

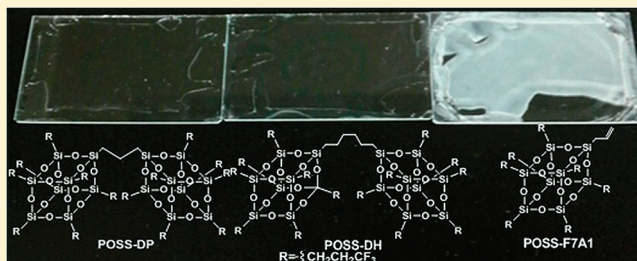
Syntheses of Dumbbell-Shaped Trifluoropropyl-Substituted POSS Derivatives Linked by Simple Aliphatic Chains and Their Optical Transparent Thermoplastic Films.

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Supporting Information

ABSTRACT: Dumbbell-shaped trifluoropropyl-substituted C2-linked POSS (POSS-DE), C3-linked POSS (POSS-DP), and C6-linked POSS (POSS-DH) were prepared by corner-capping of hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate (F7-Na) with 1,2-bis(trichlorosilyl)ethane, 1,3-bis(trichlorosilyl)propane, and 1,6-bis(trichlorosilyl)hexane, respectively. The structures of these obtained compounds were confirmed by ^1H , ^{13}C , and ^{29}Si NMR spectra and MALDI-TOF-MS analysis. In the case of POSS-DP and POSS-DH, spin coating of hexafluorobenzene solutions and subsequent baking at $100\text{ }^\circ\text{C}$ for 3 min gave optical transparent films. POSS-DE, however, formed opaque whitish films. Refractive indices of the transparent films were in the range of 1.38 to 1.39, which were the same as those of the corresponding random silsesquioxanes prepared by baking at $250\text{ }^\circ\text{C}$. POSS-DP and POSS-DH are regarded as low temperature processing low refractive materials. Thermal stabilities of the dumbbell-shaped POSS derivatives were higher than that of allylhepta(3,3,3-trifluoropropyl)-T8-silsesquioxane (POSS-F7A1). Both the glass transition and melting temperatures of the dumbbell-shaped POSS derivatives were observed by DSC analysis.



INTRODUCTION

Silsesquioxanes have been considerably utilized various materials because of their excellent thermal, mechanical, optical and electrical properties.¹ The most common silsesquioxanes are, “cage”,² “ladder”,³ and “random”⁴ structures. Among them, the random silsesquioxanes are widely applied to low-*k* interlayer insulators, low refractive index layers of antireflection films,^{5,6} etc. In particular, random silsesquioxanes containing fluorine are applied to low-*k* materials and low refractive index materials because these values of fluorocarbon compounds are the same as those of the silsesquioxanes.⁶ Molecular structures of the silsesquioxanes significantly affect their physical properties. Lee and co-workers demonstrated that both refractive indices and dielectric constant decreased with increasing cage/random ratios because a free volume of the cage structure is larger than that of the random structure.⁷ However, high temperature curing process is generally essential for the preparation of these materials. Development of lower-temperature processable material based on silsesquioxanes is desired to apply to coating on thermally unstable polymers.

Polyhedral oligomeric silsesquioxane (POSS) compounds with well-defined cube-like structures denoted as $(\text{RSiO}_{3/2})_8$ have received extensive research attention as nanoscale building blocks to form hybrid materials.² The POSS compounds are used as fillers in matrix polymers and as comonomers for

copolymerization with organic monomers.^{8–10} Another way of using the POSS compounds contains in the direct cross-linking POSS units with small organic molecules to form three dimension networks.^{11,12} Optical transparent films of a single POSS compound are hardly formed without cross-linking reagents due to their high symmetry and crystallinity. We speculated that lower the symmetries of the POSS derivatives decrease their crystallinity and would provide optical transparent film forming properties. Such kinds of materials are regarded as thermoplastic hybrids possessing low-*k* or low refractive index.

Here, we synthesized dumbbell-shaped trifluoropropyl substituted POSS derivatives linked by simple aliphatic chains to reduce their symmetries. We found that the dumbbell-shaped POSS derivatives formed optical transparent films depend on their aliphatic chains. These molecules may have not only unique structures but also different properties in comparison with normal POSS compounds. There are few reports about dumbbell-shaped POSS derivatives in the past.^{13,14} Xu and co-workers synthesized dumbbell-shaped POSS derivatives containing azobenzene chromophores which were obtained as mixtures with polymers and network structures.¹³ Lee and co-workers synthesized a

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diPOSS-substituted fluorene. No properties of this compound, however, were studied.¹⁴ The present molecules are first examples of optical transparent POSS films showing thermoplastic properties.

EXPERIMENTAL SECTION

Materials. All solvents and chemicals used here were obtained as reagent-grade quality and used without further purification. All the reactions were performed under a nitrogen atmosphere. Hepta(3,3,3-trifluoropropyl)trichloroheptasiloxane trisodium silanolate (F7-Na) was prepared by the method reported by Fukuda et al. from (3,3,3-trifluoropropyl)trimethoxysilane and sodium hydroxide.¹⁵

Measurement. ¹H (300 or 400 MHz), ¹³C (75 and 100 MHz), and ²⁹Si (100 MHz) NMR spectra were recorded on a BRUKER PDX-300. MALDI–TOF–MS was recorded on a BRUKER Autoflex II instrument. Fourier transform infrared (FTIR) spectra were obtained on a JASCO FT/IR-4100 spectrometer using KBr pellets. UV–vis spectra were recorded on a JASCO spectrophotometer V-670 KKN. Differential scanning calorimetry (DSC) was recorded on a TA Instruments 2920 Modulated DSC. Thermogravimetric analysis (TGA) was measured on a TA Instruments Hi-Res Modulated TGA 2950 thermogravimetric analyzer. Refractive indices were obtained on a Metricon Model 2010 prism coupler. Gel permeation chromatography (GPC) was measured on a TOSO HLC-8220GPC with TSKgel SuperHM-H column using THF as an eluent.

1,2-Bis(hepta(3,3,3-trifluoropropyl)-T8-silsesquioxyl)ethane (POSS-DE). F7-Na (4.0 g, 3.52 mmol) and dry THF (65 mL, 0.04 mol/L) were charged into a round-bottomed flask, and 1,2-bis(trichlorosilyl)ethane (0.499 g, 1.68 mmol) dissolved in THF (5 mL) was added at room temperature under N₂ atmosphere. Triethylamine (0.49 mL, 3.52 mmol) was added dropwise to the solution at 0 °C, and NaCl appeared as a white solid. The reaction mixture was magnetically stirred at 0 °C for 1 h and then at room temperature for 3 h. The precipitates were removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The resultant solid was dissolved in 5 mL of acetone and precipitated in 300 mL methanol, collected with a filter paper, and dried under reduced pressure. The obtained white solid (1 g) was again dissolved in acetone (25 mL) and poured into MeOH (40 mL) under stirring. The precipitate was collected with a membrane filter having 0.45 μm pores, and dried under reduced pressure to provide a white solid in 9% yield. ¹H NMR (acetone-*d*₆, 400 MHz): δ 2.40–2.23 (m, 28H, –CH₂–CF₃), 1.10–0.90 (m, 28H, Si–CH₂–CH₂–CF₃), 0.84 (s, 4H, Si–CH₂–CH₂–Si). ¹³C NMR (acetone-*d*₆, 75 MHz): δ 128.67 (q, *J* = 274 Hz), 128.65 (q, *J* = 274 Hz), 27.98 (q, *J* = 30 Hz), 27.88 (q, *J* = 30 Hz), 4.50, 4.47, 3.48. ²⁹Si NMR (acetone-*d*₆, 80 MHz): δ –66.71, –66.75, –66.87, –69.16. FT-IR (KBr): *ν* = 2981, 2955, 2919, 1449, 1422, 1375, 1318, 1270, 1221, 1118, 1070, 1028, 903, 839, 800, 706, 551, 459, 421 cm^{–1}. MALDI–TOF–MS (*m/z*, [M + Na]⁺): 2240.900 (calculated for C₄₄H₆₀F₄₂NaO₂₄Si₁₆); 2240.590 (observed).

1,3-Bis(hepta(3,3,3-trifluoropropyl)-T8-silsesquioxyl)propane (POSS-DP). POSS-DP was synthesized from F7-Na (4.0 g, 3.52 mmol) and 1,3-bis(trichlorosilyl)propane (0.34 mL, 1.41 mmol) with triethylamine (0.49 mL, 3.52 mmol) in a manner similar to that for POSS-DE except for purification. A crude product was dissolved in 5 mL of acetone and precipitated in 300 mL isopropyl alcohol, isolated with centrifugation to obtain 2.5 g of a white solid. The resultant white solid was dissolved in acetone (25 mL), and isopropyl alcohol (250 mL) was added under stirring. The precipitates were removed from the solution by centrifugation and the supernatant was concentrated under reduced pressure. The resultant solid was purified by recrystallization with acetone/MeOH = 4/6 solution to give a white solid in 12% yield. ¹H NMR (acetone-*d*₆, 300 MHz): δ 2.40–2.25 (m, 28H, –CH₂–CF₃), 1.67 (br, 2H, Si–CH₂–CH₂–CH₂–Si), 1.08–0.94 (m, 28H,

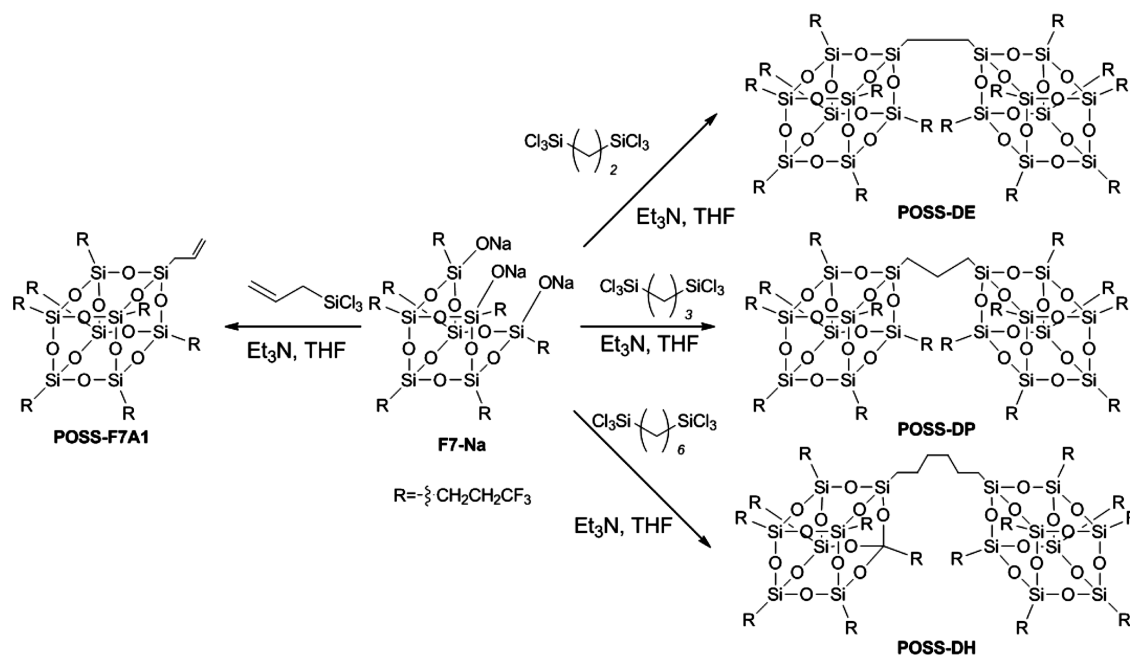
Si–CH₂–CH₂–CF₃), 0.90 (t, *J* = 6 Hz, 4H, Si–CH₂–CH₂–CH₂–Si). ¹³C NMR (acetone-*d*₆, 100 MHz): δ 128.65 (q, *J* = 274 Hz), 128.63 (q, *J* = 274 Hz), 28.04 (q, *J* = 30 Hz), 27.91 (q, *J* = 30 Hz), 16.85, 15.50, 4.58 (q (overlap), *J* = 2 Hz), 4.47 (q (overlap), *J* = 2 Hz). ²⁹Si NMR (acetone-*d*₆, 80 MHz): δ –66.06, –67.03, –67.41. FT-IR (KBr): *ν* = 2976, 2954, 2921, 2877, 1448, 1422, 1376, 1318, 1270, 1221, 1120, 1070, 1029, 903, 839, 800, 706, 658, 551, 471, 413 cm^{–1}. MALDI–TOF–MS (*m/z*, [M + Na]⁺): 2254.916 (calculated for C₄₅H₆₂F₄₂NaO₂₄Si₁₆); 2254.574 (observed).

1,6-Bis(hepta(3,3,3-trifluoropropyl)-T8-silsesquioxyl)-hexane (POSS-DH). POSS-DH was synthesized from F7-Na (5.0 g, 4.40 mmol), and 1,6-bis(trichlorosilyl)hexane (0.55 mL, 1.98 mmol) with triethylamine (0.62 mL, 4.40 mmol) in similar to that for POSS-DE except for purification. A crude product was dissolved in 5 mL of THF and precipitated in 250 mL of MeOH, collected with a filter paper, and dried under reduced pressure. The resultant white solid (1.6 g) was dissolved in acetone (16 mL), and MeOH (160 mL) was added under stirring. The precipitates were removed from the solution by centrifugation and the supernatant was concentrated under reduced pressure. The resultant solid was purified by manually recycled gel filtration chromatography (gel, Sephadex LH-20; column length, 40 cm; solvent, acetone/MeOH = 4/6; recycle, 4 times.) to give a white solid in 11% yield. ¹H NMR (acetone-*d*₆, 300 MHz): δ 2.40–2.23 (m, 28H, –CH₂–CF₃), 1.51–1.53 (br, 4H, Si–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–Si), 1.43–1.35 (br, 4H, Si–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–Si), 1.08–0.91 (m, 28H, Si–CH₂–CH₂–CF₃), 0.78 (t, *J* = 6, 4H, Si–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–Si). ¹³C NMR (acetone-*d*₆, 100 MHz): δ 128.67 (q, *J* = 274 Hz), 128.66 (q, *J* = 274 Hz), 33.21, 28.03 (q, *J* = 30 Hz), 27.91 (q, *J* = 30 Hz), 23.32, 12.01, 4.60 (q (overlap), *J* = 2 Hz), 4.50 (q (overlap), *J* = 2 Hz). ²⁹Si NMR (acetone-*d*₆, 80 MHz): δ –66.70, –67.08, –69.13. FT-IR (KBr): *ν* = 2976, 2952, 2933, 2865, 1449, 1421, 1375, 1318, 1270, 1221, 1119, 1070, 1030, 903, 837, 803, 705, 671, 551, 470, 413 cm^{–1}. MALDI–TOF–MS (*m/z*, [M + Na]⁺): 2296.963 (calculated for C₄₈H₆₈F₄₂NaO₂₄Si₁₆); 2296.638 (observed).

Allylhepta(3,3,3-trifluoropropyl)-T8-silsesquioxane (POSS-F7A1). POSS-F7A1 was synthesized from F7-Na (10.0 g, 8.8 mmol) and allyltrichlorosilane (1.66 mL, 13.2 mmol) and triethylamine (1.23 mL, 8.8 mmol) in a similar manner to POSS-DE except for purification. A crude product was purified by recrystallization with methanol to give a white solid in 43% yield. ¹H NMR (acetone-*d*₆, 300 MHz): δ 5.81 (m, 1H, –CH₃–CH=CH₂), 5.00 (m, 2H, –CH=CH₂), 2.32 (m, 14H, –CH₂–CF₃), 1.78 (d, 2H, –CH₂–Si), 1.00 (m, 14H, Si–CH₂–CH₂–CF₃). ¹³C NMR (acetone-*d*₆, 75 MHz): δ 132.6, 128.69 (q, *J* = 274 Hz), 123.21, 27.99 (q, *J* = 30.0 Hz), 27.93 (q, *J* = 30.0 Hz), 19.49, 4.58. ²⁹Si NMR (acetone-*d*₆, 80 MHz): δ –67.33, –67.38, –67.48, –70.19. FT-IR (KBr): *ν* = 2981, 2955, 2919, 1637, 1447, 1423, 1375, 1317, 1270, 1221, 1116, 1069, 1034, 903, 839, 802, 710, 656, 540, 472, 413 cm^{–1}. Anal. Calcd for C₂₄H₃₃F₂₁O₁₂Si₈: C, 25.35; H, 2.93. Found: C, 24.99; H, 2.76.

Ran-DP-Pre. To a methanol (13.7 mL) and THF (68.0 mL) solution containing (3,3,3-trifluoropropyl)trimethoxysilane (15.28 g, 70.0 mmol), propyltrimethoxysilane (0.82 g, 5.0 mmol), and tetraethoxysilane (1.04 g, 5.0 mmol) was added a mixed solution of 1 N HCl (0.80 g) aqueous and distilled water (3.64 g) dropwise at room temperature, and then a reflux condenser was attached. The mixture was refluxed for 3 h with magnetically stirring. The reactant was concentrated by a rotary evaporator and dried under reduced pressure at 50 °C for 2 h to give a viscous liquid. ¹H NMR (acetone-*d*₆, 300 MHz): δ 6.49 (br, –Si–OH), 2.30 (br, 28H, –CH₂–CF₃), 1.49 (br, 2H, Si–CH₂–CH₂–CH₃), 1.2–0.6 (m, 33H, Si–CH₂–CH₂–CF₃, Si–CH₂–CH₂–CH₃, Si–CH₂–CH₂–CH₃). ¹³C NMR (acetone-*d*₆, 75 MHz): δ 128.5 (q, *J* = 275 Hz), 28.0 (m), 15.8, 5.5 (m). FT-IR (KBr): *ν* = 3423 (s), 2955, 2917, 2874, 1449, 1422, 1375, 1318, 1269, 1218, 1127, 1072, 1030, 903, 837, 798, 706, 556, 441 cm^{–1}.

Scheme 1. Syntheses of Various POSS Derivatives



Ran-DH-Pre. Ran-DH-Pre was synthesized from (3,3,3-trifluoropropyl)trimethoxysilane (15.28 g, 70.0 mmol) and 1,6-bis(trichlorosilyl)hexane (1.88 g, 2.54 mmol) in a similar manner to Ran-DP-Pre without 1 N HCl. ^1H NMR (acetone- d_6 , 300 MHz): δ 6.49 (br, $-\text{Si}-\text{OH}$), 3.93 (br, $-\text{Si}-\text{OCHH}_3$), 2.30 (br, 28H, $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CF}_3$), 1.60–1.25 (br, 8H, $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}$), 1.0 (br, 28H, $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CF}_3$), 0.75 (br, 4H, $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}$). ^{13}C NMR (acetone- d_6 , 75 MHz): δ 128.7 (qbr, $J = 275$ Hz), 45.5 (br), 33.6 (br), 28.2 (br), 23.7 (br), 5.2 (br). FT-IR (KBr): $\nu = 3423$ (s), 2954, 2930, 2862, 1449, 1422, 1375, 1318, 1269, 1218, 1126, 1072, 1030, 902, 837, 784, 700, 551, 460 cm^{-1} .

Preparation of Coating Solutions and Coated Film. The coating solutions of the dumbbell-shaped POSS derivatives were prepared as follows. POSS-DE (0.140 g) was dissolved in hexafluorobenzene (1.246 g) and acetone (0.614 g). POSS-DP, POSS-DH, and POSS-F7A1 were prepared by dissolved in hexafluorobenzene. All the coating solutions were filtrated by a membrane filter made with polypropylene having a pore of $0.45\text{ }\mu\text{m}$ size before use. The coating solutions were spin-coated on a soda-lime glass and baked at $100\text{ }^\circ\text{C}$ for 5 min on a hot plate.

The coating solutions of the random silsesquioxanes precursors were dissolved in THF and filtrated by the membrane filter to prepare coating solutions. The coating solution was spin-coated on a soda-lime glass, and prebaked at $100\text{ }^\circ\text{C}$ for 2 min on a hot plate, and cured at $180\text{ }^\circ\text{C}$ for 5 min and $250\text{ }^\circ\text{C}$ for 15 min under air atmosphere. The cured films were lifted off from the glass with a spatula for FT-IR analysis. Ran-DP: FT-IR (KBr): $\nu = 3450$ (w), 2960, 2920, 2881, 2855, 1451, 1421, 1380, 1321, 1270, 1220, 1128, 1072, 1024, 902, 839, 798, 703, 553, 459 cm^{-1} . Ran-DH: FT-IR (KBr): $\nu = 3450$ (w), 2956, 2924, 2869, 1452, 1421, 1379, 1321, 1272, 1221, 1124, 1070, 1024, 902, 839, 799, 702, 552, 453 cm^{-1} .

RESULTS AND DISCUSSION

Synthesis and Characterization of Dumbbell-Shaped POSS Derivatives. Hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate (F7-Na) was used as a precursor for all the

POSS derivatives synthesized here. Dumbbell-shaped C2-linked POSS (POSS-DE), C3-linked POSS (POSS-DP), and C6-linked POSS (POSS-DH) were prepared by corner-capping method of F7-Na with 1,2-bis(trichlorosilyl)ethane, 1,3-bis(trichlorosilyl)propane and 1,6-bis(trichlorosilyl)hexane, respectively (Scheme 1). First purification by reprecipitation from acetone to methanol or isopropylalcohol gave crude POSS derivatives. The gel permeation chromatography (GPC) analysis of all the crude products after the first reprecipitation showed shoulders at higher molecular weight side of the main peaks as well as low molecular weight impurities (Figure 1).¹⁶ The ^1H NMR spectra of the crude products showed broader peaks (Figure S1, Supporting Information). Pure POSS-DE was obtained by subsequent fractional precipitation of the crude product. Pure POSS-DP was obtained by further recrystallization of the fractional precipitated product from acetone/MeOH = 4/6 solution. Pure POSS-DH was obtained by a gel filtration chromatography of the fractional precipitated product. The GPC analysis of the purified samples shows no high molecular weight shoulder peaks and removal of the low molecular weight impurities as shown Figure 1. Low isolated yields of the purified POSS derivatives were due to low recoveries by the fractional precipitation and recrystallization. Allylhepta(3,3,3-trifluoropropyl)-T8-silsesquioxane (POSS-F7A1) as an asymmetric POSS derivative was also synthesized from corner capping reaction of F7-Na with allyltrichlorosilane. POSS-F7A1 was purified by recrystallization from methanol.

The dumbbell structures of POSS-DE, POSS-DP, and POSS-DH were confirmed by ^1H , ^{13}C , and ^{29}Si NMR and MALDI-TOF-MS. Figure 2 shows the ^1H NMR spectra of POSS-DE, POSS-DP, and POSS-DH. The peaks of all the purified compounds were well separated compared with those of the crude samples (Figure S1, Supporting Information). The peaks derived from the trifluoropropyl groups of POSS-DE were observed at around 2.3 and 1.0 ppm. That of the ethylene group for the linker was observed at 0.84 ppm. The integral ratio of the ethylene and

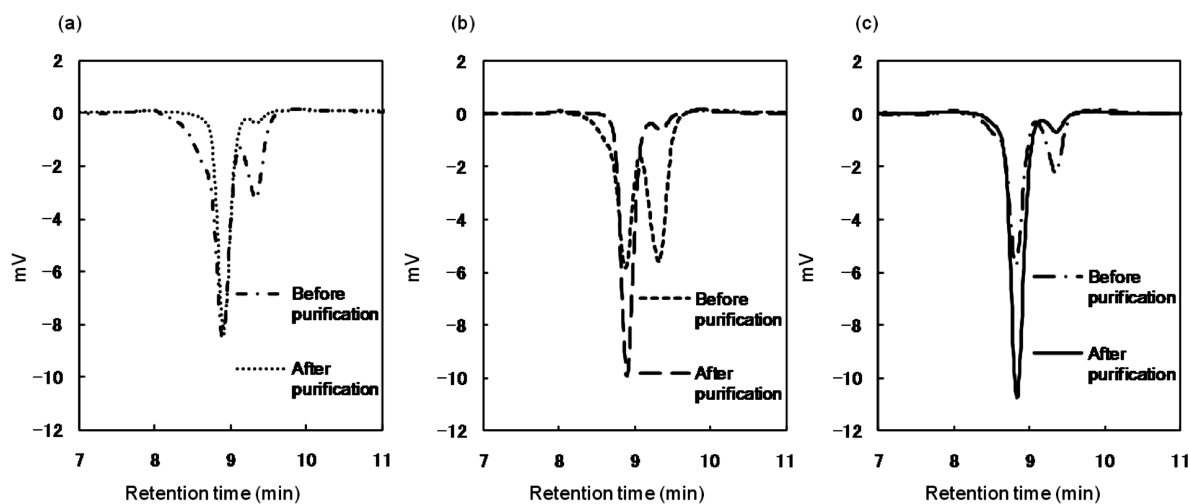


Figure 1. GPC traces of the crude and purified POSS-DE(a), POSS-DP(b), and POSS-DH(c) measured by TSK-gel super HM-H column using THF as eluent with RI detection.

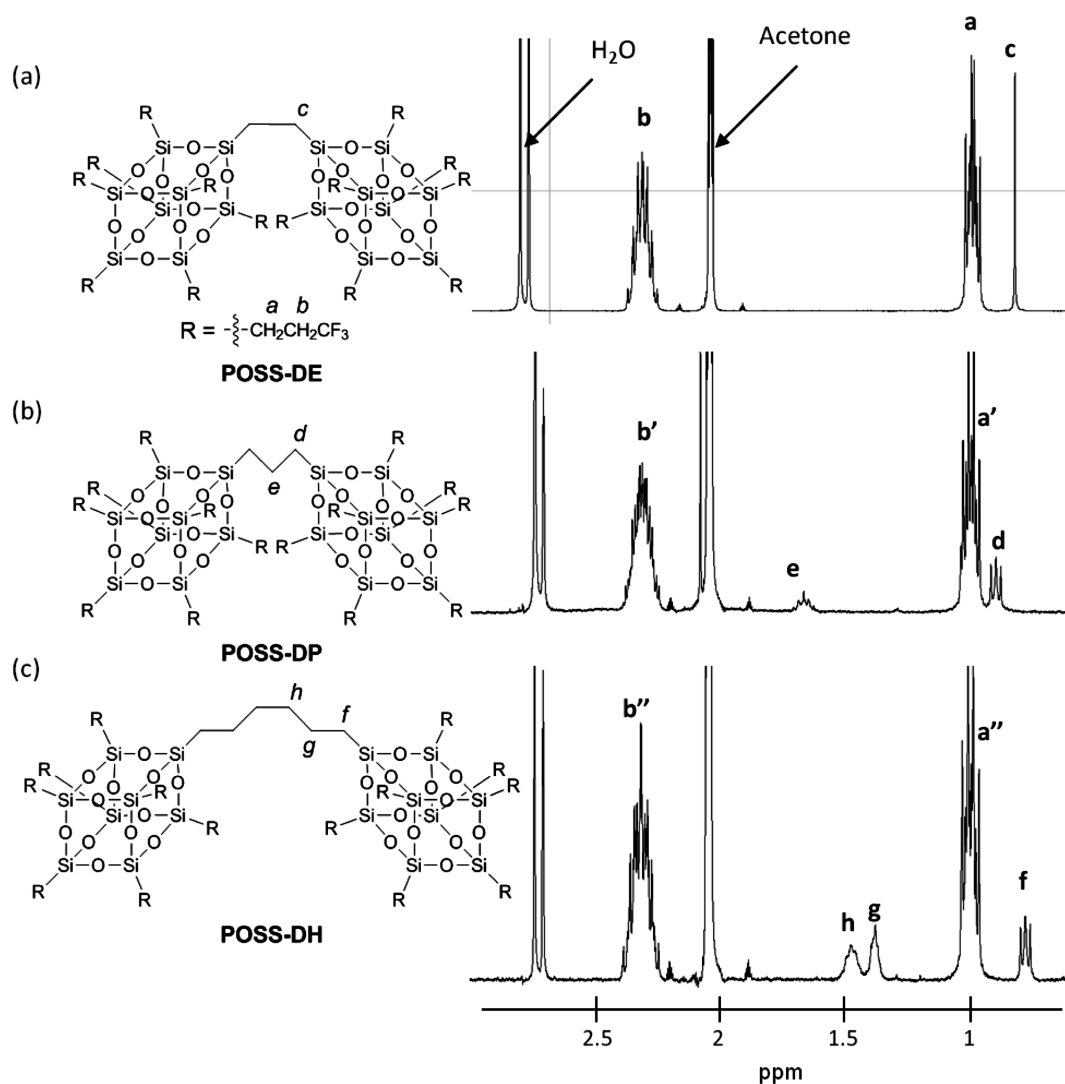


Figure 2. ¹H NMR spectra of (a) POSS-DE, (b) POSS-DP, and (c) POSS-DH in acetone-*d*₆.

trifluoropropyl groups in the ¹H NMR spectrum agreed with the theoretical value. The ¹H NMR spectra of POSS-DP and

POSS-DH also showed the peaks assignable to the trifluoropropyl groups and the propylene and the hexylene linkers, respectively.

The integral ratios of the linker parts and trifluoropropyl groups in POSS-DP and POSS-DH agreed with the theoretical values. The ^{13}C NMR and ^{29}Si NMR also suggested the dumbbell structures (see Supporting Information). The ^{13}C NMR spectrum of POSS-DE showed only one sharp peak for the linker carbons at 3.48 ppm (Figure S4, Supporting Information), suggesting the formation of the dumbbell structure. The peak patterns of the linker carbons in the ^{13}C NMR spectra of POSS-DP and POSS-DH also confirmed the dumbbell structures. Ideally, four different Si environments are observed for ^{29}Si NMR spectra of POSS derivatives prepared by corner capping of partially condensed silsesquioxanes.² The ^{29}Si NMR spectra of POSS-DE, POSS-DP, and POSS-DH showed four, three, and three peaks, respectively. These observations also suggest the dumbbell structures. The MALDI-TOF-MS results provided conclusive evidence for the formation of the dumbbell structures for all the compounds.

Trace amounts of the low molecular weight impurities were still recognized in the GPC traces of the purified POSS-DE, POSS-DP and POSS-DH (Figure 1). The GPC analysis of the THF solutions of the samples kept at room temperature for 2 days showed an increase in the peak ratios of the low molecular weight impurities (Figure S2, Supporting Information). These results suggest that the present dumbbell-shaped POSS derivatives gradually decomposed in THF solution at room temperature due to electron withdrawing properties of the trifluoropropyl groups. However, the ^1H , ^{13}C , and ^{29}Si NMR spectra of these samples in acetone- d_6 showed no additional peaks corresponding to the decomposed products even their longer scanning times.

Solubilities of the dumbbell-shaped POSS derivatives are summarized in Table 1. POSS-DP and POSS-DH were soluble in polar aprotic solvents and fluorocarbon such as acetone, THF, ethyl acetate and hexafluorobenzene. POSS-DE was soluble in acetone and partially soluble in THF, ethyl acetate, and hexafluorobenzene. Higher crystallinity of POSS-DE decreases its solubility as described later.

Optical Properties. We studied film forming properties of POSS-F7A1, POSS-DE, POSS-DP, and POSS-DH on soda lime glasses by spin coating and subsequent baking at 100 °C for 3 min using a hot plate. The coating solutions were prepared by dissolving the POSS derivatives in hexafluorobenzene at 7 wt %. We found that POSS-DP and POSS-DH formed transparent films. However, opaque whitish films were formed in the cases of POSS-F7A1 and POSS-DE. Transmittances of the films obtained from POSS-DP and POSS-DH were over 95% at visible region

between 780 and 380 nm (Figure 3). Although usual POSS derivatives are hardly form transparent films due to their high crystallinity, the present POSS-DP and POSS-DH showed well transparent films forming properties without thermosetting process. The films were easily peeled off from the substrates and brittle. It should be, however, noted that this is a first example of optical transparent films prepared from a single POSS compound.

To compare the optical properties of the present materials with those of random silsesquioxanes, random silsesquioxane precursors with the same components as those of POSS-DP and POSS-DH were also prepared as summarized in Table 2. For preparing the random silsesquioxane precursor (Scheme 2) corresponding to POSS-DP denoted as Ran-DP-Pre, additional tetraethoxysilane was required because no film was obtained without tetraethoxysilane. The random silsesquioxane precursor corresponding to POSS-DH (Ran-DH-Pre) was synthesized from (3,3,3-trifluoropropyl)trimethoxysilane and 1,6-bis(trichlorosilyl)hexane. The THF solutions of Ran-DP-Pre and Ran-DH-Pre were spin coated on soda-lime glasses and baked at 250 °C to form transparent films which are abbreviated Ran-DP and Ran-DH, respectively.

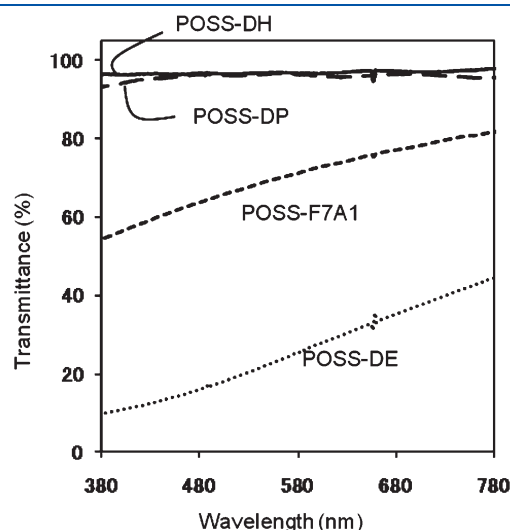


Figure 3. UV-spectra of the films obtained from POSS-DE, POSS-DP, and POSS-DH on soda lime glass. The thickness was about 1 μm .

Table 1. Solubilities of the Dumbbell-Shaped POSS Derivatives^a

	acetone	THF	EtOAc	C ₆ F ₆	hexane	MeOH	H ₂ O
POSS-DE	+	±	±	±	-	-	-
POSS-DP	+	+	+	+	-	-	-
POSS-DH	+	+	+	+	-	-	-

^a Key: +, soluble; ±, partly soluble; -, insoluble.

Table 2. Compositions of the Random Silsesquioxane Precursors

sample			
Ran-DP-Pre	(MeO) ₃ Si-CH ₂ -CF ₃	Si(OMe) ₃	Si(OEt) ₄
	14	1	
Ran-DH-Pre	(MeO) ₃ Si-CH ₂ -CF ₃	Cl ₃ Si-(CH ₂) ₆ -SiCl ₃	
	14	1	

Scheme 2. Syntheses of the Random Silsesquioxane Precursors

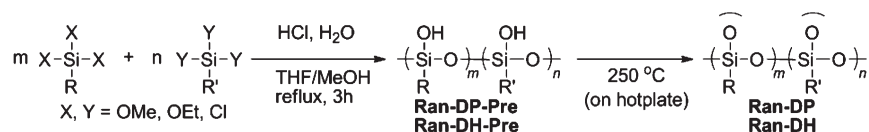


Table 3 summarized the refractive index of all the obtained transparent coated films. The values of the films of the dumbbell-shaped POSS derivatives are in the range of 1.38 to 1.39, which are the same as those of the corresponding random silsesquioxanes. These results suggested that transparent films with low refractive index based on silsesquioxane were prepared even at relatively lower processing temperature by using POSS-DP and POSS-DH. Baking of the random silsesquioxane precursors at 100 °C gave viscous liquid of which refractive index was not measurable by a prism coupler. Such low temperature baking is insufficient to complete the condensation, which increase their refractive index compared to those of sufficient condensed

Table 3. Refractive Indices of the Transparent Silsesquioxanes

sample	refractive index ^a
Ran-DP	1.388
POSS-DP	1.388
Ran-DH	1.391
POSS-DH	1.389

^a Wavelength was 632.8 nm (laser).

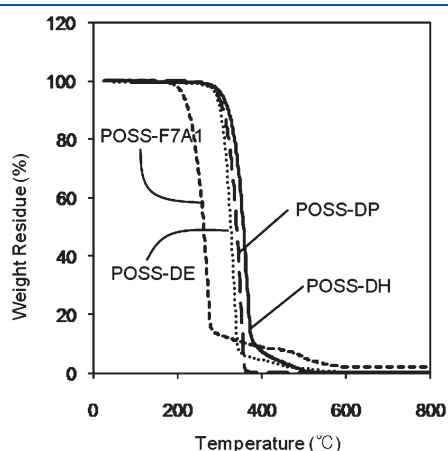


Figure 4. TGA thermograms of POSS-F7A1, POSS-DE, POSS-DP, and POSS-DH at a ramp rate of 10 °C/min in N₂ flow.

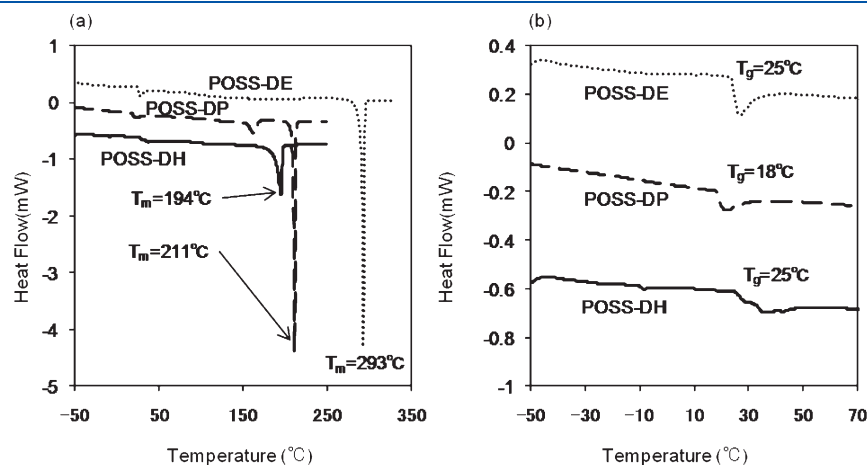


Figure 5. (a) DSC curves of POSS-DE, POSS-DP, and POSS-DH at a ramp rate of 10 °C/min in N₂ flow for the whole temperature range. (b) Expanded curves around the glass transition temperature.

silsesquioxanes.⁶ The random silsesquioxanes are thus required to be cured at high temperature. On the other hand, POSS-DP and POSS-DH showed film forming ability under lower temperature process. POSS-DP and POSS-DH are regarded new thermoplastic optical materials derived from a single POSS compound.

It was reported that an increase cage structure ratio in methyl silsesquioxane (MSQ) network structure decreases refractive index.⁷ In the present case, however, no difference was observed between the dumbbell and random structures. The weight ratios of SiO_{3/2} parts in POSS-DP and POSS-DH films are 36.8% and 35.5%, respectively. The weight ratios were calculated from molecular weight ratios of SiO_{3/2} parts in entire molecules. On the other hand, the weight ratio of SiO_{3/2} part in MSQ is 77.6%. We speculated that smaller weight fractions of the silsesquioxane parts in present cases hardly influence to the refractive index. Alternative possible reason is that cage/random ratios in Ran-DP and Ran-DH were comparable to those in the dumbbell POSS derivatives.

Thermal Properties. Thermal stabilities of the dumbbell-shaped POSS derivatives were evaluated by thermogravimetric analysis (TGA). TGA curves of the various silsesquioxanes are showed in Figure 4. Although POSS-F7A1 showed a 5 wt % loss at 214 °C due to sublimation, the dumbbell-shaped POSS derivatives significantly increase the thermal stability. POSS-DE, POSS-DP, and POSS-DH showed 5 wt % losses at 293 °C, 296 °C, and 305 °C, respectively. Thermal decomposition temperatures of the dumbbell-shaped POSS derivatives increase with increase the length of the linkers.

Differential scanning calorimeter (DSC) curves of the dumbbell-shaped POSS derivatives are showed in Figure 5. All the dumbbell-shaped POSS derivatives showed both glass-transition and melting behaviors. This means that amorphous phases were contaminated with crystal phases in these molecules. The melting point of POSS-DE, POSS-DP, and POSS-DH were observed at 293 °C, 211 °C, and 194 °C, respectively (Figure 5a). POSS-DE, POSS-DP, and POSS-DH showed glass-transition temperature at 25 °C, 18 °C, and 25 °C, respectively (Figure 5b). From these result, the dumbbell-shaped POSS derivatives have as thermoplastic materials. The melting points decreased with increase of the linker length. POSS-DE had higher melting point due to its higher crystallinity,¹⁷ which induced rough surfaces to

inhibit formation of transparent films (Figure S11, Supporting Information).

CONCLUSIONS

We synthesized novel dumbbell-shaped POSS derivatives linked by the simple aliphatic chains by corner capping reaction from the incomplete cage compounds and the bistrichlorosilane compounds. The structures of the dumbbell-shaped POSS derivatives were confirmed by ^1H , ^{13}C , and ^{29}Si NMR spectra and MALDI–TOF–MS analysis. POSS-DP and POSS-DH formed optical transparent films by spin coating and subsequent baking at 100 °C. Their refractive indices were the same as those of the corresponding random silsesquioxanes prepared by curing at 250 °C. Although the random silsesquioxanes are required to be cured at the high temperature, POSS-DP and POSS-DH showed excellent film forming properties under the lower temperature, which would open a way to apply to coating on various thermally unstable materials. The reduction of symmetries of the POSS derivatives decreased their high crystallinity and increased their thermal stabilities. POSS-DP and POSS-DH are regarded as new thermoplastic optical materials derived from a single POSS compound. Since the films were easily peeled off from the substrate and brittle, we are now currently studying new dumbbell-shaped POSS derivatives substituted with other organic units to improve film performances.

ASSOCIATED CONTENT

S Supporting Information. Figures showing ^1H , ^{13}C , and ^{29}Si NMR spectra, GPS traces, an SEM image, and DSC traces of various POSS derivatives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) The GPC traces were inverted because the refractive indices of the samples are lower than that of THF used as an eluent.

(17) No significant difference was observed in the DSC data of a sample prepared by the same condition of the opaque whitish film of POSS-DE (Figure S12, Supporting Information). This data suggests that the crystallinity of POSS-DE is not reliance on a different thermal/solvent history.