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14. ABSTRACT POSS compounds with non-reactive, aryl functionality are difficult to disperse in host materials. Recently, several new POSS compounds featuring this type of periphery demonstrated enhanced solubility in solvents and polymers. The effect of peripheral architecture on macroscale properties of aryl POSS compounds is not well understood. POSS properties should be dependent on peripheral architecture, symmetry, and packing efficiency. The aim of this work is to correlate peripheral architecture to POSS assembly and measurable thermal properties.					
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Influence of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes

28 Mar 2012

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Background



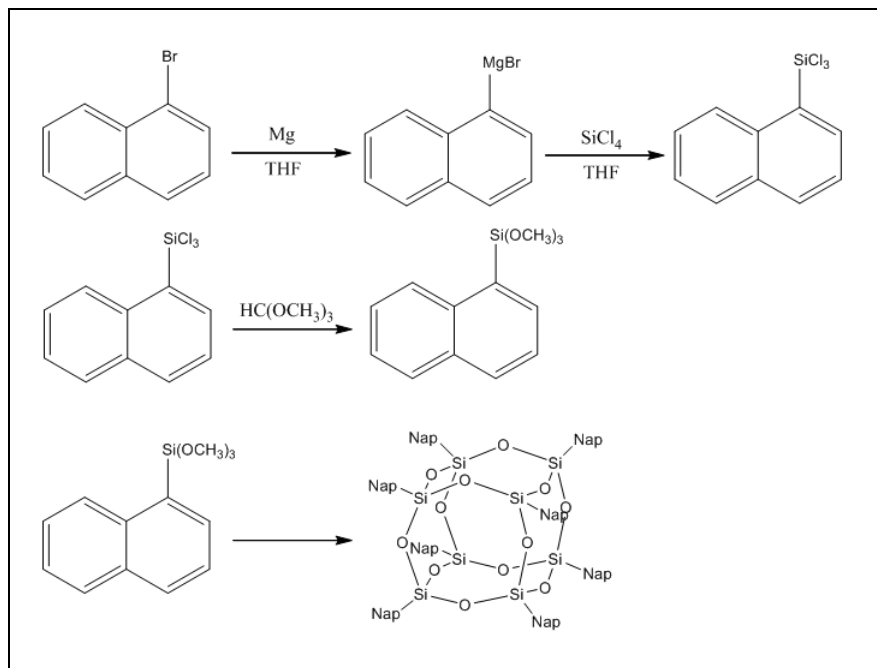
- Phenyl₈T₈ POSS and 1-Naphthyl-Phenyl₇ POSS were solubilized with Ultem 1000 in chloroform at 5 weight % POSS and 5 weight % solute
- Films subsequently cast and annealed
- The solution containing 1-Naphthyl-Phenyl₇ POSS is clear and the film exhibits reduced phase separation

Journal of Organometallic Chemistry 696 (2011), pp. 2676-2680
DOI information: 10.1016/j.jorganchem.2011.03.035

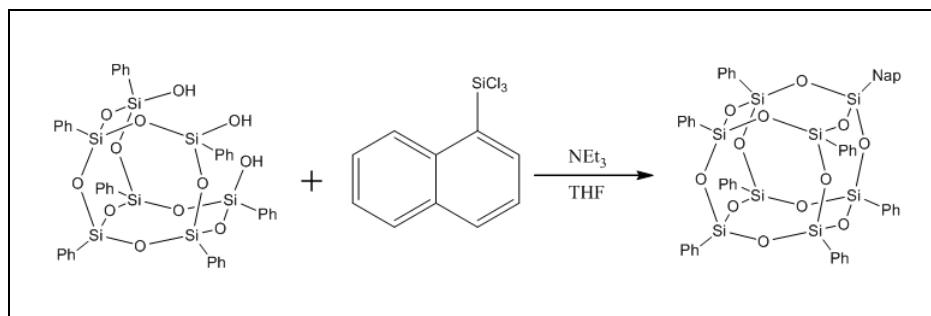
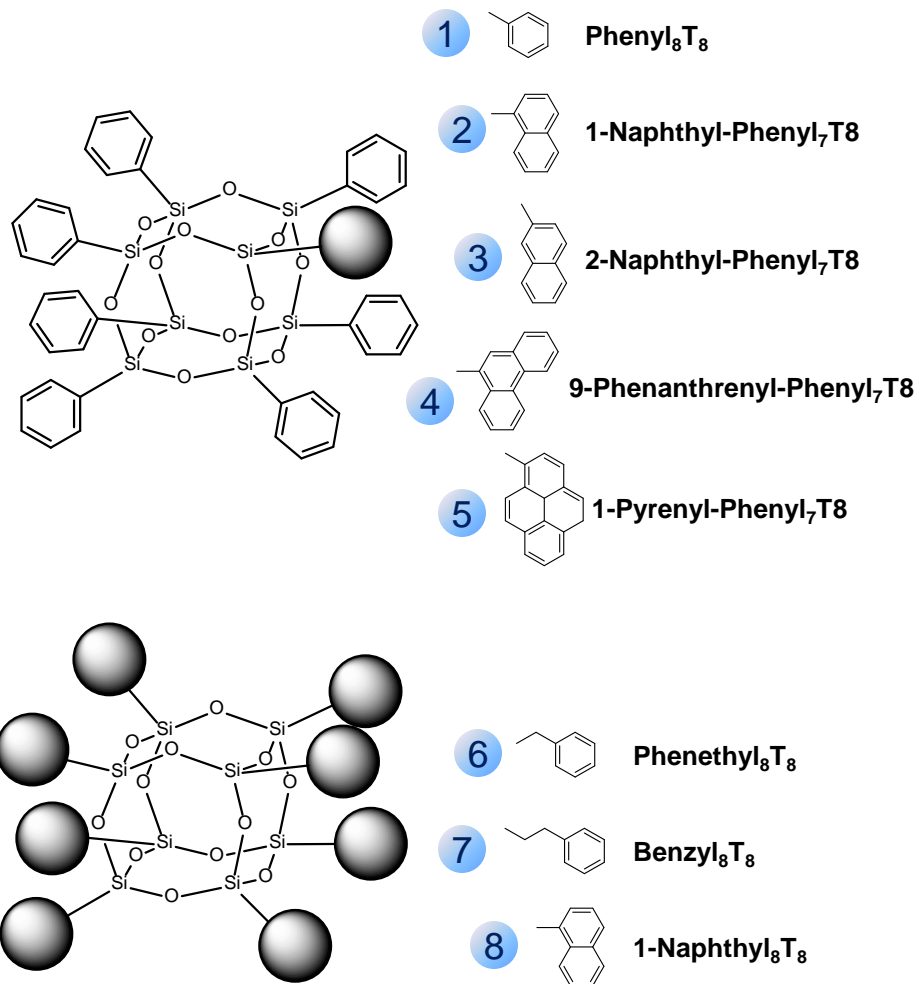
- POSS compounds with non-reactive, aryl functionality are difficult to disperse in host materials
- Recently, several new POSS compounds featuring this type of periphery demonstrated enhanced solubility in solvents and polymers
- The effects of peripheral architecture on macroscale properties of aryl POSS compounds are not well understood
- POSS properties should be dependent on peripheral architecture, symmetry, and packing efficiency
- The aim of this work is to correlate peripheral architecture to POSS assembly and measurable thermal properties



Synthesis of Ar-Functionalized POSS Compounds

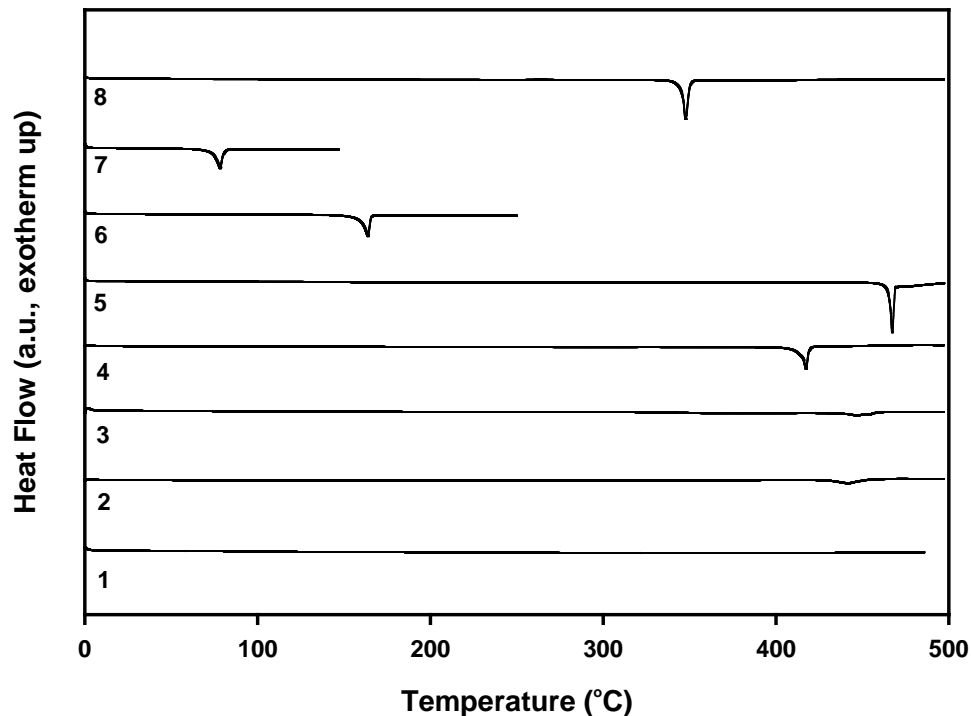


- Four symmetric T_8 compounds synthesized
- Four corner-capped T_8 compounds synthesized





Standard DSC

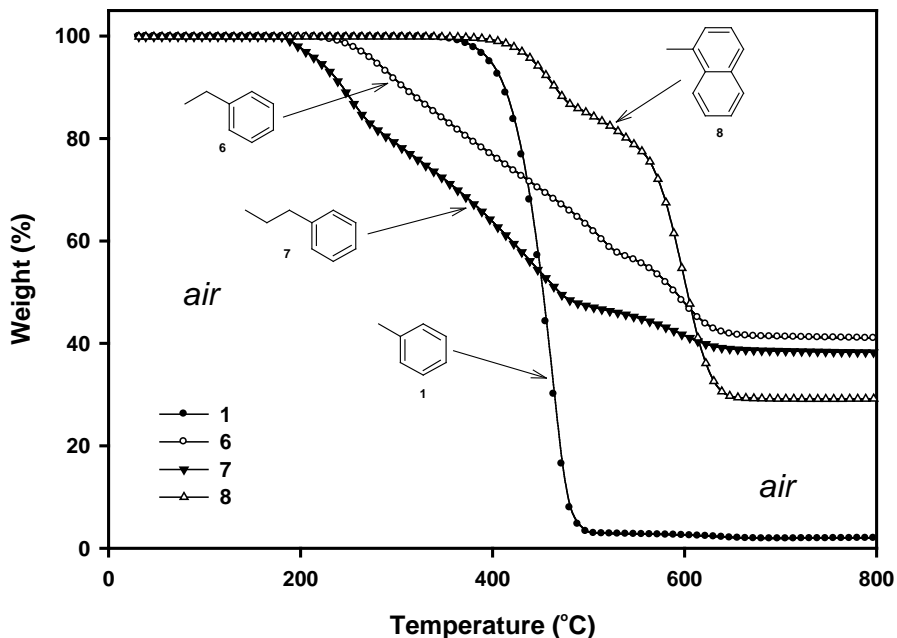
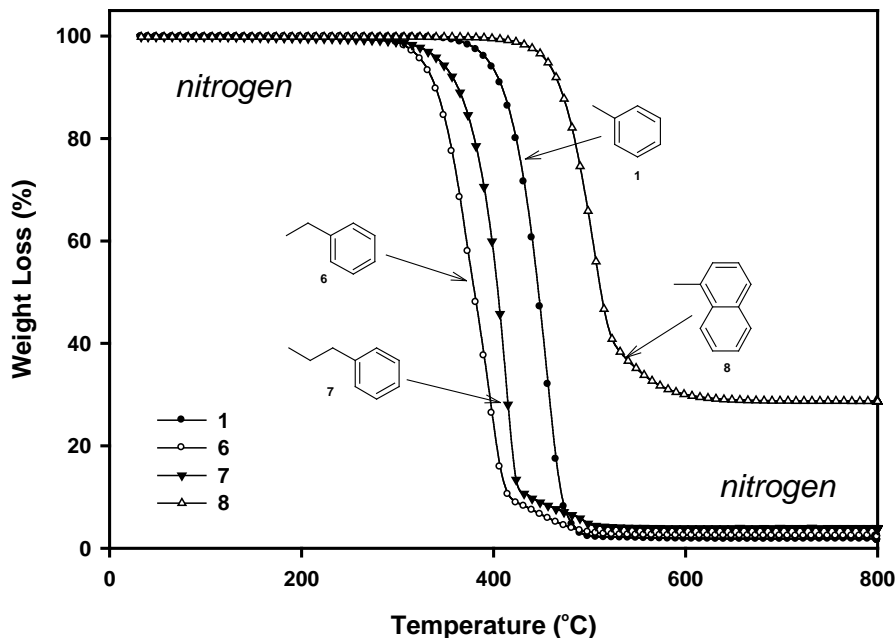


POSS	mp (°C)	ΔH (J/g)
1	n/a	n/a
2	442	26
3	447	20
4	416	47
5	467	59
6	164	52
7	78	44
8	348	69

- All compounds with the exception of 1 exhibit an endothermic peak
- 6 and 7 demonstrate relatively low melting points due to alkyl spacers in their organic peripheries



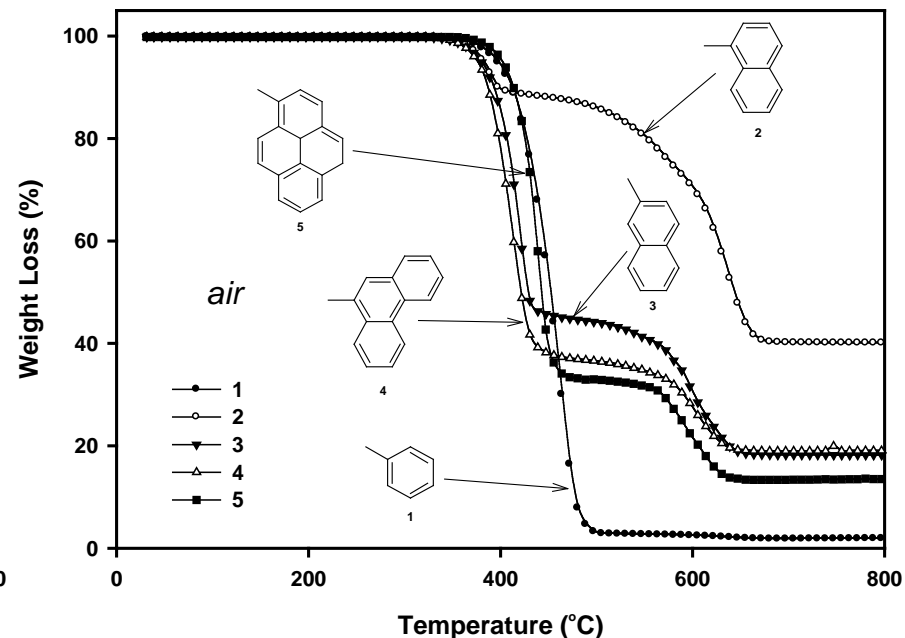
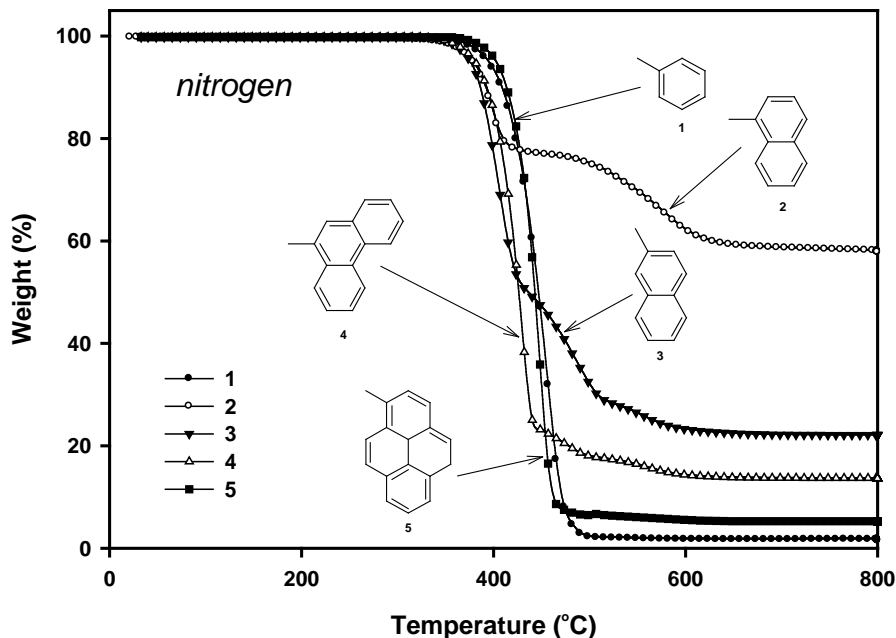
TGA of Symmetric Aryl POSS



- Anaerobically, 1 & 6-8 demonstrate single-step weight loss in most cases leaving virtually no residue
- In an oxidizing atmosphere, 6-7 begin to lose mass at ~200°C due to peroxidation of alkyl spacers and a significant residual white residue remains for all of the compounds with the exception of 1
- Mass loss of 1 during TGA is insensitive to purge atmosphere



TGA of Asymmetric POSS



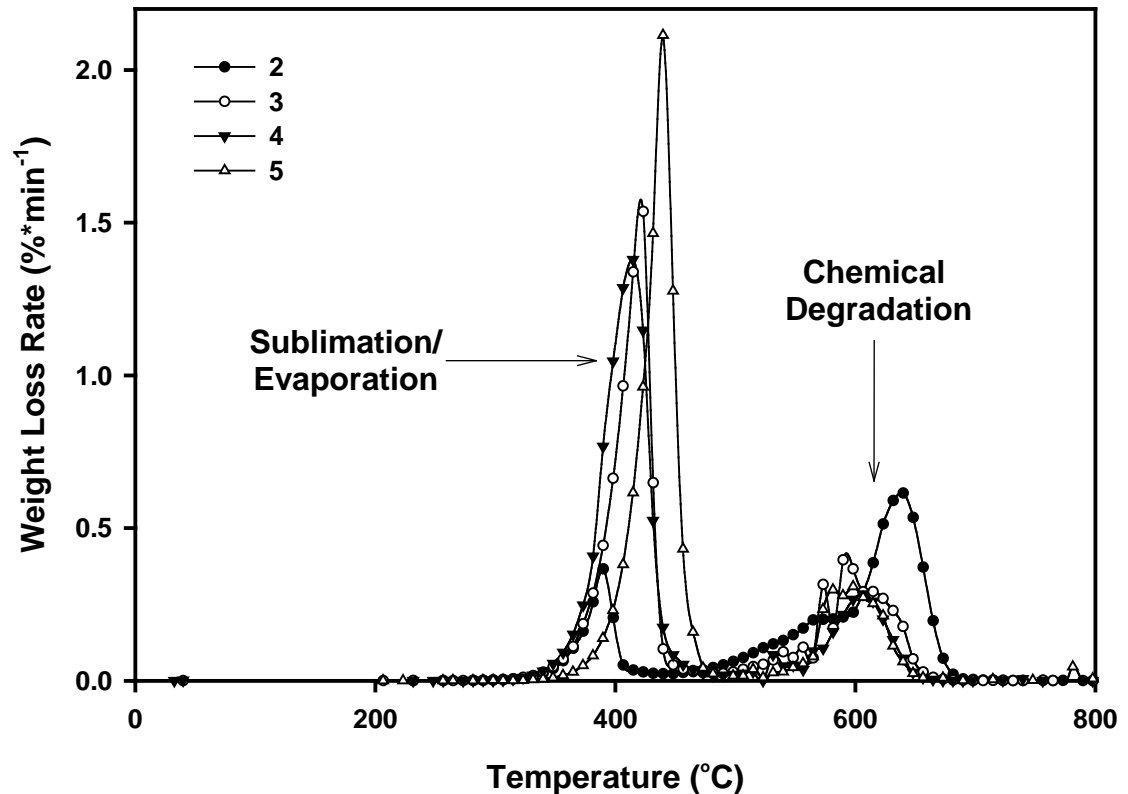
- Compounds 2-5 lose mass during two distinct events
- The magnitude of the first event appears to correlate with the geometric size of the corner cap species
- The first mass loss event for 4 and 5 is suppressed during decomposition in air likely due to activity of hydrogens on phenanthrene and pyrene groups



TGA of Asymmetric Aryl POSS



- Plot of mass loss rate vs. T for 2-5 during aerobic decomposition highlights distinction between two events
- First event is postulated to be due to sublimation / evaporation, while the second may be attributed to physical degradation at high temperature





TGA Mass Loss Statistics



POSS	ANAEROBIC DECOMPOSITION				AEROBIC DECOMPOSITION		
	Residue (%)	Approx. Sub/Evap Loss (%)	SiO ₂ Yield Theoretical† (%)	SiO ₂ Yield Experimental (%)	Approx. Sub/Evap Loss (%)	SiO ₂ Yield Theoretical (%)	SiO ₂ Yield Experimental (%)
1	1.2	98.8	0.6	0.6	95.2	2.2	1.8
2	58.7	21.7	34.8	34.8	9.8	40.1	40.2
3	14.0	82.0	8.0	7.5	58.5	18.4	18.4
4	21.7	69.0	13.2	14.0	58.0	17.8	19.2
5	8.7	91.1	3.7	6.3	67.0	13.7	13.7
6	2.4	89.9	4.2	2.1	0.0	42.0	41.1
7	4.5	88.7	4.3	4.1	0.0	38.3	38.7
8	28.6	58.9	13.8	16.8	11.6	29.7	29.2

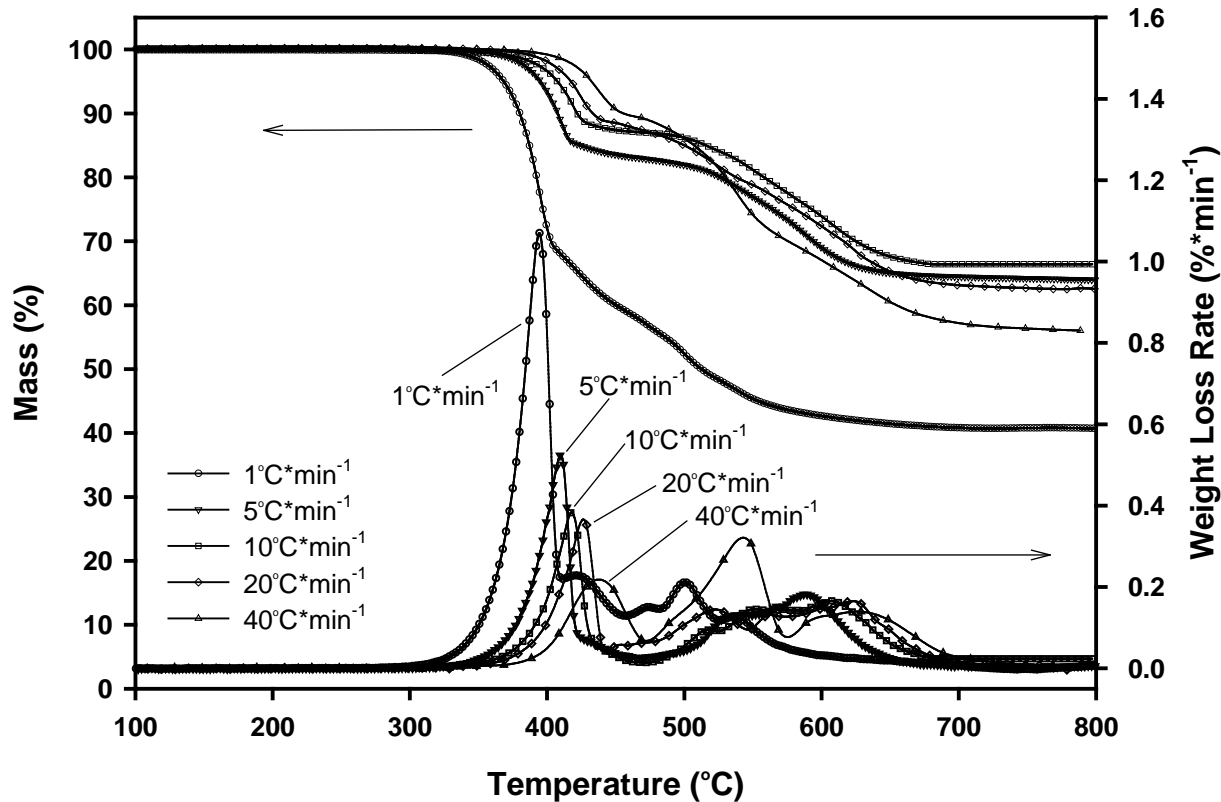
† Theoretical yield based on oxidation of residual POSS cage content after sublimation/evaporation

$$SiO_{2,theor.} = (M_i - M_s) \cdot \frac{416.8 \text{ g/mol}}{MW} \cdot 1.15355$$

- Assumption: cage loss occurs only during sublimation/evaporation events
- Statistics pertaining to SiO₂ formation support hypothesis that initial rapid mass loss events are largely attributed to sublimation/evaporation losses



Effect of Heating Rate on Mass Loss

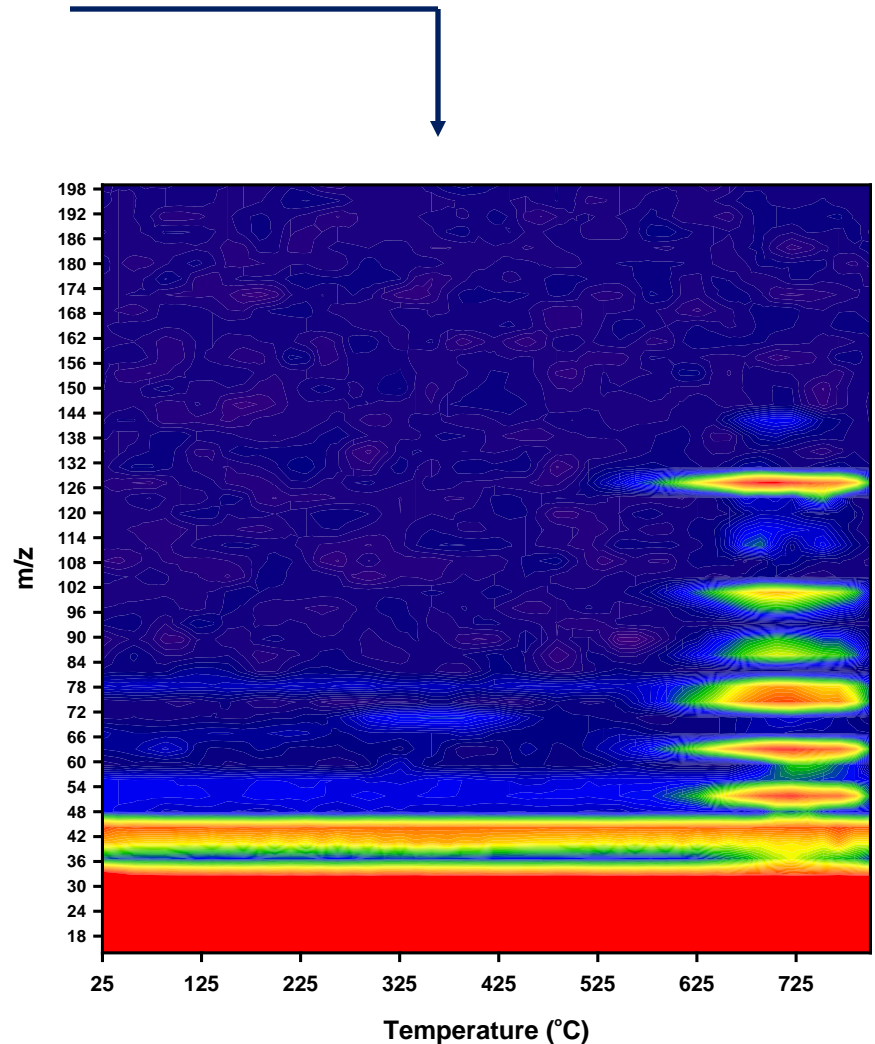
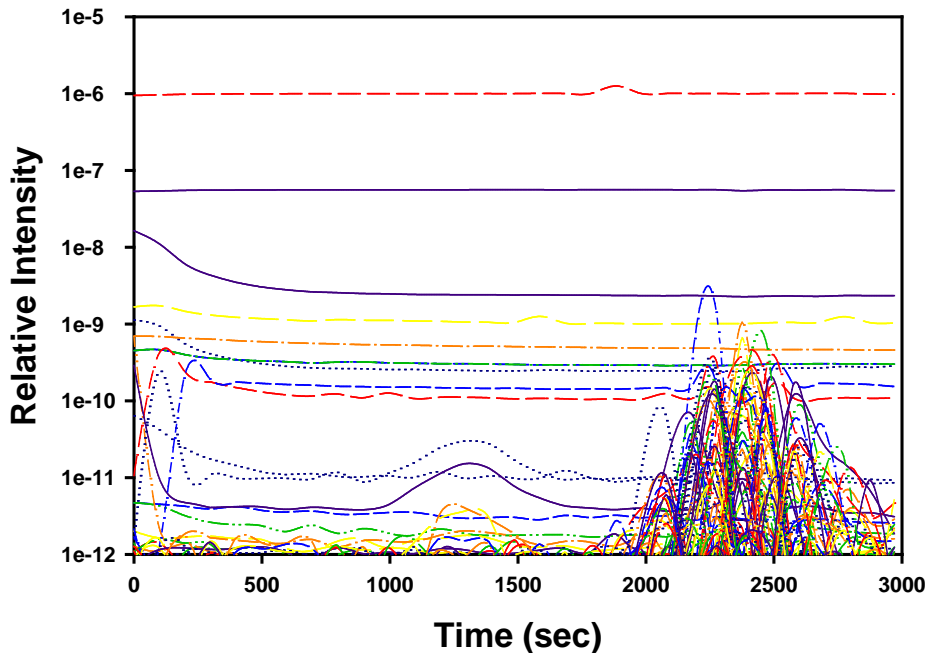


TGA analysis of 2 in nitrogen at different heating rates

- TGA heating rate affects kinetics of mass loss
- Increasing the heating rate diminishes the intensity of the first mass loss event
- 10°C·min⁻¹ leaves highest residue
- Mass loss due to second event increases with heating rate above 10°C·min⁻¹



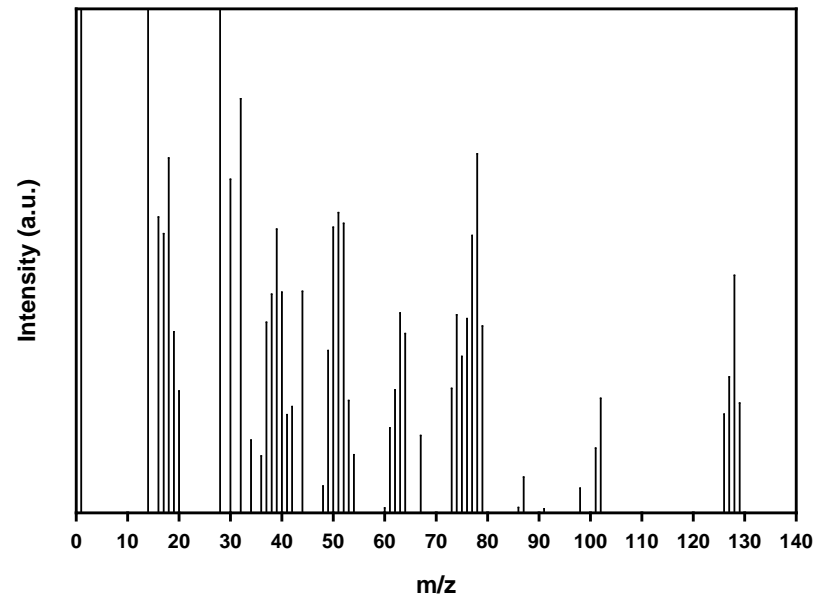
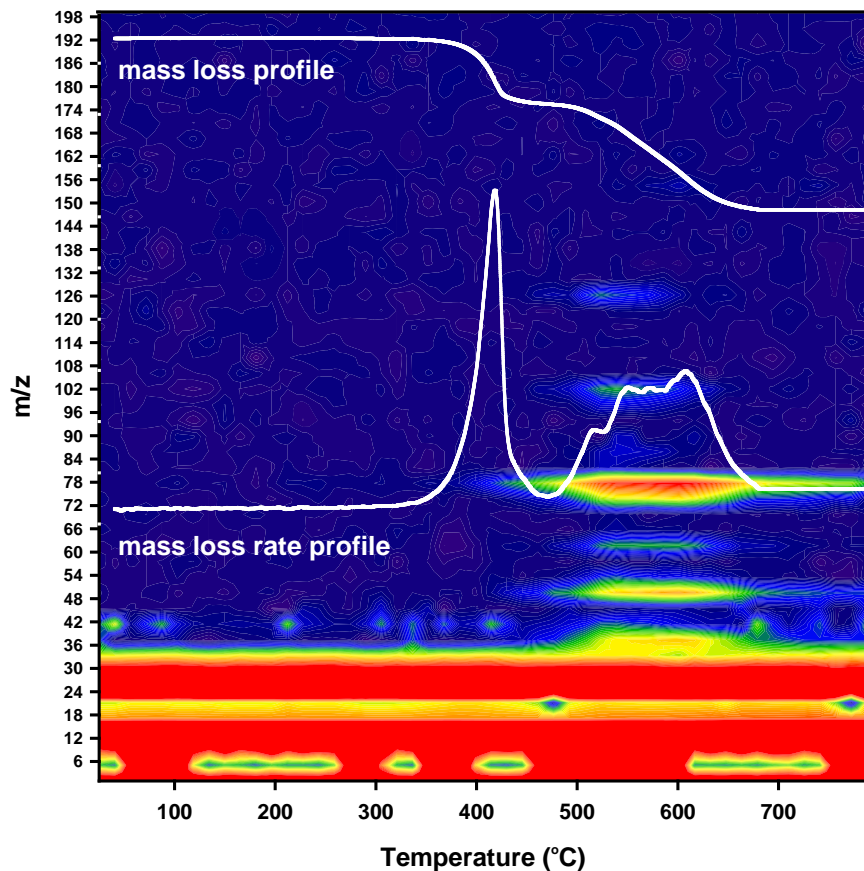
TGA-Mass Spectrometry



- Code developed to manipulate mass spectrometry data output into a 2D form of m/z vs. temperature during the TGA scan
- Use of helium or argon as the purge gas is preferable



TGA-Mass Spectrometry

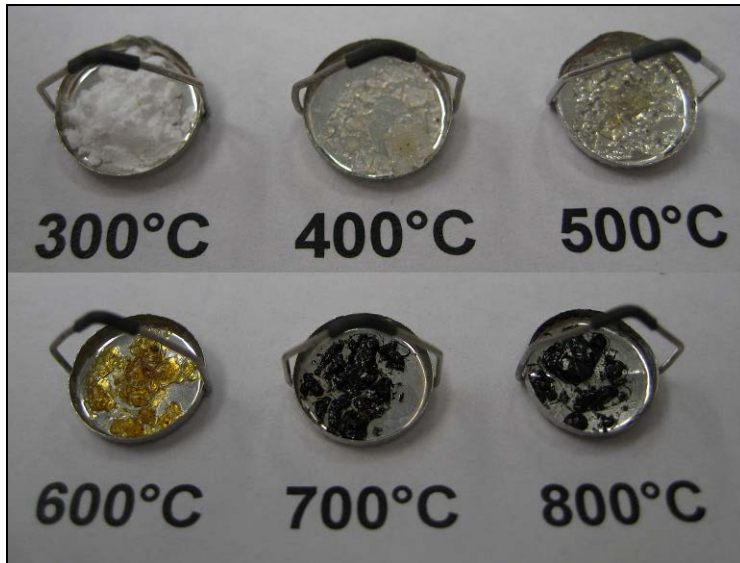


Snapshot of mass spectrum of **2** at 528 $^{\circ}\text{C}$

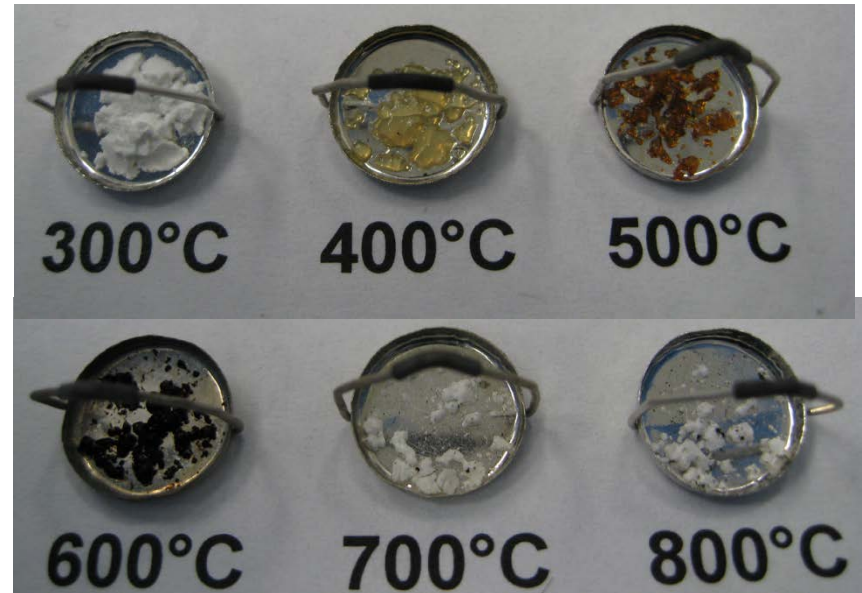
- **Data suggests chemical degradation occurs primarily through peripheral scission**
- **First mass loss event not detected, likely due to condensation of evaporated/sublimated POSS in capillary**



Residue Analysis



Inert Atmosphere

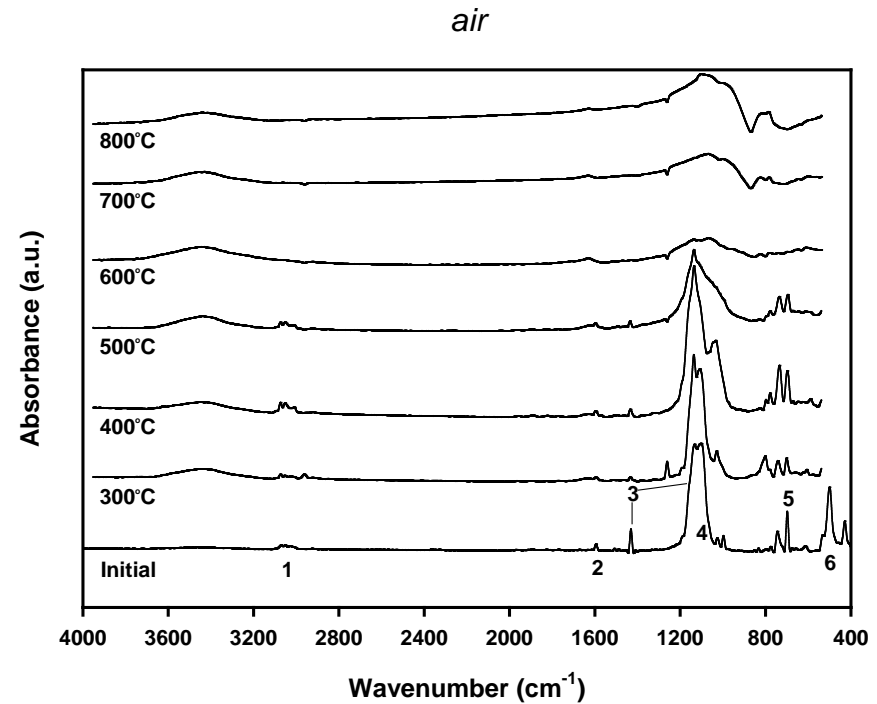
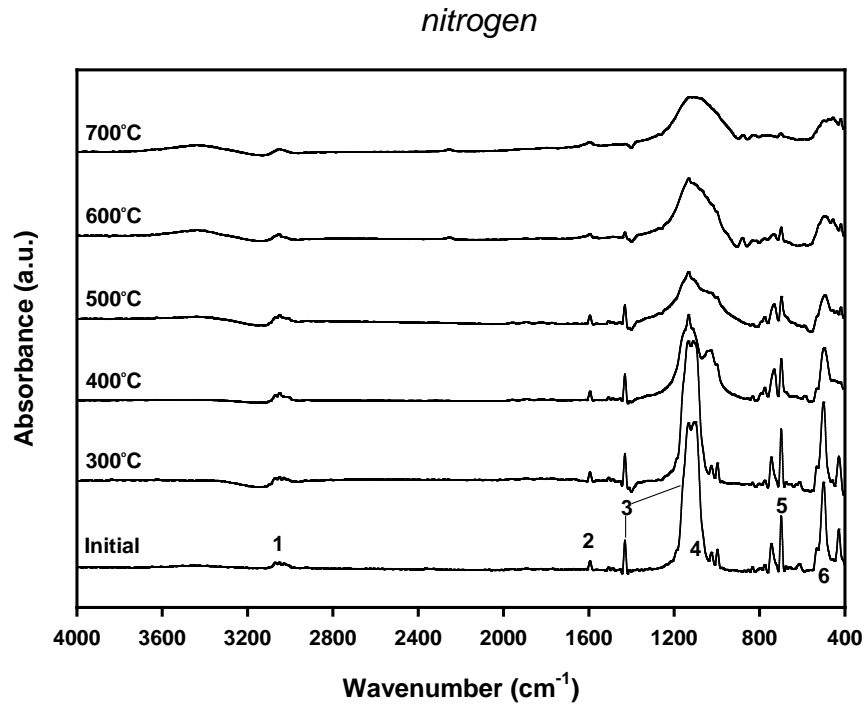


Oxidizing Atmosphere

- 10 mg samples of 2 heat treated at prescribed temperatures until equilibrium achieved
- Residues ground with KBr and analyzed in transmission by FTIR



FTIR of 2 after Heat Treatment in Nitrogen and Air

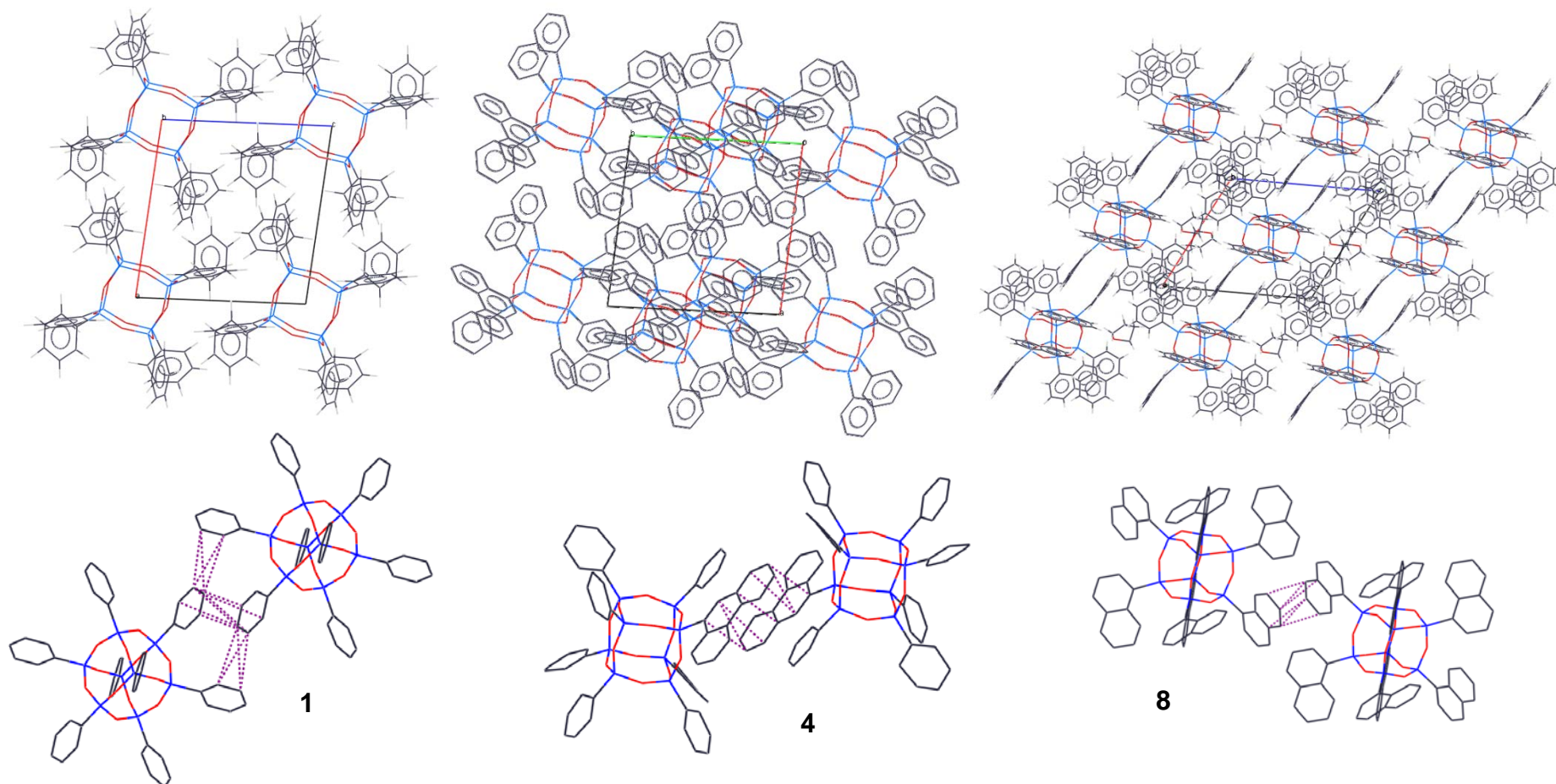


- Spectra reveal that residue is partially organic after treatment at 700°C in nitrogen
- Residue appears to be completely SiO and SiO₂ after treatment at 600°C in air

- 1 C-H Phenyl Asymmetric Stretching (3050 cm⁻¹)
- 2 Aromatic C=C Asymmetric Stretching (1600 cm⁻¹)
- 3 Si-Phenyl Deformation (1137 cm⁻¹, 1432 cm⁻¹)
- 4 Si-O deformation (1100 cm⁻¹)
- 5 Aromatic C-H Bending (700 cm⁻¹)
- 6 Si-O-Si Out-of-Plane Bending (505 cm⁻¹)



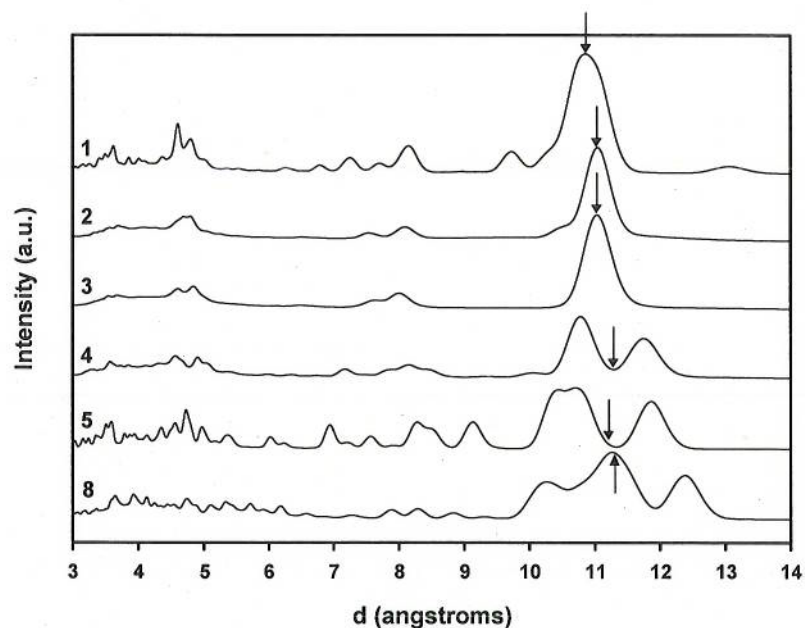
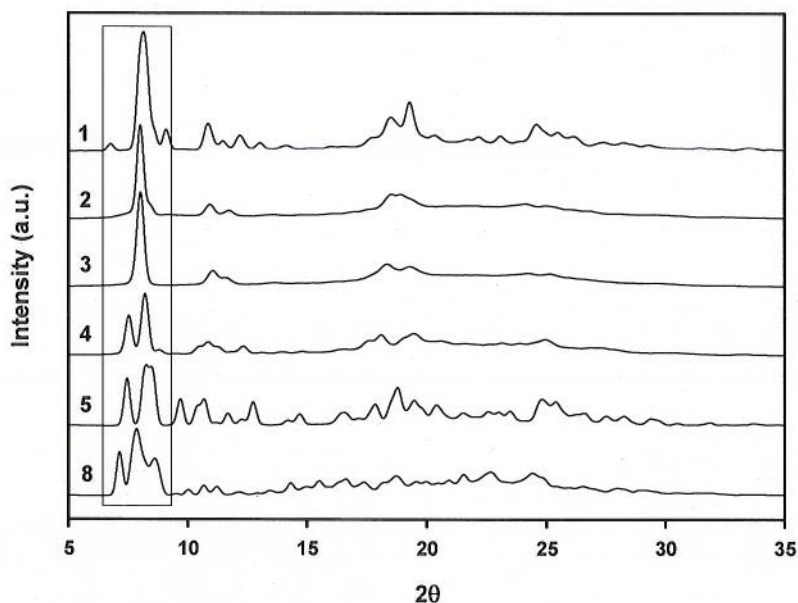
Single Crystal XRD



- **Single crystals solution grown of 1, 4, 5 and 8**
- **The unit cells of all of the compounds are monoclinic**
- **Aromatic interactions are prevalent for all of the resolved structures**



Powder XRD



- Peaks of strongest intensity occur between 5 and 10° 2θ - likely correspond to periodicity in POSS cages
- Average distance between POSS cages appears to increase with size of peripheral species



Modulated DSC

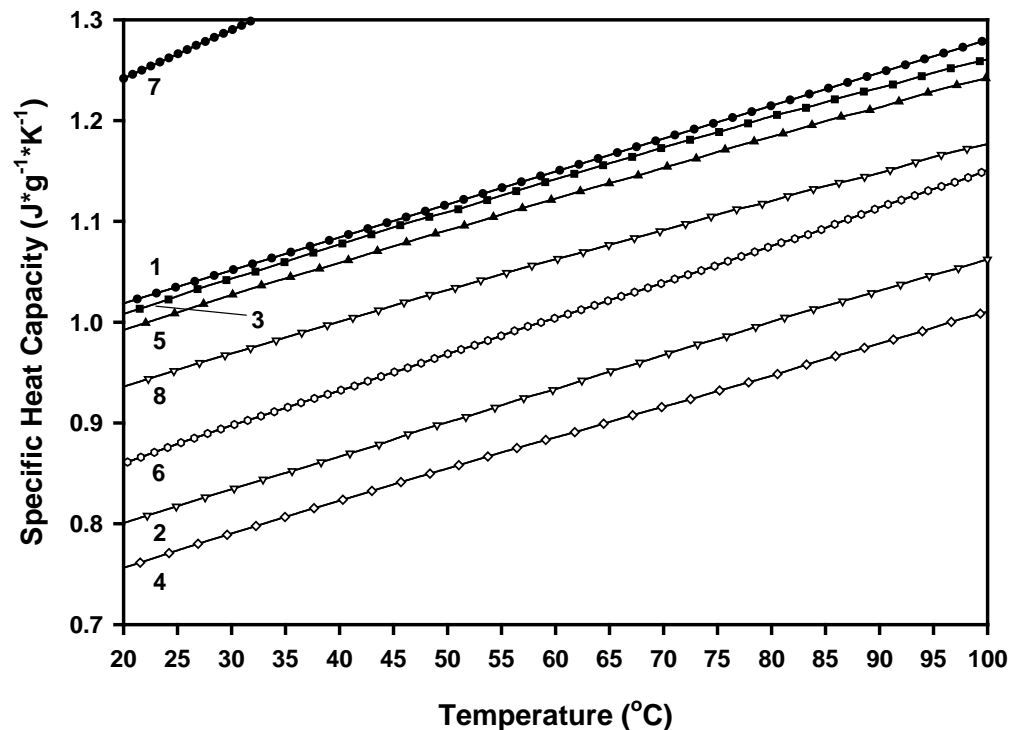
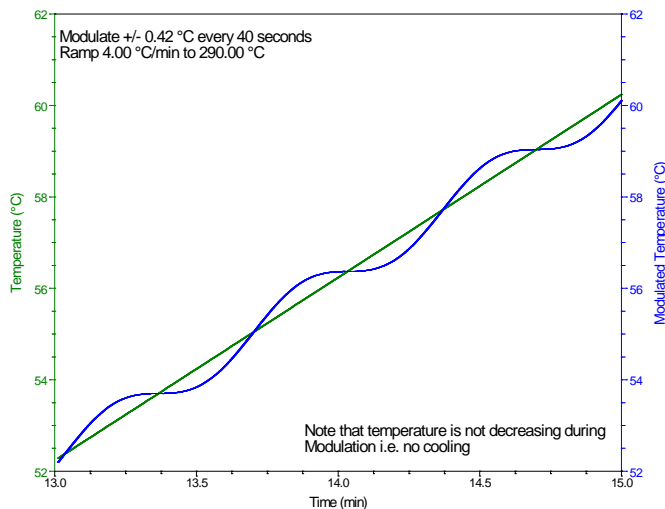
$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$

Reversing

Heat Capacity
Glass Transition
Most Melting
Transitions

Nonreversing

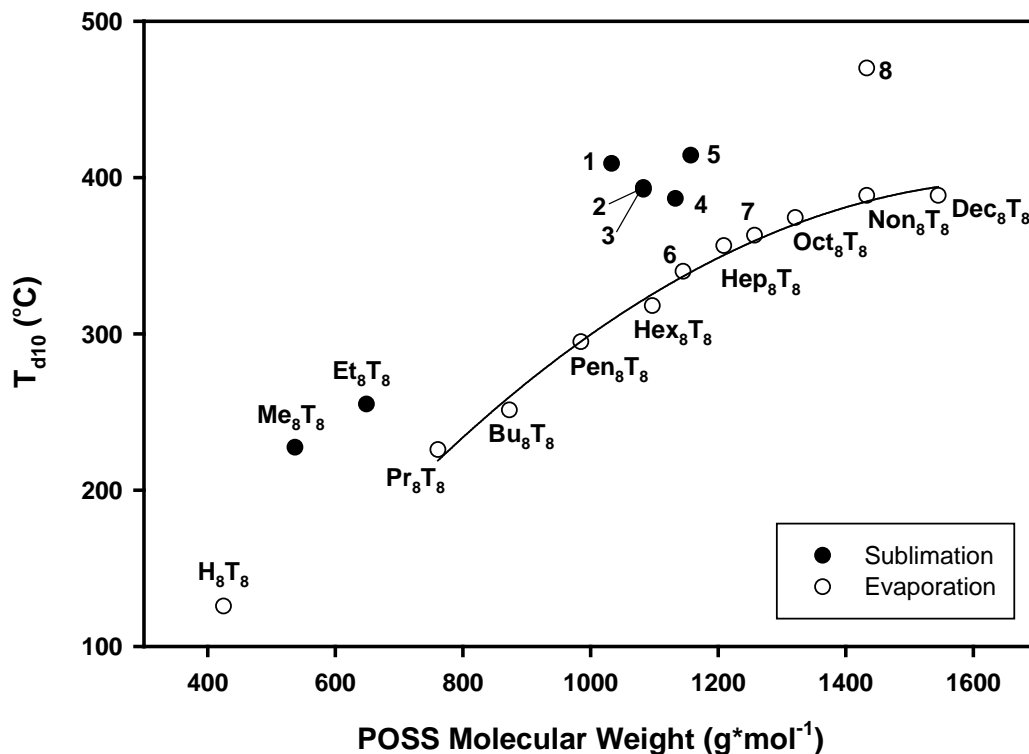
Crystallization
Thermoset Cure
Decomposition



- Slopes of 6 and 7 greater than those of purely aryl compounds
- C_ps of 2-5 seem to correlate with capable motion of peripheral groups (helicopter effect)



Influence of POSS Periphery on TGA Mass Loss



Data for alkyl POSS taken from:

- Fina, A. T., D.; Carniato, F.; Frache, A.; Boccaleri, E.; Caminoa, G., Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation. *Thermochimica Acta* **2006**, *440*, 36-42
- Bolln, C. T., A.; Frey, H.; Ihaupt, R.M., Thermal Properties of the Homologous Series of 8-fold Alkyl-Substituted Octasilsesquioxanes. *Chem. Mater.* **1997**, *9*, 1475-1479.

- Alkyl POSS compounds that evaporate due so according to their molecular weight ($R^2=0.99$)
- Weight loss of aryl POSS compounds investigated in this study is more complex due to peripheral interactions



Summary



- **Aryl POSS periphery affects molecular packing efficiency which influences thermal properties such as mass loss and heat capacity**
- **Thermal decomposition of aryl POSS is dependent on packing efficiency, temperature, and heating rate**
- **These findings can be used in the future to tailor thermally stable POSS compounds for specific properties**