**Influence of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes**

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**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.
Influence of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes

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Background

- Phenyl$_8$T$_8$ POSS and 1-Naphthyl-Phenyl$_7$ 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-Phenyl$_7$ POSS is clear and the film exhibits reduced phase separation.

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.

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Synthesis of Ar-Functionalized POSS Compounds

- Four symmetric T₈ compounds synthesized
- Four corner-capped T₈ compounds synthesized

1. Phenyl₈T₈
2. 1-Naphthyl-Phenyl₇T₈
3. 2-Naphthyl-Phenyl₇T₈
4. 9-Phenanthrenyl-Phenyl₇T₈
5. 1-Pyrenyl-Phenyl₇T₈
6. Phenethyl₈T₈
7. Benzyl₈T₈
8. 1-Naphthyl₈T₈
- 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.
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

<table>
<thead>
<tr>
<th>POSS</th>
<th>Residue (%)</th>
<th>Sub/Evap Loss (%)</th>
<th>SiO₂ Yield Experimental (%)</th>
<th>SiO₂ Yield Theoretical† (%)</th>
<th>Residue (%)</th>
<th>Sub/Evap Loss (%)</th>
<th>SiO₂ Yield Experimental (%)</th>
<th>SiO₂ Yield Theoretical (%)</th>
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<td>13.8</td>
<td>16.8</td>
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</tr>
</tbody>
</table>

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

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

- 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 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 analysis of 2 in nitrogen at different heating rates
- 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

- 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

Snapshot of mass spectrum of 2 at 528°C
Residue Analysis

- 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.
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\(_p\)s of 2-5 seem to correlate with capable motion of peripheral groups (helicopter effect)**

Note that temperature is not decreasing during modulation i.e. no cooling.
Influence of POSS Periphery on TGA Mass Loss

Data for alkyl POSS taken from:

- 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.