Full Paper

Fluoride catalyzed rearrangements of polysilsesquioxanes, mixed Me, vinyl T_8, Me, vinyl T_{10} and T_{12} cages

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Insoluble mixtures of polyvinylsilsesquioxane, -(vinyl$SiO_{1.5})_n$- PVS, and polymethylsilsesquioxanes, -(Me$SiO_{1.5})_n$- PMS, in THF at ambient when treated with catalytic amounts (1–5 mol%) of fluoride ion introduced as tBu$_4$ NF will depolymerize and dissolve. The resulting soluble species consist of [vinyl$_x$Me$_{8-x}$(SiO$_{1.5}$)]$_8$, [vinyl$_x$Me$_{8-x}$(SiO$_{1.5}$)]$_{10}$ and [vinyl$_x$Me$_{8-x}$(SiO$_{1.5}$)]$_{12}$. Ratios of 1 : 1 of PVS : PMS greatly favor formation of vinyl rich cages. Only at ratios of 1 : 5 are the proportions of vinyl : Me in the cages approximately equal. Of the T_8, T_{10} and T_{12} species produced, all conditions tried, including changing the solvent to EtOH or toluene or at reflux (THF), favor the formation of the larger cages sometimes completely excluding formation of the T_8 materials. Efforts to isolate the cage compounds by removal of solvent regenerates polysilsesquioxanes, albeit those containing mixtures of Me and vinyl groups. Introduction of CaCl$_2$ sufficient to form CaF$_2$ prior to workup prevents repolymerization, allowing recovery of the mixed cage systems. The approach developed here provides a novel way to form mixed functional group silsesquioxane cages. The fact that T_{10} and T_{12} cage formation is favored appears to suggest that these cages are more stable than the traditionally produced T_8 cages. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: Catalytic reformation of Si-O bonds; mixed functional T_{10} and T_{12} silsesquioxanes; fluoride activation of T resins

Introduction

Polymer properties are dictated by a combination of monomer structure, chain length and processing. Monomer structure can often determine how the polymer coils, crystallizes, forms electrostatic or hydrogen bonds and of course melts and/or dissolves. If the monomer unit provides extended conjugation along the polymer backbone, the polymer may offer conducting, semiconducting, emissive or light absorptive properties of use in organic electronic and photonic applications. Rigid monomers lead to polymers with excellent mechanical properties and/or liquid crystallinity. Finally monomer structure can also dictate miscibility with other polymers.

Chain length can dictate T_gs, diffusion rates, viscosities, coefficients of thermal expansion (CTEs), extents of mechanical crosslinking and, for short chains, the melt temperature. Processing provides control of chain–chain interactions on a molecular scale as a means of controlling global properties through control of molecular alignment providing, for example, toughness, transparency and conductivity, etc.

Given that specific polymer properties arise from specific types of monomers, degrees of polymerization and processing, one can state: 'One size does not fit all'. We would like to suggest to the reader that there are certain types of polymer (oligomer) systems that may offer much more tailorability than others such that 'One size fits many'. One such system, encompasses the family of compounds called silsesquioxanes, as illustrated in Fig. 1.[1–10]

Because of the breadth of their properties, silsesquioxanes are of considerable interest to both the academic and industrial communities. This interest is such that they have been the subject of 10 reviews in the last 25 years.[1–10] Furthermore, the R groups can and have been as varied as there are types of aliphatic and aromatic functional groups, offering considerable potential to control the

properties of any oligomeric, polymeric and/or organic/inorganic hybrid nanocomposites that could be made from them.[11] One drawback to the partial cages and oligomeric species is that they usually are not stable to further condensation of residual Si–OH groups, leading to the production of both H$_2$O and highly crosslinked materials. The resulting H$_2$O may affect the stability of the final product whereas further crosslinking may cause formation of insolubles that will precipitate/phase separate during processing, leading to unwanted properties, e.g. reduced transparency.

Here we describe a new approach to all of these materials (except ladder structures) that allows us to catalytically and selectively interconvert between many of the structures at ambient temperatures (RT). In particular the work reported here, representing baseline studies for a much greater set of studies, focuses on the conversion of mixtures of polymethylsilsesquioxane (PMS) and polyvinylsilsesquioxane (PVS) to mixed functional group T_{10} and T_{12} structures (Scheme 1).

Experimental

Materials

Polyvinylsilsesquioxane was prepared using literature methods;[12] tetrahydrofuran, toluene, methanol and ethanol were purchased

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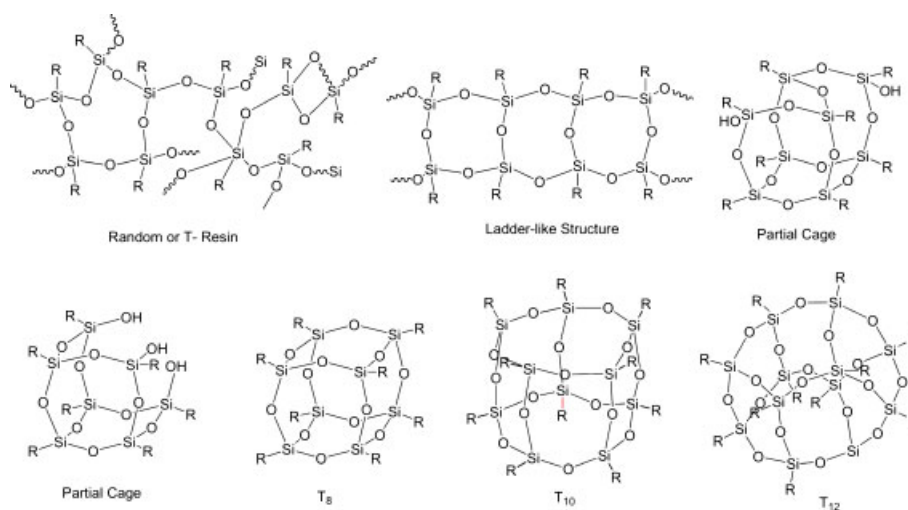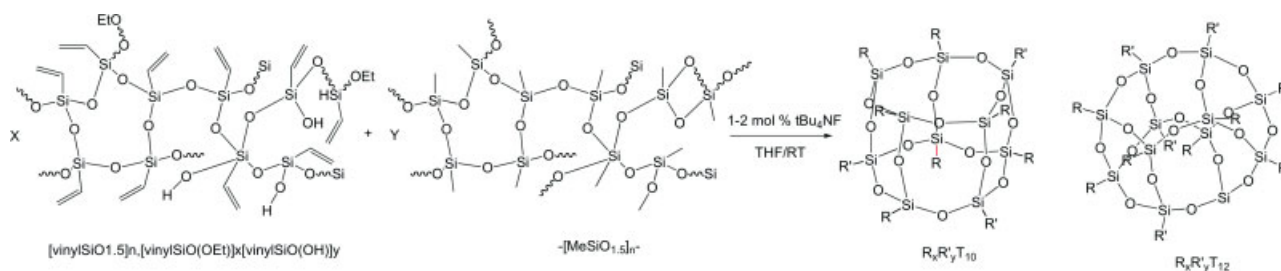
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Figure 1. Types of silsesquioxanes.[1–10] Only oligomeric rather than polymeric ladders have been made to date.[6].

Scheme 1. General concept of fluoride catalyzed rearrangement of polysilsesquioxanes to mixed T_{10} and T_{12} isomers with varying vinyl and methyl contents. Note that some T_8 isomers are seen.

from Fisher Scientific and used as received. Tetrabutylammonium fluoride and diethylether were purchased from Sigma-Aldrich and used as received. Yields are calculated based on the moles of polyvinylsilsesquioxane used.

Analytical Methods

Diffuse reflectance Fourier transform (DRIFT) spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer (Mattson Instruments Inc., Madison, WI, USA). Optical grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ, USA) 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 sample chamber was flushed continuously with N_2 prior (10 min) to data acquisition in the range 4000–400 cm^{-1}.

Gel permeation chromatography (GPC) analyses were run on a Waters 440 system equipped with Waters Styragel columns (7.8 × 300, HT 0.5, 2, 3, 4) with RI detection using Waters refractometer and THF as solvent. The system was calibrated using polystyrene standards and toluene as reference.

Matrix-assisted laser desorption/time-of-flight spectrometry (MALDI-ToF) was run on 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 solutions of 5 parts matrix (10 mg/ml in THF), 5 parts sample (1 mg/ml in THF) and 1 part $AgNO_3$ (2.5 mg/ml in water) and blotting the mixture on a target plate.

Synthetic Studies

Synthesis of polymethylsilsesquioxane

In a 100 ml one-necked round-bottom flask, 10 ml of HCl 37% were added to a solution of methyltrimethoxysilane (20 ml, 0.14 mol) in 40 ml of ethanol. The solution was stirred for 3 days, forming a white solid which was filtered off and washed with ether (3 × 10 ml) to give 8.6 g of PMS, a 90% yield. IR (KBr): ν_{C-H} (2971, 1408 cm^{-1}), ν_{Si-C} (1271 cm^{-1}), $\nu_{Si-O-Si}$ (1121, 1035 cm^{-1}).

General synthesis of T_8, T_{10} and T_{12} cages from polyvinylsilsesquioxane and polymethylsilsesquioxane

Tetrabutylammonium fluoride was added to a mixture of PVS and solvent. After complete dissolution, polymethylsilsesquioxane was added and the suspension was stirred for 2 days at room temperature or refluxed for 6 h. Unreacted material was filtered off from the solution and $CaCl_2$ (0.3 g) was added to quench the F^- catalyst. The solution was stirred for 3–4 h, the solid was removed by filtration and the product was obtained by removing the solvent *in vacuo* and/or by precipitation into methanol. All yields are based on mass of material recovered from the soluble fraction.

Experiment 1

$[ViSiO_{1.5}]_n$ (1 g, 12.6 mmol), $[MeSiO_{1.5}]_n$ (0.87 g, 12.6 mmol) and tBu_4NF (0.4 ml, 0.38 mmol) in THF (20 ml). Yield (80%). IR (KBr), Me, ν_{C-H} (2959, 1408 cm^{-1}); Vi, ν_{C-H} (3061, 1487 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1273 cm^{-1}), $\nu_{Si-O-Si}$

(1120 cm^{-1}). GPC (THF): M_n, 779; M_w, 789; PDI, 1.013. MALDI-ToF: m/z (Ag$^+$ adduct) = 691 [Si$_8$O$_{12}$(CH$_3$)$_4$(CH=CH$_2$)$_4$], 703 [Si$_8$O$_{12}$(CH$_3$)$_3$(CH=CH$_2$)$_5$], 715 [Si$_8$O$_{12}$(CH$_3$)$_2$(CH=CH$_2$)$_6$], 852 [Si$_{10}$O$_{15}$(CH$_3$)$_4$(CH=CH$_2$)$_6$], 864 [Si$_{10}$O$_{15}$(CH$_3$)$_3$(CH=CH$_2$)$_7$], 876 [Si$_{10}$O$_{15}$(CH$_3$)$_2$(CH=CH$_2$)$_8$], 998 [Si$_{12}$O$_{18}$(CH$_3$)$_5$(CH=CH$_2$)$_7$], 1010 [Si$_{12}$O$_{18}$(CH$_3$)$_4$(CH=CH$_2$)$_8$], 1022 [Si$_{12}$O$_{18}$(CH$_3$)$_3$(CH=CH$_2$)$_9$], 1024 [Si$_{12}$O$_{18}$(CH$_3$)$_2$(CH=CH$_2$)$_{10}$].

Experiment 2

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (1.74 g, 25 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (20 ml). Yield (75%). IR (KBr): Me, ν_{C-H} (2959, 1409 cm^{-1}); Vi, ν_{C-H} (3061, 3023 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1273 cm^{-1}), $\nu_{Si-O-Si}$ (1122, 1044 cm^{-1}). GPC (THF): M_n, 721; M_w, 739; PDI, 1.025. MALDI-ToF: m/z (Ag$^+$ adduct) = 729 [Si$_8$O$_{12}$(CH$_3$)(CH=CH$_2$)$_7$], 739 [Si$_8$O$_{12}$(CH=CH$_2$)$_8$], 793 [Si$_{10}$O$_{15}$(CH$_3$)$_9$(CH=CH$_2$)], 861 [Si$_{10}$O$_{15}$(CH$_3$)$_3$(CH=CH$_2$)$_7$], 899 [Si$_{10}$O$_{15}$(CH=CH$_2$)$_{10}$], 997 [Si$_{12}$O$_{18}$(CH$_3$)$_5$(CH=CH$_2$)$_7$], 1009 [Si$_{12}$O$_{18}$(CH$_3$)$_4$(CH=CH$_2$)$_8$], 1021 [Si$_{12}$O$_{18}$(CH$_3$)$_3$(CH=CH$_2$)$_9$], 1057 [Si$_{12}$O$_{18}$(CH=CH$_2$)$_{12}$].

Experiment 3

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (4.36 g, 63 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (30 ml). Yield (87%). IR (KBr): Me, ν_{C-H} (2969, 1408 cm^{-1}); Vi, ν_{C-H} (3061 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1272 cm^{-1}), $\nu_{Si-O-Si}$ (1118 cm^{-1}). GPC (THF): M_n, 760; M_w, 770; PDI, 1.013. MALDI-ToF: m/z (Ag$^+$ adduct) = 679 [Si$_8$O$_{12}$(CH$_3$)$_5$(CH=CH$_2$)$_3$], 691 [Si$_8$O$_{12}$(CH$_3$)$_4$(CH=CH$_2$)$_4$], 703 [Si$_8$O$_{12}$(CH$_3$)$_3$(CH=CH$_2$)$_5$], 715 [Si$_8$O$_{12}$(CH$_3$)$_2$(CH=CH$_2$)$_6$], 827 [Si$_{10}$O$_{15}$(CH$_3$)$_6$(CH=CH$_2$)$_4$], 837 [Si$_{10}$O$_{15}$(CH$_3$)$_5$(CH=CH$_2$)$_5$], 848 [Si$_{10}$O$_{15}$(CH$_3$)$_4$(CH=CH$_2$)$_6$], 972 [Si$_{12}$O$_{18}$(CH$_3$)$_7$(CH=CH$_2$)$_5$], 984 [Si$_{12}$O$_{18}$(CH$_3$)$_6$(CH=CH$_2$)$_6$], 997 [Si$_{12}$O$_{18}$(CH$_3$)$_5$(CH=CH$_2$)$_7$].

Experiment 4

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (1.74 g, 25 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in toluene (15 ml). Yield (39%). IR (KBr): Me, ν_{C-H} (2958, 1409 cm^{-1}); Vi, ν_{C-H} (3061 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1274 cm^{-1}), $_{Si-O-Si}$ (1120, 1049 cm^{-1}). GPC (THF): M_n, 739; M_w, 753; PDI, 1.019. MALDI-ToF: m/z (Ag$^+$ adduct) = 741 [Si$_8$O$_{12}$(CH=CH$_2$)$_8$], 899 [Si$_{10}$O$_{15}$(CH=CH$_2$)$_{10}$], 1057 [Si$_{12}$O$_{18}$(CH=CH$_2$)$_{12}$], 1689 [Si$_{20}$O$_{30}$(CH=CH$_2$)$_{20}$], 1848 [Si$_{22}$O$_{22}$(CH=CH$_2$)$_{22}$].

Experiment 5

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (4.36 g, 63 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in Toluene (30 ml). Yield (30%). IR (KBr): Me, ν_{C-H} (2958, 1409 cm^{-1}); Vi, ν_{C-H} (3061, 3023 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1274 cm^{-1}), $\nu_{Si-O-Si}$ (1126, 1047 cm^{-1}). GPC (THF): M_n, 762; M_w, 773; PDI, 1.014. MALDI-ToF: m/z (Ag$^+$ adduct) = 741 [Si$_8$O$_{12}$(CH=CH$_2$)$_8$], 899 [Si$_{10}$O$_{15}$(CH=CH$_2$)$_{10}$], 1057 [Si$_{12}$O$_{18}$(CH=CH$_2$)$_{12}$], 1690 [Si$_{20}$O$_{30}$(CH=CH$_2$)$_{20}$].

Experiment 6

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (1.74 g, 25 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (20 ml) and ethanol (20 ml). Yield (50%). IR (KBr): GPC (THF): M_n, 835; M_w, 847; PDI, 1.015. MALDI-ToF: m/z (Ag$^+$ adduct) = 739 [Si$_8$O$_{12}$(CH=CH$_2$)$_8$], 899 [Si$_{10}$O$_{15}$(CH=CH$_2$)$_{10}$], 1057 [Si$_{12}$O$_{18}$(CH=CH$_2$)$_{12}$], 1690 [Si$_{20}$O$_{30}$(CH=CH$_2$)$_{20}$].

Experiment 7

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (1.74 g, 25 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (25 ml) and ethanol (6.3 ml). Yield (52%). IR (KBr): Me, ν_{C-H} (2972, 1409 cm^{-1}); Vi, ν_{C-H} (3061 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1272 cm^{-1}), $\nu_{Si-O-Si}$ (1133, 1036 cm^{-1}). MALDI-ToF: m/z (Ag$^+$ adduct) = 828 [Si$_{10}$O$_{15}$(CH$_3$)$_6$(CH=CH$_2$)$_4$], 850 [Si$_{10}$O$_{15}$(CH$_3$)$_4$(CH=CH$_2$)$_6$], 862 [Si$_{10}$O$_{15}$(CH$_3$)$_3$(CH=CH$_2$)$_7$], 874 [Si$_{10}$O$_{15}$(CH$_3$)$_2$(CH=CH$_2$)$_8$], 996 [Si$_{12}$O$_{18}$(CH$_3$)$_5$(CH=CH$_2$)$_7$], 1009 [Si$_{10}$O$_{15}$(CH$_3$)$_4$(CH=CH$_2$)$_8$], 1020 [Si$_{12}$O$_{18}$(CH$_3$)$_3$(CH=CH$_2$)$_9$].

Experiment 8

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (1.74 g, 25 mmol) and tBu$_4$NF 0.4 ml, 0.38 mmol) in THF (6.25 ml) and ethanol (25 ml). Yield (33%). MALDI-ToF: m/z (Ag$^+$ adduct) = 793 [Si$_8$O$_{12}$(CH$_3$)$_9$(CH=CH$_2$)], 899 [Si$_{10}$O$_{15}$(CH=CH$_2$)$_{10}$], 973 [Si$_{12}$O$_{18}$(CH$_3$)$_7$(CH=CH$_2$)$_5$], 1057 [Si$_{12}$O$_{18}$(CH=CH$_2$)$_{12}$].

Experiment 9

[MeSiO$_{1.5}$]$_n$ (1 g, 14.4 mmol) and tBu$_4$NF (0.4 ml, 0.43 mmol) in THF (20 ml). Yield (25%). IR (KBr): Me, ν_{C-H} (2970, 1413 cm^{-1}), ν_{Si-C} (1270 cm^{-1}), $\nu_{Si-O-Si}$ (1123 cm^{-1}). GPC (THF): M_n, 575; M_w, 578; PDI, 1.00, MALDI-ToF: m/z (Ag$^+$ adduct) = 739 [Si$_9$O$_{12}$(CH$_3$)$_9$(OH)$_3$], 781 [Si$_{10}$O$_{15}$(CH$_3$)$_{10}$].

Experiment 10

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (0.87 g, 12.6 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (20 ml). Yield (62%). IR (KBr): Me, ν_{C-H} (2959, 1409 cm^{-1}); Vi, ν_{C-H} (3061 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1274 cm^{-1}), $\nu_{Si-O-Si}$ (1121 cm^{-1}). GPC (THF): M_n, 776; M_w, 791; PDI, 1.020. MALDI-ToF: m/z (Ag$^+$ adduct) = 679 [Si$_8$O$_{12}$(CH$_3$)$_3$(CH=CH$_2$)$_5$], 692 [Si$_8$O$_{12}$(CH$_3$)$_4$(CH=CH$_2$)$_4$], 817 [Si$_{10}$O$_{15}$(CH$_3$)$_7$(CH=CH$_2$)$_3$], 861 [Si$_{10}$O$_{15}$(CH$_3$)$_3$(CH=CH$_2$)$_7$], 875 [Si$_{10}$O$_{15}$(CH$_3$)$_2$(CH=CH$_2$)$_8$], 887 [Si$_{10}$O$_{15}$(CH$_3$)(CH=CH$_2$)$_9$], 963 [Si$_{12}$O$_{18}$(CH$_3$)$_8$(CH=CH$_2$)$_4$], 1021 [Si$_{12}$O$_{18}$(CH$_3$)$_3$(CH=CH$_2$)$_9$], 1033 [Si$_{12}$O$_{18}$(CH$_3$)$_2$(CH=CH$_2$)$_{10}$], 1045 [Si$_{12}$O$_{18}$(CH$_3$)(CH=CH$_2$)$_{11}$].

Experiment 11

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (1.74 g, 25 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (20 ml). Yield (65%). IR (KBr): Me, ν_{C-H} (2958, 1409 cm^{-1}); Vi, ν_{C-H} (3062 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1274 cm^{-1}), $\nu_{Si-O-Si}$ (1121 cm^{-1}). GPC (THF): M_n, 780; M_w, 794; PDI, 1.018. MALDI-ToF: m/z (Ag$^+$ adduct) = 715 [Si$_8$O$_{12}$(CH$_3$)$_2$(CH=CH$_2$)$_6$], 727 [Si$_8$O$_{12}$(CH$_3$)(CH=CH$_2$)$_7$], 740 [Si$_8$O$_{12}$(CH=CH$_2$)$_8$], 817 [Si$_{10}$O$_{15}$(CH$_3$)$_7$(CH=CH$_2$)$_3$], 851 [Si$_{10}$O$_{15}$(CH$_3$)$_4$(CH=CH$_2$)$_6$], 861 [Si$_{10}$O$_{15}$(CH$_3$)$_3$(CH=CH$_2$)$_7$], 875 [Si$_{10}$O$_{15}$(CH$_3$)$_2$(CH=CH$_2$)$_8$], 887 [Si$_{10}$O$_{15}$(CH$_3$)(CH=CH$_2$)$_9$], 899 [Si$_{10}$O$_{15}$(CH=CH$_2$)$_{10}$], 963 [Si$_{12}$O$_{18}$(CH$_3$)$_8$(CH=CH$_2$)$_4$], 1009 [Si$_{12}$O$_{18}$(CH$_3$)$_4$(CH=CH$_2$)$_8$], 1021 [Si$_{12}$O$_{18}$(CH$_3$)$_3$(CH=CH$_2$)$_9$], 1033 [Si$_{12}$O$_{18}$(CH$_3$)$_2$(CH=CH$_2$)$_{10}$], 1045 [Si$_{12}$O$_{18}$(CH$_3$)(CH=CH$_2$)$_{11}$].

Experiment 12

[ViSiO$_{1.5}$]$_n$ (1 g, 12.6 mmol), [MeSiO$_{1.5}$]$_n$ (4.36 g, 63 mmol) and tBu$_4$NF (0.4 ml, 0.38 mmol) in THF (25 ml). Yield (70%). IR (KBr): Me, ν_{C-H} (2959, 1408 cm^{-1}); Vi, ν_{C-H} (3061, 3023 cm^{-1}), $\nu_{C=C}$ (1602 cm^{-1}), ν_{Si-C} (1273 cm^{-1}), $\nu_{Si-O-Si}$ (1119 cm^{-1}). GPC (THF): M_n, 764; M_w, 778; PDI, 1.018. MALDI-ToF: m/z (Ag$^+$ adduct) = 679 [Si$_8$O$_{12}$(CH$_3$)$_5$(CH=CH$_2$)$_3$], 691

$[Si_8O_{12}(CH_3)_4(CH=CH_2)_4]$, 837 $[Si_{10}O_{15}(CH_3)_5(CH=CH_2)_5]$, 849 $[Si_{10}O_{15}(CH_3)_4(CH=CH_2)_6]$, 861 $[Si_{10}O_{15}(CH_3)_3(CH=CH_2)_7]$, 875 $[Si_{10}O_{15}(CH_3)_2(CH=CH_2)_8]$, 984 $[Si_{12}O_{18}(CH_3)_6(CH=CH_2)_6]$, 996 $[Si_{12}O_{18}(CH_3)_5(CH=CH_2)_7]$, 1009 $[Si_{12}O_{18}(CH_3)_4(CH=CH_2)_8]$, 1021 $[Si_{12}O_{18}(CH_3)_3(CH=CH_2)_9]$.

Results and Discussion

It is pertinent to provide some background discussion to allow the reader to understand the motivation for the work presented here. Thus, random structured silsesquioxanes or SQs for short, are often called T resins and offer a number of useful properties centered about their excellent adhesion and high temperature stability. In one form, with R = H, CH_3 they are used as interlayer dielectrics processed either by spin-on or vapor deposition methods.[13–17] They are also called organic silicates.[18–21] In other forms they are used to form molds, as clear coats for a wide variety of substrates and, for example, are a major component of silicone based caulks.[22] In other studies, they have been touted as potentially novel nanobuilding blocks for the construction of organic/inorganic hybrids with control of properties at nanometer length scales and are also noted for having unusual properties in their own right.[23–35]

The work reported here extends work by Bassindale *et al.*[36–38] targeting the synthesis of $[RSiO_{1.5}]_8$ compounds from alkoxysilanes, see reaction (1),[36] using 50 mol% TBAF (tetrabutylammonium fluoride).[36–38] Table 1 illustrates the yields for selected R groups. Of particular interest to us was the fact that no methyl cages were observed to form in these studies.

(1)
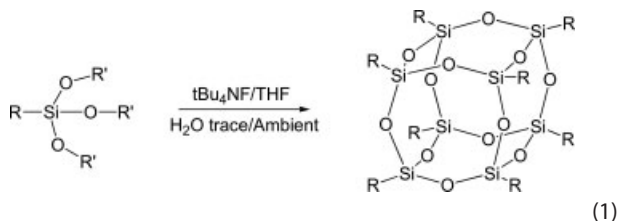
Bassindale *et al.* coincidentally discovered that the use of 50 mol% TBAF led to formation of fluoride-encapsulated compounds, as shown in the forward direction in reaction (2).[37,38] Most recently, Bowers *et al.* reported that the same products could be isolated directly from the cage by reaction of equimolar quantities of the tetramethylammonium fluoride, TMAF, as suggested in reaction (2) going from right to left.[39]

(2)
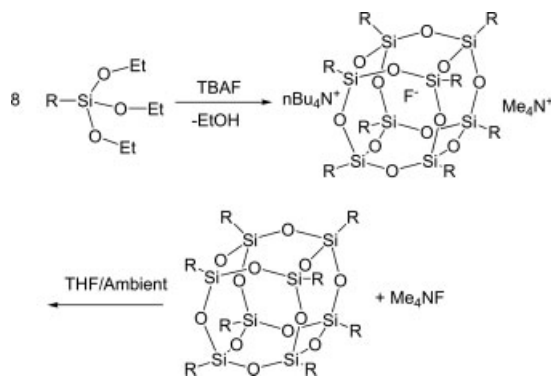
In general, both groups found that F^- encapsulation requires that the R groups be at least partially electron-withdrawing, limiting the types of $F^-@[RSiO_{1.5}]_8$ (@ refers to encapsulated F^-) to R = aryl, vinyl and partially fluorinated alkyls. Of particular note was the discovery by the Bowers/Mabry groups that reaction of the of $[iBu_7(styrene)T_8]$ with stoichiometric Me_4NF gave a mixture of products, reaction (3) with $F^-@[iBu_7(styrene)T_8]N^+$ Me_4 being a minor component. A second set of studies, reactions (4) and (5), provides additional information.

(3)

(4)

(5)
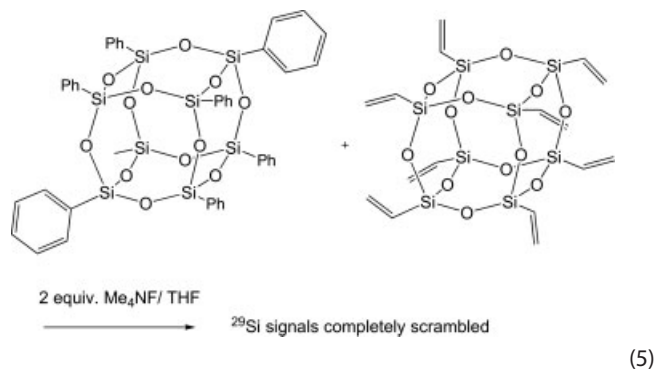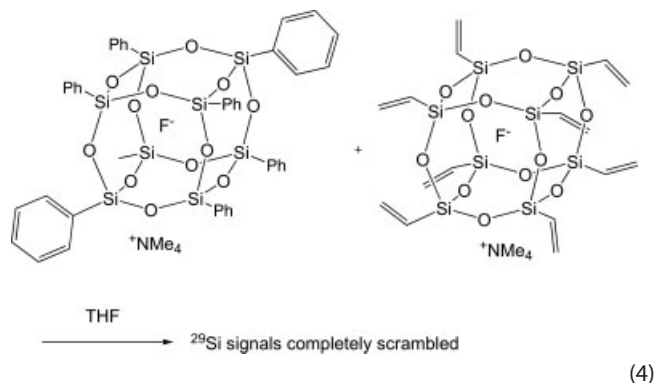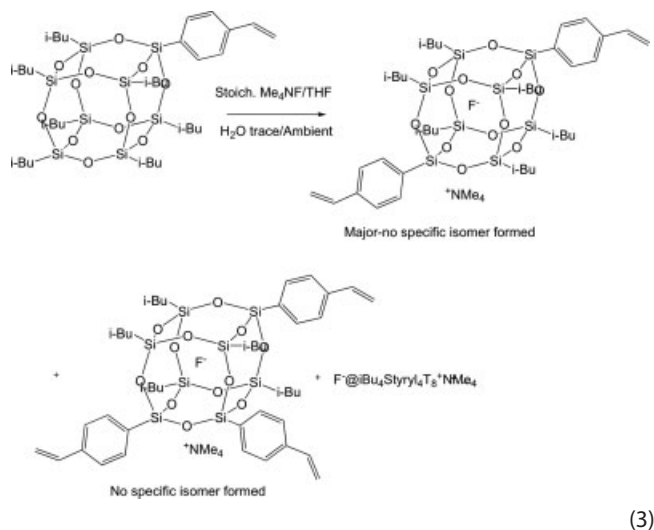
Basically, reactions (3)–(5) indicate that these cage systems are not truly stable at ambient in solution. They also suggest that the isolated F^- cage systems are actually kinetic products and that in solution they literally fall apart. This suggested to us that such reactions might actually be promoted by only catalytic amounts of F^-. We have now done extensive studies on these systems and
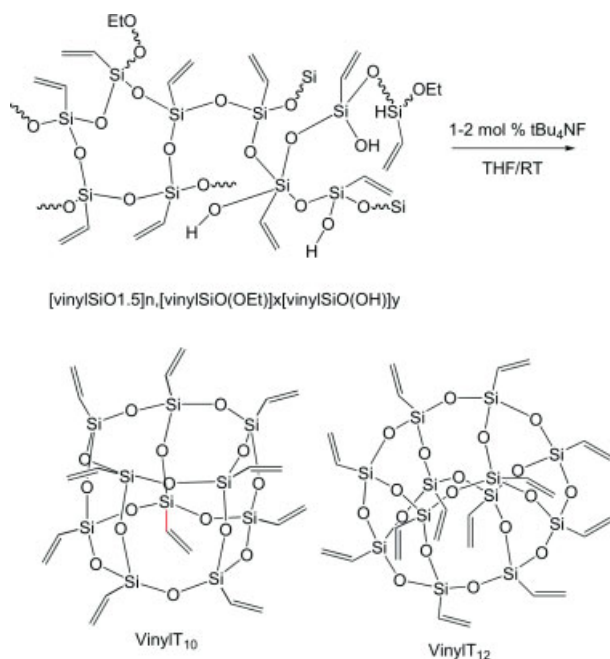
Table 1. Synthesis of cage compounds from the alkoxysilanes using TBAF

R	Percentage T_8 yield	Other cages	R	Percentage T_8 yield	Other cages
Phenyl	49	T_{12}	Hexyl	44	T_{10}
Methyl	0	–	Octyl	65	T_{10}
Vinyl	1	T_{10}, T_{12}	Isobutyl	26	T_{10}
Allyl	1	T_{10}, T_{12}	Cyclopentyl	95	–
			Cyclohexyl	84	–

report here one single aspect of this work, the depolymerization of PVS and PMS mixtures to form cage structures.

Thus, the synthesis of octavinylsilsesquioxane, $[vinylSiO_{1.5}]_8$, from hydrolysis of $vinylSiCl_3$ in aqueous EtOH provides yields of 35–45% depending on the scale of the reaction.[12] The remaining material recovered from solution consists of a mixed polymer, as suggested by $[vinylSiO_{1.5}]_n, [vinylSiO(OEt)]_x [vinylSiO(OH)]_y$. On removal of solvent, this material generates a completely insoluble and heretofore useless byproduct.

We were therefore surprised to find that treating this insoluble polymer with ∼2 mol% TBAF in THF/ambient/24 h causes it to dissolve into solution, reaction (6). MALDI-ToF of the solution shows a mixture of cages as seen in Fig. 2. However, efforts to isolate the cages led only to regenerated polymer, which however remained THF-soluble.

Figure 2. MALDI-TOF analysis of TBAF-catalyzed PVS dissolution quenched with $CaCl_2$.

$[vinylSiO1.5]n, [vinylSiO(OEt)]x[vinylSiO(OH)]y$

$1-2$ mol % tBu_4NF

THF/RT

VinylT$_{10}$ VinylT$_{12}$

(6)
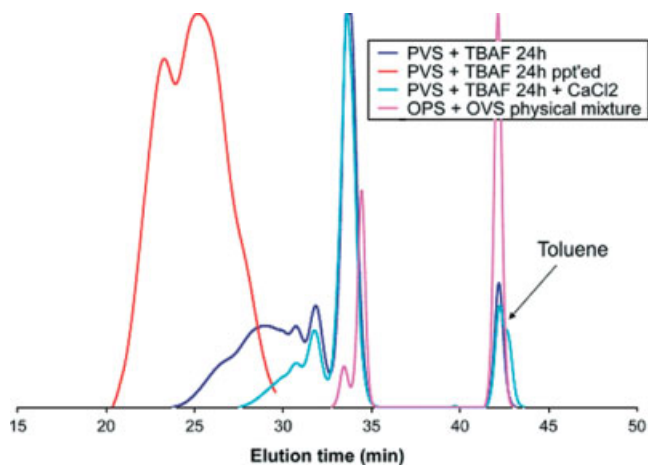
Figure 3. GPC analysis of ambient TBAF catalyzed PVS dissolution. Note that on precipitation it returns to a high MW, albeit soluble, polymer. OPS is $[PhSiO_{1.5}]_8$ used as an internal standard.

The simplest explanation for repolymerization is that given above, the cages are very labile and while easily formed they revert to the insoluble polymeric form on concentration. Consequently, we decided to trap the F^- ion by adding small amounts of $CaCl_2$ to form the insoluble CaF_2 allowing the recovery of the cage compounds, Fig. 2. Recognizing that the original PVS is insoluble, Fig. 3 illustrates the various processes observed by GPC.

It is important to point out that the major products seen by MALDI-ToF are the T_{10} and T_{12} cages. We see only small amounts of the T_8 materials. Thus, it could be argued that among the

polyhedral silsesquioxane systems the T_{10} and T_{12} cages are more stable than the T_8 cages.

One possible reason that T_8 compounds are most often recovered is that they are the least soluble of the cage systems and basically precipitate from solution first, as discussed by Brown et al.[40] Therefore, one might assume from these results that the T_8 systems are most stable cages. Clearly more work needs to be done; nonetheless the results reported here suggest whole new areas of research on the higher member cages.
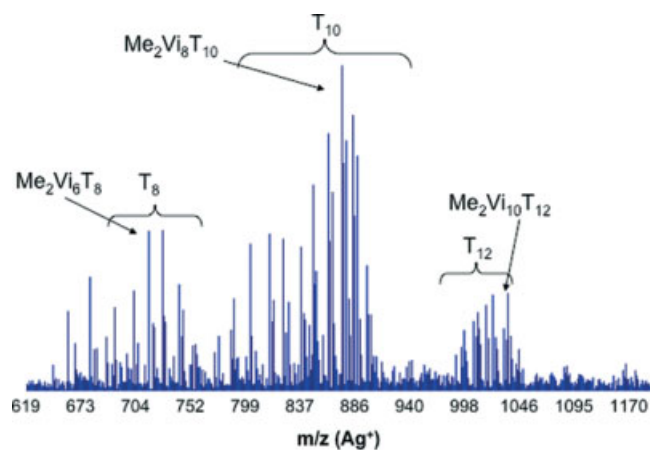
www.interscience.wiley.com/journal/aoc

Figure 4. Room temperature TBAF catalysis of OVS/OPS exchange; products are T_8, T_{10} and T_{12} PMS/PVS mixtures at a mole ratio of 1 : 1.
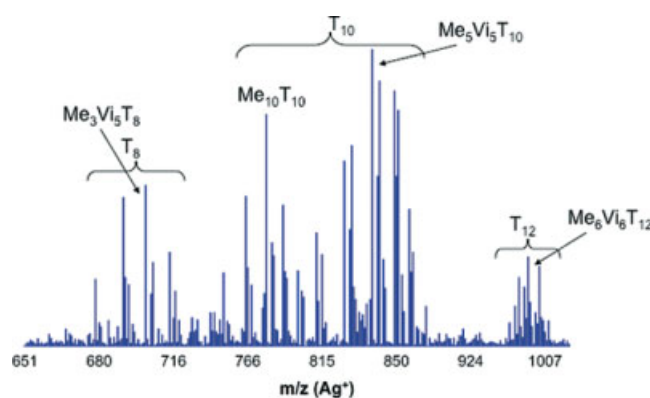

Figure 5. Room temperature TBAF catalysis of OVS/OPS exchange; products are T_8, T_{10} and T_{12} PMS/PVS mixtures at a mole ratio of 5 : 1.

We also conducted similar studies with PMS, which was insoluble in THF. The addition of ~2 mol% *t*BAF solubilized some 25% of this polymer. The isolated product gives peaks in the MALDI-ToF spectrum that can be assigned to the $Me_{10}T_{10}$ cage and what appears to be an incomplete cage $Me_9T_9(OH)_3$ missing one vertex. It is important to add that MALDI-ToF only sees species volatile under the analytical conditions. The GPC data suggest the presence of small amounts of oligomers not seen in the MALDI-ToF that may be partial cage species.
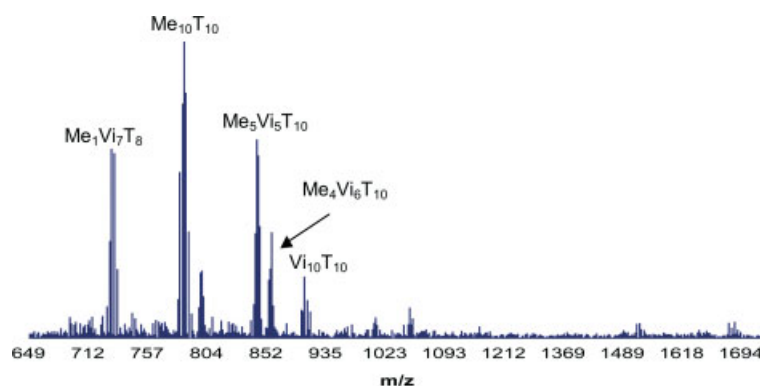
Given the apparent difficulty observed by Bassindale of producing methyl cages, we attempted to convert PMS and PVS to mixed cages per Scheme 1. As seen in Fig. 4, at a 1 : 1 mole ratio very few Me groups are incorporated into the cages arguing for lower PMS reactivity. Thus, increasing the ratio to 5 : 1 provided better Me : vinyl ratios in the soluble products, as seen in Fig. 5.

Other efforts to affect the ratios led to solvent studies using, for example, toluene and EtOH. Unfortunately, only the PVS converts to cage compounds in toluene or EtOH at ambient (RT) with PMS remaining mostly unreactive, but see above. Also, at THF reflux it was possible to isolate small amounts of mixed-group systems per Fig. 6. Note that fluoride is known to cleave Si–C bonds on heating, suggesting that this route is not useful from a synthetic standpoint.[41]

Publications from the Bassindale/Taylor group[37,38] report the use of F$^-$ as a base to promote formation of T_8 compounds and the redistribution of a cyclopentyl 'T' (CpT) resin. The T_8 compounds are produced in higher yields than obtained from other base promoted syntheses.[10] T_{10} and T_{12} cages were also observed but no yields were reported.[37] However 'T' resin studies[39b] produced Cp_8T_8 and $Cp_{10}T_{10}$ in 50 and 12% yields, respectively.

The results obtained in these papers differ from those observed here where the T_{10} and T_{12} cages are the major products and the *t*BAF concentrations were typically 1–3 mol% or 1 : 100 to 1 : 33 F$^-$: reactant ratios. This contrasts with the 1 : 1 to 0.5 : 1 F$^-$: reactant ratios used in the earlier studies. One explanation is that, although the two papers discuss the use of *t*BAF as a base in catalytic amounts, in reality these two papers[38] actually use 1 : 1 or 1 : 0.5 compound : *t*BAF mol ratios where the fluoride may act simply as a base.

Clearly more work needs to be done on this system, especially on the use of ^{29}Si and ^{19}F NMR to aid in identifying the active intermediates. However, there is sufficient information available from the above studies to make several general observations.

Observations

Given that the Si–O bond is 110–120 kcal mol^{-1} and the Si–F bond is even stronger at between 120 and 140 kcal/mol for tetravalent silicon compounds,[42] the rapid exchange seen here catalyzed by F$^-$ at solution concentrations of as little as 1 mol% of the silsesquioxane points to very unusual processes. First it is well recognized that F$^-$ will act as a nucleophile reacting with Si complexes to form highly fluxional pentacoordinate compounds where rapid exchange of the F$^-$ ligand at silicon has been postulated even at subzero temperatures.[43,44] We assume that

Figure 6. TBAF catalysis of OVS/OPS exchange in toluene at reflux, products are T_8, T_{10} and T_{12} PMS/PVS mixtures at a mole ratio of 5 : 1.

such a mechanism is occurring here; however, there are some differences, as the attack of F$^-$ must lead to rapid fragmentation of polymeric and/or cage silsesquioxanes, leading to species that can recombine to form primarily the T$_{10}$ and T$_{12}$ cages.

As noted above, the formation of F$^-$@cages requires some electron withdrawing groups on the cage. It can be assumed that electron-withdrawing groups promote fragmentation as a first step in F$^-$ encapsulation. The inability to form F$^-$@R$_8$T$_8$ where R = simple akyl would suggest therefore that F$^-$ cannot cause fragmentation of the Si−O bonds in these types of cages or in PMS. However F$^-$ can promote fragmentation when R = vinyl, which in turn apparently can react with PMS to form mixed Me : vinyl cages. This implies that the species generated, probably some type of (vinylSi)$_x$O$_y$F$^-$, is able to break Si−O bonds in PMS, leading to at least partial fragmentation of PMS Si−O bonds. It may even be that double fluorides are actually the responsible species, e.g. (vinylSi)$_x$O$_y$F$_2^-$.[45]

In future papers, we will demonstrate methods of making multiple different types of mixed-functional group cages, beads-on-a-chain oligomers and methods of recycling T-resins[46].

Acknowldgements

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