Structure and Modeling of Polyhedral Oligomeric Silsesquioxane (POSS) Monomers

by

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Why Study POSS Systems?

• A wide range of application from polymer modifiers to lubricants

• Improved physical and thermal properties of polymer systems

• Addition POSS compounds gives polymers with
  – extended temperature ranges
  – reduced flammability
  – lower thermal conductivity
  – reduced viscosity
  – resistance to atomic oxygen

• Major interest and funding by AFOSR!
Application Of Ion Mobility to POSS Characterization

- Ion Mobility
- Molecular Modeling

Collision Cross-Sections

3-D Structural Information

- Identify Mixture Distributions
- Structures of Intermediates
- How POSS attaches to polymers
- Structural differences with different “R” groups
- “impurities” in synthesis
- How structure changes with size (POSS oligomers)
Goals of POSS Work

• Create Si-O cages with various organic substituents attached to Si atoms

• Understand how structure and functionality of POSS affects polymer structure and properties

• Interact with synthetic chemists to characterize products and reaction intermediates
POSS – closed cages

\[ R_6T_6 \]

\[ R_8T_8 \]

\[ R_{10}T_{10} \]

\[ R_{12}T_{12} \]

- Si
- O

\[ R = C_6H_{11} \] (Cy)
\[ CH=CH_2 \] (Vi)
\[ CH=CH-C_6H_5 \] (Sty)
\[ CH_2-CH_2-C_6H_5 \] (PhenEt)
POSS - partially condensed

$\text{R}_4\text{D}_4(\text{OH})_4$

$\text{R} = \text{C}_6\text{H}_{11}$ (Cy)

$\text{C}_5\text{H}_9$ (Cp)

$\text{R}_6\text{D}_6(\text{OH})_2$

$\text{R}_7\text{D}_7(\text{OH})_3$
Modifications needed for POSS Modeling

- New parameters for all Si bonds, angles, dihedrals, and torsions (adapted from Si and Si-X parameters obtained from polysiloxane work).
  

- Atom charges obtained from Gaussian calculations on model systems and x-ray structures; adjusted using AMBER RESP protocol.

- Starting structures built in Hyperchem and imported into AMBER.
# POSS Cross-Sections (Å²)

<table>
<thead>
<tr>
<th>POSS System</th>
<th>x-ray$^\Delta$</th>
<th>MALDI -TOF (Na⁺) *</th>
<th>Theory (Na⁺) ♦</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cy₆T₆</td>
<td>224</td>
<td>225</td>
<td>222</td>
</tr>
<tr>
<td>Cy₆T₆(OH)₂</td>
<td>222</td>
<td></td>
<td>215</td>
</tr>
<tr>
<td>Cy₇T₇(OH)₃</td>
<td>248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cy₈T₈(OH)₂</td>
<td>252</td>
<td></td>
<td>258</td>
</tr>
<tr>
<td>Vi₁₀T₁₀</td>
<td></td>
<td>193</td>
<td>192</td>
</tr>
<tr>
<td>Vi₁₂T₁₂</td>
<td>212</td>
<td>216</td>
<td>216</td>
</tr>
<tr>
<td>Cp₄D₄(OH)₄</td>
<td>154</td>
<td>157</td>
<td>153</td>
</tr>
<tr>
<td>Ph₄D₄(OH)₄</td>
<td>167</td>
<td>162</td>
<td>168</td>
</tr>
</tbody>
</table>

$^\Delta$ from Tim Haddad at ERC Inc., Air Force Research Laboratory
* similar values for H⁺
♦♦♦♦ similar values for neutral
X-ray Structure of $\text{Sty}_8\text{T}_8$
Na⁺Sty₈T₈ ATD  (MALDI-TOF)
Na$^+$Sty$_8$T$_8$

Trans Structures

(3 pairs)

(4 pairs)

(2 pairs)
relative intensities of peaks follow statistical pairing of styrenes (nearest neighbors only)
Sty₈T₈ Cis Defect Structures
Na$^+$Sty$_8$T$_8$ ATD

Theory
3 pairs
$\Omega = 328 \text{ Å}^2$
$\Omega_{\text{EXPT}} = 330 \text{ Å}^2$

2 pairs
$\Omega = 338 \text{ Å}^2$
$\Omega_{\text{EXPT}} = 340 \text{ Å}^2$

Theory
4 pairs
$\Omega = 320 \text{ Å}^2$
$\Omega_{\text{EXPT}} = 324 \text{ Å}^2$

Theory
cis defects
$\Omega = 295, 307 \text{ Å}^2$
$\Omega_{\text{EXPT}} = 293, 310 \text{ Å}^2$

Arrival Time (µs)
Summary for Sty$_8$T$_8$

- **Most compact** structure (lowest $\sigma$) is the most stable

- **Least compact** structures are most abundant

- Quantitative agreement of experimental and theoretical $\sigma$’s

- MALDI intensities in semi-quantitative agreement with *statistical pairing* of phenyl groups

- X-ray structure quantitatively agrees with **least compact** structure
Sty₇EpT₈
Styrene Epoxy T₈ POSS System Mass Spectrum

Sty₈T₈

Sty₇EpT₈

Sty₆Ep₂T₈

Sty₅Ep₃T₈

Sty₄Ep₄T₈

Sty = \begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}

\text{Ep} = \begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
Na$^+$Sty$_7$EpT$_8$ ATDs

Arrival Time ($\mu$s)

$\sigma = 319$ Å$^2$

$\sigma = 323$ Å$^2$

$\sigma = 326$ Å$^2$
Na$^+$Sty$_7$EpT$_8$ Theoretical Structures

2 Pairs
$\sigma_{\text{Theory}} = 320 \text{ Å}^2$
$\sigma_{\text{EXPT}} = 319 \text{ Å}^2$
$\sim 13\%$

No Pairs
$\sigma_{\text{Theory}} = 328 \text{ Å}^2$
$\sigma_{\text{EXPT}} = 326 \text{ Å}^2$
$\sim 13\%$

1 Pair
$\sigma_{\text{Theory}} = 324 \text{ Å}^2$
$\sigma_{\text{EXPT}} = 323 \text{ Å}^2$
$\sim 74\%$
Na\textsuperscript{+}Sty\textsubscript{6}Ep\textsubscript{2}T\textsubscript{8} ATDs

\begin{align*}
\sigma &= 319 \text{ Å}^2 \\
\sigma &= 315 \text{ Å}^2 \\
\sigma &= 324 \text{ Å}^2
\end{align*}
Na\textsuperscript{+}Sty\textsubscript{6}Ep\textsubscript{2}T\textsubscript{8} Theoretical Structures

edge

\[ \sigma_{\text{Theory}} = 314 \text{ Å}^2 \]
\[ \sigma_{\text{EXPT}} = 315 \text{ Å}^2 \]
\[ \sim 22\% \]

face diagonal

\[ \sigma_{\text{Theory}} = 319 \text{ Å}^2 \]
\[ \sigma_{\text{EXPT}} = 319 \text{ Å}^2 \]
\[ \sim 66\% \]

cube diagonal

\[ \sigma_{\text{Theory}} = 322 \text{ Å}^2 \]
\[ \sigma_{\text{EXPT}} = 324 \text{ Å}^2 \]
\[ \sim 12\% \]
$Na^+Sty_5Ep_3T_8$ ATDs

Arrival Time ($\mu$s)

300K

$\sigma = 314 \text{ Å}^2$

$\sigma = 319 \text{ Å}^2$

$\sigma = 327 \text{ Å}^2$

110K
Na⁺Sty₅Ep₃T₈ Theoretical Structures

3 on face diagonals
σ_{Theory} = 326 Å²
σ_{EXPT} = 327 Å²
~17%

3 epoxides adjacent
on face
σ_{Theory} = 314 Å²
σ_{EXPT} = 314 Å²
~17%

2 adjacent and 1 on the opposite edge:
σ_{Theory} = 319 Å²
σ_{EXPT} = 319 Å²
~66%
Summary for Styrene Epoxy T₈ POSS System

• For a given x, y the distribution of the geometric isomers can be obtained from ion mobility studies
• Can determine x, y distributions of StyₓEpᵧT₈ from mass spectrum
In conclusion

Thanks for buying a ticket and coming....
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$\text{AFOSR}$