Structure of Polyhedral Oligomeric Silsesquioxanes (POSS) Oligomers Using Ion Mobility Mass Spectrometry and Molecular Mechanics

by

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Why Study Silicon-Based Nanomaterials??

• A wide range of application from polymer modifiers to lubricants

• Robust physical and thermal properties of polymer systems useful for space applications

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

• Major interest and funding by AFOSR!
Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS®) Molecule

Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

May possess one or more reactive groups suitable for polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.
Condensed POSS Cage Structures

- $R_6T_6$
- $R_{10}T_{10}$
- $R_8T_8$
- $R_{12}T_{12}$
Partially Condensed POSS Cage Structures Provide Synthetic Routes to Monomers

\[ \text{R}_4\text{D}_4(\text{OH})_4 \]
\[ \text{R}_6\text{D}_6(\text{OH})_2 \]
\[ \text{R}_7\text{D}_7(\text{OH})_3 \]

\[ \text{R} = \text{C}_6\text{H}_{11} \quad (\text{Cy}) \]
\[ \text{C}_5\text{H}_9 \quad (\text{Cp}) \]
Goals of POSS Work

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

• Interact with synthetic chemists to characterize reaction steps and products

• Study oligomer structures in detail

• Create polymers with tailored properties.
Concept of Ion Mobility

\[ \vec{v} = \text{const.} \]
\[ \vec{v} = K \vec{E} \]

\[ K = \text{ion mobility} \]
\[ K = f \left( T, \ p, \ q, \ \mu, \ \sigma \right) \]

\[ T = \text{temperature} \]
\[ p = \text{pressure} \]
\[ q = \text{ion charge} \]
\[ \mu = \text{reduced mass} \]
\[ K = \text{ion mobility} \]
\[ \sigma = \text{collision cross section} \]

\[ \sigma = f \left( \text{He–ion interaction}, \ \text{ion shape} \right) \]
Time-of-Flight (TOF) Mass Spectrometry

TOF Mass Spectrum

1500 1600 1700 1800

MASS

M + Li+

M + Na+

SOURCE

TOF DETECTOR

TOF REFLECTRON

DRIFT CELL

QUADRUPOLE

DETECTOR

hv

Trigger

M + Na+

Mass Spectrum
Time-of-Flight (TOF) Mass Spectrometry

Arrival Time Distribution

→ One structure

ATD

→ Multiple structures
Theoretical Method

Molecular Mechanics/Dynamics

(Annealing/Energy Minimization)

AMBER 7 parameterized for Si

• Heat guess structure for 30 ps at 600-1400K
• Cool structure exponentially to 50K for 10 ps
• Energy minimize the structure
• Use final structure as initial structure for next cycle
Theoretical Method

Structures

Collision Cross-Sections ($\sigma$)

Relative Energy (kcal/mol)

Cross-Section (Å$^2$)

-5 0 5 10 15 20 25

220 240 260 280
Putting It All Together....

Experimental Method

ARRIVAL TIME DISTRIBUTIONS (ATDs) \( \rightarrow \) MOBILITIES \( \rightarrow \) COLLISION CROSS-SECTIONS

Theoretical Method

MOLECULAR MECHANICS/DYNAMICS \( \rightarrow \) STRUCTURES \( \rightarrow \) COLLISION CROSS-SECTIONS

\( \sigma \)

\( K_0 \)

Compare

Putting It All Together....

Experimental Method

ARRIVAL TIME DISTRIBUTIONS (ATDs) \( \rightarrow \) MOBILITIES \( \rightarrow \) COLLISION CROSS-SECTIONS

Theoretical Method

MOLECULAR MECHANICS/DYNAMICS \( \rightarrow \) STRUCTURES \( \rightarrow \) COLLISION CROSS-SECTIONS

\( \sigma \)

\( K_0 \)

Compare
[MALDI-TOF Spectrum of (PMA)Cp₇T₈]ₓ·Na⁺

...adding ATDs and experimental cross-sections

\[ \sigma_{\text{expt}} = 248 \text{ Å}^2 \]

\[ \sigma_{\text{expt}} = 377, 402 \text{ Å}^2 \]

\[ \sigma_{\text{expt}} = 539 \text{ Å}^2 \]
(PMA)Cp₇T₈·Na⁺ Scatter Plot
(PMA)Cp$_7$T$_8$·Na$^+$ 1-mer Structure

$\sigma_{\text{expt}} = 248 \text{ Å}^2$

$\sigma_{\text{theory}} = 252 \text{ Å}^2$
[(PMA)Cp₇T₈]₂Na⁺ 2-mer Scatter Plot
\[(\text{PMA})\text{Cp}_7\text{T}_8\]_2\cdot\text{Na}^+ \text{ 2-mer Scatter Plot}

Cross Section (Å²)

Relative Energy (kcal/mol)
[((PMA)Cp_7T_8)_2\cdot Na^+ 2-mer Scatter Plot

Cross Section (Å²)

Relative Energy (kcal/mol)

trans
[(PMA)Cp_7T_8]_2 Na^+ 2-mer Scatter Plot

Cross Section (Å²) vs. Relative Energy (kcal/mol)

- cis
- extended trans
- trans
[(PMA)Cp₇T₈]₂Na⁺ (2-mer) Structures

trans
\[\sigma_{\text{expt}} = 378 \text{ Å}^2\]
\[\sigma_{\text{theory}} = 377 \text{ Å}^2\]

\(\sigma_{\text{expt}}\)
\(\sigma_{\text{theory}}\)

\(\sigma_{\text{expt}} = 402 \text{ Å}^2\)
\(\sigma_{\text{theory}} = 393 \text{ Å}^2\)

extended trans
\[\sigma_{\text{expt}} = 402 \text{ Å}^2\]
\[\sigma_{\text{theory}} = 393 \text{ Å}^2\]
[(PMA)Cp₇T₈]₂·Na⁺ Dynamics

Cross-sections (Å)

Time (ps)

300K

"cis"

"trans"

800K

"cis"

"trans“ + “ext. trans"
[(PMA)Cp₇T₈]₃·Na⁺ 3-mer Regioisomers

syndiotactic

\[ \begin{align*}
\text{R} &= \text{POSS(propylmethacryl)} \\
* &= \text{chiral center}
\end{align*} \]

isotactic
\((\text{PMA})\text{Cp}_7\text{T}_8\)\text{Na}^+ 3\text{-mer Scatter Plots}
\[(\text{PMA})\text{Cp}_7\text{T}_8\]_3\cdot\text{Na}^+ 3\text{-mer Scatter Plots}

Cross-section (Å²) vs. Relative Energy (kcal/mol)

- Isotactic isomer
- Syndiotactic isomer
[(PMA)Cp_7T_8]_3·Na^+ Syndiotactic Isomer

8.3 – 8.9 Å (cage centers)

\[\sigma_{\text{expt}} = 539 \text{ Å}^2\]
\[\sigma_{\text{syn}} = 540 \text{ Å}^2\]
\[\sigma_{\text{iso}} = 565 \text{ Å}^2\]
Non-POSS PMA 8-mer vs. [(PMA)Cp_7T_8^-]_8 8-mer
POSS-PMA Oligomer Summary

1. Low energy structures obtained by molecular modeling agree with experiment within ~2%.

2. Cis, trans, and extended trans structures of the 2-mer give rise to the two ATD features.

3. Structures seem to be determined primarily by non-bonded interactions of the cyclopentyl capping groups that cause the cages to pack in a variety of ways.

4. 3-mer structure is consistent with the syndiotactic regioisomer; it shows cage-cage non-bonded interactions similar to 2-mer.

5. Presence of the cation does not determine the oligomer backbone structure as in non-POSS oligomeric systems previously studied.
POSS Siloxanes

Cy = cyclohexyl

Cp = cyclopentyl
$[\text{Cp}_7 \text{T}_8]_2 \text{O} \cdot \text{Na}^+$ Siloxane 2-mer Mass Spectrum
$[\text{Cp}_7\text{T}_8]_2\text{O} \cdot \text{Na}^+$ Siloxane 2-mer Mass Spectrum

\[ \sigma_{\text{expt}} = 355 \text{ Å}^2 \]

ATD
[Cp₇T₈]₂O·Na⁺ Siloxane 2-mer Scatter Plot

σ_{calc} = 357 Å²

σ_{expt} = 355 Å²

σ_{calc} = 365 Å²
[\text{Cp}_7 \text{T}_8]^2 \text{O} \cdot \text{Na}^+ \text{ Siloxane 2-mer Comparison}

\text{Cp} = \text{cyclopentyl}

\text{Staggered:} \quad \sigma_{\text{calc}} = 357 \text{ Å}^2, \quad \sigma_{\text{expt}} = 355 \text{ Å}^2

\text{Eclipsed:} \quad \sigma_{\text{calc}} = 365 \text{ Å}^2, \quad \sigma_{\text{expt}} = 355 \text{ Å}^2
[Cy₇T₈]₂O·Na⁺ Siloxane 2-mer Structures

Cy = cyclohexyl

No folds

σ\text{calc} = 433 \text{ Å}^2
σ\text{expt} = 400 \text{ Å}^2
[Cy\textsubscript{7}T\textsubscript{8}]\textsubscript{2}O\cdotNa\textsuperscript{+} Siloxane 2-mer Structures

Cy = cyclohexyl

3 folds

σ\textsubscript{calc} = 395 Å\textsuperscript{2}
σ\textsubscript{expt} = 400 Å\textsuperscript{2}
[Cy$_7$T$_8$]$_2$O Siloxane 2-mer **X-Ray** Structures

$\text{Cy} = \text{cyclohexyl}$

100 K

All Cy’s equatorial

300 K

Cy’s disordered (chair to boat)
[Cp₇T₈]₂O·Na⁺ Siloxane 2-mer Cage Separation

8.3 – 8.6 Å Cage Centers

Covalent cage-cage (center) distance provides benchmark for non-bonded interactions!
[Cy₇T₈O-Cy₈T₆D₂-OCy₇T₈]⁺Na⁺ “3-Mer” Mass Spectrum

σₜₚₑₓₜ = 557 Å²

σₑₜ₉ₑₜₑₒ = 557 Å²
Siloxane Summary

- Low energy siloxane 2-mer and 3-mer structures obtained by molecular modeling agree with experiment within ~2%.

- Staggered or folded R group structures more compact.

- Structures seem to be determined primarily by non-bonded interactions of the cycloalkyl capping groups that cause the cages to closest pack.

- Distances between center of cages in siloxane 2-mer are in range from 8.3 – 8.6 Å. This provides a benchmark for cage-cage interactions.
Where are We Headed??

1. Larger Oligomers – we have been limited to trimers
2. Detection issues – larger oligomers without electronegative groups not detected!
3. Novel synthetic approaches to suitable oligomers:
   - Prepare amino derivatives which can be protonated (Bryan Coughlin, U. Mass.)
   - Fluoride derivatives – modify MALDI/TOF for routine negative ions or negative ion mode ESI
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