Silsesquioxanes as Synthetic Platforms. Thermally Curable and Photocurable Inorganic/Organic Hybrids

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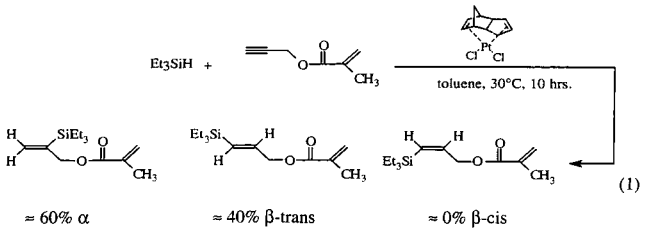
Polyhedral silsesquioxanes $(RSiO_{1.5})_n$, where R = H, Cl, or a wide variety of organic groups, are unique structures generally formed by hydrolysis and condensation of trialkoxy- or trichlorosilanes.[1] The octameric or "cubic" polyhedral silsesquioxanes resemble skeletal frameworks found in crystalline forms of silica and particular zeolites.[2] Their rigid framework offers many appealing properties that have been exploited by Feher et al. to develop unique models of silica surfaces, by Calzaferri as models of zeolites, by Klemperer et al. as novel sol−gel precursors, and by other groups for diverse applications.[2−7] Access to these materials, especially the $(HSiO_{1.5})_n$ series, results from extensive efforts by Agaskar.[8] Hasegawa et al. have developed effective routes to the related $[(RMe_2SiO)SiO_{1.5}]_8$ compounds.[9] Patents to Wacker Chemie describe routes to $[(RMe_2SiO)SiO_{1.5}]_{6/10}$ compounds.[10] Silsesquioxanes also appear to play a role in the adhesive, coupling, and coating properties of species formed on hydrolysis of glycidyl, aminopropyl, or methacroyl trialkoxysilanes.[11]

Our interest in these materials extends from the fact that their rigid framework closely resembles that of silica. In essence, cubic silsesquioxanes can be thought of as the smallest silica particles possible. Additionally, they can be octafunctional and serve as platforms that can be synthetically modified to contain groups for copolymerization, adhesion, light sensitization, binding catalyst species, and improved solubility. All or some of each type of functionality can in principle be introduced to a given platform. As "silica particles", studies of their copolymerization[6] with organic monomers may represent the simplest models of silica-reinforced composites. If silsesquioxane/organic copolymers do behave as silica-reinforced composites, then soluble, copolymerizable silsesquioxanes offer unique potential because single-phase composite processing becomes possible, as opposed to two-phase monomer/silica filler mixtures typically used.

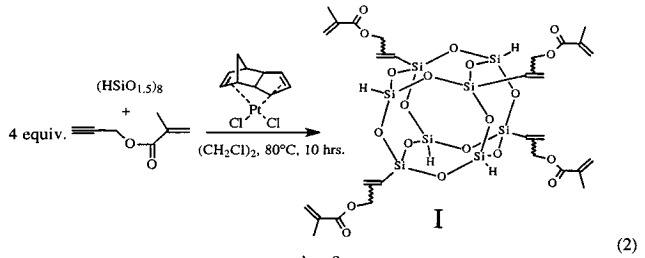
As a first step in realizing the above-described possibilities, we report here the synthesis and characterization of simple methacrylate/cube hybrids that can act as thermosets or photocurable monomers. These materials are easily manipulated, yet retain very high masked silica loadings.

The methacrylate-functionalized cubes are synthesized via Pt-catalyzed hydrosilylation of propargyl methacrylate[12,13] with $(HSiO_{1.5})_8$[8a] and $(HMe_2SiOSiO_{1.5})_8$.[9b] The propargyl route eliminates side reactions found with allyloxy chemistry.[14] Propargyl groups react in preference to methacrylate groups in Pt-catalyzed hydrosilylation, as modeled in (1) using triethylsilane.[15] Reaction of 4 equiv of propargyl methacrylate with

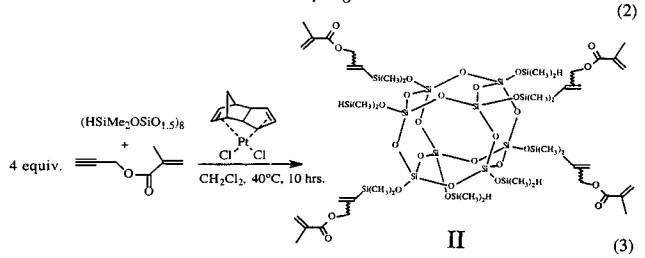


(1)

$(HSiO_{1.5})_8$ and $(HMe_2SiOSiO_{1.5})_8$, (2) and (3), gives selective reaction at the propargyl site.[16−19]



(2)



(3)

$(HSiO_{1.5})_8$ is much less reactive than $(HMe_2SiOSiO_{1.5})_8$ as evidenced by the higher reaction temperature required (80 vs 40 °C). If platinum divinyltetramethyldisiloxane [Pt(dvs)] is used in place of Pt(dcp), both reactions form cross-linked gels.

Products **I** and **II** are viscous, clear liquids that are readily characterized by ^1H, ^{13}C, and ^{29}Si NMR.[18,19] ^1H NMR indicates hydrosilylation isomer distributions similar to (1). The spectrum of **I** is clean, with all peaks accounted for.[18] Compound **II**, in addition to the expected peaks, shows a set of peaks at ≈4.1−4.0 and 2.0−1.1 ppm that result from either intramolecular hydrosilylation of the α isomer, cross (intermolecular) hydrosilylation of cubes, or a combination of the two.[19,20] Compound **II**, unlike **I**, can cyclize to form eight-membered rings, a common feature of siloxane chemistry.[21] Reaction of 10 equiv of propargyl methacrylate with $(HMe_2SiOSiO_{1.5})_8$ produces the octasubstituted cube with little evidence for intra- and/or intermolecular hydrosilylation products.[22] The as-drawn, *idealized* structures for **I** and **II** show substitutions at the opposite vertices of the cube. Although this substitution pattern is likely, no assignments regarding the exact positioning on the cube can be made at this point. Additionally, the as-drawn, idealized structures for **I** and **II** show only tetrasubstituted hybrids.

Mass spectral results for **I** using both electronic impact (EI) and fast atom bombardment (FAB) methods indicate the presence of di-, tri-, tetra-, and pentasubstituted cubes. Although hexasubstituted and higher substituted cubes are not found, their masses may be too high to be detected by EI or FAB and thus they may still be present. Compound **II** was analyzed using K^+-IDS (K^+ ionization of desorbed species) spectroscopy in addition to EI and FAB. The K^+IDS technique can successfully detect methacrylate-functionalized oligomers with molecular weights (MW) > 2000.[23] Unfor-

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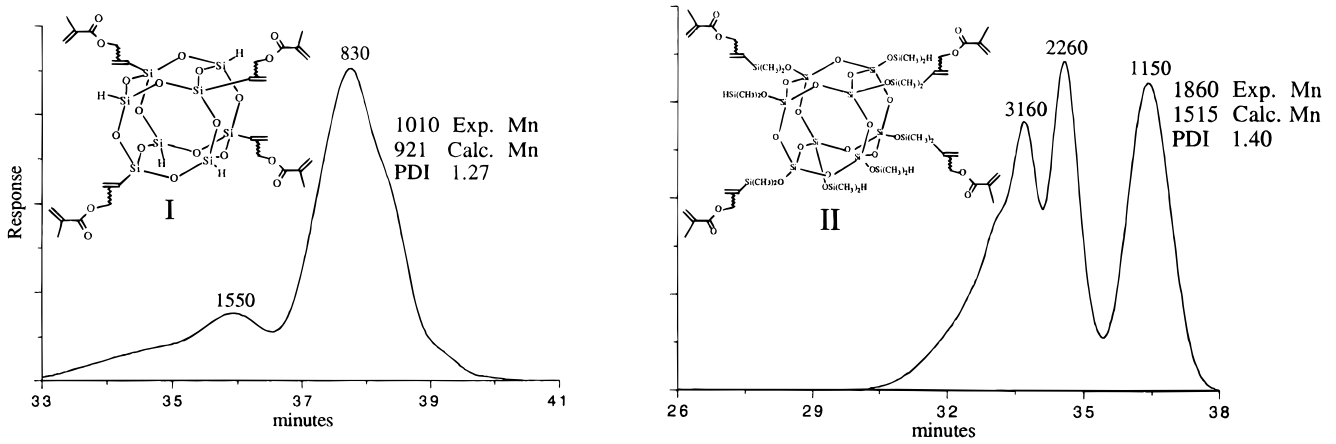

Figure 1. Size exclusion chromatograms (SEC) for compounds **I** and **II** (polystyrene standards, THF, toluene reference).

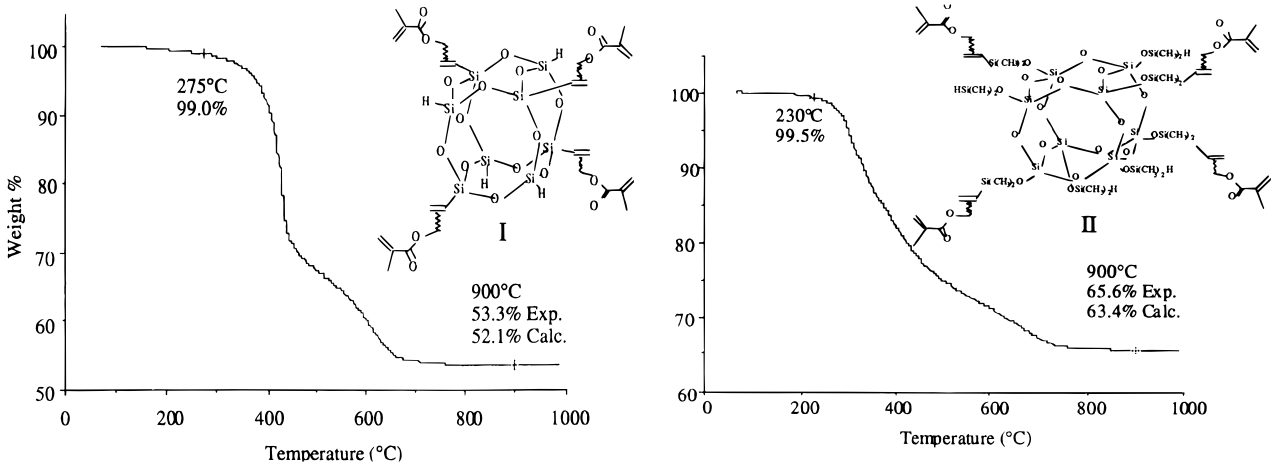

Figure 2. TGA profiles of compounds **I** and **II** in air ("Hi-Res 4 Mode", TA-Thermal Analyst 2950).

tunately, in no instance were discernible fragments observed. This suggests that the material polymerizes before volatilizing, since the skeletal framework should survive ionization.

Size exclusion chromatography, Figure 1 (SEC, polystyrene standards, THF as solvent), gives polydispersity indices (PDI) of 1.27 and 1.40 for **I** and **II**, respectively. SEC of **I** shows a *bimodal* response with no separation of di, tri, tetra, ... substituted cubes.[24] Generally, SEC can separate materials in this molecular weight range (e.g., polystyrene standard MW = 1050, PDI = 1.09, is separated into a series of peaks differing by styrene units, ≈100 g/mol). Given the cube's roughly spherical shape, it is likely that the various substituted species have very similar hydrodynamic radii, making it difficult to effect separation by SEC. SEC of **I** shows evidence for dimer formation (peak at 1550 g/mol), which was not detected in the ^{1}H, ^{13}C, and ^{29}Si NMR analyses. SEC of **II** shows a trimodal distribution of peaks at ≈1150, 2260, and 3160 g/mol, likely corresponding to intermolecular hydrosilylation forming dimers and trimers and providing support for cross coupling as suggested by the NMR studies.

DSCs of freshly prepared tetramethacrylate cubes show exotherm onsets at ≈50 °C with maxima at ≈120 °C which likely result from inter- and/or intramolecular alkene/Si−H hydrosilylation. In contrast, the octasubstituted cubes, which have no Si−H bonds, show exotherm onsets only at ≈100 °C with maxima at ≈170 °C due to methacrylate polymerization. Aged samples of the tetrasubstituted cubes or cubes prepared using a Pt/C catalyst[25] show slight onsets at 50−70 °C with maxima at ≈120 °C. If active catalyst is added to the aged samples, intense exotherms reappear with onsets at ≈50 °C. Thus, the initial exotherms likely result from Pt-catalyzed hydrosilylation. No observable thermal events occur in subsequent heating/cooling cycles.

Photochemical curing is also possible using visible light and free-radical initiators. For example, both cubes, when mixed with camphorquinone (0.15% w/w), cure almost instantaneously in the presence of visible light (450 nm), forming clear, hard, cross-linked materials insoluble in common solvents. In addition, both compounds cure at ≈100 °C without initiator to produce clear, abrasion-resistant coatings.[27]

Thermal gravimetric analysis (Figure 2) indicates that, on heating, **I** forms a quite stable network polymer, with a decomposition onset (T_d) at ≈300 °C. The much lower 230 °C T_d for **II** can be attributed to the dimethylsiloxy linkages, which are known to decompose thermally at ≈215 °C.[21] The ceramic yield to SiO_2 for **I** (1000 °C) is within 1.1% of theory (53.3% experimental vs 52.1% theory), while that of **II** is within 2.2% (65.6% experimental vs 63.4% theory). Theoretical ceramic yields are based on 4 equiv of propargyl methacrylate per cube.

Thus, we suggest that the average substitution for **I** and **II** is very close to tetrasubstitution. For example, **II** with 3 and 5 substitutions per cube would be 69.0 and 58.6%, respectively.

The two hydrocarbon-soluble, methacrylate-functionalized cubes described here are highly reactive, viscous

liquids that are readily polymerized either thermally or photochemically to produce, clear, hard hybrid polymers containing up to 65% silica. The next step will be to explore methods of producing copolymers. In complementary work, we are also developing epoxide-substituted cubes to expand the repertoire of copolymerizable cubes.[28]

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(16) All reactions were done under N_2. $(CH_2Cl)_2$, CH_2Cl_2, and toluene were distilled from CaH_2. THF was distilled from sodium benzophenone keyl. Dichlorodicyclopentadienylplatinum, Pt(dcp), was prepared by the method of Laub et al.[17] and used as 2.5 mmol solutions in $(CH_2Cl)_2$. All other chemicals were used as received.
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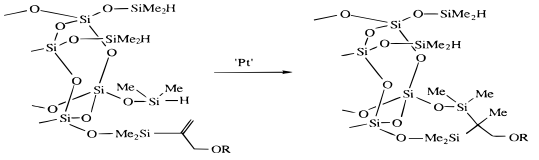
(18) Reaction 2 is run by adding $(CH_2Cl)_2$ (20 mL) and $(HSiO_{1.5})_8$ (0.600 g, 1.40 mmol) to a 25 mL Schlenk flask equipped with a stir bar and condenser. Propargyl methacrylate (0.693 mL, 5.6 mmol) in ≈2 mL of $(CH_2Cl)_2$ is added to the flask. Pt(dcp) (0.25 mL of a 2.5 mmol solution in $(CH_2Cl)_2$ (400 ppm)) is added to the mixture at 30 °C. The mixture is stirred at 80 °C for 12 h. The product is then stirred with activated charcoal (≈50 mg) for 1−2 h and filtered. Filtered solutions can be stored in foil-wrapped, brown bottles in the refrigerator for up to 1 year. If solvent is removed, the compound (in air and light) will gel over a period of 5−7 days. ^{1}H NMR (360 MHz, $CDCl_3$) 6.56 (m, 1.6H, C*H*═CHSi β-trans), 6.17, 5.60 [d, 7.8H, CH_2═CCH$_3$(CO)], 6.03−5.67 (m, 6.4H, CH_2═CSi α + CH═C*H*Si β-trans), 4.83−4.74 (m, 8H, OCH_2), 4.24 (s, 4H, Si*H*), 1.96 (d, 12H, CH$_2$═CCH_3) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): 166.9 (*C*═O), 146.6 (*C*H═CHSi β-trans), 136.7 (Si*C*═CH$_2$ α), 136.0 [CH$_2$═*C*CH$_3$-(C═O)], 131.3 (SiC═*C*H$_2$ α), 125.9 [CH$_2$═CCH$_3$(C═O)], 119.0 (CH═*C*HSi β-trans), 66.5 (O*C*H$_2$CH═CH β-trans), 65.4 (O*C*H$_2$CSi α), 18.2 [CH$_2$═C*C*H$_3$(C═O)]. ^{29}Si NMR: (79.5 MHz, $CDCl_3$) −80.1 (*Si* β-trans), −82.1 (*Si* α), −84.2 (*Si*H). *Si*−C from α and β-trans isomers resonate at −82 and −80 ppm, respectively, while the *Si*−H resonates at −84 ppm. The peaks are broad (spanning 1 ppm) and are assumed to result from the distribution of substituted cubes, e.g., di, tri, tetra, penta, etc. The distortionless enhancement by polarization transfer (DEPT) pulse sequence[26] was used to easily assign the *Si*−H, resulting in a spectrum containing one resonance at −84 ppm. *Si*−C assignments resulting from the two isomers are based on the observation that the −82 ppm resonance is larger than the −80 ppm resonance and the fact that the ^{1}H NMR shows that the α isomer is more abundant. SEC (polystyrene standards, THF as solvent, and toluene as reference) M_n = 1010, PDI = 1.27. Mass spectral results (EI): *m*/*z* and intensities for tri-, tetra-, and pentasubstituted species within **I** are 797, 4.9%; 921, 3.8%; and 1045, 1.1%, respectively.
(19) Reaction 3 is run by adding CH_2Cl_2 (15 mL), $(HSiMe_2OSiO_{1.5})_8$ (0.700 g, 0.68 mmol), and propargyl methacrylate (0.342 g, 2.75 mmol) in ≈2 mL of CH_2Cl_2 to a 25 mL Schlenk flask equipped with a stir bar and condenser. Pt(dcp) [0.13 mL of a 2.5 mmol solution in $(CH_2Cl)_2$ (400 ppm)] is added to the mixture at 30 °C. The mixture is stirred at 40 °C for 4 h and overnight at room temperature. The product is then stirred with activated charcoal (≈50 mg) for 1−2 h and filtered. Filtered solutions can be stored in foil-wrapped, brown bottles in the refrigerator for up to 1 year. If solvent is removed, the compound (in air and light) will gel over a period of 5−7 days. ^{1}H NMR (360 MHz, $CDCl_3$) 6.50 (m, 0.26H, C*H*═CHSi β-trans), 6.20−5.50 (m, 15.8H, CH_2═CCH$_3$-(CO), CH_2═CSi α, CH═C*H*Si β-trans), 4.78−4.67 (m, 10.8H, Si*H*, OCH_2C (sp^2)), 4.4−4.1 [m, 1.3H, OCH_2C(sp^3)], 1.95 [s, 12H, CH$_2$═CCH_3(C═O)], 1.2−1.1 [m, 1.5H, CH_3C(OCH$_2$Si$_2$)] ppm. ^{13}C NMR (90 MHz, $CDCl_3$) 167.1 (*C*═O), 144.6 (Si*C*═CH$_2$ α), 141.1 (*C*H═CHSi β-trans), 136.2 [CH$_2$═*C*CH$_3$-(C═O)], 130.0 (CH═*C*HSi β-trans), 127.0 (SiC═*C*H$_2$ α), 125.5 [CH$_2$═CCH$_3$(C═O)], 71.0 [OC*H*$_2$C(sp^3)], 67.4 (OC*H*$_2$-CH═CH β-trans), 66.3 (O*C*H$_2$CSi α), 18.3 [CH$_2$═C*C*H$_3$(C═O)], 11.3 [CH$_3$C(OCH$_2$Si$_2$)], −0.10 (Si(*C*H$_3$)$_2$). ^{29}Si NMR (79.5 MHz, $CDCl_3$): −108.7, 109.1 (O$_3$*Si*OSiH, O$_3$*Si*OSiC), −1.19 (*Si*H), 1.69, 1.28 (*Si* α and β trans), 13.5 [*Si*C(sp^3)]. DEPT techniques were used to assign the six different Si environments, which correspond to the α and β-trans isomers for *Si*−C at 1.28 and 1.69 ppm, *Si*−H at −1.19 ppm, *Si*(O)$_4$ at −108.7 and −109.1 ppm, and an unknown broad peak at 13 ppm. The two peaks at −108.7 and −109.1 ppm are due to O$_3$*Si*−O−SiC and O$_3$*Si*−O−SiH. The unknown peak at 13 ppm is likely due to the *Si*−C(sp^3) formed from intramolecular cyclization and/or cube coupling reactions.[20] SEC (polystyrene standards, THF as solvent, and toluene as reference) M_n = 1860, PDI = 1.40.
(20) The peak between 4.1 and 4.0 ppm is indicative of an aliphatic methylene adjacent to oxygen and sp^3 hybridization (as in the allyloxy derivatives).[14] The 2.0−1.1 ppm resonances are the result of the sp^2 methylene being hydrosilylated to a methyl group. One likely product is the intramolecular hydrosilylation product:



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(24) The product mixture, obtained on reacting 4 equiv of propargyl methacrylate with the octahydrido cubes, is very complex. Product distributions per reaction 1 ensure a set of α and β isomers. A statistical distribution of products without isomers should be ≈3% mono, ≈11% di, ≈22% tri, ≈27% tetra, ≈22% penta, ≈11% hexa, ≈3% hepta, and ≈0.4% octa. Additionally, the products contain vinylsiloxane moieties resembling the vinylsiloxane environment of Karstedt's catalyst [Pt(dvs)]. Thus, formation of one or two such moieties on the same edge of either cube might stabilize the active catalyst species and keep it on the cube face where it can react further, i.e., intra- and intermolecular hydrosilylation. Taken *in toto*, a nonstatistical product distribution is expected and found.

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