FUNCTIONALIZED FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (F-POSS)

Sean M. Ramirez, Yvonne J. Diaz, Timothy S. Haddad, Joseph M. Mahry

Incompletely-condensed fluoroalkyl-functional Polyhedral Oligomeric Silsesquioxanes (F-POSS) have been synthesized via a scaleable three-step synthetic process with an overall yield of 52%. The primary byproduct of each step in the synthesis is the completely-condensed F-POSS starting material, which enables the recycling of the starting materials. The incompletely condensed structures were readily reacted with a variety of functional dichlorosilanes to introduce reactive or unreactive functionality and produce unsymmetrical F-POSS structures. Chemical structures were confirmed by elemental analysis, multinuclear NMR (1H, 13C, 19F, and 29Si), and FT-IR methods. Single crystal X-ray diffraction was used to elucidate the crystal structure of the precursor F-POSS disilanol. The functionalized F-POSS structures were found to possess variable solubility properties, generally superior to those of the closed-cage F-POSS starting material. Dynamic contact angle measurements of these compounds were examined using water and hexadecane as the wetting liquids. Copolymers of poly(methyl methacrylate) containing F-POSS were synthesized from methacrylate F-POSS macromers. These novel structures can be used as building blocks for the development of low surface energy materials.
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Air Force Office of Scientific Research
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Hybrid Inorganic/Organic Polymers

HYBRID PROPERTIES

Ceramics

Polymers

Use Temperature & Oxidation Resistance

Toughness, Lightweight & Ease of Processing

Distribution A: Approved for public release; distribution unlimited
POSS ($\text{RSiO}_{1.5})_n$

- Organic-inorganic framework
- Well-defined, 3-D nanostructure
- Can carry functional groups
- Thermally and chemically robust
- Used in thermoset and thermoplastic polymers, temperature nanocomposites, coatings, surface modifiers, and many other applications


*Distribution A: Approved for public release; distribution unlimited*
Introduction F-POSS

- Fluorinated polyhedral oligomeric silsesquioxane (F-POSS) possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces
- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a building block material for low surface energy materials
- Applications
  - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  - Effects on polymer composite properties
    - Wetting, phase behavior, solubility, etc.

PMMA + 44 wt% POSS electrospun coating (beads on a string) morphology (water, methanol, diiodomethane, octane)

Fluorodecyl POSS

\[ R_f = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3 \]


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Fluorinated polyhedral oligomeric silsesquioxane (F-POSS)

F-POSS, a subclass of POSS which consists of a silicon-oxide core \([\text{SiO}_{1.5}]\) with a periphery of long-chain fluorinated alkyl groups.

F-POSS possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces.

Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS)

\[
\text{R}_{2}\text{Si(OEt)}_{3} \xrightarrow{\text{OH} / \text{H}_{2}\text{O}} \text{Solvent} \rightarrow \text{F-POSS}
\]

\[
\begin{align*}
\text{FH} & \quad R_i = \text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3 \\
\text{FO} & \quad \text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3 \\
\text{FD} & \quad \text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3
\end{align*}
\]

Methylene Iodide

Octane

Water

Methanol


Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. Science 2007, 318, 1618. (right)

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Functional F-POSS

• Close-caged structures are accessible and have proven versatile in polymer composites
  – Limitations
    • Solubility, mechanical robustness (surface abrasion), no sites for functionality
• Open-caged structures would allow for functionalization of F-POSS
  – Open door for use a building block material for low surface energy materials
• Applications
  – Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    • Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  – Effects on polymer composite properties
    • Wetting, phase behavior, solubility, etc....
Methods to Produce Incompletely Condensed Silsesquioxanes

- **Bottom-up approach**
  - Acid or base mediated from RSiCl$_3$ or RSi(OR)$_3$
  - Condensation reaction
  - Balance of stoichiometry, temperature, reaction time, patience, and luck
  - Stopping POSS synthesis early, before cage fully condenses
  - More common approach

- **Top-down Approach**
  - Strong acid or base mediated
  - Starting from a POSS cage
  - Conversion of Si-O-Si bonds to Si-O$^-$C$^+$ or Si-OH bonds
  - Opening up POSS cage

Which method can be applied to F-POSS?

Trifluoropropyl Example

• Small chain F-POSS (propyl) have been developed and studied
• Demonstrate the robustness of an incompletely condensed silsesquioxane to functionalization


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Methods to Produce Incompletely Condensed Silsesquioxanes

• Bottom-up approach
  – Acid or base mediated from RSiCl$_3$ or RSi(OR)$_3$
  – Condensation reaction
  – Balance of stoichiometry, temperature, reaction time, patience, and luck
  – Stopping POSS synthesis early, before cages closes
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• Top-down Approach
  – Strong acid or base mediated
  – Starting from a POSS cage
  – Conversion of Si-O-Si bonds to Si-O(-) C(+) or Si-OH bonds
  – Opening up POSS cage

Which method can be applied to F-POSS?

Incompletely Condensed Silsesquioxane

- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.*


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Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.

- Monoclinic, space group P2(1)/c, 
- a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, 
- α= 90.00°, β=92.21(10) °, γ=90.00 °, V= 12878(2) Å³

Edge Capping Reactions

\[
\begin{align*}
\text{Si} & \quad \text{Si} \\
\text{O} & \quad \text{O} \\
\text{Si} & \quad \text{Si} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\[R = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3 \]
\[R_1 = \text{CH}_3 \]
\[R_2 = \text{CH}_2\text{CH}_2\text{OC(O)}\text{CHCH}_2\]

- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes

Macromer/RBM = 4178 g/mol
Styrene Monomer Synthesis

\[ \text{Br} \xrightarrow{1) \text{Mg}} \xrightarrow{2) \text{MeSiCl}_3} \text{Si-Cl} \]

\[ \text{Si-Cl} \text{ + } \text{HO-NEt}_3 \xrightarrow{\text{C}_6\text{F}_6} \text{Si-O-Si-O-Si-O-Si} \]

Distribution A: Approved for public release; distribution unlimited
**Edge Capping Reactions**

\[
\text{Si} \quad \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Si} \\
\end{array} 
\quad + \quad \begin{array}{c}
\text{Cl}_2\text{SiR}_1\text{R}_2 \\
\text{NET}_3
\end{array} 
\]

\[
\begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Si} \\
\end{array} 
\quad + \quad \begin{array}{c}
\text{Cl}_2\text{SiR}_1\text{R}_2 \\
\text{NET}_3
\end{array} 
\]

\[
\begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Si} \\
\end{array} 
\quad + \quad \begin{array}{c}
\text{Cl}_2\text{SiR}_1\text{R}_2 \\
\text{NET}_3
\end{array} 
\]

\[
\begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Si} \\
\end{array} 
\quad + \quad \begin{array}{c}
\text{Cl}_2\text{SiR}_1\text{R}_2 \\
\text{NET}_3
\end{array} 
\]

- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**

29Si NMR taken in fluorinated solvent
Separation of T₈ from Product

Before

-18.20

After

-17.78

²⁹Si NMR taken in fluorinated solvent

²⁹Si NMR taken in diethyl ether-d₁₀

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$\textbf{1}^H$ NMR Characterization of Compounds

$\text{H}^1\text{NMR}$ taken in diethyl ether. $\text{H}^1\text{NMR}$ taken in $\text{C}_6\text{F}_6/\text{CDCl}_3$ mixture.

$\text{F}^{19}\text{NMR}$ taken in diethyl ether. $\text{H}^1\text{NMR}$ taken in $\text{C}_6\text{F}_6/\text{CDCl}_3$ mixture.
$^{13}$C NMR Characterization of Compounds
13C NMR Characterization of Compounds
$^1$H NMR Characterization of Compounds

$^{19}$F NMR taken in diethyl ether. $^1$H NMR taken in C$_6$F$_6$/CDCl$_3$ mixture.

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F-POSS Structures Synthesized

-29.5 ppm

-17.8 ppm

-32.1 ppm

-17.8 ppm

-45.5 ppm

-17.1 ppm

-17.9 ppm

R = CH₂CH₂(CF₂)₇CF₃
Contact Angle Measurements

- Non-wetting surfaces can be developed by a combination of three parameters
  - Chemical functionality (high fluorine content)
  - Roughness (micro- and nanoscale)
  - Surface Geometry (re-entrant curvature)
- What type of influence will functional groups have on F-POSS surface properties?
- Solvent impact?
Contact Angle Measurements

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  - Chemical functionality (high fluorine content)
  - Roughness (micro- and nanoscale)
  - Surface Geometry (re-entrant curvature)
- What type of influence will functional groups have on F-POSS surface properties?
- Solvent impact?

Static contact angles of Si wafer surfaces coated with compounds disilanol (a) and (b), dioctyl (c) and (d), and diphenyl (e) and (f). Image of hexadecane droplet (10 μL) rolling off surface coated with compound diphenyl (g).
F-POSS Silane Coupling Reaction

- Chlorosilyl-functional fluoroPOSS compound synthesized from the Pt(II) catalyzed hydrosilylation of vinyl-functional fluoroPOSS and dimethylchlorosilane
- Desired compound successfully synthesized in high yield
- Characterized by $^1$H, $^{13}$C, $^{19}$F, and $^{29}$Si NMR
## Dynamic Contact Angle Measurements

<table>
<thead>
<tr>
<th>Functional Group on F-POSS</th>
<th>water</th>
<th>hexadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\theta_{\text{adv}})</td>
<td>(\theta_{\text{rec}})</td>
</tr>
<tr>
<td>F-POSS*</td>
<td>124 ± 0.5°</td>
<td>109.6 ± 0.7°</td>
</tr>
<tr>
<td>Si-(OH)(_2)</td>
<td>116.8 ± 0.4°</td>
<td>111 ± 0.6°</td>
</tr>
<tr>
<td>Si-(CH(_3))(CH=CH(_2))</td>
<td>116.2 ± 0.4°</td>
<td>100.6 ± 0.8°</td>
</tr>
<tr>
<td>Si((CH(_3))((CH(_2))(_3))OC(O)CCH=CH(_2))</td>
<td>118.2 ± 1.0°</td>
<td>90.6 ± 1.0°</td>
</tr>
<tr>
<td>Si-(CH(_3))((CH(_2))(_3))OC(O)C(CH(_3))=CH(_2))</td>
<td>117.1 ± 0.6°</td>
<td>93.8 ± 1.5°</td>
</tr>
<tr>
<td>Si-(CH(_3))((CH(_2))(_2))CH(_3))</td>
<td>117.9 ± 0.4°</td>
<td>96.9 ± 1.9°</td>
</tr>
<tr>
<td>Si-(C(_6)H(_5))(_2)</td>
<td>116.2 ± 0.4°</td>
<td>110.5 ± 0.5°</td>
</tr>
<tr>
<td>Si-((CH(_2))(_7))CH(_3))</td>
<td>117.9 ± 0.5°</td>
<td>95.5 ± 0.4°</td>
</tr>
</tbody>
</table>

Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).


**Distribution A: Approved for public release; distribution unlimited**
Initial Copolymerizations

MMA
(MW = 100 g/mol)

MMA-F-POSS
(MW = 4179 g/mol)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Weight (g)</th>
<th>Weight (g)</th>
<th>Weight (g)</th>
<th>Monomer (mmol)</th>
<th>Monomer (mmol)</th>
<th>Mol Ratio (MMA:MMA-F-POSS)</th>
<th>Initiator</th>
<th>Conversion</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA-F-POSS</td>
<td>MMA</td>
<td>MMA-F-POSS</td>
<td>MMA</td>
<td>MMA-F-POSS</td>
<td>(%)</td>
<td>(%) F-POSS</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>1</td>
<td>0.085</td>
<td>1.31</td>
<td>6.3</td>
<td>0.02</td>
<td>13.1</td>
<td>655</td>
<td>0.5</td>
<td>42</td>
<td>2.74</td>
</tr>
<tr>
<td>2</td>
<td>0.362</td>
<td>1.31</td>
<td>21.6</td>
<td>0.09</td>
<td>13.1</td>
<td>145</td>
<td>0.2</td>
<td>71</td>
<td>14.4</td>
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<tr>
<td>3</td>
<td>0.50</td>
<td>3.50</td>
<td>12.5</td>
<td>0.12</td>
<td>35.0</td>
<td>291</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>3.00</td>
<td>25.0</td>
<td>0.24</td>
<td>30.0</td>
<td>125</td>
<td>1</td>
<td>62.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.00</td>
<td>2.00</td>
<td>50.0</td>
<td>0.47</td>
<td>20.0</td>
<td>42</td>
<td>0.2</td>
<td>92.5</td>
<td></td>
</tr>
</tbody>
</table>

*Weight (%) of F-POSS was calculated from elemental analysis of Fluorine content in the final polymer.

Distribution A: Approved for public release; distribution unlimited
NMR Characterization of Copolymers

19F NMR

1H NMR

Distribution A: Approved for public release; distribution unlimited
# Initial Copolymerization

**MMA**

\[
\text{MMA} \quad (\text{MW} = 100 \text{ g/mol})
\]

**MMA-F-POSS**

\[
\text{MMA-F-POSS} \quad (\text{MW} = 4179 \text{ g/mol})
\]

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Weight (%F-POSS)</th>
<th>Mol Ratio (MMA:MMA-F-POSS)</th>
<th>Conversion (%)</th>
<th>Weight (%) FPOSS*</th>
<th>(T_g) (°C)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.3</td>
<td>655</td>
<td>42</td>
<td>2.74</td>
<td>165</td>
<td>PMMA solvents</td>
</tr>
<tr>
<td>2</td>
<td>21.6</td>
<td>145</td>
<td>71</td>
<td>14.4</td>
<td>165</td>
<td>PMMA solvents (takes time)</td>
</tr>
<tr>
<td>3</td>
<td>12.5</td>
<td>291</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>25.0</td>
<td>125</td>
<td>62.5</td>
<td></td>
<td>126</td>
<td>PMMA solvents with small amount of AK-225G</td>
</tr>
<tr>
<td>5</td>
<td>50.0</td>
<td>42</td>
<td>92.5</td>
<td></td>
<td>127</td>
<td>THF-AK225G mixture (suspension)</td>
</tr>
</tbody>
</table>

*Note: Conversion and weight are approximate values.*
Summary

• Structures were demonstrated to be reactive towards a variety of dichlorosilanes
• Solubility of F-POSS compounds were shown to be influenced by chemical functionality
• Functionality was shown to be influential on contact angle measurements
• F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or omniphobic polymer composites.
  — Reaction mechanisms, polymer composites, block copolymers, etc....