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Octa(aminophenyl)silsesquioxane as a Nanoconstruction Site

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The field of nanomaterials science and engineering has a continuing need for well-defined building blocks that allow the construction of a wide variety of materials nanometer-by-nanometer with precise control of the nanoarchitecture and that imbue functionality.[1,2] Octahedral or cubic silsesquioxanes (cubes) and the related polyhedral oligomeric silsesquioxanes (POSS) offer one solution to this need in that they provide the opportunity to design and "construct" materials with extremely well-defined dimensions and behavior.[3−11] In this regard, we have prepared a wide variety of octafunctional cubes with polymerizable moieties that offer access to highly cross-linked (thermoset) nanocomposites having: (1) controlled porosities with high surface areas,[9] (2) novel mechanical properties,[10−12] and (3) high thermal stabilities (see below). In a complementary fashion, POSS materials offer access to robust thermoplastics with good-to-excellent properties including resistance to atomic oxygen.[3−7]

Our approach to generating functionalized cubic silsesquioxane macromonomers that offer access to nanocomposites has relied primarily on introducing functionality by hydrosilylation using $(HSiO_{1.5})_8$[13] or $(HMe_2SiOSiO_{1.5})_8$ nanoplatforms.[13−15] We have successfully introduced functional groups including methacrylates,[1] mesogenic groups,[8] epoxies,[2,10] and alcohols.[11]

In a departure from this approach, we recently reported the synthesis of octa(aminopropyl)silsesquioxane which offers access to novel amides and imides with good high-temperature properties and hints of liquid crystalline behavior.[16] Feher et al. reported the same synthesis almost simultaneously.[17]

A key problem with almost all of the materials explored to date is that the aliphatic components limit the thermal stability of the resulting nanocomposites, strongly influence (lower) T_g, and decrease mechanical properties potentials. Hence we sought more rigid, thermally stable nanoplatforms while expanding the types of functionality available for nanoconstruction projects.

We report here the synthesis of octa(aminophenyl)silsesquioxane (OAPS), an aromatic amine-functionalized silsesquioxane free from aliphatic components. OAPS appears to offer excellent potential as a nanoconstruction site for preparing materials ranging from high-temperature nanocomposites, to precursors to organic light-emitting diodes, to multiarmed stars, to templates for high-temperature porous materials of use in catalysis, sensing, separations, etc.

OAPS is easily prepared in two steps by nitration of octaphenylsilsesquioxane (OPS)[18] in fuming nitric acid to form octa(nitrophenyl)silsesquioxane (ONPS),[19] followed by mild reduction. OPS nitration was described briefly 40 years ago, but the resulting product was poorly characterized, and the material was reported to be unreactive. Slight modification of this procedure[20] provides ONPS with one nitro group per phenyl (see Supporting Information). ONPS is easily transformed to OAPS by hydrogen-transfer reduction[21−23] using formic acid and triethylamine (Pd/C catalyst 60 °C/N_2/5 h) resulting in quantitative conversion (Scheme 1).[21]

^{1}H and ^{13}C NMR data (Supporting Information) support the formation of equal quantities of the *meta* and *para* nitration and amine products. ^{29}Si NMR spectra of ONPS show two peaks at −79.2 and −83.0 ppm for the *para* and *meta* isomers, respectively. Likewise, ^{29}Si NMR spectra of OAPS also show two respective peaks at −73.3 and −77.4 ppm. Thermal gravimetric and chemical analyses (TGA) of the ONPS and OAPS products are shown in Table 1. The TGA ceramic yield for ONPS was 33.7 versus 34.5 wt % theory. The TGA ceramic yield for OAPS was 41.1 versus 41.7 wt % theory. More importantly C, H, and N analyses agree with the calculated values. These results support formation of monosubstituted ONPS and its quantitative conversion to

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(1) Sellinger, A.; Laine, R. M. *Macromolecules* **1996**, *29*, 2327.

(2) Sellinger, A.; Laine, R. M. *Chem. Mater.* **1996**, *8*, 1592.

(3) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromlecules* **1995**, *28*, 8435.

(4) Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *379*, 33.

(5) Feher, F. J.; Soulivong, D.; Eklud, A. G.; Wyndham, K. D. *Chem. Commun.* **1997**, 1185.

(6) (a) Jeon, H. G.; Mather, P. T.; Haddad, T. S. *Polym. Int.* **2000**, *49*, 453. (b) Haddad, T. S.; Mather, P. T.; Jeon, H. G.; Romo-Uribe, A.; Farris, A. R.; Lichtenhan, J. D. In *Organic/Inorganic Hybrid Materials*; Laine, R., Sanchez, Brinker, Giannelis, Eds.; MRS Symp. Ser. 519; Materials Research Society: Warrendale, PA, 1998; pp 381−386.

(7) (a) Gilman, J. W.; Schlitzere, D. S.; Lichtenhan, J. D. *J. Appl. Polm. Sci.* **1996**, *60*, 591. (b) Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. *J. Spacecr. Rockets* **2000B**, *37*, 463.

(8) Sellinger, A.; Laine, R. M.; Chu, V.; Viney, C. *J. Polym. Sci., Part A: Polym. Chem.* **1994** *32*, 3069.

(9) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380.

(10) Laine, R. M.; Choi, J.; Lee, I. *Adv. Mater.* **2001**, *13*, 800.

(11) Zhang, C.; Laine, R. M. *J. Am. Chem. Soc.* **2000** *122*, 6979.

(12) Laine, R. M.; Asuncion, M.; Baliat, S.; Dias Filho, N. L.; Harcup, J.; Sutorik, A. C.; Viculis, L.; Yee, A. F.; Zhang, C.; Zhu, Q. In *Organic/Inorganic Hybrid Materials*; Klein, L., De Guire, M., Lorraine, F., Mark, J., Eds.; MRS Symp. Ser. 576; Materials Research Society: Warrendale, PA, 1999; pp 3−14.

(13) (a) Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2707. (b) Hasegawa, I.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2279.

(14) Hasegawa, I.; Sakka, S.; Sugahara, Y.; Kuroda, K.; Kato, C. *J. Chem. Soc., Chem. Commun.* **1989**, 208.

(15) Hasegawa, I.; Motojima, S. *J. Organomet. Chem.* **1992**, *441*, 373.

(16) Gravel, M.-C.; Zhang, C.; Dinderman, M.; Laine, R. M. *Appl. Organomet. Chem.* **1999**, *13*, 329.

(17) Feher, F. J.; Wyndham, K. D. *Chem. Commun.* **1998**, 323.

(18) Brown, J. F., Jr.; Vogt, L. H., Jr.; Prescott, P. I. *J. Am. Chem. Soc.* **1964**, *86*, 1120.

(19) Olsson, K.; Grönwall, C. *Arkiv. Kemi.* **1961**, *17*, 529.

(20) **ONPS** was prepared per Olsson and Grönwall[19] with several modifications. OPS, 50 g (48.4 mmol) was added in small portions to 300 mL of fuming nitric acid with stirring at 0 °C. After addition was complete, the solution was stirred for an additional 30 min and then at room temperature for 20 h. After filtration through glass wool, the solution was poured onto 250 g of ice. A very faintly yellow precipitate was collected, washed with water (∼100 mL × 5 until pH ≈ 6.0) and then with ethanol (∼100 mL × 2). The obtained powder was dried at ambient to remove residual solvent to yield 60.8 g (43.6 mmol, 90.1%) of material. ^{1}H NMR (acetone-d_6, ppm): 8.7 (*t*, 1.0H), 8.4−8.0 (*m*, 4.1H), 7.8 (*m*, 2.7H); ^{13}C NMR (acetone-d_6, ppm): 154.0, 148.9, 141.0, 138.6, 136.5 (small), 135.3, 134.1, 132.3 (small), 130.8, 129.5, 127.0, 125.2, 123.6 (small); ^{29}Si NMR (THF, TMS, acetone-d_6, ppm): −79.2, −83.0.

(21) **OAPS** was prepared by introducing ONPS (10.0 g, 7.16 mmol, $-NO_2$ 57.4 mmol) and 5 wt % Pd/C (1.22 g, 0.574 mmol) into a 250-mL Schlenk flask equipped with a condenser under N_2. Distilled THF (80 mL) and triethylamine (80.0 mL, 0.574 mmol) were then added. The mixture was heated to 60 °C, and 85% formic acid (10.4 mL, 0.230 mol) was added slowly at 60 °C. Carbon dioxide evolved, and the solution separated into two layers. After 5 h, the THF layer was separated, and 50 mL of THF and 50 mL of water were added until the slurry formed a black suspension. The suspension and the THF solution separated previously were mixed and filtered through Celite. Another 20 mL of THF and 20 mL of water were added to the flask to dissolve the remaining black slurry, and the suspension was filtered again. All of the filtrates were combined with 50 mL of ethylacetate and washed 4× with 100 mL H_2O. The organic layer was dried after 5 g of $MgSO_4$ and precipitated by addition to 2 L of hexane. A white precipitate was collected by filtration, redissolved in 30:50 THF/ethyl acetate and reprecipitated into 1 L hexane. The obtained powder was dried under vacuum. Yield 6.80 g (5.89 mmol, recovery 82%). ^{1}H NMR (acetone-d_6, ppm): 7.8−6.2 (*b*, 4.0H), 5.2−3.7 (*b*, 2.0H); ^{13}C NMR (acetone-d_6, ppm): 154.0, 148.1, 136.6, 132.8, 129.3, 123.4, 120.8, 117.3, 115.8, 114.4; ^{29}Si NMR (THF, TMS, acetone-d_6, ppm): −73.3, −77.4.

(22) Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1977**, *42*, 3491.

(23) Johnstone, R. A. W.; Wilby, A. H. *Chem. Rev.* **1985**, *85*, 129.

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Scheme 1

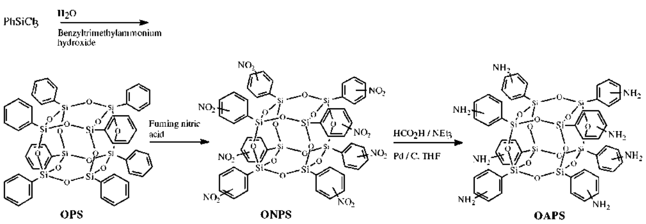
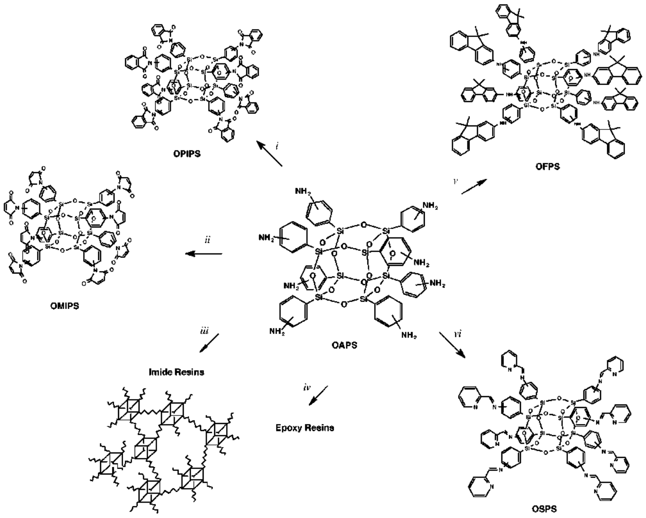


Table 1. Properties of the Silsesquioxanes[a]

POSS (FW)	M_n	M_w	M_w/M_n	C % (cal)	H % (cal)	N % (cal)	ceramic yield (%)[b] (cal)
OPS (1033.5)	718	733	1.022	–	–	–	9.1[c] (46.5)
ONPS (1393.5)	1030	1111	1.078	41.3 (41.4)	2.3 (2.4)	8.0 (8.0)	33.7[d] (43.5)
OAPS (1153.7)	1057	1133	1.072	49.4 (50.0)	4.3 (4.2)	9.2 (9.7)	41.1[e] (41.7)

[a] Obtained by GPC using THF as eluent and calibrated with polystyrene standards. [b] Calculated by TGA at 1000 °C in air. [c] OPS sublimes. [d] Allowing for residual solvent (slight decrease below 300 °C) the ceramic yield was calculated as 33.7% at 1000 °C. [e] The OAPS ceramic yield was calculated as 41.1 wt TGA for both ONPS and OAPS demonstrated the decomposition onset temperatures of ~350 °C.

Scheme 2. Reactions of Octaminophenylsilsesquoxane[a]



[a] i) 1:8.4 OAPS:phthalic anhydride in NMP 350 °C/N_2 /4 h. ii) 1:8 OAPS:maleic anhydride in DMA 60 °C/N_2/3 h with acetic anhydride and Et_3N. iii) 1:8 OAPS:pyromellitic anhydride in NMP 350 °C/N_2/3 h; iv) 1:8 OAPS:epoxy neat at 200 °C/6 h/N_2; v) 1:8.8 OAPS:2-bromo-9,9-dimethylfluorene, $Pd_2(dba)_3$, (dcbp)P, glyme 100 °C/N_2/5.5 h; vi) 1:8 OAPS:2-pyridinecarboxaldehyde Na_2SO_4/ THF/rt/N_2/22 h.

OAPS. The decomposition onset for both ONPS and OAPS is ~350 °C.

Table 1 also provides GPC (THF) data giving molecular weights for ONPS, OAPS, and OPS of 1394, 1154, and 1034 Da, respectively. These values differ from calculated values because polystyrene was used as a calibration standard. All of the compounds exhibit narrow polydispersities, even after reaction, indicating the absence of polymeric materials resulting from core decomposition.

To demonstrate the potential OAPS offers as a nanoconstruction site, several model compounds were synthesized per Scheme 2. See Table 2 for yields and derivatization details (Supporting Information).

Phthalimide Derivatives. As a prelude to making 3-D imide nanocomposites, efforts were directed toward making a prototype imide, a potential nanofiller. The octaphthalimide (OPIPS) forms simply on heating an NMP solution of OAPS and phthalic anhydride at 350 °C/N_2/4 h (Supporting Information). The obtained powder is soluble in common polar organic solvents and behaves as expected per NMR, TGA, and GPC analyses. The corresponding maleimide (OMIPS) was also easily made (Supporting Information). Both compounds are stable to ~430 °C (5% mass loss temperature). No exotherms corresponding to maleimide polymerization were observed by DSC although the heated product was no longer soluble. The maleimide group offers access to diverse thermosets via self-polymerization or via Michael-addition reactions with dithiols or diamines to form high-temperature resins.[24, 25]

Nanocomposites. OAPS when reacted with diepoxides or dianhydrides should provide high cross-link density materials with good thermal stability, and good-to-excellent tensile and compressive strengths.[10] Reacting OAPS, with pyromellitic anhydride (PMA) at >300 °C, provides complete curing and a material that exhibits a 5% mass loss temperature of 540 °C (air and N_2) and 75 wt % char yield at >1000 °C/N_2. This robustness is exemplary and offers potential for many diverse applications. The properties of these materials will be discussed elsewhere.[26]

Fluorene Derivative (OFPS). Pd-catalyzed coupling of bromofluorene to OAPS (Supporting Information) provides a potential route to hole-transport materials for organic light-emitting diodes.[27,28] Potassium phosphate was found to be superior to other bases tested[27] in limiting Si–O bond cleavage. On average, 0.66 fluorene groups/N (~5 fluorene groups/cube) were introduced as confirmed by ^{1}H NMR. Steric hindrance may make complete substitution difficult. Diverse coupling reactions are available for adding other functional species to the aromatic nitrogen. [27, 28]

Schiff Base Derivative (OSPS). OAPS reacts rapidly with the 2-pyridinecarboxaldehyde under mild conditions, giving an imine that emits green light under UV illumination. This type of imine offers potential for forming metal chelate complexes for sensor, electrochemical, photonic, and catalytic applications.[29−31]

OAPS contains an inorganic core as a foundation and rigid arylamine moieties that serve as highly functional anchors to this foundation. As suggested in Scheme 2, it provides access to numerous materials with a high density of functional groups in a very small volume, ~1 nm. Some of these materials can be used as starting points to construct a large number of thermally robust nanocomposite materials nanometer-by-nanometer. For example, we successfully prepared core−shell materials.[26] Still other derivatives appear to offer potential for numerous nonstructural applications. OAPS represents the first example of a new class of materials that are very promising nanoconstruction sites. In future papers, we will describe the syntheses of ketones, esters, bromo- and acid-functionalized octaphenylsilsesquioxane nanoconstruction sites.

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Supporting Information Available: NMR data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) White, J. E.; Snider, D. A. *J. Appl. Polym. Sci.* **1984**, *29*, 891.

(25) Kwiatkowski, G. T.; Robeson, L. M.; Brode, G. L.; Bedwin, A. W. *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 961.

(26) (a) Laine, R. M.; Choi, J.; Lee, I. *Adv. Mater.* **2001**, *13*, 800 and references therein. (b) Choi, J.; Harcup, J.; Yee, A. F.; Zhu, Q.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*. ASAP on Web October 26, 2001. (c) Tamaki, R.; Choi, J.; Laine, R. M. *Abstracts of Papers*, 221st National Meeting of the American Chemical Society, San Diego, CA, April 1−5, 2001; American Chemical Society: Washington, DC, 2001; PMSE 312.

(27) Harris, M. C.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5327.

(28) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158.

(29) Winpenny, R. E. P. *Chem. Soc. Rev.* **1998**, *27*, 447.

(30) Yoshida, N.; Oshio, H.; Ito, T. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 975.

(31) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110.