Synthesis and Free Radical Polymerization of Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers: Precursors for Low Surface Energy Materials and Devices

In this presentation, 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. Scientists are currently working on other monomers and polymers for F-POSS. F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or omniphobic polymer composites.
Synthesis and Free Radical Polymerization of Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers: Precursors for Low Surface Energy Materials and Devices

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April 2012
AFRL Propulsion Directorate
(AFRL/RZ)

Space & Missile Propulsion
Hypersonics
Energy, Power & Thermal

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AFRL Propulsion Directorate

RZ-West
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RZ-East
(Wright Patterson AFB OH)

- Rocket Engines & Motors
- Satellite Propulsion
- Advanced Propulsion
- Fuels and Propellants
- System Analysis

- Turbine Engines
- Ramjet Engines
- Combined-Cycle Engines
- Hypersonic Engines
- Aircraft Power
- Thermal Management
- Fuels and Propellants
- System Analysis
Basic and Applied Research

**Basic Research**

- Basic POSS research funded by AFOSR

**Solid Rocket Motors**

- Polymers are >50% of inert mass
- Nanocomposites allow significant weight reduction
- Transition target - Boost, strategic, & tactical SRMs
- Use possible in other Air Force applications

**Liquid Rocket Engines**

- Fluorinated polymer nanocomposites
- Reduce cost and improve performance
- Most hydrophobic crystalline solids known
- Superoleophobic surfaces produced
- Fuel separation

**Polymer Matrix Composites**

- Replace metals for mass reduction
- Resistance to oxidation seen in nanocomposite PMCs
- Developing PMC resins for high-temperature applications
- Moisture uptake properties improved with added nano-materials

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Hybrid Inorganic/Organic Polymers

Ceramics

Polymers

HYBRID PROPERTIES

Use Temperature & Oxidation Resistance

Toughness, Lightweight & Ease of Processing

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**POSS (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

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*Inorganic Si-O core*

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*Organic peripheral*

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Introduction to F-POSS

(1,1,2,2-tetrahydroperfluorodecyl)$_8$Si$_8$O$_{12}$ Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS
- hybrid organic-inorganic structure
- well-defined polyhedral architecture
- long-chain fluoroalkyl substituents on periphery of cage

Due to its unique structure, fluorodecyl POSS has one of the lowest surface energies of any crystalline solid currently known
- fluorodecyl POSS 9.3 mN/m
- polytetrafluoroethylene 18-20 mN/m
- CF$_3$ monolayer 6.7 mN/m

Low surface energy and other unique properties of fluorodecyl POSS has enabled the development of various types of tunable non-wetting polymeric surfaces

Superhydrophobic/oleophilic dip-coated fabric
Tuteja et al, Science, 2007, 318, 1618

Superamphiphobic dip-coated fabric
Choi et al, Adv Mater, 2009, 21, 2190

Superamphiphobic electrospun surfaces
Tuteja et al, PNAS, 2008, 105, 18200
Synthesis of F-POSS

\[ \text{RfSi(OEt)}_3 \xrightarrow{\text{KOH/H}_2\text{O}} \text{EtOH} [\text{RfSiO}_{1.5}]_n \]
Functional F-POSS (Open-Caged)

• 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....

• Open cages lead to functional POSS structures
• Reactions are simple
• High yields typically reported
Methods to Produce Incompletely Condensed Silsesquioxanes

• Bottom-up approach
  – Acid or base mediated from RSiCl₃ or RSi(OR)₃
  – Condensation reaction
  – Balance of stoichiometry, temperature, reaction time, patience, and luck
  – Stopping POSS synthesis early, before cages closes
  – 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?

Synthesis of F-POSS-(OH)$_3$

- Synthesis discussed in patents*
- Works for trifluoropropyl groups
- Solubility is critical in this reaction
- Fluorinated compounds not miscible in most organics once condensation begins to occur
- *Does not work for long-chain F-POSS*
- Tried under various conditions
  - Solvent, temperature, reaction time, base

Open cages lead to functional POSS structures
- Reactions are simple
- High yields typically reported

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Methods to Produce Incompletely Condensed Silsesquioxanes

• Bottom-up approach
  – Acid or base mediated from RSiCl$_3$ or RSi(OR)$_3$
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• Top-down Approach
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Which method can be applied to F-POSS?

Initial Reactions with Triflic Acid

- Fluorodecyl $T_8$
- Reacted with triflic acid to open cage structure
- Structures analyzed with $^{29}$Si NMR
- Equivalents of triflic acid to POSS cage is important to success of reaction
- Disappointing results

$^{29}$Si NMR taken in fluorinated solvent

Synthesis of F-POSS-(OTf)$_2$

- After a little bit of refining
- An open cage structure is partially visible
- Starting material is still present
- Reaction not very clean
- Si ratio (1:1:2)

$2^9$Si NMR taken in fluorinated solvent

Mixture of unknown incompletely caged silsesquioxanes and resin
Synthesis of F-POSS-SO$_2$

$R = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$

- Bridge sulfate cleans up reaction
- Structure significantly more stable than then F-POSS-(OTf)$_2$, however still difficult to isolate
- Removal of starting material extremely difficult
- Si ratio (1:1:2)

$^{29}\text{Si NMR taken in fluorinated solvent}$
Synthesis of F-POSS-(OH)$_2$

- Acidic conditions are used to remove the bridge sulfate complex
- Silanol peak at -58.8 ppm
- F-POSS-(OH)$_2$ is more stable than both F-POSS-(OTf)$_2$ and F-POSS-SO$_2$
- Anal. Calcd. for C$_{80}$H$_{34}$F$_{136}$O$_{13}$Si$_8$ (found): C, 23.94 (23.99), H, 0.85 (0.75), F, 64.44 (64.72)
- Dehydration of disilanol leads to T$_8$ formation
- Si ratio (1:1:2)

$\text{R} = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$

$^{29}\text{Si}$ NMR taken in fluorinated solvent
Incompletely Condensed Silsesquioxane

\[ R_f = CH_2CH_2(CF_2)_7CF_3 \]


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X-Ray Crystal Structure of Disilanol

- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- \( M_r = \text{monoclinic, space group P2(1)/c, } a=11.84(10) \text{ Å, } b=57.11(6) \text{ Å, } c=19.06(2) \text{ Å, } \alpha = 90.00^\circ, \beta = 92.21(10)^\circ, \gamma = 90.00^\circ, V = 12878(2) \text{ Å}^3 \)

Edge Capping Reactions

\[
\text{Cl}_2\text{SiR}_1\text{R}_2 + \text{NET}_3 \rightarrow \text{Cl}_2\text{SiR}_1\text{R}_2
\]

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

- 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
Edge Capping Reactions

\[ R = CH_2CH_2(CF_2)_7CF_3 \]
\[ R_1 = CH_3 \]
\[ R_2 = CH_2CH_2CH_2OC(O)CHCH_2 \]

- 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!
F-POSS Structures Synthesized

R = CH₂CH₂(CF₂)₇CF₃

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

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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

- 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?**

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).
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$_3$)$_2$</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).

Free Radical Polymerization

**Polymer**

A (Monomer)

$\text{AAAAA} \Rightarrow \frac{\text{A}}{\text{A}}$  

$\left(\text{A}\right)_n$

- Initiator $k_d$ → 2 I.
- $\text{I.} + \text{Monomer} \xrightarrow{k_i} \text{P}_n^*$

**Copolymer**

A + B (Monomers)

$\text{ABAABABAB}$

- Propagation
- $\text{P}_n^* + \text{Monomer} \xrightarrow{k_p} \text{P}_n^*$

- Termination
- 2 Radicals $k_t$ → Polymer

-Monomers make polymers
- Multiple different types of monomers in a polymer make copolymers
- Choosing a type of monomer will decide what type of polymer you have
  - trash bags, cotton, paint, DNA, protein, plastic bottles, etc....most things you use in your life
Free Radical Polymerization

Initiation

Initiator \[ \rightarrow \] 2 \( I \).

\( I \) + Monomer \[ \rightarrow \] \( P_n \).

Propagation

\( P_n \) + Monomer \[ \rightarrow \] \( P_n \).

Termination

2 Radicals \[ \rightarrow \] Polymer

Example: Polystyrene

- Standard polymerization method
- Simple, cheap, easy
- Does not allow for much control
- No block copolymers
- Molecular weight difficult to control

Two most important factors for polymers:
1) Structure
2) Molecular Weight

Ethylene glycol (monomer) (antifreeze)
Polyethylene glycol
Low MW (laxatives, lubricants, toothpaste binder)
Higher MW (medical uses, paintballs, etc.)
Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization

Initiation

Initiator $\overset{k_d}{\rightarrow} 21.$

$\text{I.} + \text{Monomer} \rightarrow P_n^*$

$P_n^* + \frac{S=C=S}{Z} \leftrightarrow P_n^*S\hat{C}\hat{S}R \leftrightarrow P_n^*S\hat{C}\hat{S} + R.$

Propagation

$R. + \text{Monomer} \rightarrow P_m^*$

$P_n^* + \text{Monomer} \rightarrow P_n^*$

Termination

$P_m^* + \frac{S=C=S}{Z}P_n \leftrightarrow P_m^*S\hat{C}\hat{S}P_n \leftrightarrow P_m^*S\hat{C}\hat{S} + P_n^*$

Monomer

2 Radicals $\rightarrow$ Dead polymer

Chain Transfer Agent

RAFT Polymerization

• Controlled polymerization
• Allows for block copolymers
• Tune molecular weight

Free Radical Copolymerizations

MMA
(MW = 100 g/mol)

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

+ AIBN, 60°C

• Standard free radical polymerization of methyl methacrylate and MMA-F-POSS monomers:
  — F-POSS monomer is active towards polymerization
  — F-POSS incorporation (1-20% by weight)
  — Molecular weights range from 10-50,000 g/mol
  — Higher F-POSS and polymerization causes problems
RAFT Copolymerizations

- Controlled/"living" free radical polymerization of methyl methacrylate, CPD, and MMA-F-POSS monomers:
  - Promising results with molecular weights ranging from 20-40,000 gm/mol
  - Narrow polydispersity indices (1.04-1.1)
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
• Currently working on other monomers and polymers for F-POSS
• 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....
Acknowledgements

The Polymer Working Group at Edwards Air Force Base:

Dr. Joseph Mabry
Mr. Pat Ruth
Ms. Vandana Vij
Dr. Greg Yandek
Dr. Josiah Reams
Ms. Yvonne Diaz
Mr. Raymond Compos

Mr. Brian Moore
Mr. Kevin Lamison
Dr. Tim Haddad
Dr. Andy Guenthner
Ms. Dana Pinson
Capt. Rebecca Stone

We thank Peter Müller at the Massachusetts Institute of Technology (MIT) and the American Crystallography Association (ACA) summer course for their assistance with small molecule X-ray crystal structure determination and refinement.

Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate
Propulsion & Power are Important!

- 50-70% of satellite weight, 25-40% of system cost, the life-limiting factor
- 70-90% of launch weight, 40-60% of system cost
- 60-80% of tactical missile weight; the critical factor in range & time-to-target
- 40-70% of cruise missile weight; the critical factor in survivability, lethality, & reach
- 45-80% of directed energy weapon weight and volume
- 40-60% of aircraft TOGW, 20-40% of system life cycle cost

Air Force fuel costs were $6B in FY07 alone.
Designing Superoleophobic Surfaces

- Goal: a design framework for constructing super-repellent surfaces
- Demonstrated electrospun mats (single step process)
- Three key ingredients

- Roughness \( (r) \)
- Surface Chemistry \( (\theta_e) \)
- Surface Geometry \( (\psi) \)

Superhydrophobic \( \theta > 150^\circ \)

PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology