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Octaalkynylsilsesquioxanes, Nano Sea Urchin Molecular Building Blocks for 3-D-Nanostructures

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ABSTRACT: The design and construction of 3-D molecular scaffolds is currently an area of extreme interest for a variety of reasons including hydrogen storage, gas separation and molecular sieving. Octahedral silsesquioxanes, $[RSiO_{1.5}]_8$, represent a class of unusually robust, nanometer size molecules with cubic symmetry that places each functional group in a different octant in Cartesian space. This 3-D array of functional groups offers the potential to design nanobuilding blocks to construct multifunctional, nanocomposite materials including molecular scaffolds. We describe here detailed studies on the synthesis of octaalkyne silsesquioxanes using Sonogashira coupling of octaiodophenylsilsesquioxane, $[p\text{-}IC_6H_4SiO_{1.5}]_8$ (I_8OPS) and a related bromine derivative with terminal alkynes. We describe versatile and reliable methods for synthesizing octaalkyne silsesquioxanes in moderate to high yields with 100% conversion of the I_8OPS to the octaalkynes. The inorganic core provides 3-D rigidity and the heat capacity of crystalline SiO_2 making them quite robust in many environments. The alkyne "spines" provide excellent solubility in organic solvents and the ability to polymerize on heating, to form robust 3-D polyalkyne networks with air stabilities to >500 °C suggesting potential utility as matrix materials for high temperature composites. With appropriate functionality on the external point of the spine, all of these molecules should also serve as 3-D connection points for the construction of molecular scaffolds.

Introduction

The design and construction of 3-D molecular scaffolds is currently an area of extreme interest for a variety of reasons including hydrogen storage, gas separation and molecular sieving, for molecular recognition, nonlinear optical properties, synthesis of hyperbranched and dendrimeric species, protection and stabilization of catalytic sites, the creation of well-defined arrays of addressable functional groups for computational purposes, and for micromechanical devices, etc.[1−14] Extensive work has been devoted to developing rigid rod components for molecular scaffolds,[1,2] and through the use of transition metal centers there are now extensive sets of work on developing connection points for these rigid rods.[3−8] To date, however, very little work has been directed toward developing connection points with symmetry higher than tetrahedral.[1,2,4] To our knowledge there are no components that provide connection points with cubic symmetry although the potential utility of cubane materials as difunctional connection points has been described.[1]

Part of the problem lies in the fact that aside from cubane, only one other easily accessible class of materials offers perfect cubic symmetry, the cubic silsesquioxanes.[9−15] We have recently developed a synthetic route to $[p\text{-}I\text{-}C_6H_4SiO_{1.5}]_8$,[16] with the pure octasubstituted isomer isolated in ≥40% yields (at scales of 100 g of starting material) following recrystallization and where iodide substitution is reproducibly ≥93% para offering the potential to create cubic connection points for 3-D molecular scaffolds. Given the considerable interest in using alkyne and oligoalkyne rods as the bridging components in such scaffolds, we have undertaken to develop synthetic routes to a number of alkynes some of which offer potential as octafunctional, cubic connection points. These same systems polymerize on heating to generate materials that exhibit very high temperature oxidative stability offering the potential to serve as composite matrix materials.

Experimental Section

Materials. Dioxane was purchased from Fisher and distilled under N_2 prior to use. Octa(iodophenyl)silsesquioxane was synthesized according to recently published methods.[16] All other chemicals were purchased from Fisher or Aldrich and used as received. All work was performed under nitrogen unless otherwise stated. The $Br_{5.3}$ octaphenylsilsesquioxane was synthesized as described in ref 21.

Analytical Methods. *Gel Permeation Chromatography.* 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.

NMR Analyses. All ^{1}H and ^{13}C NMR analyses were done in $CDCl_3$ and recorded on a Varian INOVA 400 spectrometer. ^{1}H -NMR spectra were collected at 400.0 MHz using a 6000 Hz spectral width, a relaxation delay of 3.5 s, a pulse width of 38°, 30K data points, and $CHCl_3$ (7.27 ppm) as an internal reference. ^{13}C NMR spectra were collected at 100 MHz using a 25000 Hz spectra width, a relaxation delay of 1.5 s, 75K data points, a pulse width of 40°, and $CDCl_3$ (77.23 ppm) as the internal reference.

Thermal Gravimetric Analysis (TGA). Thermal stabilities of materials under N_2 or air were examined using a 2960 simultaneous DTA-TGA Instrument (TA Instruments, Inc., New Castle, DE). Samples (5−10 mg) were loaded in platinum pans and ramped to 1000 °C (10 °C/min/N_2). The N_2 or air flow rate was 60 mL/min.

FTIR Spectra. Diffuse reflectance Fourier transform (DRIFT) spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer (Mattson Instruments, Inc., Madison, WI). Optical grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ) were ground, with 1.0 wt% of the sample to be analyzed. For DRIFT analysis, samples were packed firmly and leveled off at the upper edge to provide a smooth surface. The FTIR

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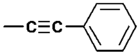
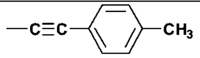
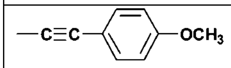
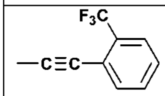
Table 1. Alkyne Product Yields, Conversions, and GPC Data from $Br_{5.3}OPS$[21] and I_8OPS[16]

	$Br_{5.3}OPS$[20]				I_8OPS				
acetylene	yield (%)[a]	% convn[b](NMR)	GPC PDI	ceramic yield (%)	yield (%)[a]	% convn[b](NMR)	GPC PDI	ceramic yield (%)	theor ceramic yield (%)
phenylacetylene	90	n/a	1.14	25.4	90	n/a	1.02	26.4	27.0
4-ethynyltoluene	86	130	1.09	22.5	89	>99	1.01	24.5	25.4
4-ethynylanisole	87	130	1.15	21.2	90	>99	1.01	22.6	23.8
4-ethynyl-α,α,α-trifluorotoluene	64	120	1.21	22.5	70	>99	1.15	21.1	20.7
trimethylsilyl-acetylene	80	110	1.23	17.8	81	>99	1.02	27.6	27.5
methylpropiolate	56	110	1.23	17.8	67	>99	1.02	29.3	29.3

[a] Isolated yield calculated relative to complete conversion of aryl halide. [b] Conversion calculated as ratio of aromatic to nonaromatic protons in ^1H NMR compared to the theoretical ratio.

Table 2. $T_{d5\%}$ for Octaalkynes from I_8OPS (in Air)

R	$T_{d5\%}$ (°C)
	526
	475
	508
	423
$—C{\equiv}C—Si(CH_3)_3$	418
$—C{\equiv}C—COOCH_3$	403

sample chamber was flushed continuously with N_2 prior to data acquisition in the range 4000−400 cm^{-1}.

Differential Scanning Calorimetry (DSC). Calorimetry was performed on materials using a DSC 2910 (TA Instruments, Inc., New Castle, DE). The N_2 flow rate was 60 mL/min. Samples (10−15 mg) were placed in a pan and ramped to 400 °C (5 °C/min/N_2) without capping.

Melting Point. Melting point determinations were performed on samples using a Mel-Temp 3.0 (Laboratory Devices, Inc. Dubuque, IA) with a ramp rate of 5 °C/min.

Matrix-Assisted Laser-Desorption/Time-of-Flight Spectrometry. MALDI−TOF was performed on a Micromass TofSpec-2E equipped with a 337 nm nitrogen laser in positive ion reflection mode using poly(ethylene glycol) as the calibration standard, 1,8,9-anthracenetriol as the matrix, and $AgNO_3$ as the ion source. Samples were prepared by mixing solutions of five parts dithranol (10 mg/mL in THF), five parts sample (1 mg/mL in THF) and one part $AgNO_3$ (10 mg/mL in water) and blotting the mixture on the target plate.

Synthetic Methods. *General Sonogashira Reaction Conditions from $Br_{5.3}OPS$.* To a dry 50 mL Schlenk flask under N_2 and equipped with a magnetic stir bar was added 0.500 g of $Br_{5.3}OPS$ (1.83 mmol Br), CuI (18.2 mg, 0.096 mmol, 5%), $Pd_2(dba)_3$ (22.08 mg, 0.048 mmol), bis(tri-*tert*-butylphosphine)-palladium(0) (24.5 mg, 0.096 mmol), 5.0 mL 1,4 dioxane (previously distilled under N_2), 0.36 mL (2.6 mmol) of triethylamine, and phenylacetylene (0.21 mL, 1.8 mmol). The solution was stirred at 25 °C for 48 h, during which time it turned dark gray-brown. The mixture was poured into excess methanol to deactivate the catalyst. Volatiles were removed by rotary evaporation. The residue was dissolved in 5.0 mL of ethyl acetate, filtered through celite, and precipitated into 100 mL of methanol. The light orange powder was collected by filtration and dried in vacuo for 5 h, giving 0.454 g (85% yield).

General Sonogashira Reaction Conditions from I_8OPS. To a dry 50 mL Schlenk flask under N_2 and equipped with a magnetic stir bar under was added 0.5 g of I_8OPS (2.4 mmol I-Phenyl), 0.29 mL (2.6 mmol) of phenylacetylene, 18.2 mg (0.096 mmol, 4%) of CuI, 194 mg (0.168 mmol, 7%) of tetrakis(triphenylphosphine)palladium(0), 5.0 mL of 1,4-dioxane (previously distilled and degassed), and 0.808 mL (4.9 mmol) of triethylamine. The solution was stirred at 60 °C for 24 h. The solution turned dark gray-brown. The mixture was passed through a short celite column and poured into an excess of methanol to deactivate the catalyst. The resulting precipitate was collected by filtration. The residue was redissolved in 5.0 mL ethyl acetate and precipitated into 100 mL of methanol. The light brown-orange powder was collected by filtration and dried *in vacuo* for 5 h, giving 0.4 g (90%).

Results and Discussion

The objectives of the current study are to develop molecular "sea urchins," molecules that have alkyne groups pointing to each octant in Cartesian space (cubic symmetry). Such structures offer the opportunity to build 3-D molecular scaffolds by serving as connection points, especially for example the trimethylsilyl compound which can be expected to be susceptible to facile proto-desilylation providing a point for further elaboration.[17] In addition, reaction of the alkyne groups with perphenylcyclopentadienones can be expected to provide access to 3-D graphene like structures akin to the novel 2-D structures developed by the Mullen group over the past decade.[18] Finally, alkyne monomers are known to undergo polymerization to provide novel, high temperature matrix materials for high strength carbon fiber reinforced composite materials for aerospace applications.[19] A further possible application of these materials is as starting points for the synthesis of robust 3-D star networks of polyacetylenes.[20]

Our initial approach focused on using $Br_{5.3}OPS$ as the substrate for alkynation via Pd catalyzed Songashira reactions.[21] Unfortunately the complex substitutions patterns found for $Br_{5.3}OPS$ were not conducive to producing highly symmetrical products. In addition, this approach suffered other problems as noted below. Thus with the successful synthesis of very pure *p*-I_8OPS, we switched to this substrate for more extensive efforts.

Sonogashira Reactions from $Br_{5.3}OPS$. Both I_8OPS and the previously reported[20] $Br_{5.3}OPS$ were reacted with various terminal acetylenes (Table 1) under slightly different conditions with different Pd catalysts (see Experimental Section). A catalyst system containing bis(tri-*tert*-butylphosphine)palladium(0) and $Pd_2(dba)_3$ was employed for $Br_{5.3}OPS$ because previous work showed that this system catalyzed both Heck and Sonogashira reactions from aryl bromides at ambient temperature, exclusive of unwanted side polymerizations associated with higher temperature reaction conditions.[21]

$Br_{5.3}OPS$ was used as the starting aryl halide since "octafunctional" Br_8OPS is actually a mixture of mono- and disubstituted isomers.[21] The use of $Br_{5.3}OPS$ ensures that the majority (>97%) of the resulting products are monosubstituted and predominantly (40%) *p*-isomers.

Early attempts to synthesize *p*-alkynes from $Br_{5.3}OPS$ resulted in the coincident formation of alkenyl bromides, as evidenced by characteristic alkenyl C−H peaks (≈6.5 ppm) present in the ^1H NMR of each sample. These peaks suggest that HBr byproduct adds across the alkyne triple bond, resulting in a C=C

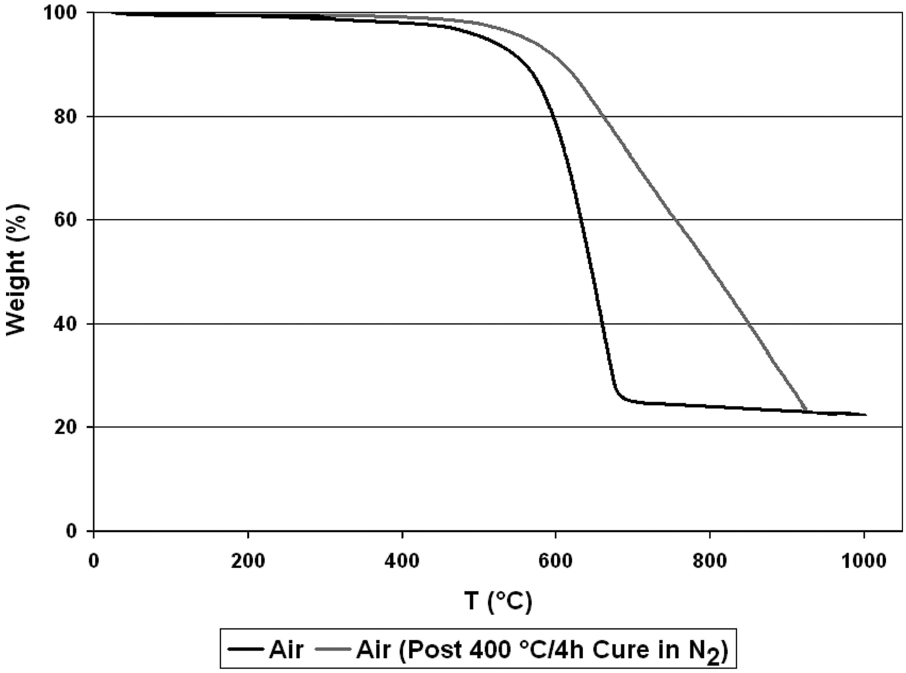
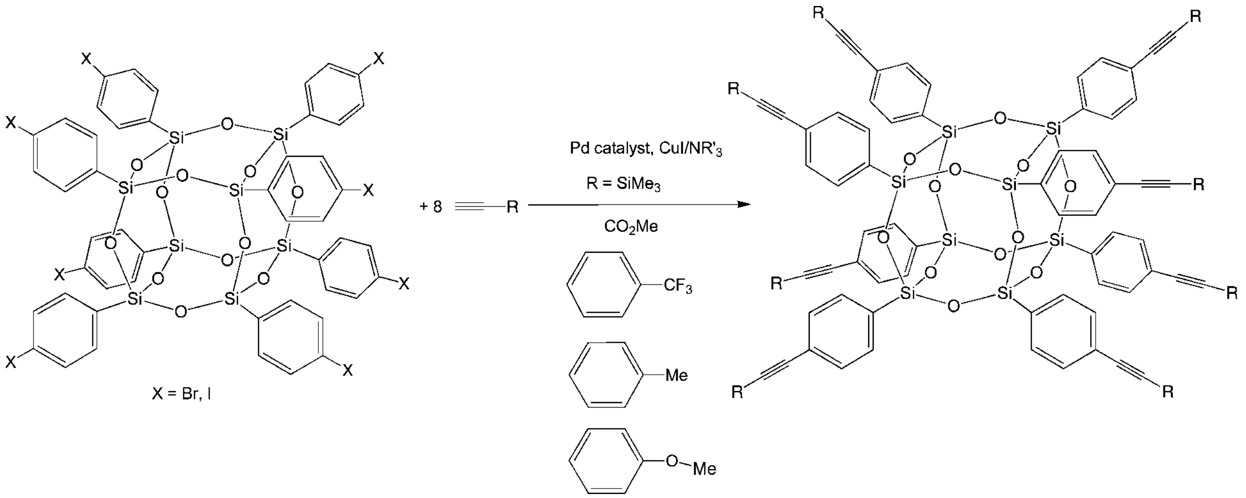


Figure 1. TGA of *p*-methoxydiphenylethyne derivative before/after 400 °C/4 h heat treatment.



bond and a vinyl bromide that offers another site for further reaction. Multiple substitution products are reflected in greater-than-unity % conversions (determined by ^{1}H NMR as the ratio of aromatic to nonaromatic protons compared to the theoretical ratio) for alkyne products from Br$_{5.3}$OPS. Consequently, MALDI−TOF data collected for the reaction of Br$_{5.3}$OPS with 4-ethynyltoluene indicates an average degree of substitution of 7.5 whereas the starting material was only 5.3. Residues at 1000 °C in air, which indicate the SiO$_2$ content (ceramic yields) of the materials, are all lower than theory, indicating higher-than-expected substitution. Furthermore, the PDIs determined by GPC are somewhat broader than expected for typical octa-substituted cubic silsesquioxanes (which usually have very narrow polydispersities), and may signify the presence of asymmetrical, multiply substituted products. Even when a deficiency of acetylene is used compared to the aryl bromide (4 equiv of acetylene: 5.3 equiv of Ph−Br), the presence of multisubstituted products is detected by ^{1}H NMR and TGA.

In an effort to capitalize on such uncontrolled substitution, we attempted to create exhaustively substituted "hyperbranched" oligoalkynes. Thus, Br$_{5.3}$OPS was reacted with a 2:1 excess of phenylethyne under Sonogashira conditions. Unfortunately, attempts to obtain effective alkyne hyper-branching were unsuccessful, as determined by the TGA, the maximum degree of substitution was $\approx$9 for Br$_{5.3}$OPS, regardless of further additions of catalyst or alkyne.

Since Br$_{5.3}$OPS is a mixture of isomers with only 40% *p*-isomer and the remaining 61% a mixture of unsubstituted phenyl and *m*- and *o*-isomers, the resulting Sonogashira products are expected to be a mixture of isomers as well. This fact is reflected in the rather broad ^{1}H NMR signals for phenyl-CH$_3$ and phenyl-OCH$_3$ substituted alkynes. Since highly symmetric octaalkynes offer considerable potential for the reasons discussed above, the low symmetry of alkynes from Br$_{5.3}$OPS increases the probability of defects in higher ordered structures derived from them.

Sonogashira Reactions from I$_8$OPS. The problem of multiple substitution products and isomer mixtures was remedied by using I$_8$OPS as the starting aryl halide. Apart from the aryl iodide being more reactive[16] in Sonogashira and similar coupling reactions, I$_8$OPS is $\geq$93% *p*-substituted and 99% octa-substituted after recrystallization, highly soluble in organic solvents and preparable in 100 g quantities.[16] In theory, the use of highly symmetrical I$_8$OPS should lead selectively to symmetrical *p*-octaalkynes, "sea urchin"-like molecules.

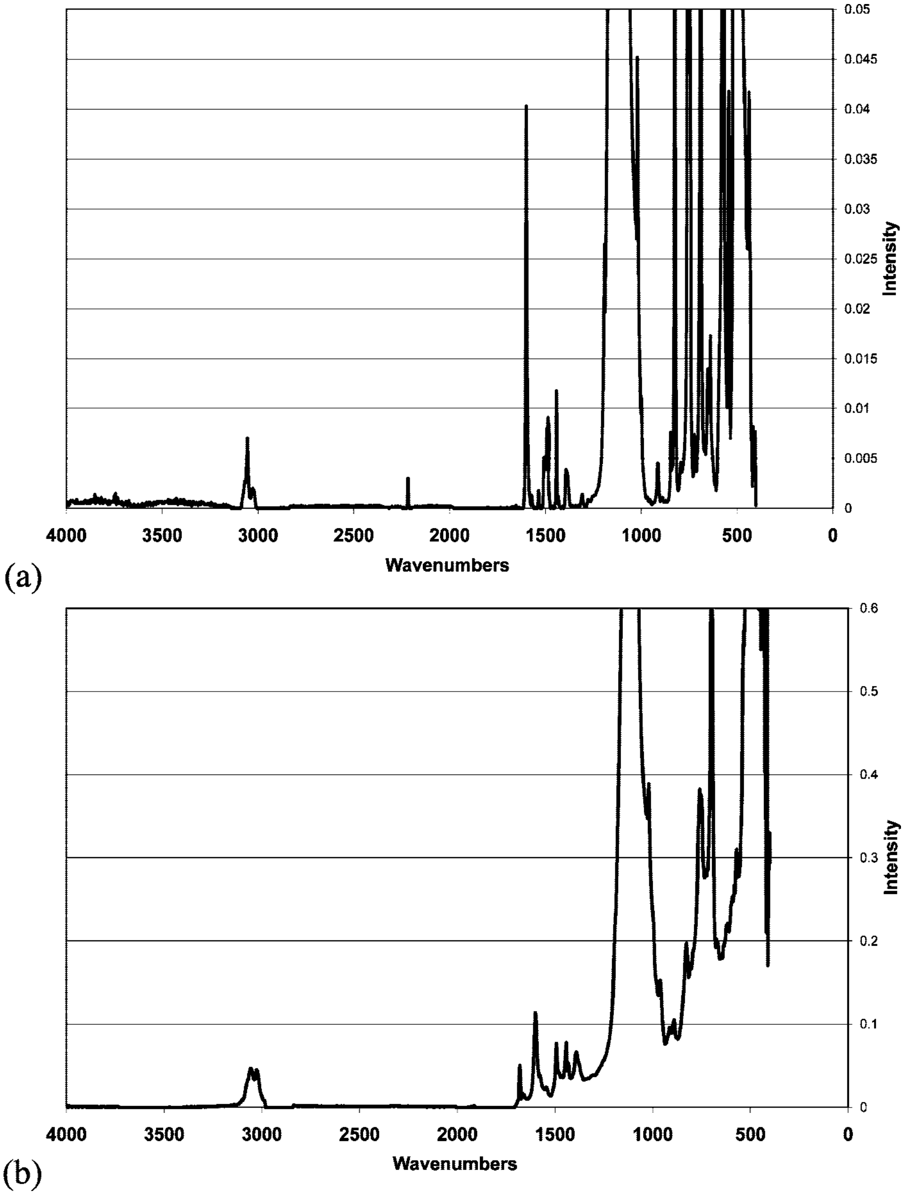


Figure 2. DRIFT spectra of [diphenylethyneSiO$_{1.5}$]$_8$ (a) before and (b) after heating to 400 °C/4 h.

The catalyst system for alkynylation from I$_8$OPS was changed from (tri-*tert*-butyl-phosphine)palladium(0)/Pd$_2$(dba)$_3$ to the less expensive (Ph$_3$P)$_4$Pd, due to the increased reactivity of the aryl iodide toward substitution. We found that heating the reaction mixture at 60 °C for 24 h drove the reactions to completion in the shortest possible time. As expected from aryl iodides, I$_8$OPS is so reactive toward substitution that $\approx$70% conversion can be achieved even at ambient temperature if stirred for 2.5 d. However, we found that mild heating could provide higher conversions in less time. There was no evidence of unwanted double addition of the starting alkyne on heating.

Compared to alkyne products from Br$_{5.3}$OPS, I$_8$OPS products by GPC are very monodisperse, representative of typical octa-functionalized cubic silsesquioxanes (see Table 1). Moreover, ^{1}H NMR does not reveal the presence of any alkenyl H's from addition side reactions as for Br$_{5.3}$OPS. Note that we were unable to obtain MALDI−TOF data for this set of materials although we tried multiple times using several procedures, e.g. with and without Ag$^+$.

Thermal Studies. The octaalkynes from I$_8$OPS exhibit exceptional thermal robustness in air (Table 2). The 5% mass loss temperatures ($T_{d5\%}$) determined by TGA predictably are the highest for the phenylethyne derivatives (475−526 °C) and the lowest for the nonaromatic propiolate and trimethylsilyl derivatives (ca. 400 and 420 °C, respectively). Residues at 1000 °C (ceramic yields, Table 1) in air for all derivatives are very close to theory (±1 wt %).

When heated treated to 400 °C/4 h, the materials thermally cross-link. Following polymerization, the cross-linked materials exhibit even greater stability. The $T_{d5\%}$ for Ph−OCH$_3$ increases from $\approx$ 510 to 560 °C as shown in Figure 1, which is typical behavior for these materials.[19,22] These properties make octaalkynes ideal cross-linking agents for high performance resins.[22]

Evidence for self-polymerization is seen in the DRIFTS spectra of the diphenylethyne derivative before and after heat treatment. Before heating, we see typical $\nu_{C\equiv C}$ at $\approx$ 2217 cm^{-1}, as well as νC−H aromatic ring and ν_{Si-O} stretches at $\approx$3050 and 1120 cm^{-1}, respectively, which are consistent with the proposed structure of the material. After heating at 400 °C/4 h, however, there is a notable absence of $\nu_{C\equiv C}$ peaks in the spectrum (Figure 2 b). This seems to indicate exhaustive polymerization of the alkyne groups. ν_{C-H} aromatic ring and ν_{Si-O} stretching peaks are still found in the DRIFTS spectrum

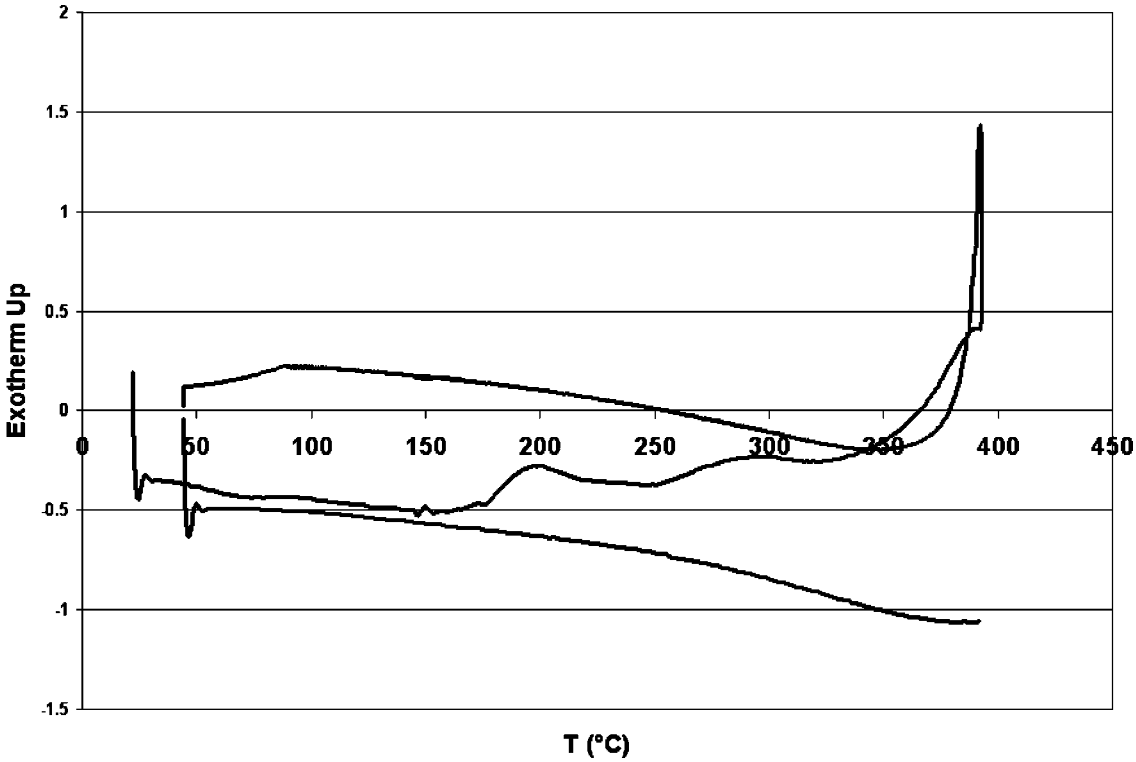


Figure 3. DSC thermogram of diphenylethyne derivative (N_2).

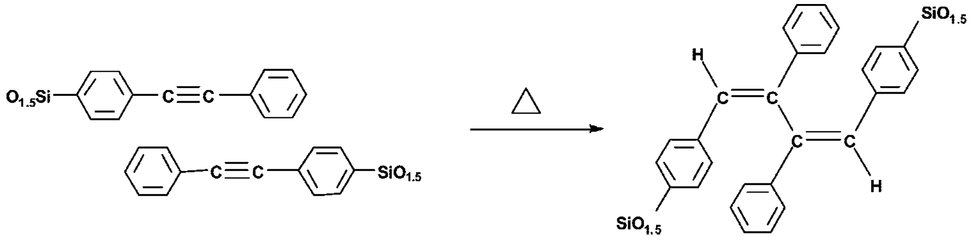


Figure 4. Possible structure of octaacetylenes after thermal polymerization.

after heat treatment, indicating retention of the tether aromatic rings as well as the silica cage. Thus the material is still polymeric (and not charred) after heating.

The DSC of [diphenylethyne$SiO_{1.5}$]$_8$ is shown in Figure 3. Most notable are two exotherms with maxima at 190 and 285 °C, and an exotherm onset at ≈325 °C. We believe that the first exotherm corresponds some form of ordering, e.g. T_c, since materials heated to this temperature and subsequently cooled remain soluble. However, heating to temperatures ≥285 °C, results in much reduced solubility, suggesting some form of polymerization occurs during the second exotherm. Materials heated past this temperature are brittle and completely insoluble in any organic solvents suggesting that the 325 °C exotherm onset corresponds to bulk polymerization. While we do not observe the appearance of an endotherm corresponding to T_m, it is possible that the endotherm is masked by the other two exotherms (simultaneous melting and polymerization). The other octaalkyne derivatives exhibit similar DSC plots. In no instance are we able to observe melting via DSC or using standard melting point studies.

While the precise mode of cross-linking is unclear, the presence of IR peaks ≈ 1680 cm^{-1} in the heat treated material (Figure 2b) could be attributed to C=C bond peaks resulting from polymerization. If this is indeed the case, the resulting thermoset could have a structure such as shown in Figure 4. The weakness of this reasoning is that there does not seem to be a reasonable source of protons during thermal self-polymerization to support this mechanism. However, thermolysis of aromatic acetylenes has been reported to give various π-conjugated products, such as fused rings, by means of intra- and intermolecular cyclization.[22-26]

While further analysis is needed to identify the exact cross-linking mechanism whereby these materials polymerize, we find that they readily self-polymerize at temperatures ≈ 400 °C to produce cross-linked materials with thermal stabilities in air above 500 °C. This level of thermal stability is among the best for alkyne derived polymers currently known.[22-26] In part these stabilities must result as a consequence of generating fully dispersed nanosilica particles within the polymer matrix that provide extra heat capacity not found in simple cross-linked polyalkynes.

In a future paper we will explore the reaction of selected octaalkynes with tetraphenylcyclopentadienone to first produce, for example, an Octahexaphenylbenezene silsesquioxane, a soluble, robust molecule with 56 phenyl rings that offers potential access to an octagraphene silsesquioxane.

Conclusions

Octaalkynes are readily synthesized in >70% yields with 100% conversions from I_8OPS via Sonogashira reactions under mild conditions. While the formation of octaalkynes from $Br_{5.3}$OPS resulted in unwanted addition reactions, the reactivity of the aryl iodide and near-perfect symmetry makes I_8OPS a suitable platform for the construction of octaalkynes with corresponding geometry. The resulting alkyne compounds are thermally robust, yet highly soluble and have been shown to self-polymerize at temperatures ≈ 400 °C to form highly cross-linked star polyalkynes with exceptional high temperature oxidative stability in air.

Finally, given that we now have developed a simple, high yield route to 3-D "Nano-Sea Urchin" molecules, it appears reasonable to suggest that the introduction of appropriate functionality at the external alkyne position will offer the potential to use these compounds as 3-D connectors for the construction of nanostructured materials. It also appears that these compounds, made in two steps from octaphenylsilsesquioxane could be used as new matrix materials for structural composites.

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