

Octa(3-chloroammoniumpropyl) Octasilsesquioxane

M.-C. Gravel, C. Zhang, M. Dinderman and R. M. Laine*

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

The octahydrochloride salt of octa(3-aminopropyl)octasilsesquioxane can be isolated in 30% yields by controlled hydrolytic condensation of 3-aminopropyltriethoxysilane in strongly acidic methanol. The analytically pure product can be filtered from the reaction solution. The product was characterized by standard analytical and spectroscopic tools. Efforts were made to explore the potential utility of the product for preparing amide and imide compounds that serve as models of polyimides with the goal of making novel materials, especially those that offer high strength and that are flame-resistant. Efforts to make the octa-acetamide were unsuccessful as the hexadeca-acetamide was formed in preference. These results provided the motivation to explore the synthesis of the succinic-anhydride-derived octa-imide. This reaction was found to proceed quite readily. The latter compound is stable in nitrogen to $\approx 500^\circ\text{C}$ and more importantly, it appears to behave as a liquid-crystalline material in the temperature range $90\text{--}190^\circ\text{C}$. This behavior is unusual, given that no aromatic or mesogenic groups are present on the cube. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Inorganic–organic hybrid materials are expected to combine the hardness and abrasion resistance of an inorganic phase with the compliance and formability of an organic phase, to produce materials that are more than simply the sum of the component parts. To do this effectively in a predictable, repeatable and tailorable manner, it is necessary to design components that can be combined at the smallest length scales possible, e.g. the atomic or molecular (nano) scales. Cubic silsesquioxanes offer considerable potential for producing hybrid materials because the cube itself is the smallest particle of sand (reinforcing inorganic phase) that can be formed, yet the vertices of these cubes can be ‘decorated’ with organic moieties to provide mechanisms for linking these ‘sand particles’ to and within an organic matrix.^{1–6}

Because of this potential, extensive efforts have been made to develop synthetic routes to: (1) partially oligomerized ‘T’-type silsesquioxanes as represented by the products of Scheme 1; (2) octahedral ‘T’-type silsesquioxanes as illustrated by the products of Scheme 2, and (3) octahedral ‘DQ’-or ‘spacer’-type silsesquioxanes as produced via Schemes 3–5.^{6–9}

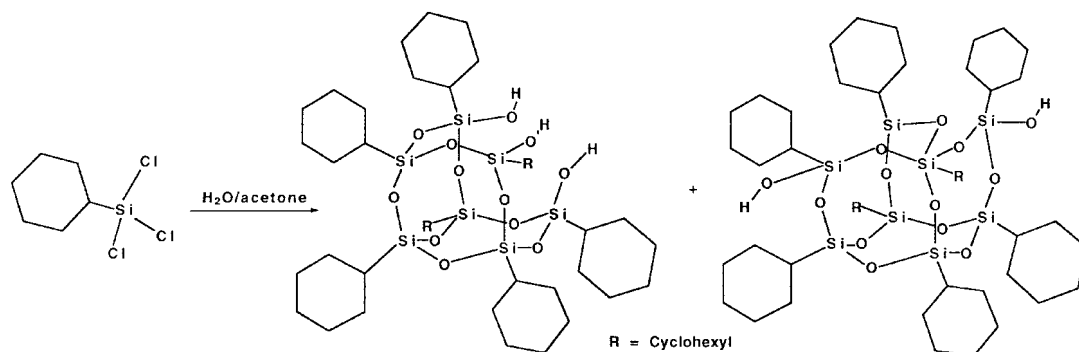
The general objectives that guide the research presented here are twofold. One is to develop low-cost routes to polyfunctional octahedral silsesquioxanes (cubes) and the second is to use these ‘macromonomers’ to process hybrid nanocomposites that offer potential as structural materials for dental, aerospace, electronic (etc.) applications.

We have previously prepared methacrylate, epoxide and liquid-crystalline functionalized cubes.^{6–9} In an effort to expand the types of functionality available, we sought to prepare the octa(aminopropyl) cube as a potential hybrid macromonomer. The synthesis of this cube was first described in a Wacker Chemie patent,¹⁰ then by Roziers and co-workers.^{11,12} However, the octa(aminopropyl) product claimed in these two

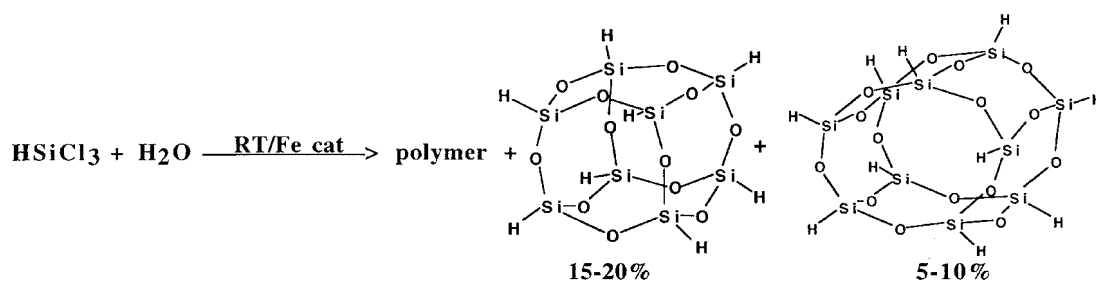
* Correspondence to: R. M. Laine, Department of Chemistry and Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA.

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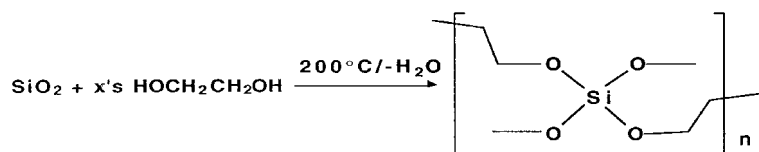
Contract/grant sponsor: Federal Aviation Administration; Contract/grant number: 95-G-026.



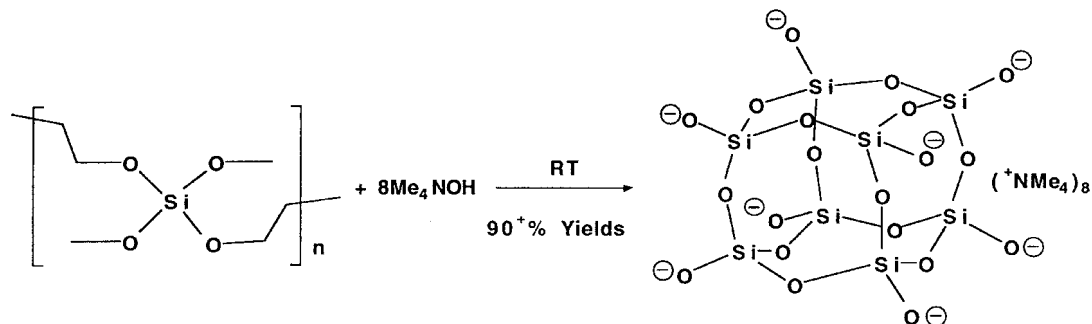
Scheme 1



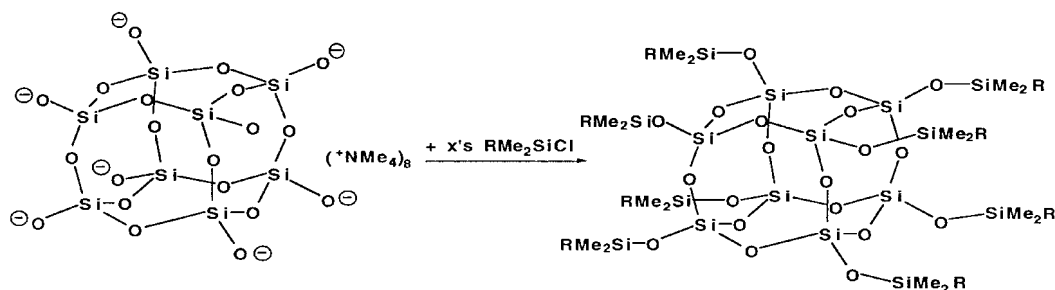
Scheme 2



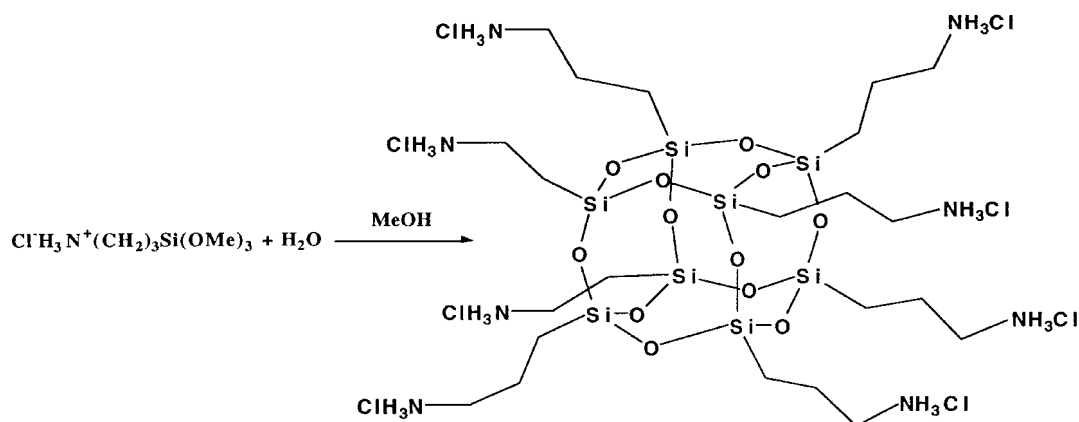
Scheme 3



Scheme 4



Scheme 5



Scheme 6

reports was not actually isolated; indeed, Petridis and co-workers note that amino-functionalized silsesquioxanes cannot be isolated.¹³

Despite these reports, we recently described the synthesis and isolation of octa(aminopropyl) octasilsesquioxane hydrochloride salt (OCAPS) via Scheme 6, simply by hydrolysis of aminopropyltriethoxysilane in aqueous acidic methanol.¹⁴ These results were confirmed in a brief report by Feher and Wyndham.¹⁵ In this paper, we provide more details about the OCAPS synthesis and characterization. We also present preliminary evidence that suggests the potential utility of OCAPS for synthesizing polyamide and polyimide hybrid materials.

EXPERIMENTAL

Analytical methods

NMR analyses

All NMR spectra were obtained in CDCl₃ with ¹H

and ¹³C NMR recorded on a Varian INOVA 400 Hz spectrometer. ¹H NMR spectra obtained at 400 MHz were collected using a 6000 Hz spectral width, a relaxation delay of 3.5 s, a pulse width of 38 ° and 30K data points. ¹³C{¹H} NMR spectra were obtained at 100.6 MHz using a 25 000 Hz spectral width, a relaxation delay of 1.5 s, a pulse width of 40 ° and 75K data points. CHCl₃ was used as internal reference for ¹H NMR (7.259 ppm) and CDCl₃ for ¹³C NMR (77.23 ppm). ²⁹Si NMR spectra were recorded on a Bruker AM 360 Hz spectrometer operating at 71.5 MHz using a 32 000 Hz spectral width, a pulse width of 90 °, a relaxation delay of 10.0 s, 32K data points tetramethylsilane and (TMS) as external reference.

Thermal analysis

TGA was performed on a Perkin–Elmer TGA-7 thermogravimetric analyzer (Perkin–Elmer Co., Norwalk, CT, USA). The instrument was calibrated with alumel and iron standards supplied by Perkin–Elmer. The measurements were performed under a

continuous flow of nitrogen or synthetic air (25 ml min^{-1}), at $20^\circ\text{C min}^{-1}$ to 900°C .

Differential scanning calorimeter (DSC) was performed on a Perkin–Elmer DSC-7 differential scanning calorimeter. The instrument was calibrated with indium supplied by Perkin–Elmer. The measurements were performed under a continuous flow of nitrogen (25 ml min^{-1}). The samples (1–2 mg) were typically equilibrated at 30°C , ramped to 225°C ($10^\circ\text{C min}^{-1}$), and allowed to cool back to 30°C at $10^\circ\text{C min}^{-1}$. Three heating–cooling cycles were recorded for each sample.

DRIFT spectra

These were recorded on a Mattson Galaxy Series FTIR 300 spectrometer (Mattson Instruments, Inc., Madison, WI, USA) with a DTGS detector. Random cuttings of crystalline, optical-grade KBr from International Crystal Laboratories were used to prepare the sample. About 600 mg of KBr was ground in a mortar with a pestle, and enough sample was ground with KBr to make a 0.6 wt% mixture. After the sample was loaded, the sample chamber was purged with nitrogen for a minimum of 10 min before data collection. A minimum of 250 scans were collected for each sample at a resolution of $\pm 4 \text{ cm}^{-1}$.

Mass spectrometry

Mass spectra were obtained on a VG analytical model 70-250S mass spectrometer using a DCI probe for both electron-impact and NH_3 -ionization techniques (FAB). The electron ionization energy was 70 eV.

Analytical mass spectra for lower-molecular-weight samples (i.e. <500) were recorded on a Finnigan model 4021 quadrupole GC/mass spectrometer by electron-impact ionization using the Galwin software package. Low-resolution mass spectra for higher-molecular-weight samples were obtained on a VG analytical model 70-250S mass spectrometer using a DCI probe for both electron-impact and NH_3 -ionization techniques. The electron ionization energy was 70 eV for all analyses.

Elemental analyses

These were performed by the University of Michigan, Department of Chemistry, analytical services for analysis of carbon, hydrogen and nitrogen content (CHN). At the University of Michigan, a Perkin–Elmer 2400 CHN Elemental Analyzer was operated at 1075°C with helium as a carrier gas. Powder specimens (1.5 mg) were loaded into tin capsules with powdered tin (6–

10 mg) as a combustion aid. Acetanilide was used as a reference standard, and was analyzed in the same manner as the samples.

Synthetic methods

Octa(3-chloroammoniumpropyl) silsesquioxane (OCAPS)

OCAPS synthesis optimization studies were conducted by varying the reaction conditions by using different acid and 3-aminopropyltrimethoxysilane concentrations, different temperatures and different reaction times. The total overall yields, no matter what the conditions, were never above 40% of theory, and most typically about 30%. The following example is for a 30% yield.

OCAPS was prepared in a Schlenk flask equipped with a magnetic stirrer and nitrogen purge. First, the methanol was placed in the flask, then the 3-aminopropyltrimethoxysilane (APTS, Gelest Inc.) was introduced dropwise. The hydrochloric acid (36.5 wt%, 12 M) was then poured quickly and the flask was closed when the fume production stopped (about 5 minutes). The reaction mixture was then stirred under nitrogen until the OCAPS precipitated as a white powder (typically 5–10 days). The resulting OCAPS was then washed with cold, dry methanol and dried under vacuum. The compound was extremely hygroscopic and must be stored in sealed containers in a desiccator.

Preparation of succinimide of OCAPS

Succinic anhydride (3.41 g, 34.1 mmol) and OCAPS (0.500 g, 0.426 mmol) were placed in a 25-ml Schlenk flask equipped with a reflux condenser and a magnetic stirrer. The reaction was heated in a silicone-oil bath. Succinic anhydride melts at $\approx 130^\circ\text{C}$, and a clear yellowish solution was obtained at $\approx 180^\circ\text{C}$. After heating at this temperature for $\approx 2 \text{ h}$, the reaction mixture was allowed to cool in air into a hard solid. CH_2Cl_2 (20 ml) was added and the reaction mixture was stirred at room temperature (RT) for 2 h, by which time the product had dissolved and a white suspension of the unreacted succinic anhydride was obtained. The succinic anhydride was filtered off, and CH_2Cl_2 was blown off under a stream of N_2 to yield the crude product, succinimide, as a white solid. Trace amounts of succinic anhydride remaining in the product were removed by sublimation under vacuum at $\approx 120^\circ\text{C}$. The crude product was recrystallized in CH_2Cl_2 /methanol to yield a white powder (0.398 g, 61% of theoretical). Selected characterization data are as follows: IR

Table 1. NMR data for OCAPS and derivatives

Cube	^1H (δ , D_2O)	^{13}C ($[\text{D}_6]$ DMSO)	^{29}Si ($[\text{D}_6]$ DMSO)
OCAPS	0.81 (t, 2H, $-\text{CH}_2\text{Si}$), 1.81 (m, 2H, $-\text{CH}_2-$), 3.02 (t, 2H, $-\text{CH}_2\text{NH}_2$)	8.44 ($-\text{CH}_2\text{Si}$), 20.63 ($-\text{CH}_2-$), 41.04, ($-\text{CH}_2\text{NH}_2$)	-66.4
OAOCAPS	0.65 (t, 2H, $-\text{CH}_2-\text{Si}$), 1.58 (m, 2H, $-\text{CH}_2-$), 1.93 (s, 3H, $\text{CH}_3\text{CO}-$), 2.78 (t, 2H, $-\text{CH}_2-\text{NHCO}-$), (CDCl ₃)	—	—
HOAAPS	0.61 (t, 2H, $-\text{CH}_2-\text{Si}$) 1.60 (m, 2H, $-\text{CH}_2-$) 2.37 (s, 6H, $-\text{CO}-\text{CH}_3$) 3.58 (t, 2H, $-\text{CH}_2-\text{N}$)	(CDCl ₃) 9.19 $-\text{CH}_2-\text{Si}$ 22.40 ($-\text{CH}_2-$) 26.37 $-\text{CO}-\text{CH}_3$ 47.23 $-\text{CH}_2-\text{N}$ 173.06 (C=O)	(CHCl ₃) -67.5
SOCAPS	0.54 (t, 2H, $-\text{CH}_2-\text{Si}$), 1.53 (p, 2H, $-\text{CH}_2-$), 2.67 (s, 4H, $-\text{CH}_2-\text{CO}-$), 3.41 (t, $-\text{CH}_2-\text{N}-$).	9.27 $-\text{CH}_2-\text{Si}$, 21.26 ($-\text{CH}_2-$), 28.31 $-\text{CH}_2-\text{CO}$, 41.13 ($-\text{CH}_2-\text{N}$), 177.53 ($-\text{C}=\text{O}$).	-67.26

(KBr, cm^{-1}): 2939s, 2890m (ν (C—H)), 1701s (ν (C=O)), 1440m (δ (C—H)), 1405s (ν (C—N)), 1232m (ν (Si—O)), 1141s (ν (Si—O)). Mass spectrum [FAB in 3-nitrobenzyl alcohol (NBA), relative percentage]: m/z = 1537 (M+1, 1.6), 1397 (0.3), 307 (25), 154 (NBA+1, 100), 136 (73). Elemental analysis: Found: C, 43.88; H, 5.20; N, 7.10; Si, 14.30 (calculated from ceramic yield in air); O, 29.52. Calcd: C, 43.73; H, 5.24; N, 7.29; Si, 14.61; O, 29.13%.

Hexadecylacetamide cube

To a 15-ml round-bottomed flask equipped with a magnetic stirrer and a condenser were added 0.200 g (0.171 mmol) octa-amino cube and 5 ml (52.0 mmol) acetic anhydride. The solution was refluxed at 140 °C for 24 h under nitrogen. The resulting product was dried under vacuum at 60 °C for 4 h and methanol was then used to wash the product and remove any remaining acetic anhydride. Methanol was evaporated under a nitrogen flow and 0.192 g (yield 92.5%) of the final product was obtained. Analytical data are Table 1.

RESULTS AND DISCUSSION

A number of groups have already demonstrated that silica/amide (e.g. nylon) and imide hybrid systems produced via sol-gel techniques offer enhanced thermal stability and improved mechanical properties compared with either component alone.^{16–21} Our intention in the work reported here is to extend

these efforts to molecular-level silica particles, e.g. cubes with direct chemical links to the polymer backbone.

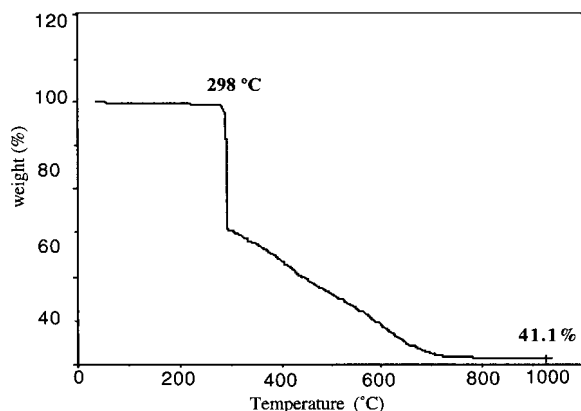
The first step was to attempt to synthesize octa(aminopropyl) octasilsesquioxane (OCAPS) macromonomer by acid-catalyzed condensation of 3-aminopropyltrimethoxysilane in MeOH. To our surprise, we were unable to prepare the octamino compound; however, we did find that OCAPS was precipitated out of solution in low yields. In an attempt to raise the yield of OCAPS, we explored the effects of variations in reaction conditions on isolated yields. Following extensive efforts, we were unable to obtain yields greater than $\approx 30\%$ reproducibly, and these yields required reaction times of 5–10 days for the OCAPS product to precipitate out of solution. Note that our reaction times seem to be shorter than the six weeks described by Feher and Wyndham.¹⁵

OCAPS is highly hygroscopic, as might be expected for an octa-(ammonium chloride) salt. It is quite soluble in water or dimethyl sulfoxide, giving a neutral pH in aqueous solution. Table 1 shows the results of NMR analysis, and Table 2 shows CHN and mass spectral analyses. The ^1H NMR data differ slightly from those reported by Feher and co-workers, as spectra were taken in D_2O rather than $[\text{D}_6]\text{DMSO}$; however, the ^{13}C and ^{29}Si data are identical. The TGA analysis (Fig. 1) of the OCAPS hydrochloride shows surprising stability, as the compound decomposes in air only at ≈ 300 °C, suggesting that amide and imide derivatives might exhibit reasonable stabilities.

The next step was to attempt a simple acetylation

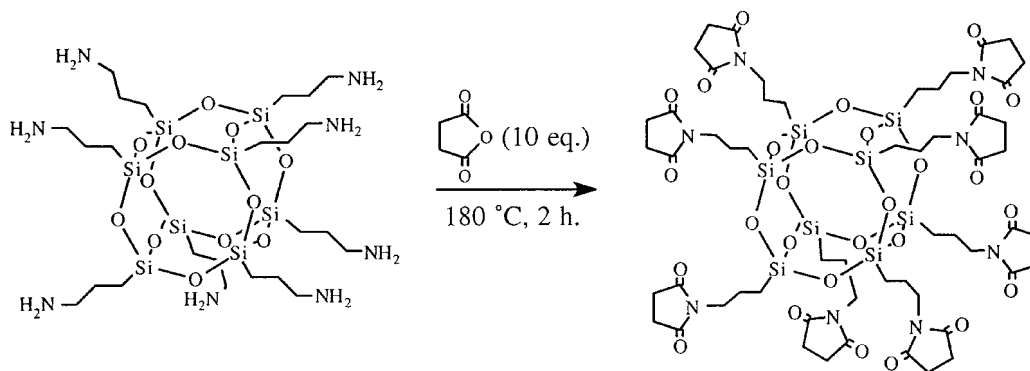
Table 2. Mass spectral and chemical analyses for OCAPS and derivatives

Cube	Mass spectrum m/z (intensity, %) ^a	Elemental analysis: Found (calcd) (%)			
		C	H	N	Si
OCAPS	881 (M^+)	24.21 (24.60)	6.20 (6.20)	9.31 (9.60)	
OAOCAPS	1217 (M^+), 881 ($M-CH_3CO$).				
HOAAPS	1553 (M^+ , 61.6), 1511 ($M-COCH_3$, 100), 1469 ($M-2COCH_3$, 47.7), 1428 ($M-3COCH_3$, 25.9), 1387 ($M-4COCH_3$, 14.3), 1345 ($M-5COCH_3$, 7.4), 1304 ($M-6COCH_3$, 4.3), 1268 ($M-7COCH_3$, 4.0), 1217 ($M-8COCH_3$, 8.0)				
SOCAPS	1537 ($M+1$, 1.6), 1397 (0.3), 307 (25), 154 (NBA+1, 100), 136 (73)	43.88 (43.73)	5.20 (5.24)	7.10 (7.29)	14.30 (14.61) ^b

^a Fast atom bombardment (FAB) in nitrobenzyl alcohol matrix.^b Calculated from ceramic yield.**Figure 1** TGA (air/10 °C min⁻¹) of octa(3-chloroammoniumpropyl) octasilsesquioxane octahydrochloride.

to determine the facility with which OCAPS undergoes amide-type reactions. To simplify our efforts, the isolated octahydrochloride was used directly for the acetylation reaction and somewhat forcing conditions were employed, refluxing acetic anhydride. Surprisingly, rather than isolating the octa-acetamide (OAOCAPS), the product recovered (>90% yield) was the hexadecylacetamide (HOAAPS), as determined by mass spectral analysis and NMR (see Tables 1 and 2).

Efforts to produce pure OAOCAPS by reducing reaction temperatures to 60–80 °C and using longer reaction times were not successful as the OAOCAPS appears to be more reactive towards further acetylation than OCAPS is to acetylation. Thus, the mass spectral data and NMR data found in Tables 1 and 2 were gleaned from spectra of mixtures of the

**Scheme 7**

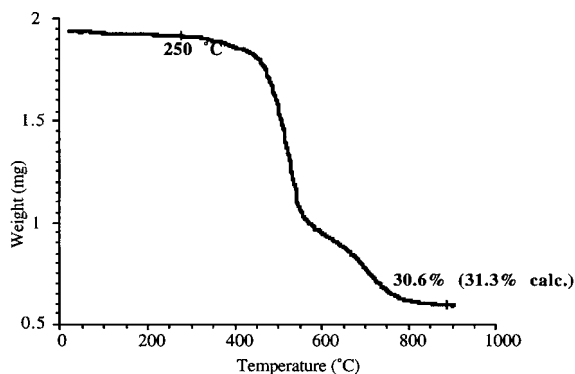


Figure 2 TGA (air/ $10\text{ }^{\circ}\text{C min}^{-1}$) of octa(3-succinimido-propyl) octasilsesquioxane.

two products with or without starting material, where the OAOCAPS never amounted to more than 30–40% of the product.

Our inability to isolate the OAOCAPS made it impossible to study the potential properties of this material as a model for polyamides. However, the peracetylation suggested that imides might be easily accessible. Therefore, we explored this possibility by replacing acetic anhydride with succinic anhydride as reactant, as shown in Scheme 7. Scheme 7 goes to completion in a short time (2 h) and provides nearly quantitative yields of the octasuccinimide (SOCAPS). No evidence for any intermediates or incomplete reaction is seen in the NMR and mass spectral analyses.

The TGA analyses in air and nitrogen are quite informative. First the air TGA (Fig. 2) shows a final ceramic yield of 30.6 wt%, which is very close to the calculated ceramic yield of 31.3 wt%, indicating a high-purity product. Second, the absence of

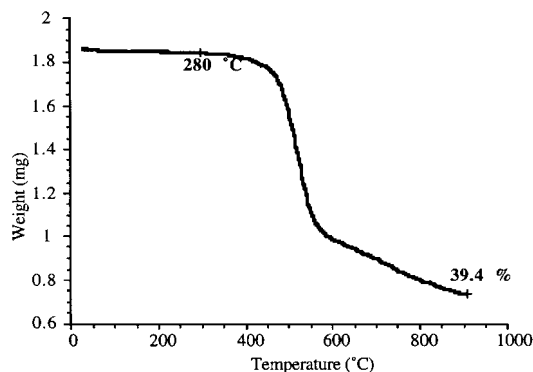


Figure 3 TGA (nitrogen/ $10\text{ }^{\circ}\text{C min}^{-1}$) of octa(3-succinimido-propyl) octasilsesquioxane.

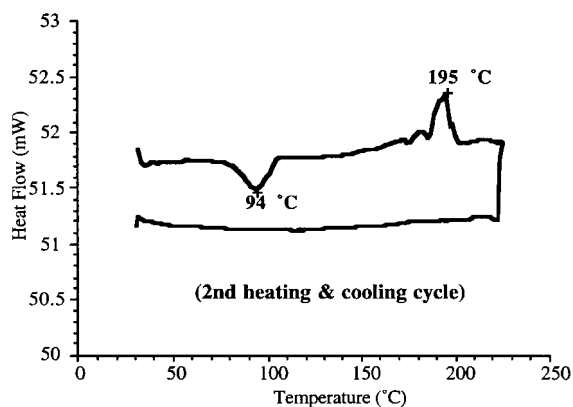


Figure 4 DSC (nitrogen/ $10\text{ }^{\circ}\text{C min}^{-1}$) of octa(3-succinimido-propyl) octasilsesquioxane.

any major mass losses before $\approx 400\text{ }^{\circ}\text{C}$ in air is very promising in that it suggests high stability for any polyimides or copolyimides that might be prepared using cubic silsesquioxanes. This is very important because the high silica content plus the high-temperature stability suggest that these materials will be very useful for applications requiring flame resistance and high strength.

The SOCAPS TGA in nitrogen (Fig. 3) shows stability to temperatures of almost $500\text{ }^{\circ}\text{C}$. Taken together, these data suggest that polyimides made with aromatic anhydrides might be even more temperature-resistant.

The DSC results (second heat-cool cycle) shown in Fig. 4 provide still more interesting results. During the heating stage, an exotherm centered at $\approx 94\text{ }^{\circ}\text{C}$ is followed by a small endotherm that begins at $\approx 180\text{ }^{\circ}\text{C}$ and is followed by a larger endotherm at $190\text{ }^{\circ}\text{C}$. A sample placed on the hot stage of a polarizing microscope exhibits isotropic behavior below $90\text{ }^{\circ}\text{C}$ (second heat-cool cycle) and then it exhibits birefringence on heating above $180\text{ }^{\circ}\text{C}$. The birefringence remains until the material is heated above $190\text{ }^{\circ}\text{C}$. At this point it flows freely on the hot stage. We interpret these results to suggest that on heating a crystallization event occurs first (exotherm). Heating to $\approx 180\text{ }^{\circ}\text{C}$ leads to formation of what we tentatively assigned as a liquid-crystalline (LC) phase. On continued heating, the LC phase becomes isotropic at $\approx 190\text{ }^{\circ}\text{C}$ (endotherm). The cooling curve shows a slight upturn that a referee has suggested might be due to a vitrification process. The fact that no rigid aromatic groups are attached to the cube makes the observation of LC behavior quite unique, if it is indeed an LC phase. We plan to report in detail on

this behavior in a future publication (C. Zhang, L. Gonzalez, D. Martin and R.M. Laine, unpublished results).

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