Applied Organometallic Chemistry

Synthesis of acetoxyphenyl- and hydroxyphenyl-terminated polyfunctional T_8, T_{10}, T_{12} silsesquioxanes and initial studies on their use in the formation of highly crosslinked polyesters

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There is continuing interest in the synthesis of polyhydroxy-terminated molecular species for diverse applications ranging from photolithographic materials to intermediates in the synthesis of porous, crosslinked polymers as media for molecular separations, drug delivery etc. We describe here the use of [vinylSiO$_{1.5}$]$_8$ and [vinylSiO$_{1.5}$]$_{10/12}$ mixtures to synthesize first- and second-generation acetoxyphenyl compounds via metathesis with *p*-acetoxystyrene (generation 1, GEN1) or metathesis with *p*-bromostyrene followed by Heck coupling with *p*-acetoxystyrene (generation 2, GEN2). The resulting acetoxy compounds were then hydrolyzed to produce octa-, deca- and dodecahydroxy GEN1 and GEN2 compounds. These compounds were purified and then reacted with adipic acid chloride to form the first examples of highly crosslinked polyesters based on silsesquioxanes. The coupling products, their hydrolyzed products and the crosslinked polymers were characterized using a variety of spectroscopic methods. In general, the observed specific surface areas were less than 5 m^2 g^{-1}; however, the T_8 GEN1 derivative gave a surface area of 25 m^2 g^{-1} and was the only crosslinked polymer with a TGA ceramic yield that matched theory for 'perfect' crosslinking. This crosslinked polyester has the shortest organic linker between cages and despite the highly flexible C$_6$ linker provides continuing evidence that it is possible to use the cubic symmetry in these materials to build well-ordered 3-D nanocomposite structures. Copyright © 2013 John Wiley & Sons, Ltd.

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Introduction

Polyhedral silsesquioxanes (SQs), with the formulae [RSiO$_{1.5}$]$_{8,10,12}$, are organic–inorganic hybrid materials that consist of nanometer-sized silica cages surrounded by organic functional groups. While the inorganic core provides mechanical stiffness and thermal stability, the organic pendant groups provide solubility in organic solvents and the opportunity for chemical modification. In particular, the T_8 SQs have cubic symmetry offering the potential for use as three-dimensional nano-building blocks.[1–14] Such 3-D building blocks may offer nanocomposites and/or nanoporous materials for a range of applications, including low-dielectric-constant interlayer dielectrics for semiconductor interconnects, encapsulants for drug delivery, porous media for hydrogen storage, separation of pollutants or fine chemicals, and as catalyst substrates.[15–24]

The work presented here details our efforts to develop acetoxy- and hydroxy-terminated nanobuilding blocks based on different vinyl SQs, T_8 and mixtures of T_{10} and T_{12}. Vinyl SQs are easily modified by metathesis and Heck coupling reactions.[25–31] First-generation (GEN1) acetoxySQs were prepared by metathesis of the vinyl SQs and *p*-acetoxystyrene, as illustrated by reaction (1), and second-generation (GEN2) acetoxySQs were prepared by Heck coupling of *p*-acetoxystyrene with Br-StyrenylSQs as shown in reaction (2). These *p*-acetoxy GEN1 and GEN2 SQs were converted to the *p*-hydroxySQs by mild hydrolysis, reaction (3).
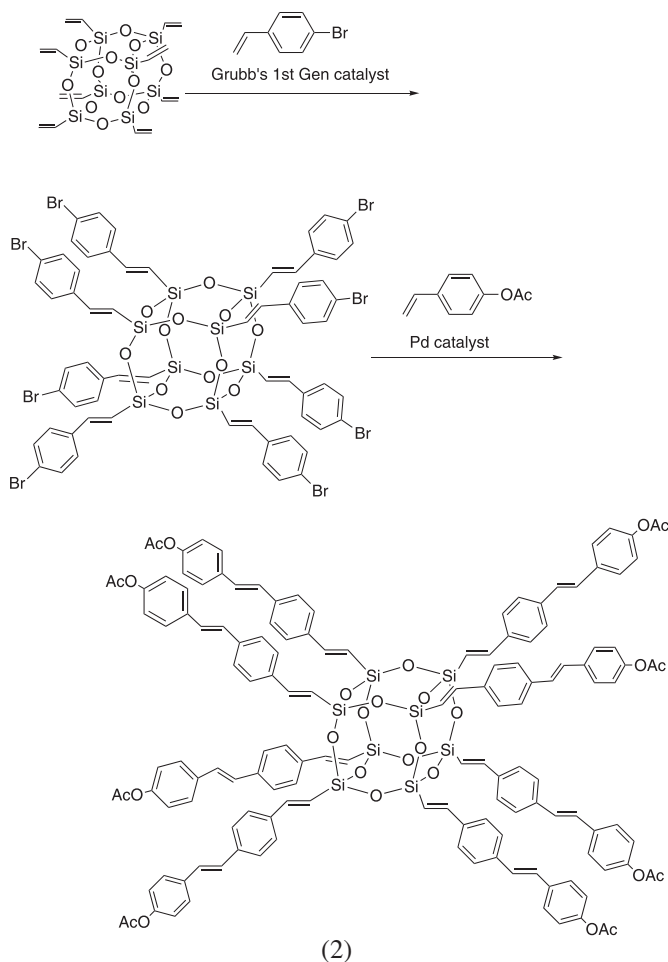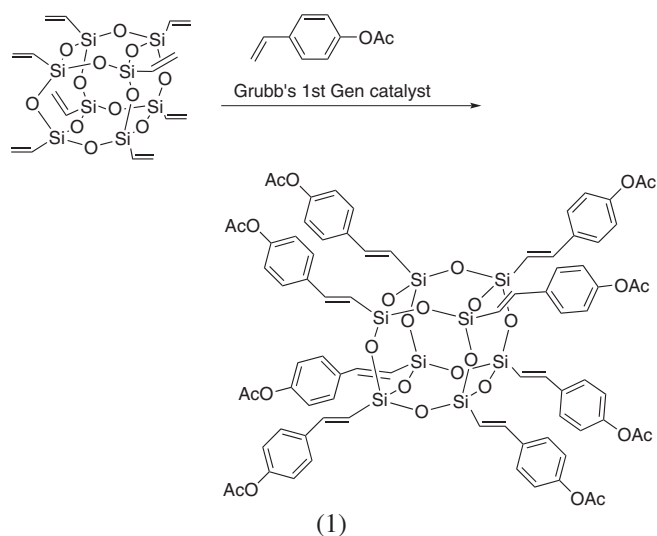
The *p*-hydroxy GEN1 and GEN2 SQs were reacted with stoichiometric amounts of adipoyl chloride to prepare crosslinked polymers (Scheme 1) with some limited porosity.

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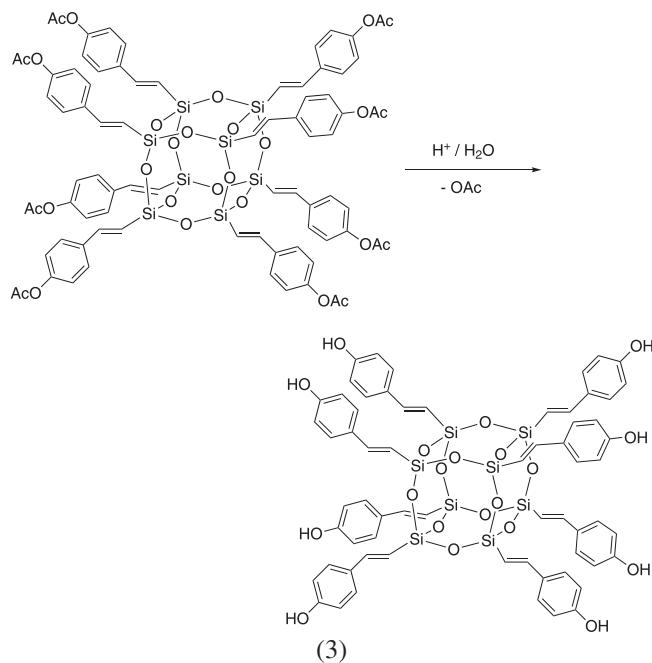
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Grubb's 1st Gen catalyst

(1)

H^+ / H_2O
- OAc

(3)

Grubb's 1st Gen catalyst

Pd catalyst

(2)

Experimental

Materials

Octavinylsilsesquioxane (OVS) was prepared using the literature method[32] or was a gift from Mayaterials Inc. Vinyl $T_{10/12}$ silsesquioxane and p-Br-styrenyl T_8 and $T_{10/12}$ silsesquioxanes were prepared using literature methods.[30–32] 1,4-Dioxane was distilled from sodium benzophenone ketyl under nitrogen prior to use. Methylene chloride (CH_2Cl_2) was purchased from Fisher and distilled from CaH_2 under N_2 prior to use. A first-generation Grubbs catalyst was purchased from Aldrich. All other chemicals were purchased from Aldrich or Fisher and used as received.
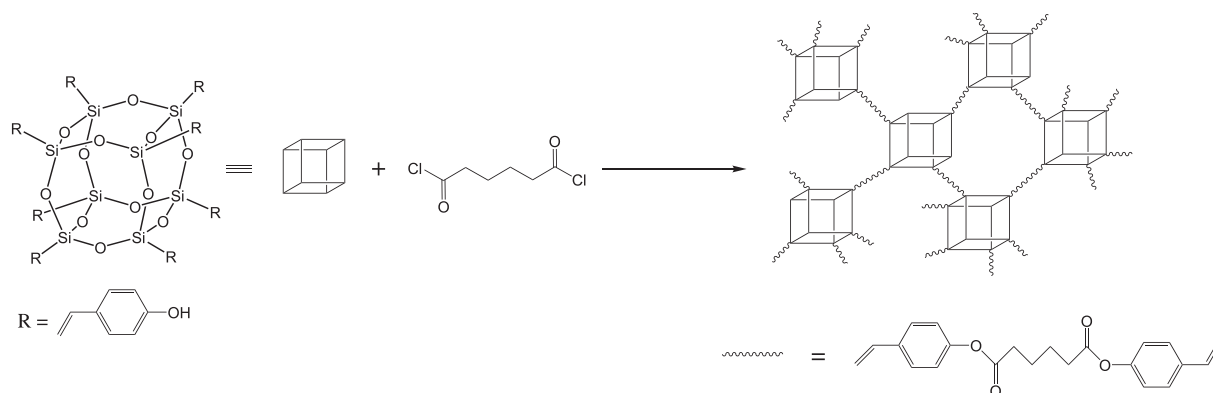
Analytical Methods

Gel permeation chromatography (GPC)

All GPC analyses were done on a Waters 440 system equipped with Waters Styragel columns (7.8 × 300, HT 0.5, 2, 3, 4) with RI detection using Optilab DSP interferometric refractometer and THF as solvent. The system was calibrated using polystyrene standards and toluene as reference. Analyses were performed using PL Caliber 7.04 software (Polymer Labs, Church Stretton, UK).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrometry

MALDI-TOF spectra were obtained using a Micromass TofSpec-2E equipped with a 337 nm nitrogen laser in positive-ion reflectron mode using poly(ethylene glycol) as calibration standard, dithranol as matrix and $AgNO_3$ as ion source. Samples were prepared by mixing a solution of 5 parts matrix (10 mg ml^{-1} in THF), 5 parts sample (1 mg ml^{-1} in THF), and 1 part $AgNO_3$ (2.5 mg ml^{-1} in water) and blotting the mixture on the target plate.

The goal of the current work was to develop simple routes to high densities of phenolic groups in small 3-D volumes with the objective of providing simple routes to a wide variety of 3-D polyphenolics for applications as noted above and simply as potential crosslinking agents for polyphenolic resins.

Scheme 1. General scheme for reaction of GEN1 hydroxy T_8 and adipoyl chloride.

NMR analyses

All ^{1}H were run in DMSO on a Varian INOVA 500 spectrometer. ^{1}H NMR spectra were collected at 500 MHz using a 7998.4 Hz spectral width, a relaxation delay of 0.5 s, a pulse width of 45°, 65 k data points and TMS (0.00 ppm) as an internal reference.

Fourier-transform infrared spectroscopy (FT-IR)

Diffuse reflectance Fourier transform (DRIFT) spectra were recorded on a Nicolet 6700 Series FT-IR spectrometer (Thermo Fisher Scientific, Inc., Madison, WI, USA). Optical-grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ, USA) were ground, with 1.0 wt% of sample to be analyzed. For DRIFT analyses, samples were packed firmly and leveled off at the upper edge to provide a smooth surface. The FT-IR sample chamber was flushed continuously with N_2 prior to data acquisition in the range 4000–400 cm^{-1} with a precision of $\pm 4\, cm^{-1}$.

Thermal gravimetric analyses (TGA)

Thermal stabilities of materials under N_2 or air were examined using a 2960 simultaneous DTA-TGA (TA Instruments, Inc., New Castle, DE, USA). Samples (5–10 mg) were loaded in alumina pans and ramped to 1000 °C while heating at 10 °C min^{-1}. The N_2 or air flow rate was 60 ml min^{-1}.

Brunauer–Emmett–Teller surface area analysis (BET)

Surface area analysis was carried out by the BET method using an ASAP 2020 system from Micromeritics Inc. A sample of each powder was loaded into a sample tube of known mass, and the weight of the tube and sample was measured. The sample was then degassed at 150 °C under vacuum for 8 h and weighed again. The sample tube was then transferred to the analysis port of the machine and an 11-point adsorption isotherm over the pressure range $0.5 \leq P/P_0 \leq 0.35$ was obtained at 77 K in liquid N_2.

Syntheses

General metathesis reactions of vinyl T_8 (OVS) and $T_{10/12}$ SQs

To a dry 250 ml Schlenk flask under N_2 was added 4.0 g (9.60 mmol) vinyl SQ and 63.0 mg (0.08 mmol) of first-generation Grubbs catalyst. Dry CH_2Cl_2 (60 mL) was added by syringe followed by 11.6 g (113 mmol) *p*-acetoxystyrene. The mixture was stirred for 168 h at 40 °C and conversion of starting materials was monitored via MALDI-TOF. The solution was quenched by precipitation into 500 ml hexane and then filtered. The resulting solid was vacuum dried for 4 h and was obtained as a white solid.

The product was further purified by column chromatography to remove residual catalyst. (silica, 4:1 THF:hexane).

Metathesis reactions of OVS (GEN1 *p*-acetoxy T_8 SQ)

OVS and *p*-acetoxystyrene were allowed to react according to the above general procedure (8.3 g, 80.0% yield). Characterization data: ^{1}H-NMR (DMSO, δ ppm): 2.3 (s, 3H, —CH_3), 6.4 (d, H, $J = 20\, Hz$, Si—C*H* CH—), 7.1 (d, 2H, $J = 26\, Hz$, Ar—*H*), 7.3 (t, H, $J = 20\, Hz$, Si—CH C*H*—), 7.5 (d, 2H, $J = 48\, Hz$, Ar—*H*). ^{13}C NMR (CDCl$_3$, δ ppm): 21.2 (—CH_3), 119.1 (Si—C *C*—), 121.9 (Ar —CH), 128.0 (Ar —CH), 135.1 (Si—*C* C—), 147.6 (Ar *C*—C), 151.2 (Ar *C*—O), 169.4 (*C* O). MALDI-TOF: m/z (Ag$^+$ adduct) = 1813.47 [Ag(SiO$_{1.5}$)$_8$(C$_8$H$_6$)$_8$(C$_2$H$_3$O$_2$)$_8$]. FT-IR (cm^{-1}): 1096 (Si—O), 1203 (C—O), 1603 (C C), 1505 (Si—C), 1763 (C O), GPC: $M_n = 2070$, $M_w = 2150$, PDI = 1.04. TGA (air, 1000 °C): found 27.9%, calcd 28.2%, $T_{d5\%} = 345\,°C$.

Metathesis reactions of vinyl $T_{10/12}$ SQ (GEN1 *p*-acetoxy $T_{10/12}$ SQ)

Vinyl $T_{10/12}$ SQ and *p*-acetoxystyrene were allowed to react according to the above general procedure using 6.0 g vinyl $T_{10/12}$ SQ, 94.5 mg of first-generation Grubbs catalyst and 17.4 ml *p*-acetoxystyrene (13.6 g, 84.1% yield). Characterization data: ^{1}H NMR (DMSO, δ ppm): 2.3 (s, 3H, —CH_3), 6.4 (d, H, $J = 20\, Hz$, Si—C*H* CH—), 7.1 (d, 2H, $J = 8\, Hz$, Ar—*H*), 7.3 (d, H, $J = 20\, Hz$, Si—CH C*H*—), 7.5 (d, 2H, $J = 8\, Hz$, Ar—*H*). ^{13}C NMR (CDCl$_3$, δ ppm): 21.2 (—CH_3), 117.5 (Si—C *C*—), 121.9 (Ar —CH), 128.0 (Ar —CH), 135.1 (Si—*C* C—), 148.2 (Ar *C*—C), 151.2 (Ar *C*—O), 169.4 (*C* O). MALDI-TOF: m/z (Ag$^+$ adduct) = 2240.37 [Ag(SiO$_{1.5}$)$_{10}$(C$_8$H$_6$)$_{10}$(C$_2$H$_3$O$_2$)$_{10}$], 2666.67 [Ag(SiO$_{1.5}$)$_{12}$(C$_8$H$_6$)$_{12}$(C$_2$H$_3$O$_2$)$_{12}$]. FT-IR (cm^{-1}): 1117 (Si—O), 1205 (C—O), 1505 (Si—C), 1603 (C C), 1763 (C O), GPC: $M_n = 2500$, $M_w = 2560$, PDI = 1.02. TGA (air, 1000 °C): found 28.4%, calcd 28.2%, $T_{d5\%} = 345\,°C$.

General Heck reaction converting *p*-Br-styrenyl T_8 and $T_{10/12}$ SQ to *p*-acetoxy GEN2

To a dry 50 ml Schlenk flask under N_2 was added 1.0 g (4.28 mmol Br) of Br-styrenylSQ, 43.70 mg bis(tri-*tert*-butylphosphine)-palladium catalyst, and 39.15 mg tris(dibenzylideneacetone)-dipalladium catalyst. Dry 1,4-dioxane (20 ml) was added via syringe, followed by 0.61 ml (2.24 mmol) *N*-methyldicyclohexylamine, and 1.96 ml (8.88 mmol) *p*-acetoxystyrene. The mixture was stirred at room temperature for 72 h and then quenched by filtering through 1 cm Celite. The solution was then precipitated into 200 ml methanol and filtered. The resulting solid was vacuum dried for 4 h and was obtained as a yellow solid. The product was further purified by column chromatography to remove residual Pd catalyst. (silica, 2:1 THF:hexane).

Heck coupling reactions of p-Br-styrenyl T$_8$ SQ (GEN2 p-acetoxy T$_8$ SQ)

p-Br-styrenyl T$_8$ SQ and *p*-acetoxystyrene were allowed to react according to the above general procedure (1.25 g, 93% yield). Characterization data: ^{1}H-NMR (DMSO, δ ppm): 2.3 (s, 3H, —CH$_3$), 6.5 (d, H, *J* = 20 Hz, Si—C*H* CH—), 7.3–7.6 (m, 11H, Ar—*H*, Si—CH C*H*—, Ar—C*H* CH—Ar). ^{13}C NMR (CDCl$_3$, δ ppm): 21.2 (—CH$_3$), 117.2 (Si—*C C*—), 121.9 (Ar —*C*H), 126.9 (Ar —*C*H), 127.5 (Ar —*C*H), 128.3 (Ar —*C*H CH—Ar), 135.1 (Si—*C* C—), 136.7 (Ar *C*—C), 138.0 (Ar *C*—C), 148.9 (Ar *C*—C), 150.2 (Ar *C*—O), 169.5 (*C* O). MALDI-TOF: *m/z* (Ag + adduct) = 2629.59 [Ag(SiO$_{1.5}$)$_8$(C$_8$H$_6$)$_{16}$ (C$_2$H$_3$O$_2$)$_8$]. FT-IR (cm^{-1}): 1095 (Si—O), 1202 (C—O), 1510 (Si—C), 1598 (C C), 1760 (C O), GPC: M_n = 4080, M_w = 4240, PDI = 1.04. TGA (air, 1000 °C): found 19.2%, calcd 19.1%, $T_{d5\%}$ = 335 °C.

Heck coupling reactions of p-Br-styrenyl T$_{10/12}$ SQ (GEN2 p-acetoxy T$_{10/12}$ SQ)

p-Br-styrenyl T$_{10}$/T$_{12}$ SQ and *p*-acetoxystyrene were allowed to react according to the above general procedure (1.2 g, 89% yield). Characterization data: ^{1}H NMR (DMSO, δ ppm): 2.3 (s, 3H, —CH$_3$), 6.5 (m, H, Si—C*H* CH—), 7.0–7.6 (m, 11H, Ar—*H*, Si—CH C*H*—, Ar—C*H* CH—Ar). ^{13}C NMR (CDCl$_3$, δ ppm): 21.2 (—CH$_3$), 117.2 (Si—*C C*—), 121.9 (Ar —*C*H), 126.9 (Ar —*C*H), 127.5 (Ar —*C*H), 128.3 (Ar —*C*H CH—Ar), 135.1 (Si—*C* C—), 136.7 (Ar *C*—C), 138.0 (Ar *C*—C), 148.9 (Ar *C*—C), 150.2 (Ar *C*—O), 169.5 (*C* O). MALDI-TOF: *m/z* (Ag$^+$ adduct) = 3261.0 [Ag(SiO$_{1.5}$)$_{10}$(C$_8$H$_6$)$_{20}$ (C$_2$H$_3$O$_2$)$_{10}$], 3891.3 [Ag(SiO$_{1.5}$)$_{12}$(C$_8$H$_6$)$_{24}$-(C$_2$H$_3$O$_2$)$_{12}$]. FT-IR (cm^{-1}): 1009 (Si—O), 1202 (C—O), 1510 (Si—C), 1598 (C C), 1759 (C O), GPC: M_n = 4130, M_w = 4270, PDI = 1.03. TGA (air, 1000 °C): found 19.5%, calcd 19.1%, $T_{d5\%}$ = 305 °C.

General hydrolysis reaction to prepare p-hydroxySQs

To a dry 50 ml Schlenk flask under N$_2$ was added 0.50 g (2.34 mmol for GEN1 compounds and 1.59 mmol for GEN2 compounds) *p*-acetoxy SQ and 12.5 ml of THF. 0.2 ml of 37% HCl solution and 0.5 ml deionized water were added to the reaction by syringe and the reaction flask was wrapped in aluminum foil to limit light-promoted oxidation. The reaction was stirred at room temperature and monitored by disappearance of the C-O peak using FT-IR. The reaction was neutralized using saturated NaHCO$_3$ and the product was extracted using methylene chloride. The solution was then dried over Na$_2$SO$_4$ and evaporated by vacuum to give a white solid as product and stored in the refrigerator.

Hydrolysis reactions of GEN1 p-acetoxy T$_8$ SQ (GEN1 p-hydroxy T$_8$ SQ)

GEN1 *p*-acetoxy T$_8$ SQ was allowed to react according to the above general procedure. The resulting solid was vacuum dried for 4 h and was obtained as a white solid (0.33 g, 82.2 % yield). Characterization data: ^{1}H NMR (DMSO, δ ppm): 6.2 (d, H, *J* = 20 Hz, Si—C*H* CH—), 6.7 (d, 2H, *J* = 26 Hz, Ar—*H*), 7.1 (t, H, *J* = 20 Hz, Si—CH C*H*—), 7.3 (d, 2H, *J* = 48 Hz, Ar—*H*), 9.8 (s, H, —O*H*). MALDI-TOF: *m/z* (Ag$^+$ adduct) = 1477.47 [Ag(SiO$_{1.5}$)$_8$(C$_8$H$_6$)$_8$(OH)$_8$],1519.48 [Ag(SiO$_{1.5}$)$_8$(C$_8$H$_6$)$_8$(OH)$_7$-(C$_2$H$_3$O$_2$)$_1$]. FT-IR (cm^{-1}): 1112 (Si—O), 1510 (Si—C), 1606 (C C), 3326 (O—H), GPC: M_n = 2000, M_w = 2030, PDI = 1.01. TGA (air, 1000 °C): found 34.6 %, calcd 35.1%, $T_{d5\%}$ = 235 °C.

Hydrolysis reactions of GEN1 p-acetoxy T$_{10/12}$ SQ (GEN1 p-hydroxy T$_{10/12}$ SQ)

GEN1 acetoxy T$_{10/12}$ SQ was allowed to react according to the above general procedure. The resulting solid was vacuum dried for 4 h and was obtained as a white solid (0.32 g, 79.7% yield). Characterization data: ^{1}H NMR (DMSO, δ ppm): 6.2 (d, H, *J* = 20 Hz, Si—C*H* CH—), 6.7

(d, 2H, *J* = 8 Hz, Ar—H), 7.1 (d, H, *J* = 20 Hz, Si—CH C*H*—), 7.3 (d, 2H, *J* = 8 Hz, Ar—H), 9.7 (s, H, —O*H*). MALDI-TOF: *m/z* (Ag$^+$ adduct) = 1819.44 [Ag(SiO$_{1.5}$)$_{10}$(C$_8$H$_6$)$_{10}$(OH)$_{10}$], 2162.48 [Ag(SiO$_{1.5}$)$_{12}$(C$_8$H$_6$)$_{12}$ (OH)$_{12}$]. FT-IR (cm^{-1}): 1115 (Si—O), 1511 (Si—C), 1605 (C C), 3328 (O—H), GPC: M_n = 2240, M_w = 2300, PDI = 1.03. TGA (air, 1000 °C): found 34.4%, calcd 35.1%, $T_{d5\%}$ = 280 °C.

Hydrolysis reactions of GEN2 p-acetoxy T$_8$ SQ (GEN2 p-hydroxy T$_8$ SQ)

GEN2 *p*-acetoxy T$_8$ SQ was allowed to react according to the above general procedure. The resulting solid was vacuum dried for 4 h and was obtained as a white solid (0.35 g, 80.8% yield). Characterization data: ^{1}H NMR (DMSO, δ ppm) 6.7–7.6 (m, 12H, Si—C*H* CH—, Ar—*H*, Si—CH C*H*—, Ar—C*H* CH—Ar), 9.6 (s, H, —O*H*). MALDI-TOF: *m/z* (Ag$^+$ adduct) = 2293.10 [Ag(SiO$_{1.5}$)$_8$ (C$_8$H$_6$)$_{16}$(OH)$_8$]. FT-IR (cm^{-1}): 1097 (Si—O), 1513 (Si—C), 1597 (C C), 2962 (O—H), GPC: M_n = 3410, M_w = 3560, PDI = 1.04. TGA (air, 1000 °C): found 22.2%, calcd 22.0%, $T_{d5\%}$ = 360 °C.

Hydrolysis reactions of GEN2 p-acetoxy T$_{10/12}$ SQ (GEN2 p-hydroxy T$_{10/12}$ SQ)

GEN2 acetoxy T$_{10/12}$ SQ was allowed to react according to the above general procedure. The resulting solid was vacuum dried for 4 h and was obtained as a white solid (0.36 g, 83.1% yield). Characterization data: ^{1}H-NMR (DMSO, δ ppm): 6.5–7.8 (m, 12H, Si—C*H* CH—, Ar—*H*, Si—CH C*H*—, Ar—C*H* CH—Ar), 9.6 (s, H, —O*H*). FT-IR (cm^{-1}): 1115 (Si—O), 1514 (Si—C), 1597 (C C), 3022 (O—H), GPC: M_n = 3490, M_w = 3590, PDI = 1.03. TGA (air, 1000 °C): found 22.3%, calcd 22.0%, $T_{d5\%}$ = 345 °C.

General polyesterification reaction of p-hydroxySQs and adipoyl chloride

To a dry 10 ml Schlenk flask under N$_2$ was added 0.50 g (2.92 mmol for GEN1 compounds and 1.83 for GEN2 compounds) of *p*-hydroxySQ, 3 ml of 1,4-dioxane, and 0.42 ml (3.07 mmol for GEN1 compounds, 1.92 mmol for GEN2 compounds) of adipoyl chloride. 0.81 ml (5.8 mmol) of triethylamine diluted in 3 ml of 1,4-dioxane was added dropwise to the reaction, which formed a white–yellow precipitate. The reaction was stirred at 40 °C for 1 h and was then filtered. The solid was then stirred with deionized water for 1 h at room temperature to dissolve any remaining acid and filtered again.

Polyesterification reactions of GEN1 p-hydroxy T$_8$ SQ (GEN1 T$_8$ polymer SQ)

GEN1 hydroxy T$_8$ SQ was allowed to react according to the above general procedure with a yield of 0.36 g, 72.0% yield. Characterization data: FT-IR (cm^{-1}): 1119 (Si—O), 1504 (Si—C), 1602 (C C), 1758 (C O), 1292, 1361, 2947 (C—H). TGA (air, 1000 °C): found 19.4%, $T_{d5\%}$ = 230 °C.

Polyesterification reactions of GEN1 p-hydroxy T$_{10.12}$ SQ (GEN1 T$_{10/12}$ polymer SQ)

GEN1 hydroxy T$_{10/12}$ SQ was allowed to react according to the above general procedure with a yield of 0.33 g, 66.0% yield. Characterization data: FT-IR (cm^{-1}): 1119 (Si—O), 1505 (Si—C), 1603 (C C), 1758 (C O), 1360, 2954 (C—H). TGA (air, 1000 °C): found 20.6%, $T_{d5\%}$ = 240 °C.

Polyesterification reactions of GEN2 p-hydroxy T$_8$ SQ (GEN2 T$_8$ polymer SQ)

GEN2 hydroxy T$_8$ SQ was allowed to react according to the above general procedure with a yield of 0.37 g, 74.0% yield. Characterization data: FT-IR (cm^{-1}): 1116 (Si—O), 1511 (Si—C), 1598 (C C), 1738 (C O), 1261, 1359, 2961 (C—H). TGA (air, 1000 °C): found 22.0%, $T_{d5\%}$ = 210 °C.

Polyesterification reactions of GEN2 p-hydroxy T$_{10/12}$ SQ (GEN2 T$_{10/12}$ polymer SQ)

GEN2 hydroxy T$_{10/12}$ SQ was allowed to react according to the above general procedure using 0.15 g (0.55 mmol) GEN2 hydroxy T$_{10/12}$ SQ, 0.13 ml (0.55 mmol) of adipoyl chloride, and 0.24 ml (1.72 mmol) triethylamine with a yield of 0.16 g, 106.7% yield. Characterization data: FT-IR (cm^{-1}): 1122 (Si—O), 1511 (Si—C), 1598 (C C), 1755 (C O), 1358 (C—H). TGA (air, 1000 °C): found 10.1%, $T_{d5\%}$ = 230 °C.

Results and Discussion

In the following sections, we discuss the synthesis and characterization of various *p*-acetoxy SQs (GEN1 T$_8$, GEN1 T$_{10/12}$, GEN2 T$_8$, GEN2 T$_{10/12}$). We then discuss their hydrolysis to form the corresponding hydroxy SQs and thereafter a first example of their polymerization by reaction with adipoyl chloride to form 3-D crosslinked polyesters.

Synthesis of *p*-Acetoxysilsesquioxanes

Reaction (1) or (2) was used to synthesize four different *p*-acetoxySQs from the vinyl T$_8$ SQ and T$_{10/12}$ SQs through metathesis and Heck coupling reactions. Vinyl T$_{10/12}$ SQs were prepared by F$^-$ catalyzed rearrangement of polyvinylsilsesquioxane (PVS), [vinylSiO$_{1.5}$]$_x$, as we recently reported.[30] Vinyl T$_{10/12}$ SQs are a mixture of isomers with the dominant ionizable species being the deca- and dodecavinyl compounds. MALDI reveals the presence of a small amount of vinyl T$_{14}$ as well (Fig. 1). Because these compounds have similar chemical and physical properties, we have not found a simple method of separating T$_{10}$ from T$_{12}$. Therefore, it is important to note that vinyl T$_{10/12}$ should be considered to be relatively well-defined oligomers rather than distinct molecular species.

Table 1 summarizes the characterization data for the *p*-acetoxySQs. In general, the GPC, MALDI and TGA data are all
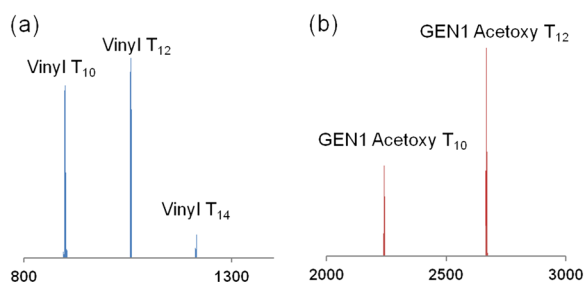
in agreement with those expected for the isolated compounds. The narrow molecular weight distribution of these SQ compounds in the GPC indicates that they retain their cage structures. The MALDI-TOF spectrum of GEN1 T$_{10/12}$ *p*-acetoxySQ indicates that this compound is fully substituted. The ^{1}H NMR spectra of these compounds confirm their complete conversion from their parent material as well.

Synthesis of *p*-Hydroxysilsesquioxanes

The *p*-acetoxySQs were gently hydrolyzed with HCl to give the corresponding *p*-hydroxySQs. These reactions were monitored by FT-IR until the characteristic νC O (1760 cm^{-1}) of *p*-acetoxySQs disappeared (Fig. 2). Since the synthetic procedures and subsequent characterization are analogous for all *p*-acetoxySQs, only the hydrolysis of the GEN1 T$_8$ *p*-acetoxySQ is discussed in further detail.

The FT-IR of GEN1 T$_8$ *p*-acetoxySQ shows characteristic νO—H (3300 cm^{-1}) and νSi—O (1112 cm^{-1}) bands (Fig. 2). FT-IR spectra for the corresponding compounds are given in Fig. S-1 (supporting information). As expected, all the spectra are very similar given the essentially identical chemical and structural compositions.

MALDI-ToF spectra of the product do not show any unreacted *p*-acetoxy T$_8$ species (Fig. 1b) and no methyl peaks (δ 2.3–2.4 ppm) are seen in the ^{1}H NMR spectrum, indicating that all of the acetoxy groups hydrolyze off (Fig. 3). The characterization data for the *p*-hydroxySQs are given in Table 2. Figures S-2 to S-4 provide similar characterization data for all the other analogs. Again no significant differences are seen or expected.
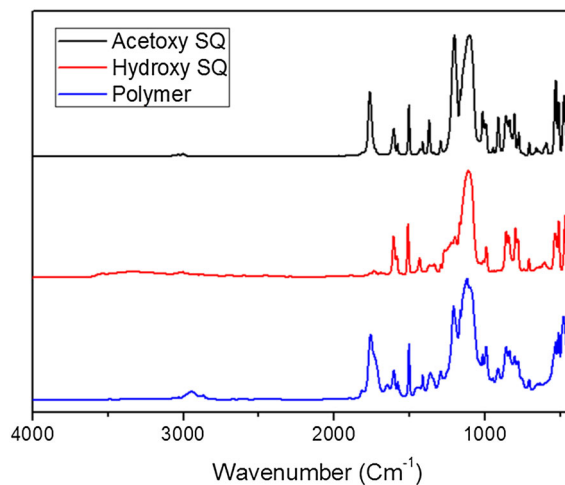

Figure 1. MALDI-TOF spectrum of vinyl T$_{10/12}$ (a) and GEN1 *p*-acetoxy T$_{10/12}$ (b).

Figure 2. FT-IR of GEN1 T$_8$ *p*-acetoxySQ, *p*-hydroxySQ and crosslinked polyester.

Table 1. Characterization of *p*-acetoxySQs

	GPC			m/z (Ag$^+$ adduct)				TGA	
	M_n	M_w	PDI	Calcd	MALDI	CY	Theo. CY	$T_{d5\%}$ (°C)	
GEN1 T$_8$	2070	2150	1.04	1813.9	1813.5	27.9 %	28.2 %	345	
GEN1 T$_{10/12}$	2500	2560	1.02	T$_{10}$: 2240.4	2240.4	28.4 %	28.2 %	345	
				T$_{12}$: 2666.9	2667.5				
GEN2 T$_8$	4080	4270	1.04	2630.9	2629.6	19.2 %	19.1 %	335	
GEN2 T$_{10/12}$	4130	4270	1.03	T$_{10}$: 3261.7	3261.0	19.5 %	19.1 %	305	
				T$_{12}$: 3892.5	3892.3				
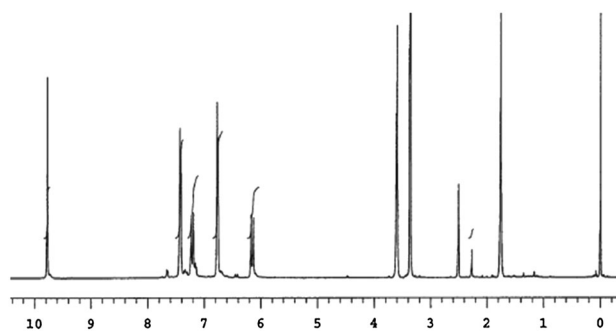
Figure 3. ^{1}H NMR (DMSO) of GEN1 T_8 p-hydroxy SQ.

Figure 4. TGA of GEN1 T_8 p-acetoxySQ, p-hydroxySQ and crosslinked polyester (air, 10 °C min^{-1}).

In accord with the NMR, GPC and MALDI-TOF data, the found and calculated ceramic yields of all the compounds are identical, within the error limits of analysis, again supporting the fact that these compounds are compositionally and structurally identical on a per silicon basis.

Polymerization of *p*-hydroxysilsesquioxanes and adipoyl chloride

The p-hydroxySQs were reacted with adipoyl chloride in an effort to form crosslinked nanoporous polyesters per Scheme 1. The FT-IR spectrum of synthesized polyester showed characteristic $\nu C\,O$ (1760 cm^{-1}), νC—O (1210 cm^{-1}) and aliphatic νC—H (2950 cm^{-1}) (Fig. 3). Figure 4 provides the TGA traces for GEN1 T_8 p-acetoxySQ, p-hydroxySQ and crosslinked polyester. Figure S-5 provides analogous TGAs for the related compounds. The lower ceramic yields for the polyester compared with p-hydroxySQ indicates that adipoyl groups were incorporated into the polymer.

Although the exceptional flexibility of the adipate crosslinker would suggest that we should not observe any degree of porosity, BET-specific surface areas (SSAs) were measured. Only one polymeric compound, the GEN1 T_8 polymer, had a surface area of 25 m^2 g^{-1} (Table 3). Given that this system has the shortest spacer between cages and the highest symmetry, one might infer that there is sufficient restriction of chain motion that ingress and egress of N_2 during the measurements is possible.

One might therefore extend this idea to suggest that while some pores probably exist in the crosslinked systems, they are not easily accessible for N_2 absorption and desorption, perhaps because of highly torturous paths. However, there is a simpler explanation. Except for the GEN1 T_8 polymer, the ceramic yields of other polymers are lower than the theoretical value based on 100 % conversion to the crosslinked form. This means that excess
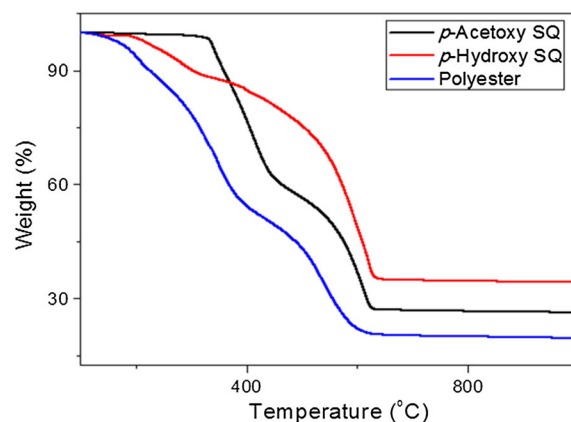
Table 3. Characterization of crosslinked polyesters

	TGA			BET SSAs (m^2 g^{-1})
	CY	Theo. CY	$T_{d5\%}$ (°C)	
GEN1 T_8	26.7%	26.6%	260	24
GEN1 $T_{10/12}$	20.7%	26.6%	210	5
GEN2 T_8	14.8%	18.3%	190	1
GEN2 $T_{10/12}$	15.3%	18.3%	200	4

of adipoyl chloride reacts with p-hydroxySQs, leading to dangling, unreacted carboxyl groups after water workup. Thus the crosslink densities are much lower and, while there may be extensive porosity, the resulting mesopores are too large to be 'seen' by BET.

We could also expect the $T_{10/12}$ SQ polyesters to show lower SSAs than that of GEN1 T_8 SQ. Because the T_{10} and T_{12} cages are larger than T_8 cage, they offer smaller angles between C6 linkers, perhaps leading to stronger interactions that reduce pore size. To produce nanoporous materials having high surface areas and to investigate the relationship between the porosity and chemical structure of nanobuilding blocks, it is necessary to control the reaction conditions to make highly crosslinked nanocomposites with emphasis on using more rigid crosslinkers. Furthermore, it appears likely that high symmetry as found with the T_8 systems will provide better access to nanoporous materials, with better controlled crosslink densities and therefore better control of pore size distributions.

Table 2. Characterization data for the various *p*-hydroxy SQs

	GPC			m/z (Ag$^+$ adduct)		TGA		
	M_n	M_w	PDI	Calcd	MALDI	CY	Theo. CY	$T_{d5\%}$ (°C)
GEN1 T_8	2000	2030	1.01	1477.6	1477.5	34.6 %	35.1 %	235
GEN1 $T_{10/12}$	2240	2300	1.03	T_{10}: 1820.1	1819.4	34.4 %	35.1 %	280
				T_{12}: 2162.5	2162.8			
GEN2 T_8	3410	3560	1.04	2294.6	2293.1	22.2 %	22.0 %	360
GEN2 $T_{10/12}$	3490	3590	1.03	T_{10}: 2841.3	3261.0	22.3 %	22.0 %	345
				T_{12}: 3388.0	3892.3			

Conclusions

We have demonstrated the synthesis of a variety of *p*-acetoxy- and *p*-hydroxySQs based on T_8 and $T_{10/12}$ vinylSQs as 3-D nanobuilding blocks. We have begun to explore the application of these *p*-hydroxySQs as precursors to nanoporous polymeric materials by studying their reaction with adipoyl chloride. The crosslinked polyester prepared from GEN1 T_8 SQ exhibited up to 25 m^2 g^{-1} of BET surface area in spite of the flexible C_6 linker. This comes as a result of the very high symmetry of the SQ coupled with the shortest linker between cages. Moreover, the TGA data suggest that all corners of the cage are fully reacted. The results reported here are in keeping with other recent studies comparing T_8 with T_{10} and T_{12} nanoporous structures.[21] In the near future we anticipate exploring reactions with rigid diacid chlorides and also working with the T_8 amine analogs.[30,31]

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Supporting Information

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