle ausdem SchmelzfuB; Thallium Bromide-Iodide) or KBr. After the solvent evaporated, the spectrum was acquired (128 scans, 4 cm<sup>-1</sup> resolution).

The number-average molecular weight  $(M_n)$  and molecular weight distribution (weight-average molecular weight/number-average molecular weight  $(M_w/M_n)$ ) values of the polymers were estimated on a TOSOH size exclusion chromatography system (HLC-8220, TOSOH Corp., Tokyo, Japan) equipped with two consecutive polystyrene gel columns (TSK gels: SuperHZM-M×2), a refractive index detector (RI-8220) and an ultraviolet detector (UV-8220) at 40 °C. The system was operated at a flow rate of 0.35 ml min<sup>-1</sup> with tetrahydrofuran as an eluent.

The glass transition temperature  $(T_g)$  was measured with an EXSTAR 6000/DSC6200 (Seiko Instruments Inc, Chiba, Japan) at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere (monitoring range: -30 to 200 °C).

The thermal decomposition temperature  $(T_d)$  was measured with an EXSTAR 6000/TG/DTA6200 (Seiko Instruments Inc.) at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere (monitoring range: 50–600 °C).

The refractive index of the polymer film was determined by ellipsometry (DHA-OLX/S4, Mizojiri Optical Co. Ltd, Tokyo, Japan). The thin film (about 1000 Å in thickness) was prepared from the polymer solution (toluene or tetrahydrofuran), followed by spin coating on a silicon wafer and drying *in vacuo* at room temperature overnight (>12 h). The temperature dependence of the refractive index was measured by an ellipsometer equipped with a controllable heating stage (Linkam TP94, Japan Hightech Co. Ltd, Chiba, Japan).

#### Polymerization

Synthesis of the linear polymer. Linear polymer (LP)-1: DDSQ (1) (150 mg, 130 µmol), dimethyldivinylmethylsilane (5) (14.6 mg, 130 µmol) and dry toluene (0.5 ml) were transferred to a vessel under argon. Karstedt's catalyst (Pt(dvs)) (2.6 µl, 0.26 µmol, 0.1 mol% Si–H) was added to the solution, and the reaction mixture was stirred at 50 °C for 24 h. After the precipitation from toluene to methanol (100 ml), the precipitate was collected and dried under vacuum to give an off-white solid LP-1 (144 mg, 88%);  $M_n$ =1.8×10<sup>4</sup> ( $M_w/M_n$ =2.79); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.40 to 0.90 (m, 20 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 6.95–7.65 (m, 48 H, phenyl); IR (cm<sup>-1</sup>): 2982, 2963, 2870, 2852, 1130, 1090;  $T_d^{5\%}$ =537 °C,  $T_d^{10\%}$ =573 °C;  $n_D$ =1.550.

*LP-2*: LP-2 was synthesized by the reaction of 1,4-bis(dimethylsilyl)benzene (4) with 5 according to the same procedure as LP-1. Yield=89%;  $M_n$ =1.2×10<sup>4</sup> ( $M_w/M_n$ =1.99); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.08 (m, 65 H, CH<sub>3</sub>), 0.04 (s, 3.1 H, terminal CH<sub>3</sub>), 0.231 (s, 133 H, CH<sub>3</sub>), 0.38-0.65 (m, 89 H, CH<sub>2</sub>), 5.646 (dd, *J*=4, 20 Hz, 0.4 H, terminal CH<sub>2</sub>), 5.941 (dd, *J*=4, 12 Hz, 0.4 H, terminal CH<sub>2</sub>), 6.119 (dd, *J*=12, 20 Hz, 0.4 H, terminal CH), 7.42-7.55 (m, 40 H, phenyl); IR (cm<sup>-1</sup>): 3046, 2953, 2904, 2790;  $T_d^{5\%}$ =441 °C,  $T_d^{10\%}$ =453 °C;  $n_D$ =1.58.

Synthesis of HBP-1: DDSQ (1) (150 mg, 130 µmol), trivinylmethylsilane (6) (11 mg, 86.7 µmol) and dry toluene (0.5 ml) were transferred to a vessel under argon. Pt(dvs) (2.6 µl, 0.26 µmol, 0.1 mol% Si–H) was added into the solution, and the reaction mixture was stirred at 50 °C for 1 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-1 (150 mg, 93%);  $M_n$ =9.8×10<sup>4</sup> ( $M_w/M_n$ =5.30); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.30 to 1.20 (m, 21H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 5.28–5.95 (m, 2.8 H, vinyl), 6.90–7.75 (m, 48 H, phenyl). IR (cm<sup>-1</sup>): 2982, 2965, 2869, 1130, 1090;  $T_d^{5\%}$ =483 °C,  $T_d^{10\%}$ =547 °C;  $n_D$ =1.551.

*HBP-2*: DDSQ (1) (150 mg, 130 µmol), 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (7) (22 mg, 86.7 µmol) and dry toluene (0.5 ml) were transferred to a vessel under argon. Pt(dvs) (2.6 µl, 0.26 µmol, 0.1 mol% Si–H) was added, and the reaction mixture was stirred at 50 °C for 1.5 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-2 (117 mg, 68%);  $M_n$ =5.2×10<sup>3</sup> ( $M_w/M_n$ =2.80); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.35 to 1.10 (m, 23 H CH<sub>2</sub>, Si–CH<sub>3</sub>), 6.90–7.70 (m, 48 H, phenyl); IR (cm<sup>-1</sup>): 3074, 3051, 3032, 2961, 1219, 1130, 772;  $T_d^{5\%}$ =383 °C,  $T_d^{10\%}$ =447 °C;  $n_D$ =1.541.

*HBP-3*: DDSQ (1) (76.7 mg, 66.5 μmol), 1,3,5-tetravinyl-1,3,5,7-tetramethyl-cyclotetrasiloxane (**8**) (50.0 mg, 44.3 μmol) and dry toluene (0.5 ml) were transferred to a vessel under argon. Pt(dvs) (1.3 μl, 0.13 μmol) was added, and the reaction mixture was stirred at 50 °C for 1 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-3 (95.8 mg, 76%);  $M_n$ =1.2×10<sup>4</sup> ( $M_w/M_n$ =3.28); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.50 to 1.05 (m, 14 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 4.97 (br s, 0.37 H, Si–H), 5.50–6.05 (m, 1.89 H, vinyl), 6.85–7.70 (m, 48 H, phenyl); IR (cm<sup>-1</sup>): 3074, 3052, 2963, 1219, 1130, 772;  $T_d^{5\%}$ =396 °C,  $T_d^{10\%}$ =470 °C;  $n_D$ =1.544.

*HBP-4*: DDSQ (1) (76.7 mg, 66.5 μmol), *endo*-3,7,14-tris(dimethyl-vinylsilyloxy)-1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane (2) (50 mg, 44.3 μmol) and toluene (0.5 ml) were transferred to a vessel under argon. Pt(dvs) (1.3 μl, 0.13 μmol, 0.1 mol% Si–H) was added, and the reaction mixture was stirred at 50 °C for 1 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-4 (95.8 mg, 76%);  $M_n$ =1.3×10<sup>4</sup> ( $M_w/M_n$ =3.32); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.20 to 0.95 (m, 24 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 1.20–1.80 (m, 63 H, cyclopentyl), 5.60–6.10 (m, 0.53 H, terminal vinyl), 6.90–7.80 (m, 48 H, phenyl); IR (cm<sup>-1</sup>): 2951, 2866, 1219, 1130, 772;  $T_d^{5%}$ =458 °C,  $T_d^{10\%}$ =509 °C;  $n_D$ =1.531.

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*HBP-5:* Endo-3,7,14-tris(dimethylsilyloxy)-1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane (**3**) (80 mg, 76.2 µmol), trivinylmethylsilane (**6**) (9.5 mg, 76.2 µmol) and toluene (1 ml) were transferred to a vessel under argon. Pt(dvs) (1.5 µl, 0.15 µmol, 0.1 mol% Si–H) was added, and the reaction mixture was stirred at 50 °C for 18 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-5 (65.6 mg, 73%);  $M_n$ =3.5×10<sup>3</sup> ( $M_w$ / $M_n$ =1.48); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.20 to 1.10 (m, 246 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 1.30–1.85 (m, 420 H, cyclopentyl), 5.50–6.30 (br m, 10 H, terminal vinyl); IR (cm<sup>-1</sup>): 2950, 2911, 2866, 1250, 1113, 1087, 1062, 825, 788;  $T_d^{5\%}$ =362 °C,  $T_d^{10\%}$ =428 °C;  $n_D$ =1.495.

*HBP-6:* Endo-3,7,14-tris(dimethylsilyloxy)-1,3,5,7,9,11,14-heptacyclopentyl-tricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane (**3**) (80 mg, 76.2 µmol), 1,3,5-trivinyl-1,3, 5-trimethylcyclotrisiloxane (**7**) (19.7 mg, 76.2 µmol) and toluene (1 ml) were transferred to a vessel under argon. Pt(dvs) (1.5 µl, 0.15 µmol, 0.1 mol% Si–H) was added, and the reaction mixture was stirred at 50 °C for 24 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-6 (71.6 mg, 72%);  $M_n$ =5.7×10<sup>3</sup> ( $M_w/M_n$ =1.63); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.10 to 1.15 (m, 400 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 1.30–1.88 (m, 620 H, cyclopentyl), 5.50–6.30 (br m, 10 H, terminal vinyl); IR (cm<sup>-1</sup>): 2951, 2911, 2866, 1256, 1112, 1088, 1015, 835, 799, 774;  $T_d^{5\%}$ =413 °C,  $T_d^{10\%}$ =461 °C;  $n_D$ =1.488.

*HBP-7:* Endo-3,7,14-tris(dimethylsilyloxy)-1,3,5,7,9,11,14-heptacyclopentyl-tricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane (**3**) (100 mg, 83.2 µmol), 1,3,5-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (**8**) (24.6 mg, 24.7 µmol) and toluene (3 ml) were transferred to a vessel under argon. Pt(dvs) (2.9 µl, 0.29 µmol, 0.1 mol% Si–H) was added, and the reaction mixture was stirred at 50 °C for 3 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-7 (86.5 mg, 69%);  $M_n$ =2.4×10<sup>3</sup> ( $M_w/M_n$ =1.58); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.05 to 1.10 (m, 20.5 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 1.35–1.85 (m, 25.9 H, cyclopentyl), 5.75–6.10 (m, 1.0 H, terminal vinyl); IR (cm<sup>-1</sup>): 2951, 2911, 2866, 1257, 1077, 833, 791;  $T_d^{5\%}$ =478 °C,  $T_d^{10\%}$ =508 °C;  $n_D$ =1.487.

*HBP-8:* Endo-3,7,14-tris(dimethylsilyloxy)-1,3,5,7,9,11,14-heptacyclopentyl-tricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane (**3**) (74.5 mg, 70.9 µmol), endo-3,7,14-tris (dimethylvinylsilyloxy)-1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane (**2**) (80 mg, 70.9 µmol) and toluene (1 ml) were transferred to a vessel under argon. Pt(dvs) (1.4 µl, 0.14 µmol, 0.1 mol% Si–H) was added, and the reaction mixture was stirred at 50 °C for 1 h. After the precipitation from toluene to methanol, the precipitate was collected and dried under vacuum to give a white solid HBP-8 (131.1 mg, 85%);  $M_n$ =3.2×10<sup>3</sup> ( $M_w$ / $M_n$ =1.44); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =−0.05 to 1.10 (m, 402 H, CH<sub>2</sub>, Si–CH<sub>3</sub>), 1.30–1.90 (m, 884 H, cyclopentyl), 3.40–3.60 (br s, 4.6 H, Si–H), 5.70–6.20 (m, 10 H, terminal vinyl); IR (cm<sup>-1</sup>): 2951, 2911, 2866, 1251, 1114, 1081, 833, 786;  $T_d^{5%}$ =446 °C,  $T_d^{10\%}$ =492 °C;  $n_D$ =1.49.

### **RESULTS AND DISCUSSION**

# Synthesis of linear and hyperbranched polymer based on

silsesquioxane derivatives via  $(A_x \times B_y)$  reaction (x=2 or 3, y=2-4) DDSQ (1) was prepared using the procedure in the literature with ~25% yield in two steps (Scheme 2).<sup>5</sup> The copolymerization of 1 and divinyldimethylsilane (5) was carried out in toluene at 50 °C in the presence of Karstedt's catalyst (Pt(dvs)) to give LP-1 (88%). Instead of 1, the copolymerization of 4 and 5 was examined in a similar reaction condition. However, this copolymerization progressed more smoothly at room temperature to give the corresponding LP-2 with a yield of 89%.

Hyperbranched polysiloxane based on a DDSQ was synthesized by the polyhydrosilylation of 1 and vinyl derivatives (2, 6, 7 and 8) in the presence of 0.1 mol%/Si–H Karstedt's catalyst (Scheme 3). All the reactions were carried out with a feed ratio of  $[A_2]/[B_3]=1.5/1$  and  $[A_2]/[B_4]=2/1$ . The other reaction conditions and results are summarized in Table 1. HBPs were obtained with  $M_n=5.2\times10^3-9.8\times10^4$ and with a 66–93% yield. When 110 °C was used as the reaction temperature, gel products appeared with copolymerization, which means that the reaction was not easily controlled. In contrast, the copolymerization was readily controllable at 50 °C.

Instead of 1, we examined a different POSS (3) derivative using  $A_3$  monomer, which had three functional groups while maintaining the characteristic cage structure. The reaction was carried out with 3 and vinyl derivatives (2, 6, 7 and 8) in the presence of Karstedt's catalyst at 50 °C (Scheme 4). The feed monomer ratio was fixed at  $[A_3]/[B_3]=1/1$  and  $[A_3]/[B_4]=4/3$ . The other reaction conditions and results are summarized in Table 2. HBPs were obtained with  $M_n = \sim 3 \times 10^3$  and with a 62–85% yield. The molecular weights of the polymers obtained were relatively low due to the sterically hindered  $A_3$  monomer.

#### Thermal properties

The thermal properties of the obtained polymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis. The  $T_{\rm g}$  value dropped significantly when cyclic siloxane was used as a co-monomer because the cyclic siloxane behaved as a flexible unit in the polymer structure. Notably, an exothermic peak beginning around 100 °C was observed in HBP-2, -3, -6 and -7 during DSC measurements. The DSC profile in the second heating for these polymers did not show any significant peak under the measurement conditions because these polymers consisted of cyclosiloxane unit that



Scheme 2 Synthesis of linear polymer.



LP-2: 4+5



Scheme 3 Synthesis of HBP-1 to -4.

#### Table 1 Synthesis of HBP<sup>a</sup>

Sample	Time (h)	Yield (%) <sup>b</sup>	М <sub>л</sub> (×10 <sup>4</sup> ) <sup>с</sup>	M <sub>w</sub> ∕ M <sub>n</sub> c	T <sub>d</sub> <sup>5%</sup> (°C) <sup>d</sup>	T <sub>d</sub> <sup>10%</sup> (°C) <sup>d</sup>	T <sub>g</sub> (°C)⁰	n <sub>D</sub> f
HBP-1	1.0	93	9.8	5.30	483	547	103	1.551
HBP-2	1.5	68	0.52	2.80	383	447	65	1.541
HBP-3	1.0	66	1.2	3.28	396	470	61	1.544
HBP-4	1.0	76	1.3	3.32	458	509	g	1.531

Abbreviations: DSC, differential scanning calorimetry; HBP, hyperbranched polymer; Pt(dvs), Karstedt's catalyst; TG-DTA, thermogravimetric analysis–differential thermal analysis, THF, tetrahydrofuran.

<sup>a</sup>Polymerization conditions: toluene ([C]=0.25 M) with 0.1 mol % of Pt(dvs) at 50 °C. <sup>b</sup>Insoluble fraction in methanol.

<sup>d</sup>Determined by size exclusion chromatography (eluent: THF) based on polystyrene standards. <sup>d</sup>Determined by TG-DTA at heating rate 10 <sup>°</sup>Cmin<sup>-1</sup> under N<sub>2</sub>.

<sup>e</sup>Determined by DSC at heating rate 10 °C/min under N<sub>2</sub>.

fAverage value of refractive index determined by the ellipsometer with 632.8 nm laser ray

 $^{\rm g}{\rm No}~T_{\rm g}$  was observed under the measurement condition.

could be thermally polymerized under heating conditions. All of the obtained HBPs were soluble in common organic solvents and exhibited good thermal stability ( $T_d^{5\%} > 350$  °C) under nitrogen. However, in the series HBP-1 to -4, the thermal stabilities of HBP-2 and -3 were significantly lower than that of HBP-1 and -4, which may be explained by the lower thermal stability of cyclic siloxane. In contrast, a similar  $T_d$  value was observed in the series HBP-5 to -8 because of the low molecular weight of the HBPs. However, HBP-5 showed a relatively low  $T_d$  value compared with the other HBPs. Owing to its small size, co-monomer **6** might be difficult to give the branch structure.

#### Refractive index

A tetrahydrofuran solution of polymer was spin coated onto a silicon wafer and dried *in vacuo* at room temperature over 12 h to prepare a thin film with a thickness of about 0.1 µm. The refractive indices of polymer films were determined by ellipsometry. The refractive indexes  $(n_{\rm D})$  of LP-1 and -2 were 1.550 and ~1.58, respectively. Even monomer 1 showed a larger refractive index  $(n_{\rm D}=1.55)$  than 4  $(n_{\rm D}=1.500)$ , and the corresponding polymer (LP-1) displayed a lower  $n_{\rm D}$  value, which might be because the bulky cage-like structure of 1, which produced a low density  $(\rho)$ , affected the lower  $n_{\rm D}$  in the

polymer system. The refractive indexes of LP-1 and HBP-1 were similar, which probably suggests that the branching synthesized from the large monomer structure (POSS) and the small vinyl silane derivative had little influence on the refractive index of polysilsesquioxane. On the other hand, HBP obtained from 4 and 6 (HBP-9) gave a lower value than LP-2, which indicates that the combination of co-monomers is important in creating the branched structure. It is possible that the HBPs had a low density because of their threedimensional globular structure with many branched arms. The refractive index tended to decrease when using the larger monomer structure. The refractive indexes of HBP-5 to -8 were much smaller than those of HBP-1 to -4, because of the molecular refraction difference between 1 and 3, which probably depended on the difference between the phenyl and cyclopentyl substitution. A preliminary measurement of the dielectric constant ( $\varepsilon$ ) for the polymers films selected was examined. The dielectric constant is known to be proportional to  $n^2$ . The obtained HBP showed  $\varepsilon$  around 2.6–2.8, which were higher than the expected values.

The temperature dependence of the refractive index was measured by an ellipsometer equipped with a heating stage. The results are summarized in Table 3. The  $n_{\rm D}$  decreased linearly as the temperature increased. In the case of HBP-9, the inflection point was observed around 50 °C, which was coincident with the glass transition temperature  $(T_g)$  of HBP-9. The thermo-optic coefficients were -175 p.p.m./K below  $T_g$  ( $R^2$ =0.989) and -364 p.p.m./K above  $T_{\rm g}$  ( $R^2$ =0.999). LP-1 derived from 1 also showed an inflection point around 100 °C ( $T_g$ =103 °C), and the coefficients were -221 p.p.m./K below  $T_{\rm g}$  ( $R^2$ =0.996) and -319 p.p.m./K above  $T_{\rm g}$  ( $R^2$ =0.995). The slope above  $T_{\rm g}$  was higher than that below  $T_{\rm g}$ . On the other hand, other HBPs did not show any clear inflection point during the same experiment (<300 °C). However, the HBPs showed higher thermo-optic and thermal expansion coefficients because of the large free volume associated with the cage structure of DDSQ and POSS derivatives. It is expected that the difference between the HBPs correlates with the softness of the A3 monomer. HBP-2 showed a low value of the thermo-optic coefficient because the thermal polymerization proceeded to give rigid thermosetting polymers. No refractive index value change was observed before or after heating.



Scheme 4 Synthesis of HBP-5 to -8.

#### Table 2 Synthesis of HBP<sup>a</sup>

Sample	Time (h)	Yield (%) <sup>b</sup>	М <sub>л</sub> (×10 <sup>3</sup> ) <sup>с</sup>	M <sub>w</sub> ∕ M <sub>n</sub> c	T <sub>d</sub> <sup>5%</sup> (°C) <sup>d</sup>	T <sub>d</sub> <sup>10%</sup> (°C) <sup>d</sup>	Τ <sub>g</sub> (°C) <sup>e</sup>	n <sub>D</sub> f
HBP-5	20	73	3.5	1.48	362	428	g	1.495
HBP-6	24	62	5.7	1.63	417	468	53	1.488
HBP-7	3.0	69	2.4	1.58	450	497	56	1.487
HBP-8	1.0	85	3.2	1.44	446	492	g	(1.49) <sup>†</sup>

Abbreviations: DSC, differential scanning calorimetry; HBP, hyperbranched polymer; Pt(dvs), Karstedt's catalyst; TG-DTA, thermogravimetric analysis–differential thermal analysis, THF, tetrahydrofuran.

<sup>a</sup>Polymerization conditions: toluene ([C]=0.25 M) with 0.1 mol % of Pt(dvs) at 50 °C.

<sup>b</sup>Insoluble fraction in methanol.

 $^c\text{Estimated}$  by size exclusion chromatography (eluent: THF) based on polystyrene standards. <code>dDetermined</code> by TG-DTA at heating rate 10  $^c\text{C}\,\text{min}^{-1}$  under N<sub>2</sub>.

<sup>e</sup>Determined by DSC at heating rate 10 °C min<sup>-1</sup> under N<sub>2</sub>.

<sup>f</sup>Average value of refractive index determined by the ellipsometer with 632.8 nm laser ray.  ${}^{s}$ No  $T_{g}$  was observed under the measurement condition. <sup>h</sup>Poor film forming.

#### Table 3 Thermo-optic coefficient of HBP

Polymer	Thermo-optic coefficient (below T <sub>g</sub> ), p.p.m./K		Thermo-optic coefficient (above T <sub>g</sub> ), p.p.m./K
LP-1	-221		-319
HBP-9	-175		-364
HBP-1		-297	
HBP-2		-275	
HBP-4		-310	

Abbreviations: HBP, hyperbranched polymer; LP, linear polymer.

#### CONCLUSIONS

In this study, we synthesized hyperbranched polysiloxanes using silsesquioxane derivatives, which have a unique nanometer-sized cage structure with  $A_2$  or  $A_3$  monomers. HBPs based on DDSQ showed large thermal–optical coefficients compared with the corresponding LP. The values of the refractive index of the polymers obtained tended to decrease with increasing structure size of

co-monomers. To obtain low refractive index materials, it is important that there are many vacancies in the polymer structure (that is, film) while maintaining the thermal and physical properties.<sup>12</sup> Further investigations for HBPs using a larger cavity structure and fewer aromatic ring compounds are in progress.

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