Supporting Information

Open-cage silsesquioxane necklace polymers having closed-cage silsesquioxane pendants

Hiroaki, Imoto; Ryoichi, Katoh; Kensuke, Naka*

Faculty of Molecular Chemistry and Engineering, Graduate School of Science and Technology, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan. E-mail: kenaka@kit.ac.jp

Contents:
1. Materials
2. Measurements
3. Synthetic procedure and characterization data
4. NMR spectra
5. MALDI-TOF MS spectra
6. X-ray diffraction patterns
7. Detail of cyclic compound
8. Study on $M_n$ values
1. Materials

Tetrahydrofuran (THF), toluene, triethylamine (NEt₃), and magnesium sulfate anhydrous (MgSO₄) were purchased from Nacalai Tesque (Kyoto, Japan). Distilled water was purchased from Wako Pure Chemical Industry (Osaka, Japan). Chlorodimethylvinylsilane, 1,1,3,3-tetramethyldisiloxane (5b) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Xylene solution (0.1 M) of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt(dvs)), 1,1,3,3,5,5-hexamethyltrisiloxane (5a), and 1,4-bis(dimethylsilyl)benzene (5c) were purchased from Sigma-Aldrich (Hattiesburg, Mississippi, US). Heptaphenyl trisilanol POSS (1ₚₚ) and heptaisobutyl trisilanol POSS (1ᵢBu) was purchased from Hybrid Plastics Inc (Hattiesburg, Mississippi, US). SiliaMetS(R) Thiol (40-63 μmol 60 Å, functionalized Silica) was purchased from SiliCycle, Inc. Dimethylvinylsilane-substituted heptaphenyl IC-POSS (2ₚₚ) and heptaisobutyl IC-POSS (2ᵢBu), and hydride-substituted heptaphenyl CC-POSS (3ₚₚ) and heptaisobutyl CC-POSS (3ᵢBu) were prepared by following the literatures.

2. Measurements

¹H (400MHz) and ¹³C (100MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany) in CDCl₃ using Me₄Si as an internal standard. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Molecular weights were determined by size exclusion chromatography (SEC) of LC-6AD (Shimadzu, Kyoto, Japan) with Shodex KF-805L (Showa Denko, Tokyo, Japan), and then analysed by refractive index with RID-20A (Shimadzu, Kyoto, Japan). Preparative high-performance liquid chromatography (HPLC) for purification was performed on LC-6AD (Shimadzu, Kyoto, Japan) with a KF-2002 (for polymers, Showa Denko, Tokyo, Japan) or a tandem column system of two columns selected from Shodex KF-2001 and KF-2002 (for monomers, Showa Denko, Tokyo, Japan) using chloroform as an eluent. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was recorded on a Bruker Autoflex II instrument (Bruker Daltonics, Billerica, MA, USA): trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix (20 mg/mL in CHCl₃) and sodium trifluoroacetate cationizing agents (1 mg/mL in THF). TGA and DSC measurements were performed by Shimadzu DTG-60 and DSC-60 Plus (Shimadzu, Kyoto, Japan), respectively, under nitrogen atmosphere at a heating rate of 10 °C/min. Transmittance spectra were recorded on a JASCO
spectrophotometer V-670 KNN (JASCO, Tokyo, Japan). Refractive index (RI) values were measured by Abbe’s method with an Atago refractometer (Atago, Tokyo, Japan).

3. Synthetic procedure and characterization data

**Bis(dimethylvinylsilyloxy) heptaphenyl IC-POSS with heptaphenyl CC-POSS (**4Ph-Ph**). A Toluene solution (8.4 mL) of **2**Ph (1.00 g, 0.84 mmol), **3**Ph (0.96 g, 1.00 mmol) and Pt(dvs) (0.1 M in xylene, 0.05mL, 5.0 × 10⁻³ mmol) was stirred at 50 °C for 6 h under N₂ atmosphere. The solvents were removed in vacuo, and the residue was subjected to preparative HPLC to give **4**Ph-Ph (0.94 g, 0.44 mmol, 52%). 

**1H-NMR** (CDCl₃, 400 MHz) δ 7.78-7.68 (m, 14H), 7.59-7.56 (m, 2H), 7.48-7.40 (m, 14H), 7.40-7.24 (m, 28H), 7.18-7.08 (m, 10H), 6.96-6.91 (t, J = 2.8Hz, 2H), 6.24-5.77 (m, 6H), 0.75 (s, 4H), 0.30-0.28 (m, 12H), 0.24-0.22 (m, 6H) ppm.

**13C-NMR** (CDCl₃, 100 MHz) δ 138.7, 134.4, 134.3, 134.2, 134.1, 134.0, 139.9, 132.9, 132.8, 132.6, 131.2, 130.8, 130.6, 130.5, 130.2, 130.1, 128.0, 127.7, 127.6, 9.1, 3.6, 0.5, -0.2 ppm. 

**29Si-NMR** (CDCl₃, 80 MHz) δ 12.3, 0.1, -64.6, -77.4, -77.6, -77.8, -78.1, -78.2, -78.4, -78.7 ppm. MALDI-TOF MS (m/z): calcd for C₉₆H₉₈O₂₄Si₁₈Na [M+Na]⁺: 2161.2; found: 2161.2.

**Bis(dimethylvinylsilyloxy) heptaisobutyl CC-POSS (**4Ph-iBu**). The same procedure as that of **4**Ph-Ph using **3**iBu instead of **3**Ph. The isolated yield was 52%. 

**1H-NMR** (CDCl₃, 400 MHz) δ 7.59-7.56 (m, 2H), 7.43-7.38 (m, 7H), 7.38-7.24 (m, 14H), 7.17-7.08 (m, 12H), 6.27-5.81 (m, 6H), 1.91-1.80 (m, 7H), 0.98-0.91 (m, 42H), 0.63-0.56 (m, 18H), 0.34-0.32 (m, 12H), 0.26-0.24 (m, 6H) ppm. 

**13C-NMR** (CDCl₃, 100 MHz) δ 138.6, 134.1, 134.0, 133.9, 132.9, 132.5, 132.2, 132.5, 131.2, 130.7, 130.6, 130.1, 130.0, 129.9, 127.6, 127.5, 25.8, 25.7, 23.9, 22.6, 22.5, 8.9, 3.7, 0.4, -0.3 ppm. 

**29Si-NMR** (CDCl₃, 80 MHz) δ 12.5, -0.2, -66.9, -67.5 -67.6, -67.8, -67.9, -77.3, -77.7, -77.8, -78.0, -78.1 ppm. MALDI-TOF MS (m/z): calcd for C₈₂H₁₂₆O₂₄Si₁₈Na [M+Na]⁺: 2021.4; found: 2021.4.

**Bis(dimethylvinylsilyloxy) heptaisobutyl CC-POSS (**4iBu-Ph**). The same procedure as that of **4**Ph-Ph using **2**iBu instead of **2**Ph. The isolated yield was 54%. 

**1H-NMR** (CDCl₃, 400 MHz) δ 7.86-7.78 (m, 14H), 7.55-7.45 (m, 7H), 7.45-7.38 (m, 14H), 6.25-5.75 (m, 6H), 1.99-1.82 (m, 7H), 1.08-0.95 (m, 42H), 0.90-
0.75 (m, 4H), 0.67-0.57 (m, 14H), 0.26-0.24 (m, 12H), 0.20-0.18 (m, 6H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 139.1, 134.3, 134.2, 131.9, 130.8, 130.6, 130.4, 130.3, 130.2, 129.7, 127.9, 26.1, 26.0, 25.9, 25.7, 25.0, 24.1, 24.0, 23.9, 23.8, 22.5, 9.1, 3.7, 0.4, -0.3 ppm. $^{29}$Si-NMR (CDCl$_3$, 80 MHz) δ 9.8, -2.6, -64.3, -67.2 -67.6, -67.7, -67.8, -68.0, -77.8, -78.2, -78.3, -78.6 ppm. MALDI-TOF MS (m/z): calcd for C$_{82}$H$_{126}$O$_{24}$Si$_{18}$Na [M+Na]$^+$: 2021.4; found: 2021.4.

**Synthesis of polymer 6a.** A Toluene solution (0.3 mL) of 4$_{Ph-Ph}$ (300 mg, 0.144 mmol), 5a (29 mg, 0.14 mmol) and Pt(dvs) (0.1 M in xylene, 8 × 10$^{-3}$ mL, 8.0 × 10$^{-4}$ mmol) was stirred at 50 °C for 2 h under N$_2$ atmosphere. The solvents were removed in vacuo, and the residue was subjected to preparative HPLC to give 5 (157 mg, 48%). $^1$H-NMR (CDCl$_3$, 400 MHz) δ 7.89-7.80 (m, 14H), 7.70-7.65 (m, 2H), 7.56-7.46 (m, 14H), 7.46-7.32 (m, 28H), 7.27-7.16 (m, 10H), 7.05-6.97 (m, 2H), 0.85 (s, 4H), 0.64-0.47 (m, 8H), 0.42-0.34 (m, 18H), 0.24-0.02 (m, 18H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 134.3, 134.2, 134.1, 134.0, 133.9, 133.1, 132.8, 130.9, 130.6, 130.4, 130.2, 130.0, 127.7, 127.6, 9.5, 9.1, 3.6, 1.5, -0.2, -0.5 ppm. $^{29}$Si-NMR (CDCl$_3$, 80 MHz) δ 12.7, 12.3, 8.3, -21.1, -64.5, -77.3, -77.6, -77.7, -78.0, -78.2, -78.5 ppm.

**Synthesis of polymer 6b.** The same procedure as that of 6a using 5b instead of 5a. The isolated yield was 62%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ 7.95-7.82 (br, 14H), 7.74-7.68 (br, 2H), 7.60-7.53 (br, 14H), 7.53-7.34 (br, 28H), 7.29-7.18 (br, 10H), 7.09-7.01 (br, 2H), 0.92-0.84 (br, 4H), 0.65-0.47 (br, 8H), 0.47-0.35 (br, 18H), 0.20-0.01 (br, 12H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 134.4, 134.3, 134.2, 134.1, 134.0, 133.1, 132.8, 131.4, 131.3, 130.9, 130.6, 130.5, 130.4, 130.2, 130.0 128.0, 127.7, 9.6, 9.5, 9.1, 3.6, -0.2, -0.3 ppm. $^{29}$Si-NMR (CDCl$_3$, 80 MHz) δ 12.7, 12.4, 8.4, -64.4, -77.2, -77.6, -77.7, -78.2, -78.5 ppm.

**Synthesis of polymer 6c.** The same procedure as that of 6a using 5c instead of 5a. The isolated yield was 58%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ 7.94-7.85 (m, 14H), 7.74-7.70 (m, 2H), 7.60-7.53 (m, 14H), 7.53-7.36 (m, 32H), 7.30-7.19 (m, 10H), 7.12-7.05 (m, 2H), 0.92 (s, 4H), 0.83-0.64 (m, 8H), 0.47-0.37 (m, 18H), 0.34-0.26 (m, 12H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 134.4, 134.3, 134.2, 134.1, 134.0, 133.1, 133.0, 132.9, 131.4, 131.3, 130.9, 130.8, 130.6, 130.5, 130.3, 130.2, 130.1 128.0, 127.7, 10.3, 9.1, 7.0, 3.7, -0.1, -3.5 ppm. $^{29}$Si-NMR (CDCl$_3$, 80 MHz) δ 12.6, 12.4, -1.5, -64.4, -77.2, -77.5, -77.7, -77.9, -78.1, -78.5 ppm.
Synthesis of polymer 7. The same procedure as that of 6a using $4_{\text{Ph-iBu}}$ instead of $4_{\text{Ph-Ph}}$, and reaction time was changed from 2 h to 4 h. The isolated yield was 31 %. $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.64-7.56 (m, 2H), 7.48-7.38 (m, 7H), 7.38-7.24 (m, 14H), 7.22-7.06 (m, 12H), 1.95-1.83 (m, 7H), 1.02-0.95 (m, 42H), 0.66-0.59 (m, 18H), 0.58-0.40 (m, 8H), 0.34-0.26 (m, 18H), 0.13-0.04 (m, 18H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 134.0, 133.9, 133.0, 131.2, 130.1, 129.9, 127.9, 127.5, 25.8, 25.7, 23.9, 22.6, 22.5, 9.4, 8.9, 3.7, 1.2, 1.1, 1.0, -0.3, -0.6 ppm. $^{29}$Si-NMR (CDCl$_3$, 80 MHz) $\delta$ 12.6, 12.4, 8.1, -21.2, -67.0, -67.6, -67.8, -67.9, -77.4, -77.8, -78.1 ppm.

Synthesis of polymer 8. The same procedure as that of 6a using $4_{\text{iBu-Ph}}$ instead of $4_{\text{Ph-Ph}}$, and reaction time was changed from 2 h to 4 h. The isolated yield was 31 %. $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.84-7.74 (m, 14H), 7.52-7.44 (m, 7H), 7.44-7.34 (m, 14H), 1.96-1.78 (m, 7H), 1.06-0.90 (m, 42H), 0.88-0.72 (m, 4H), 0.64-0.54 (m, 14H), 0.52-0.44 (m, 8H), 0.23-0.13 (m, 18H), 0.13-0.04 (m, 18H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 134.3, 134.2, 130.7, 130.6, 130.4, 127.9, 26.1, 26.0, 25.9, 25.8, 25.7, 25.1, 25.0, 24.1, 24.0, 23.9, 23.8, 22.5, 9.5, 9.1, 3.6, 1.4, 1.3, 1.1, 0.4, 0.2, -0.4, -0.5 ppm. $^{29}$Si-NMR (CDCl$_3$, 80 MHz) $\delta$ 9.9, 9.7, 8.2, -2.6, -21.3, -64.4, -67.3, -67.6, -67.7, -67.8, -67.9, -68.1, -78.3, -78.6 ppm.
4. NMR spectra

**Figure S1.** $^1$H NMR spectrum (400 MHz) of 4_{Ph-Ph} in CDCl$_3$.

**Figure S2.** $^{13}$C NMR spectrum (100 MHz) of 4_{Ph-Ph} in CDCl$_3$.
Figure S3. $^{29}\text{Si}$ NMR spectrum (80 MHz) of $4_{\text{Ph-Ph}}$ in $\text{CDCl}_3$.

Figure S4. $^1\text{H}$ NMR spectrum (400 MHz) of $4_{\text{Ph-iBu}}$ in $\text{CDCl}_3$. 
Figure S5. $^{13}$C NMR spectrum (100 MHz) of $4_{Ph-iBu}$ in CDCl$_3$.

Figure S6. $^{29}$Si NMR spectrum (80 MHz) of $4_{Ph-iBu}$ in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum (400 MHz) of 4$_{3}$Bu-Ph in CDCl$_3$.

Figure S8. $^{13}$C NMR spectrum (100 MHz) of 4$_{3}$Bu-Ph in CDCl$_3$. 
**Figure S9.** $^{29}$Si NMR spectrum (80 MHz) of 4$_{\text{Bu-Ph}}$ in CDCl$_3$.

**Figure S10.** $^1$H NMR spectrum (400 MHz) of 6a in CDCl$_3$. 
Figure S11. $^{13}$C NMR spectrum (100 MHz) of 6a in CDCl$_3$.

Figure S12. $^{29}$Si NMR spectrum (80 MHz) of 6a in CDCl$_3$. 
Figure S13. $^1$H NMR spectrum (400 MHz) of 6b in CDCl$_3$.

Figure S14. $^{13}$C NMR spectrum (100 MHz) of 6b in CDCl$_3$. 
Figure S15. $^{29}\text{Si}$ NMR spectrum (80 MHz) of 6b in CDCl$_3$.

Figure S16. $^1\text{H}$ NMR spectrum (400 MHz) of 6c in CDCl$_3$. 
Figure S17. $^{13}$C NMR spectrum (100 MHz) of 6c in CDCl$_3$.

Figure S18. $^{29}$Si NMR spectrum (80 MHz) of 6c in CDCl$_3$. 
Figure S19. $^1$H NMR spectrum (400 MHz) of 6d in CDCl$_3$.

Figure S20. $^{13}$C NMR spectrum (100 MHz) of 6d in CDCl$_3$. 
Figure S21. $^{29}$Si NMR spectrum (80 MHz) of 6d in CDCl$_3$.

Figure S22. $^1$H NMR spectrum (400 MHz) of 6e in CDCl$_3$. 
Figure S23. $^{13}$C NMR spectrum (100 MHz) of 6e in CDCl$_3$.

Figure S24. $^{29}$Si NMR spectrum (80 MHz) of 6e in CDCl$_3$. 
Figure S25. $^{29}\text{Si}$ NMR spectra (80 MHz in CDCl$_3$) and assignments of 4$_{\text{Ph-Bu}}$ and 4$_{\text{Bu-Ph}}$. 
5. MALDI-TOF-MASS spectra

**Figure S26.** MALDI TOF MS spectrum of 4_{Ph-Bu}. Matrix: DCTB (20 mg/mL in CHCl₃), cationizing agents: TFANa (1 mg/mL in THF). (a) Full spectrum and (b) expanded view.
Figure S27. MALDI TOF MS spectrum of 4_{Bu-Ph}. Matrix: DCTB (20 mg/mL in CHCl₃), cationizing agents: TFANa (1 mg/mL in THF).
6. X-ray diffraction patterns

![X-ray diffraction patterns](image)

**Figure S28.** Powder X-ray diffraction patterns of 6a, 7, and 8.

7. Detail of cyclic compound

In the course of polymerization, low molecular weight by-products were observed in the SEC charts though the conversions of the monomers were approximately 100%. Thus, the by-product was isolated by preparative HPLC in the case of polymer 6a. The $^1$H-NMR spectrum of the isolated by-product showed no signals due to vinyl (4$_\text{Ph-Ph}$, 6.19-5.80 ppm) and Si–H (5a, 4.71 ppm) groups (Figure S29). In the $^{29}$Si-NMR spectrum, the signals due to dimethylvinylsilyl (4a, -0.1 ppm) and dimethylsilyl (5a, -6.6 ppm) groups also disappeared (Figure S30). The MALDI-TOF MS spectra showed a peak at 2369.3 Da (C$_{102}$H$_{118}$O$_{26}$Si$_{21}$Na: [M+Na]$^+$ calcld. 2369.3) (Figure S31). These results indicate that the isolated by-product is cyclic compound as shown in Chart S1.

![Chart S1](image)

**Chart S1.** Chemical structure of the cyclic by-product.
Figure S29. $^1$H-NMR spectra (400 MHz in CDCl$_3$) of 4$_{\text{Ph-Ph}}$, 5a, and the cyclic by-product.

Figure S30. $^{29}$Si-NMR spectra (80 MHz in CDCl$_3$) of 4$_{\text{Ph-Ph}}$, 5a, and the cyclic by-product.
Figure S31. MALDI TOF MS spectrum of the cyclic by-product. Matrix: DCTB (20 mg/mL in CHCl₃), cationizing agents: TFANa (1 mg/mL in THF).
8. Study on $M_n$ values

For the evaluation of $M_n$ by $^1$H-NMR spectroscopy, vinyl groups were introduced to the end groups. That is, polymerization of 1.5 equivalent 4$_{Ph-Ph}$ with 5a was carried out under the optimized condition (Run 4 in Figure 2). The low molecular weight molecules were removed by preparative HPLC (eluent: chloroform), and the obtained polymer products were subjected to $^1$H-NMR and SEC measurements. The $^1$H-NMR spectrum indicated that the $M_n$ was approximately 21000 ($n \approx 8$ in Figure S32), while the $M_n$ estimated by the SEC was 7200. This result means that the molecular weight of the polymer was much underestimated using SEC.

![Figure S32. $^1$H-NMR (400 MHz in CDCl$_3$) of the end-labeled polymer.](image-url)