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**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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For presentation to the Chemistry Department of the Air Force Academy, Colorado Springs, CO, 12 April 2012.

**14. ABSTRACT**

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.

**15. SUBJECT TERMS**

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| | | | | | Dr. Joseph M. Mabry |
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| Unclassified | Unclassified | Unclassified | SAR | 37 | N/A |

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

*Sean M. Ramirez*

*ERC Inc., Air Force Research Laboratory*

*Propulsion Directorate*

*Edwards Air Force Base, CA*

*April 2012*



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# AFRL Propulsion Directorate

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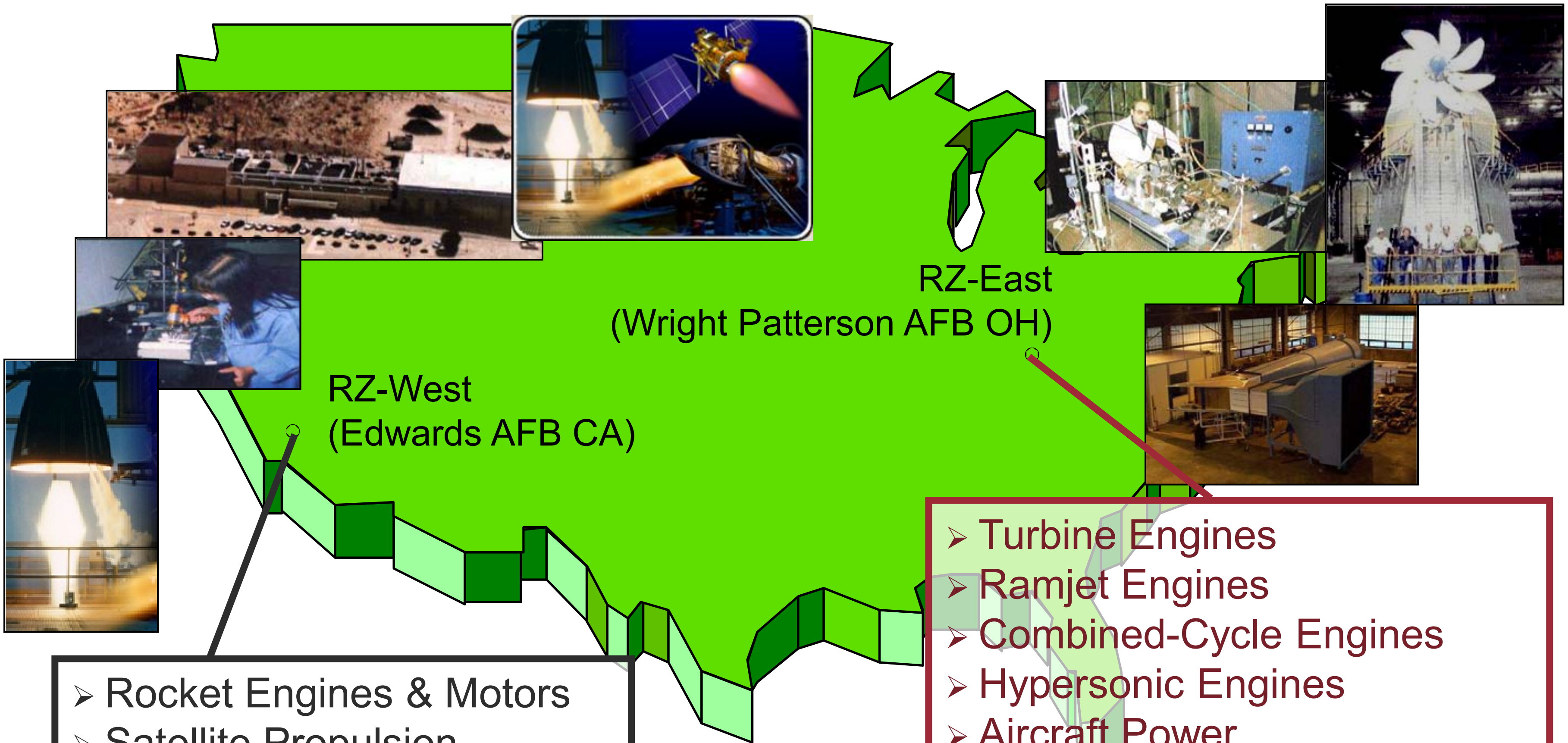
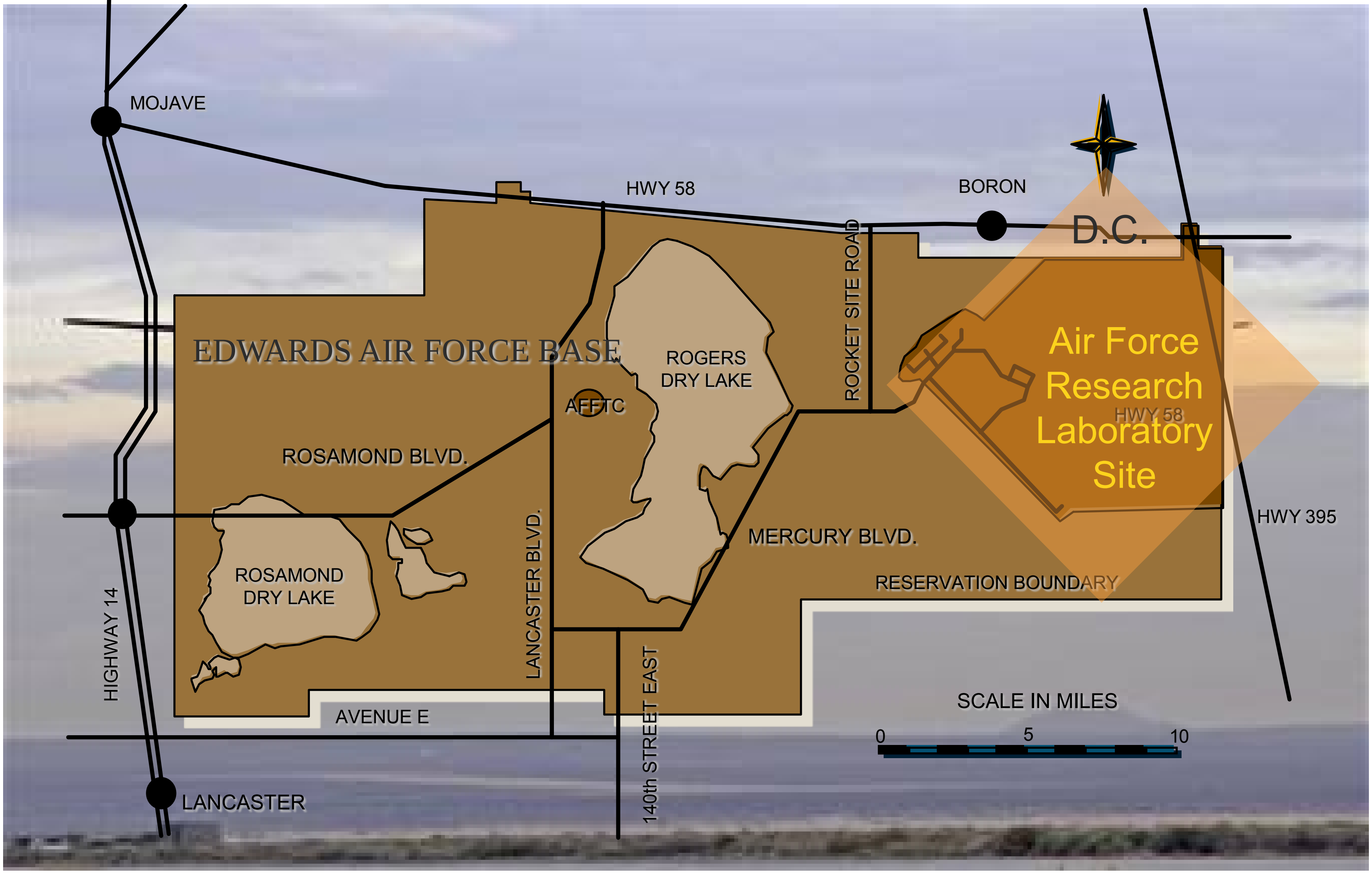
# AFRL Propulsion Directorate




- 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

# Edwards AFB



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ROCKET SITE ROAD
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AFFTC
ROSAMOND BLVD.
MERCURY BLVD.
HWY 395
ROSAMOND DRY LAKE
LANCASTER BLVD.
RESERVATION BOUNDARY
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AVENUE E
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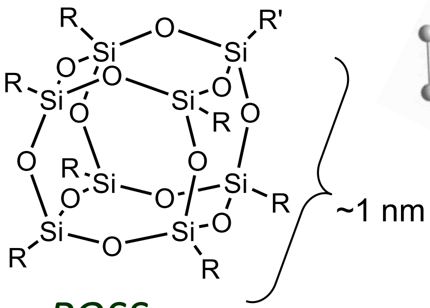
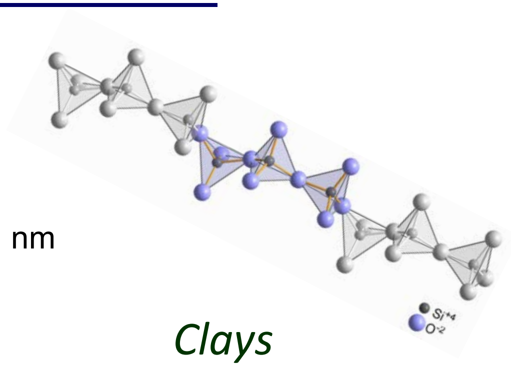
# Basic and Applied Research

## Basic Research




*POSS*



*Clays*

- 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

*Atlas V*

## Liquid Rocket Engines

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

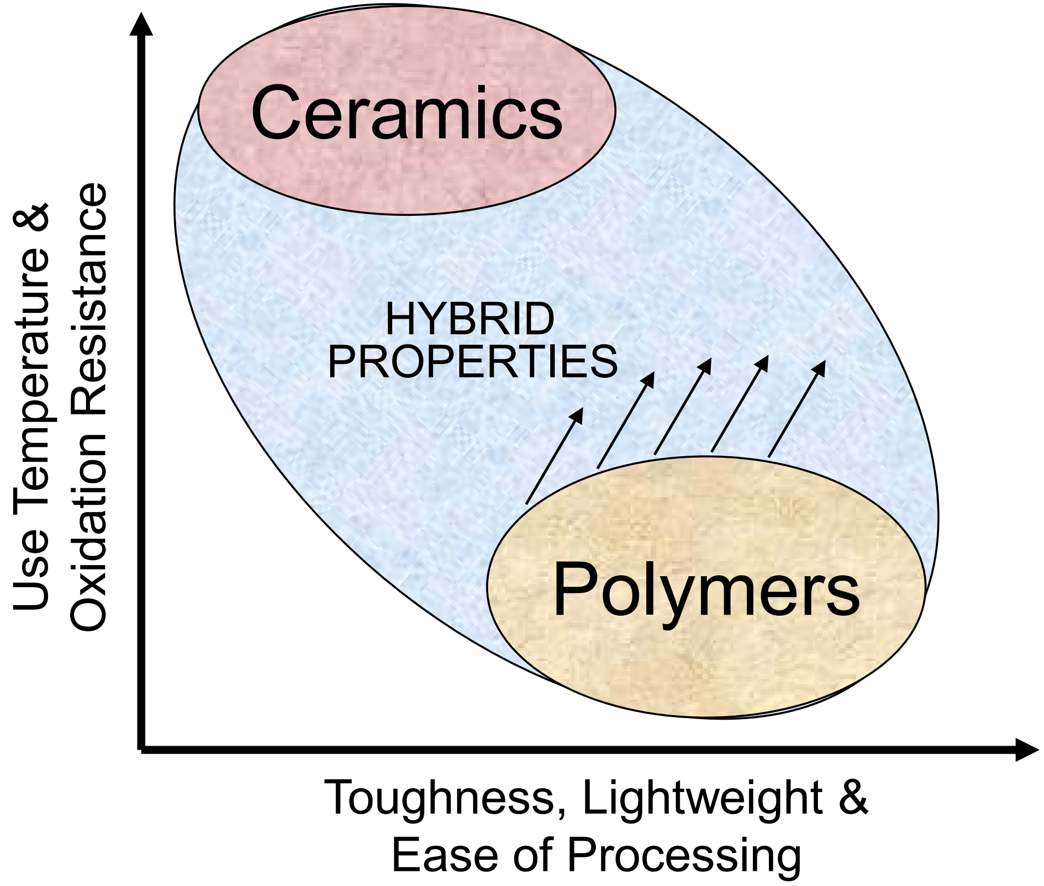
*Liquid Demo Engine*

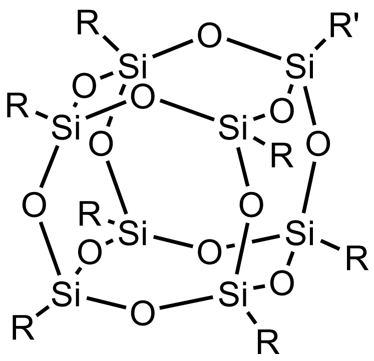
## Polymer Matrix Composites

- 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

*Bushings*

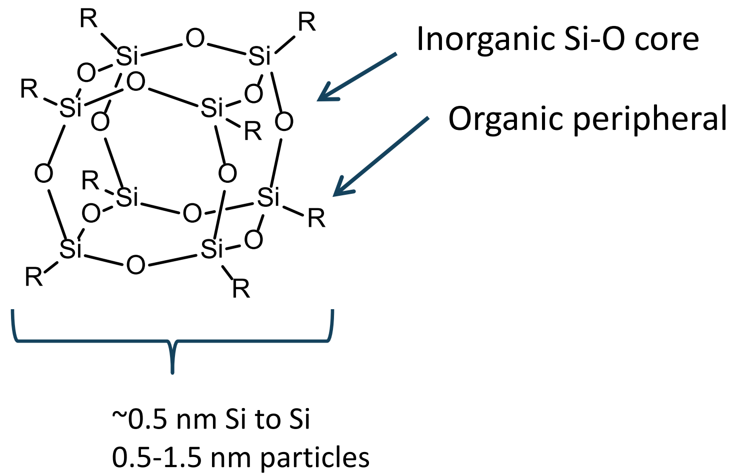
# Hybrid Inorganic/Organic Polymers



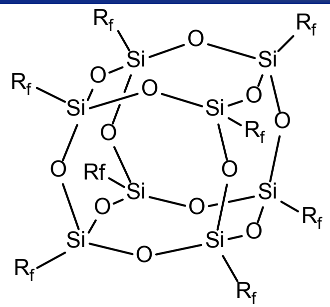
# POSS $(RSiO_{1.5})_n$

- 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




Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* ***2010****, 110, 2081.*
Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* ***2004****, 8, 21.*

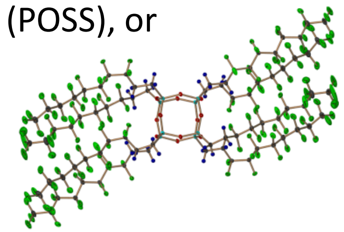
# Introduction to F-POSS



$R_f = -(CH_2)_2(CF_2)_7CF_3$

(1,1,2,2-tetrahydroperfluorodecyl)$_8Si_8O_{12}$ Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS

- hybrid organic-inorganic structure
- well-defined polyhedral architecture
- long-chain fluoroalkyl substituents on periphery of cage

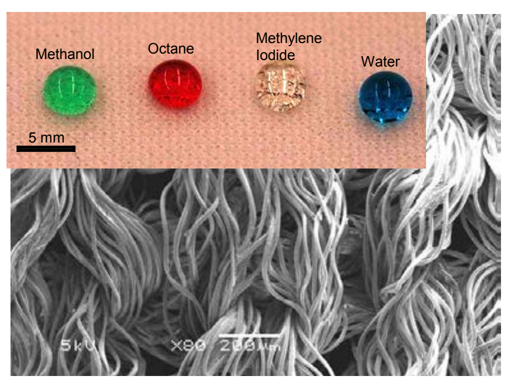


Due to its unique structure, fluorodecyl POSS has one of the lowest surface energies of any crystalline solid currently known

| | |
|---|---|
| - 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

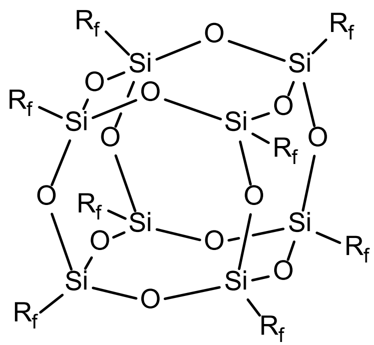



Superamphiphobic dip-coated fabric
Choi *et al*, Adv Mater, **2009**, 21, 2190

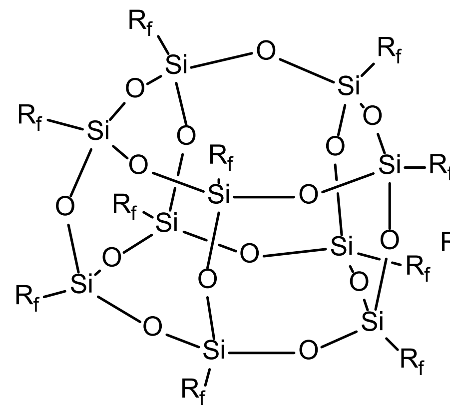

Superamphiphobic electrospun surfaces
Tuteja *et al*, PNAS, **2008**, 105, 18200

# Synthesis of F-POSS

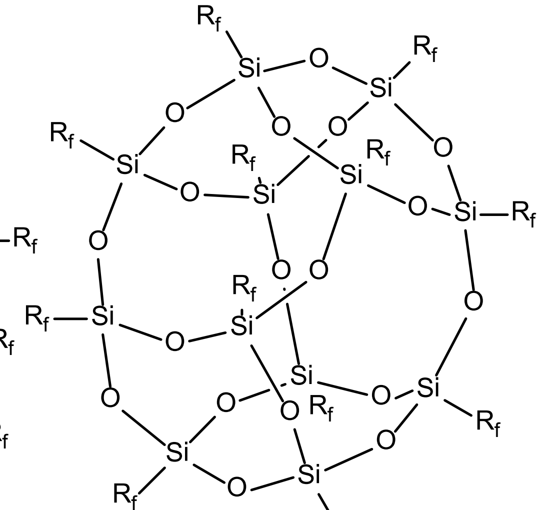
$$R_fSi(OEt)_3 \xrightarrow[EtOH]{KOH/H_2O} [R_fSiO_{1.5}]_n$$



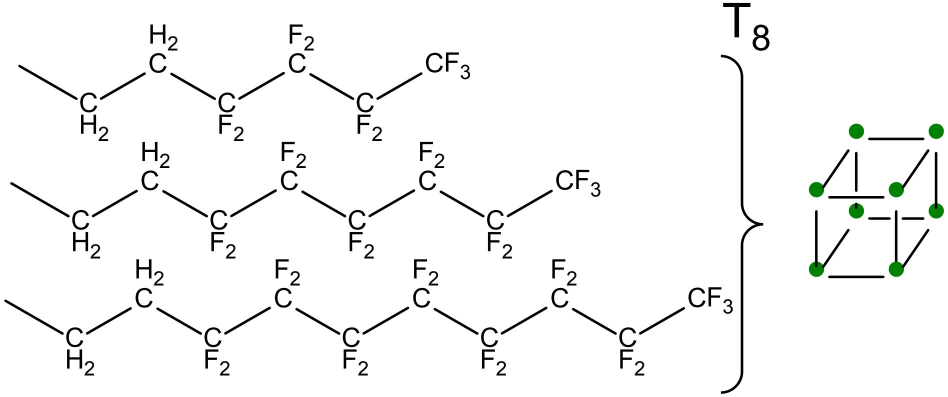

$T_8$

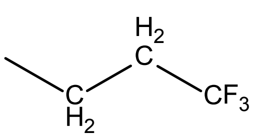


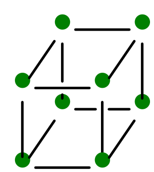

$T_{10}$

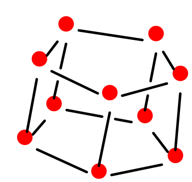


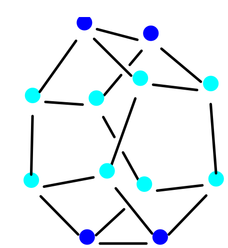

$T_{12}$



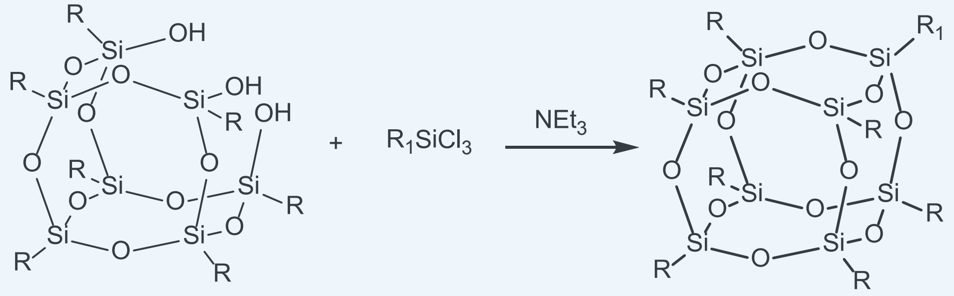







# Functional F-POSS (Open-Caged)

- 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

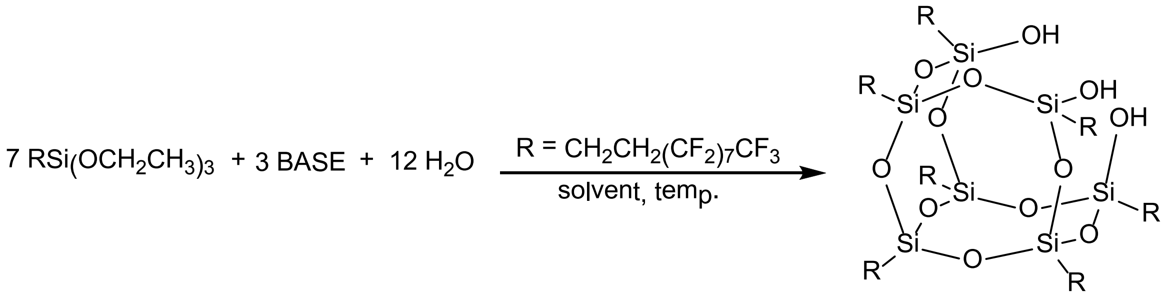
- Bottom-up approach
  - Acid or base mediated from $RSiCl_3$ or $RSi(OR)_3$
  - Condensation reaction
  - Balance of stoichiometry, temperature, reaction time, patience, and luck
  - Stopping POSS synthesis early, before cages closes
  - More common approach

- Top-down Approach
  - Strong acid or base mediated
  - Starting from a POSS cage
  - Conversion of Si-O-Si bonds to $Si\text{-}O^{(-)}C^{(+)}$ or Si-OH bonds
  - Opening up POSS cage

Which method can be applied to F-POSS?

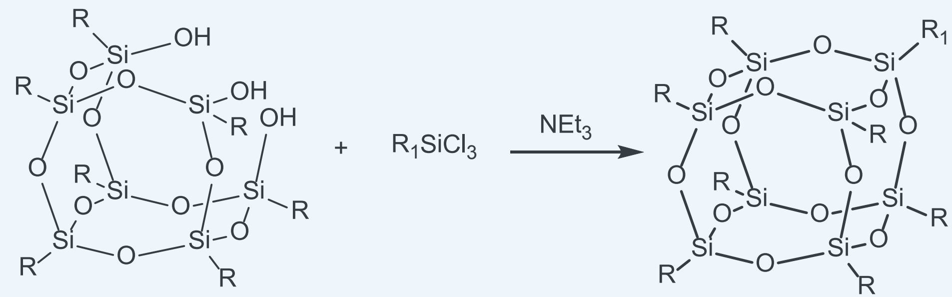
Feher, F. J.; Terroba, R.; Ziller, J. W. *Chemical Communications* ***1999***, 2309. Feher, F. J.; Newman D.A;. Walzer, J.M., *J. Am. Chem. Soc.,* **1989**, 111, 1741. Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W. *Angew.Chem. Inter. Ed.* ***1998***, *37,* 2663. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* ***1998,*** 1279.

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




**R = $CH_2CH_2(CF_2)_nCF_3$**

- 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

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*Yamashita, Y.; Hayashi, K.; Ishihara, M.; (Mitsubishi Materials Corp., Japan; Dai Nippon Toryo Co., Ltd.). Application: JP, 2000; pp 12 pp. Yamashita, Y.; Hayashi, K.; Ishihara, M.; (Mitsubishi Materials Corp., Japan; Dai Nippon Toryo Co., Ltd.). Application: JPJP, 2000; pp 9 pp.

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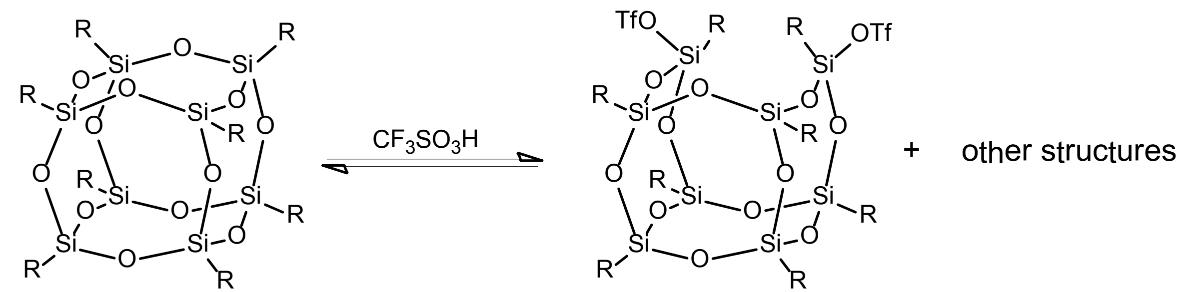
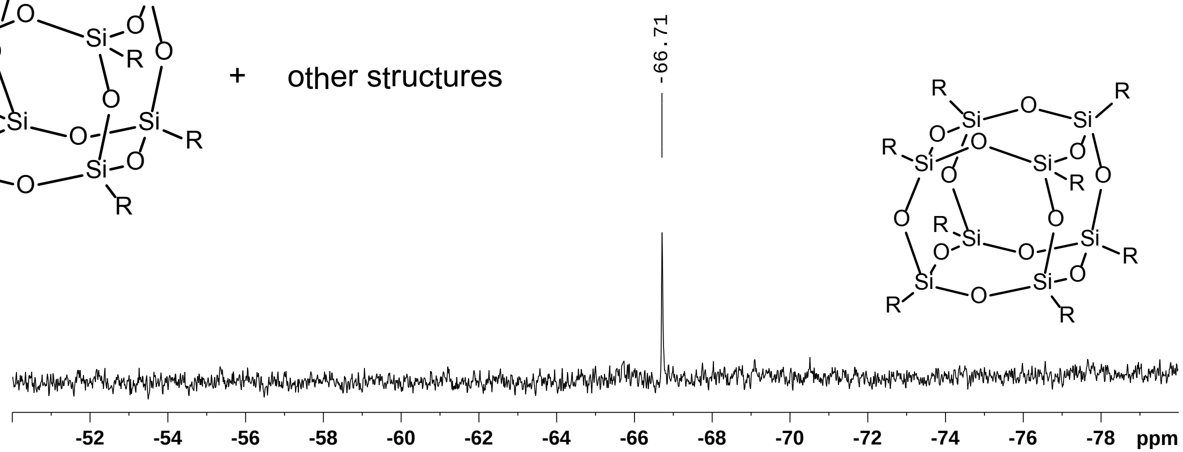
Feher, F. J.; Terroba, R.; Ziller, J. W. *Chemical Communications* ***1999***, 2309. Feher, F. J.; Newman D.A;. Walzer, J.M., *J. Am. Chem. Soc.,* **1989**, 111, 1741. Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W. *Angew.Chem. Inter. Ed.* ***1998**, 37,* 2663. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* ***1998,*** 1279.

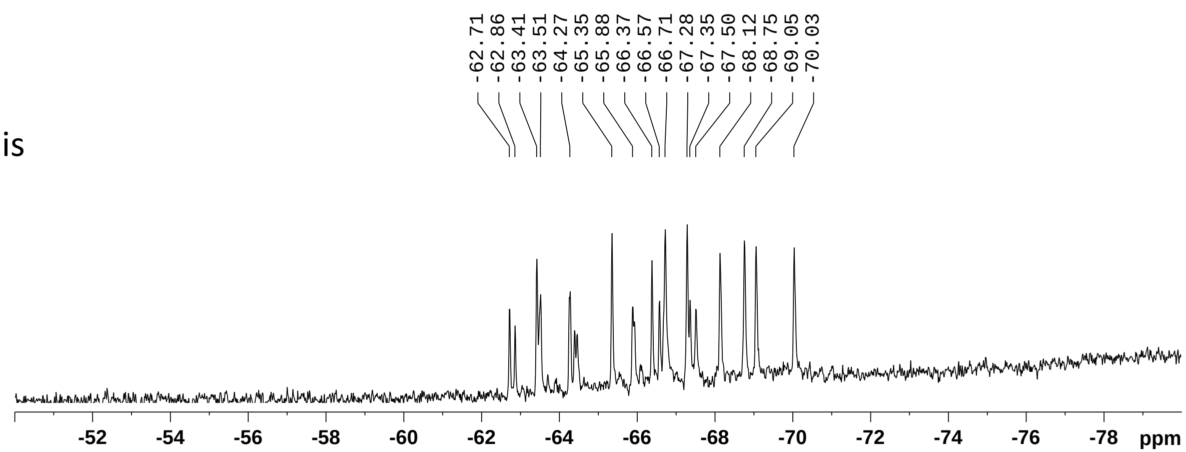
# Initial Reactions with Triflic Acid




R = $CH_2CH_2(CF_2)_7CF_3$

- 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

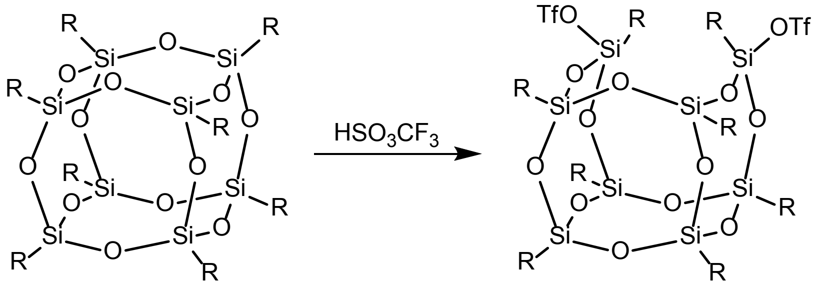



$^{29}$Si NMR taken in fluorinated solvent

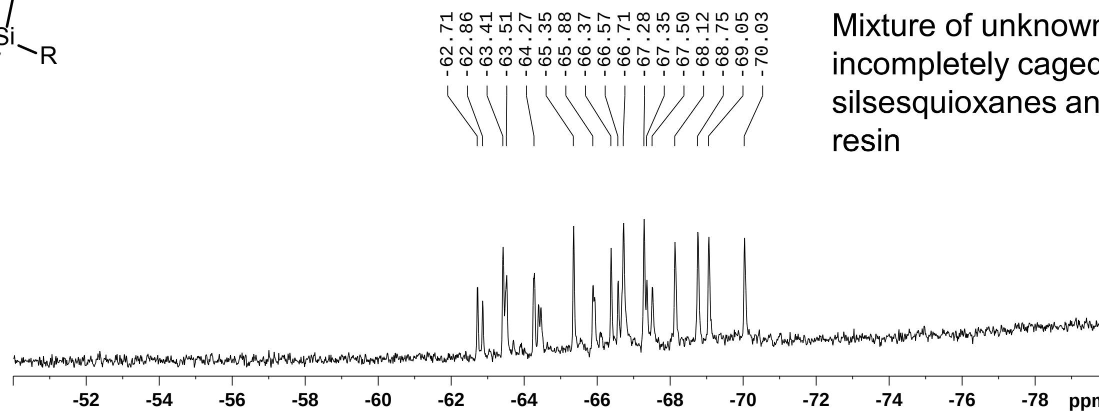

. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* ***1998,*** 1279.

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

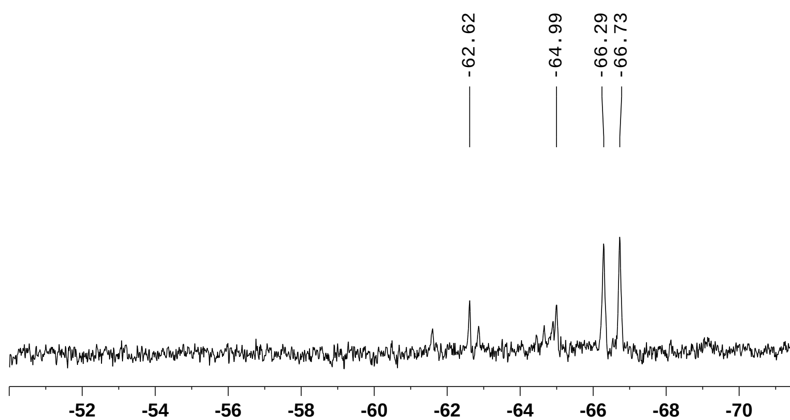


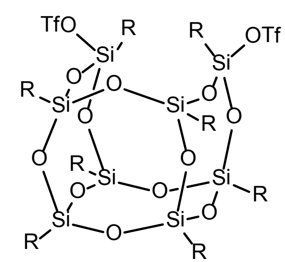

R = $CH_2CH_2(CF_2)_7CF_3$

- 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)



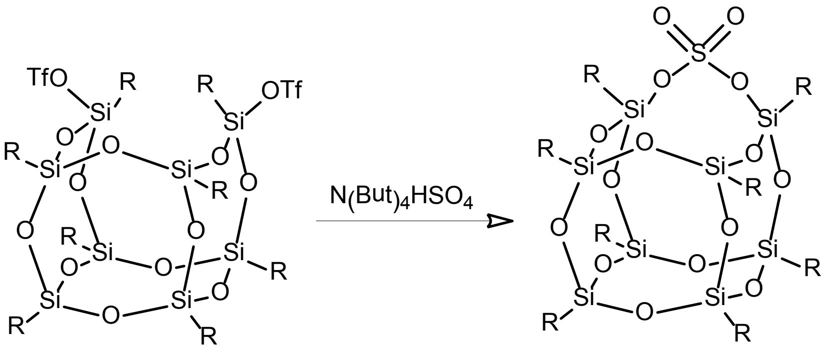

Mixture of unknown incompletely caged silsesquioxanes and resin



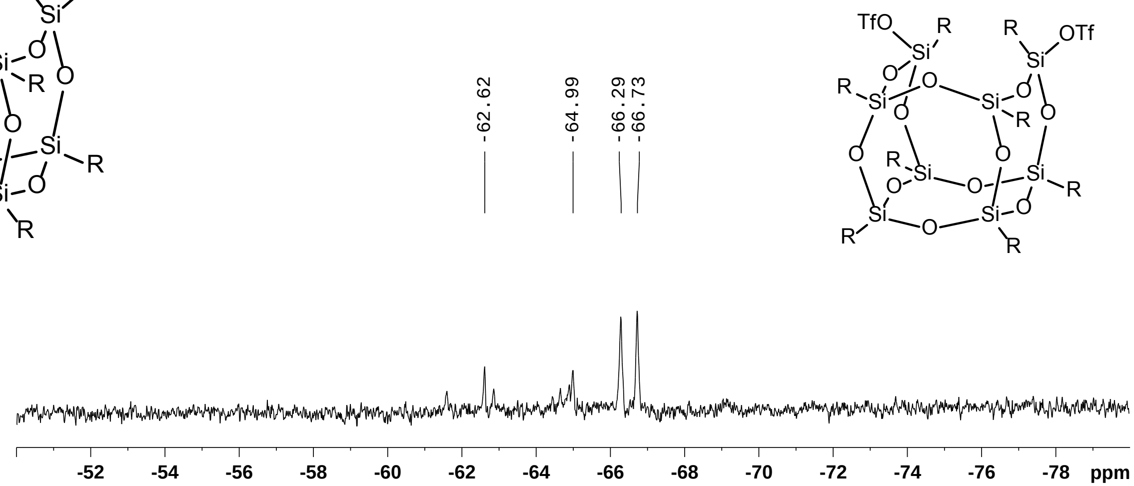

$^{29}Si$ NMR taken in fluorinated solvent

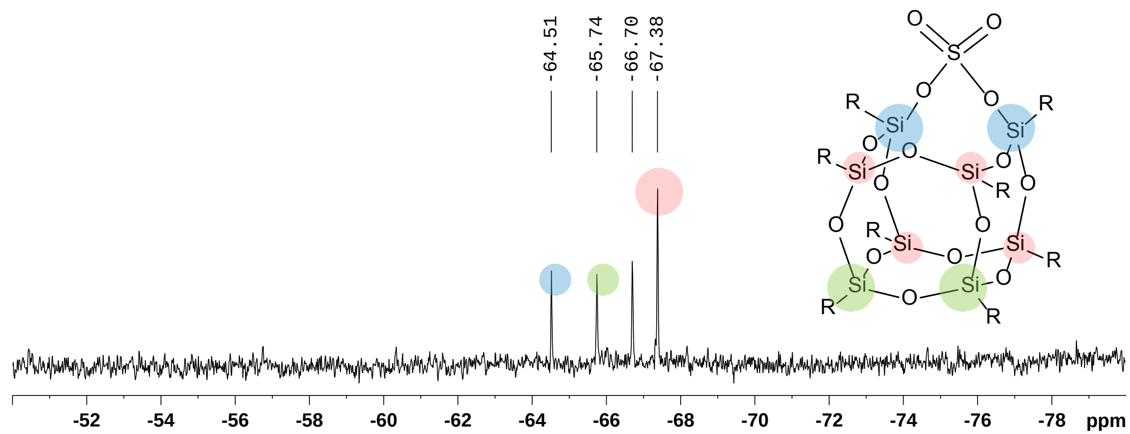
# Synthesis of F-POSS-$SO_2$




**R = $CH_2CH_2(CF_2)_7CF_3$**

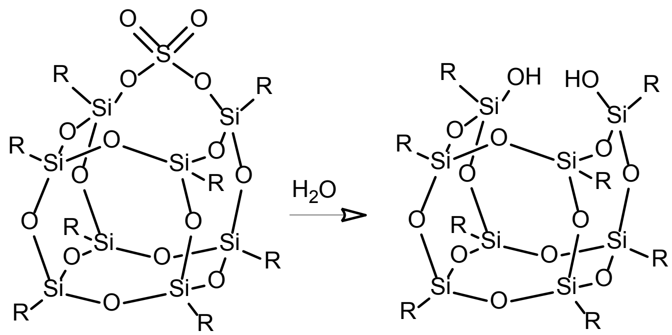
- Bridge sulfate cleans up reaction
- Structure significantly more stable than then F-POSS-$(OTf)_2$, however still difficult to isolate
- Removal of starting material extremely difficult
- Si ratio (1:1:2)



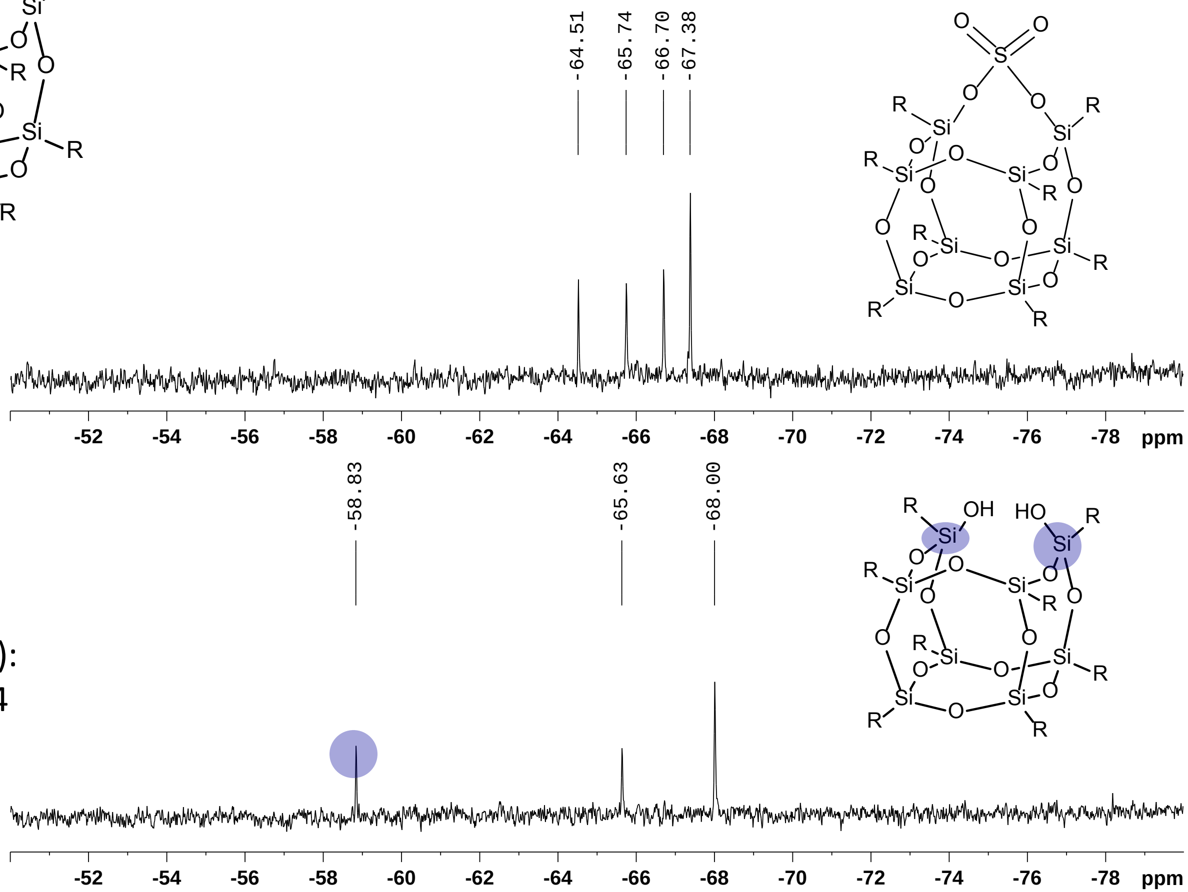

$^{29}Si$ NMR taken in fluorinated solvent

# Synthesis of F-POSS-$(OH)_2$



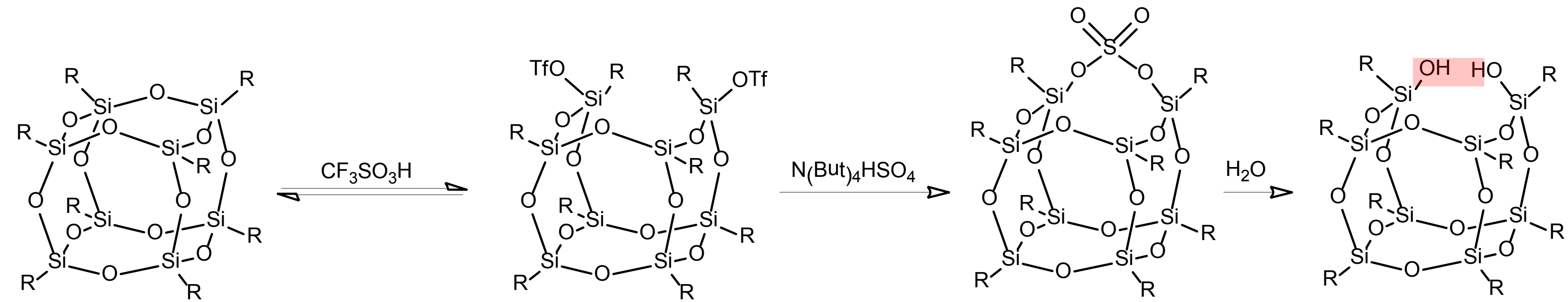

**R = $CH_2CH_2(CF_2)_7CF_3$**

- 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)




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

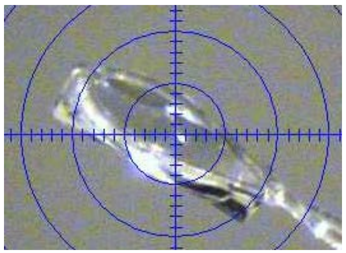
# Incompletely Condensed Silsesquioxane

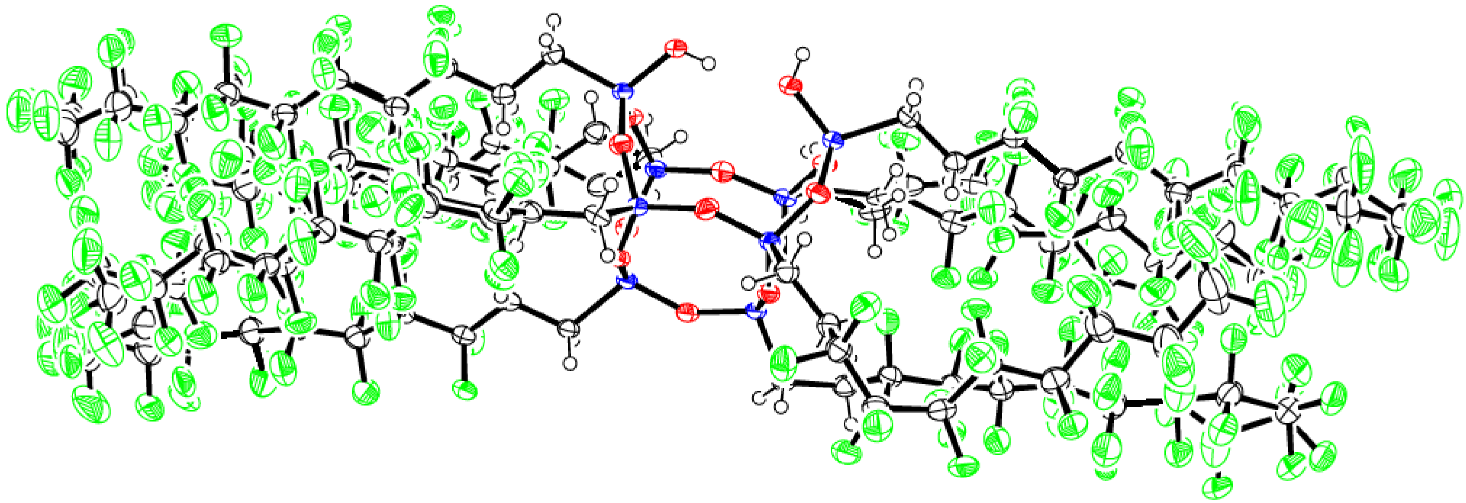



$R_f = CH_2CH_2(CF_2)_7CF_3$

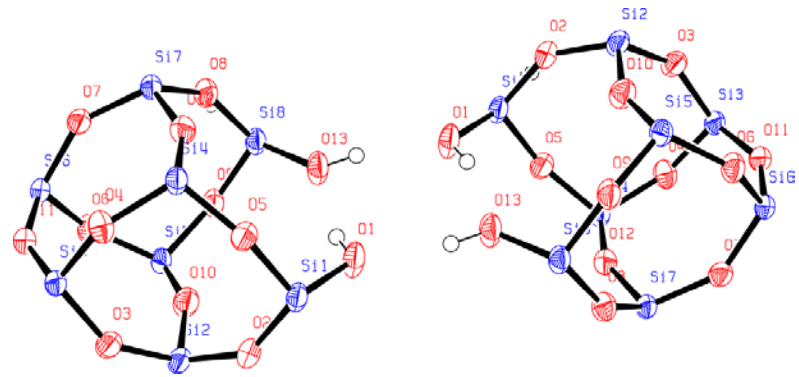
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* **2011**, *133*, 20084.

# X-Ray Crystal Structure of Disilanol



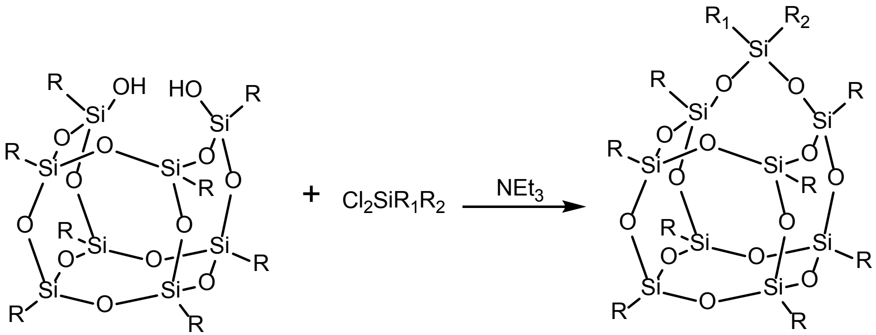


- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- $M_r$=,monoclinic, space group P2(1)/c , a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, $\alpha$= 90.00°, $\beta$=92.21(10) °, $\gamma$=90.00 °, V= 12878(2) Å$^3$



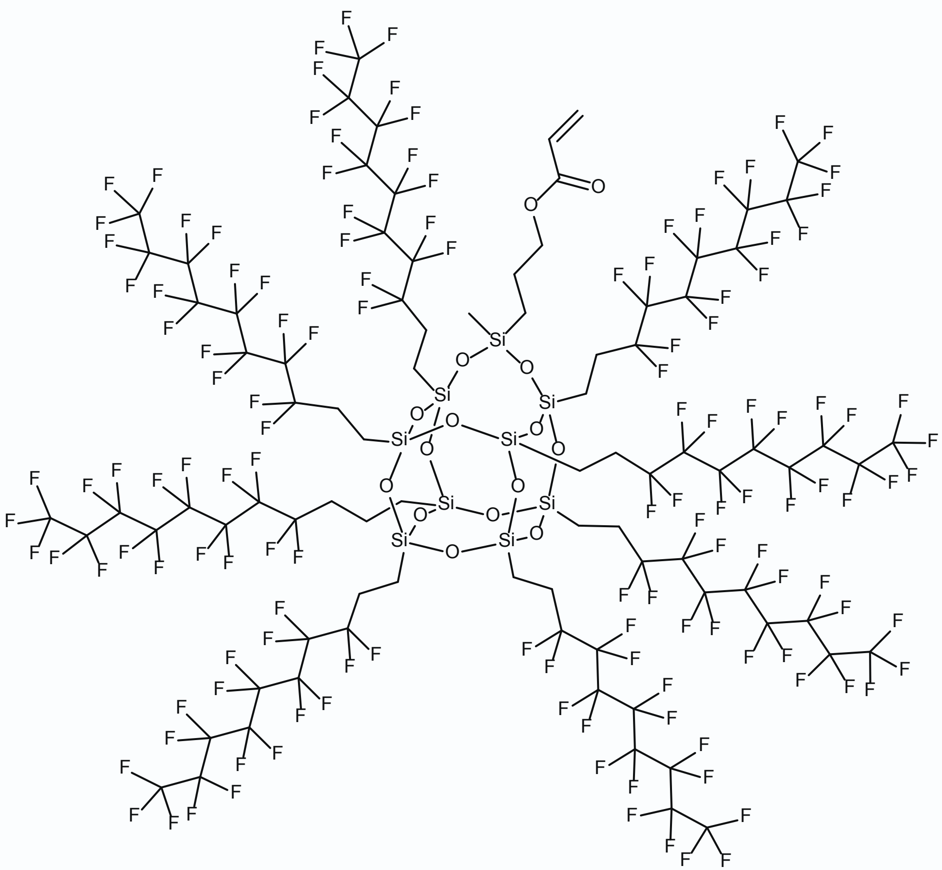
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, *133*, 20084.

# Edge Capping Reactions



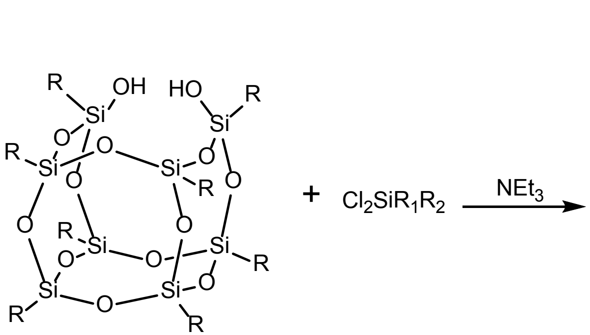

**R = $CH_2CH_2(CF_2)_7CF_3$**
**$R_1$ = $CH_3$**
**$R_2$ = $CH_2CH_2CH_2$ OC(O)CHCH$_2$**

- 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

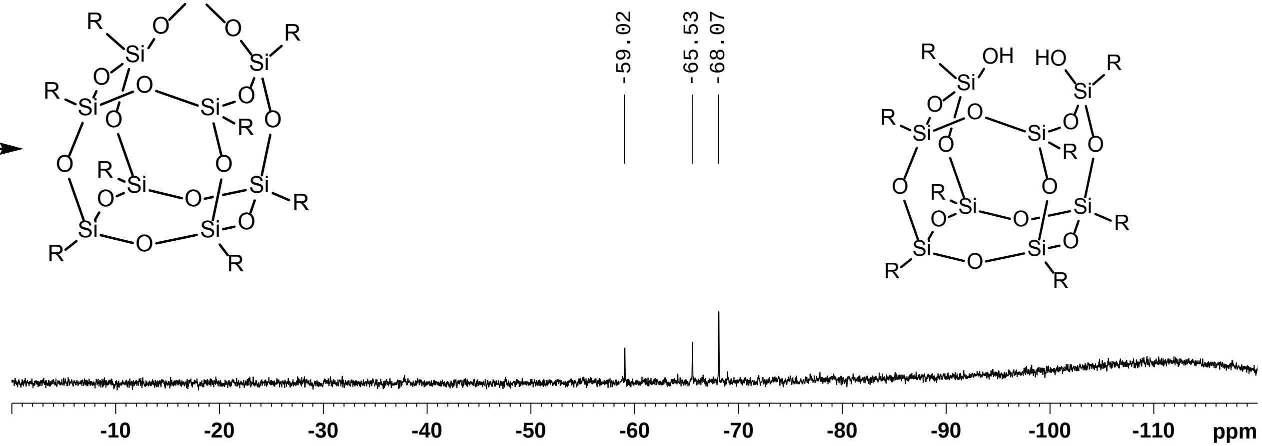


Macromer/RBM = 4178 g/mol

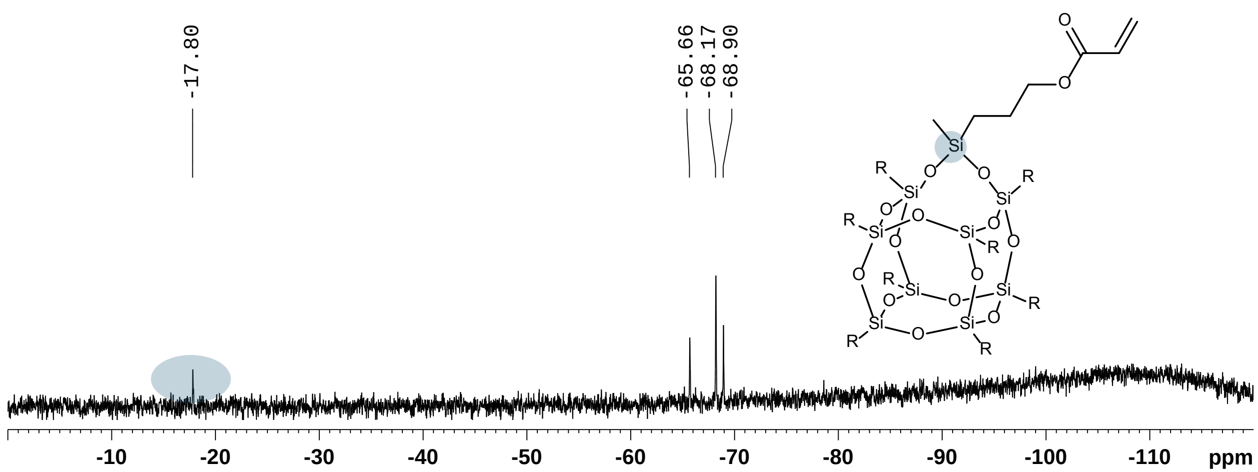
# Edge Capping Reactions




**R = $CH_2CH_2(CF_2)_7CF_3$**
**$R_1$ = $CH_3$**
**$R_2$ = $CH_2CH_2CH_2\ OC(O)CHCH_2$**



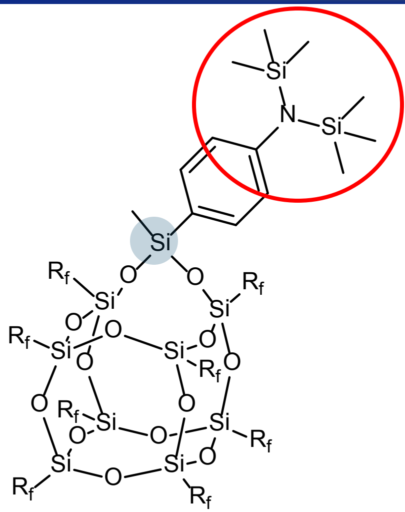

- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**



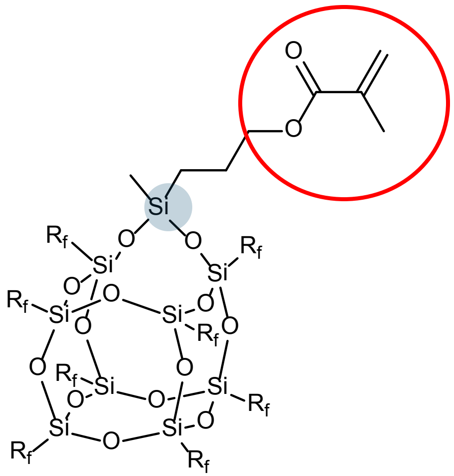

$^{29}$Si NMR taken in fluorinated solvent

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

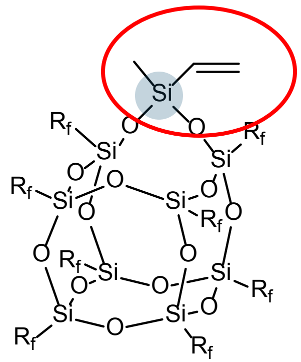
# F-POSS Structures Synthesized



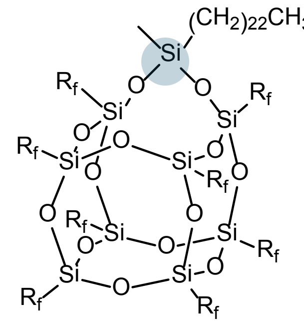
-29.5 ppm



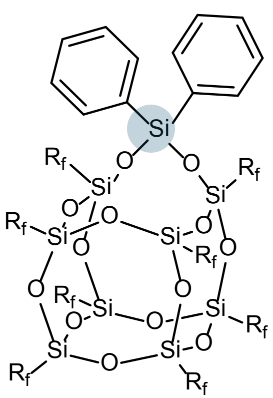
-17.8ppm



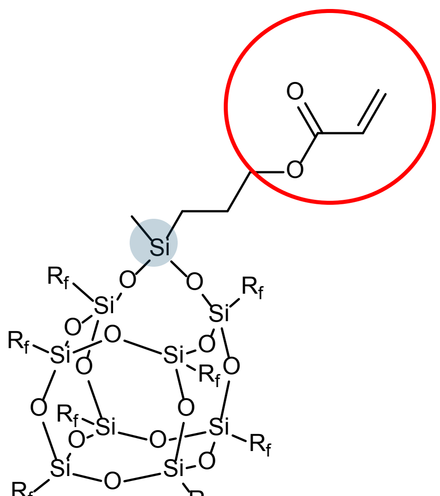
-32.1 ppm



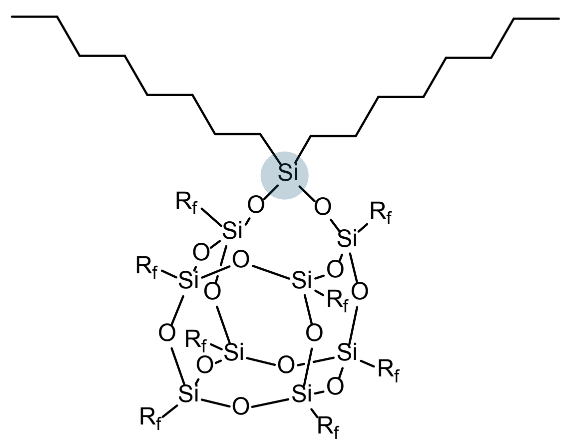
-17.8 ppm



-45.5 ppm



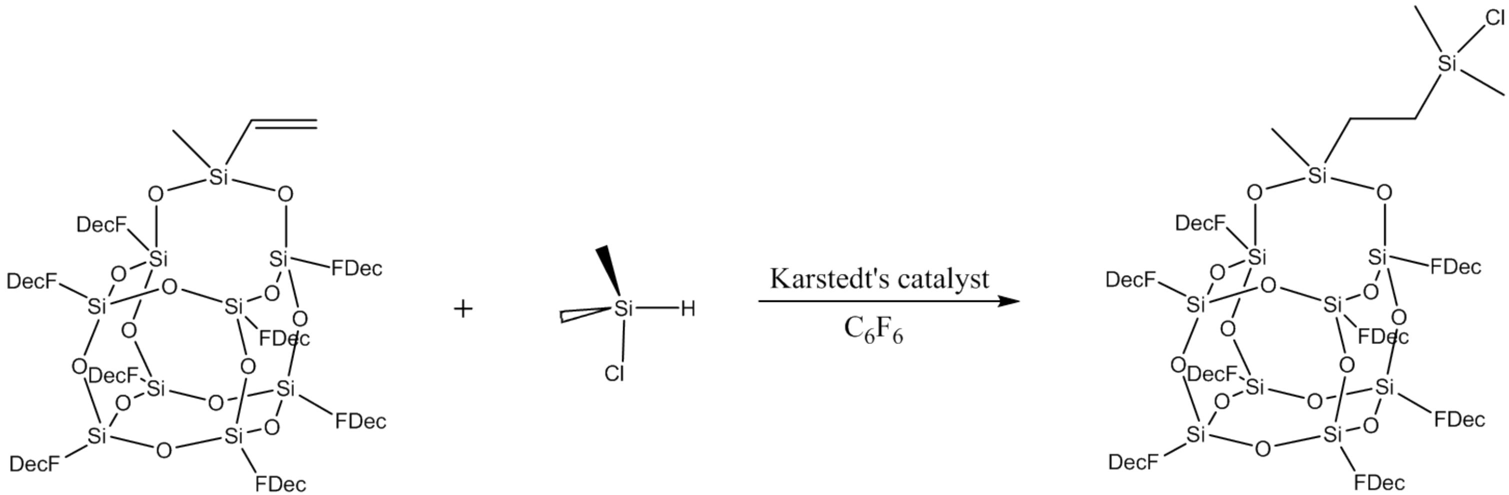
-17.1 ppm



-17.9 ppm

**R = $CH_2CH_2(CF_2)_7CF_3$**

# F-POSS Silane Coupling Reaction

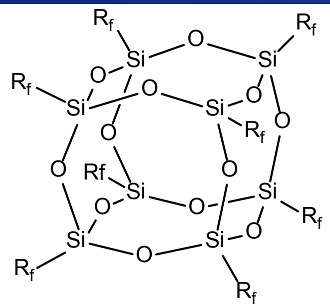



• Chlorosilyl-functional fluoroPOSS compound synthesized from the Pt(II) catalyzed hydrosilyation of vinyl-functional fluoroPOSS and dimethylchlorosilane

• Desired compound successfully synthesized in high yield

• Characterized by $^{1}H$, $^{13}C$, $^{19}F$, and $^{29}Si$ NMR

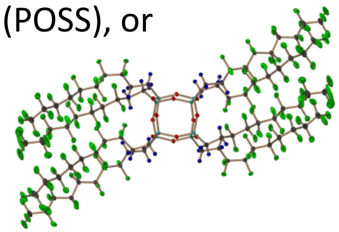
# Introduction to F-POSS



$R_f = -(CH_2)_2(CF_2)_7CF_3$

$(1,1,2,2\text{-tetrahydroperfluorodecyl})_8Si_8O_{12}$ Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS

- hybrid organic-inorganic structure
- well-defined polyhedral architecture
- long-chain fluoroalkyl substituents on periphery of cage

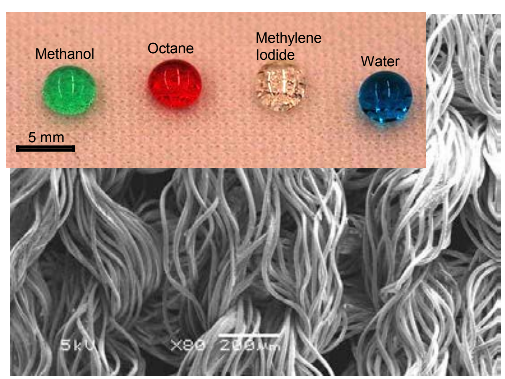


Due to its unique structure, fluorodecyl POSS has one of the lowest surface energies of any crystalline solid currently known

| | |
|---|---|
| - 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

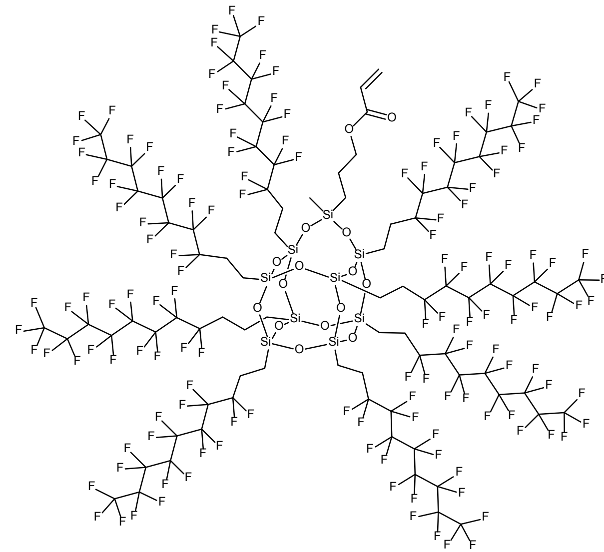


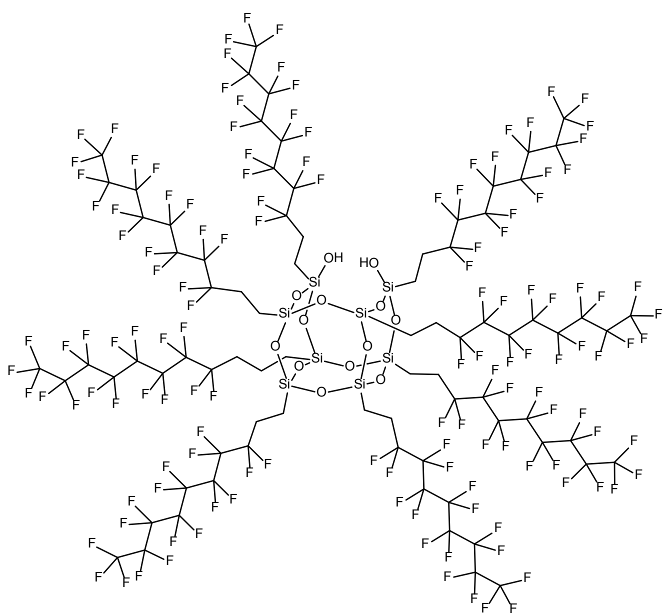

Superamphiphobic dip-coated fabric
Choi *et al*, Adv Mater, **2009**, 21, 2190


Superamphiphobic electrospun surfaces
Tuteja *et al*, PNAS, **2008**, 105, 18200

# 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?*





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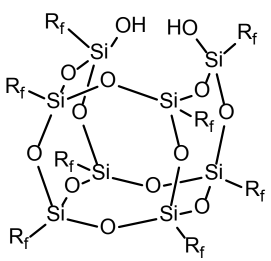
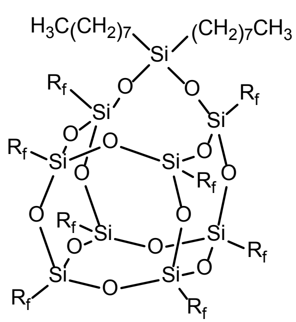
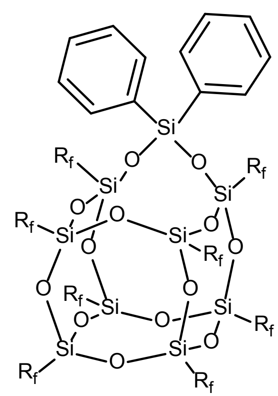
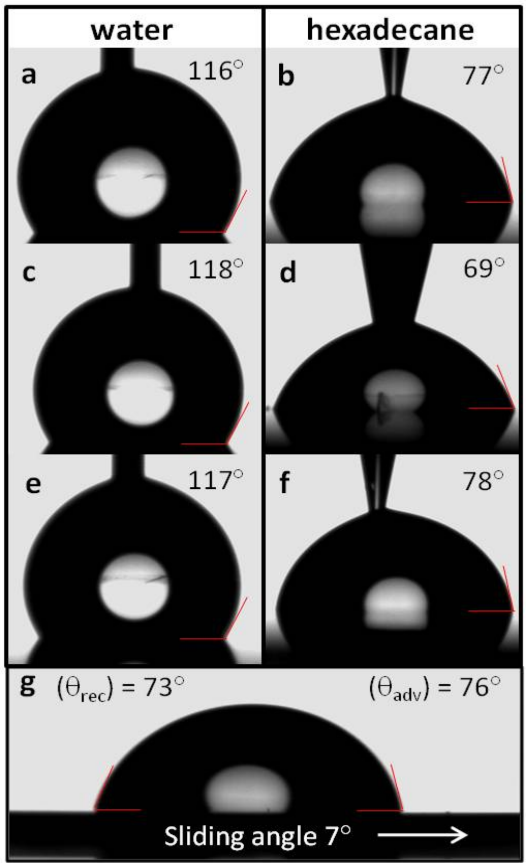


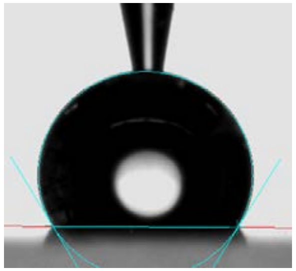







Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10$\mu$L) rolling off surface coated with compound **diphenyl** (g).

# Dynamic Contact Angle Measurements



| *Functional Group on F-POSS* | *water* | | *hexadecane* | |
|---|---|---|---|---|
| | ($\theta_{adv}$) | ($\theta_{rec}$) | ($\theta_{adv}$) | ($\theta_{rec}$) |
| F-POSS* | 124 ± 0.5° | 109.6 ± 0.7° | 79.1 ± 0.4° | 65.1 ± 0.5° |
| Si-$(OH)_2$ | 116.8 ± 0.4° | 111 ± 0.6° | 77.4 ± 0.4° | 74.4 ± 0.8° |
| Si-$(CH_3)(CH=CH_2)$ | 116.2 ± 0.4° | 100.6 ± 0.8° | 78.4 ± 0.3° | 70.6 ± 2.3° |
| Si$((CH_3)((CH_2)_3OC(O)CCH=CH_2)$ | 118.2 ± 1.0° | 90.6 ± 1.0° | 76.8 ± 0.3° | 64.8 ± 1.0° |
| Si-$(CH_3)( (CH_2)_3OC(O)C(CH_3)=CH_2)$ | 117.1 ± 0.6° | 93.8 ± 1.5° | 78.1 ± 0.4° | 63.0 ± 1.2° |
| Si-$(CH_3)((CH_2)_{22}CH_3)$ | 117.9 ± 0.4° | 96.9 ± 1.9° | 78.0 ± 0.4° | 16.2 ± 5.5° |
| Si-$(C_6H_5)_2$ | 116.2 ± 0.4° | 110.5 ± 0.5° | 76.0 ± 0.8° | 73.2 ± 0.4° |
| Si-$((CH_2)_7CH_3)_2$ | 117.9 ± 0.5° | 95.5 ± 0.4° | 69.1 ± 1.2° | 23.1 ± 1.2° |

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).

*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544.

# Free Radical Polymerization

A (Monomer)

Polymer AAAAAAAAAAAA

$-\!(A)\!-_n$

A + B (Monomers)

Copolymer ABAABABAB

AAAAAAABBBBBBB

Initiation

$$\text{Initiator} \xrightarrow{k_d} 2\,\text{I}\bullet$$

$$\text{I}\bullet + \text{Monomer} \xrightarrow{k_i} P_n\bullet$$

Propogation

$$P_n\bullet + \text{Monomer} \xrightarrow{k_p} P_n\bullet$$

Termination

$$2\ \text{Radicals} \xrightarrow{k_t} \text{Polymer}$$

-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

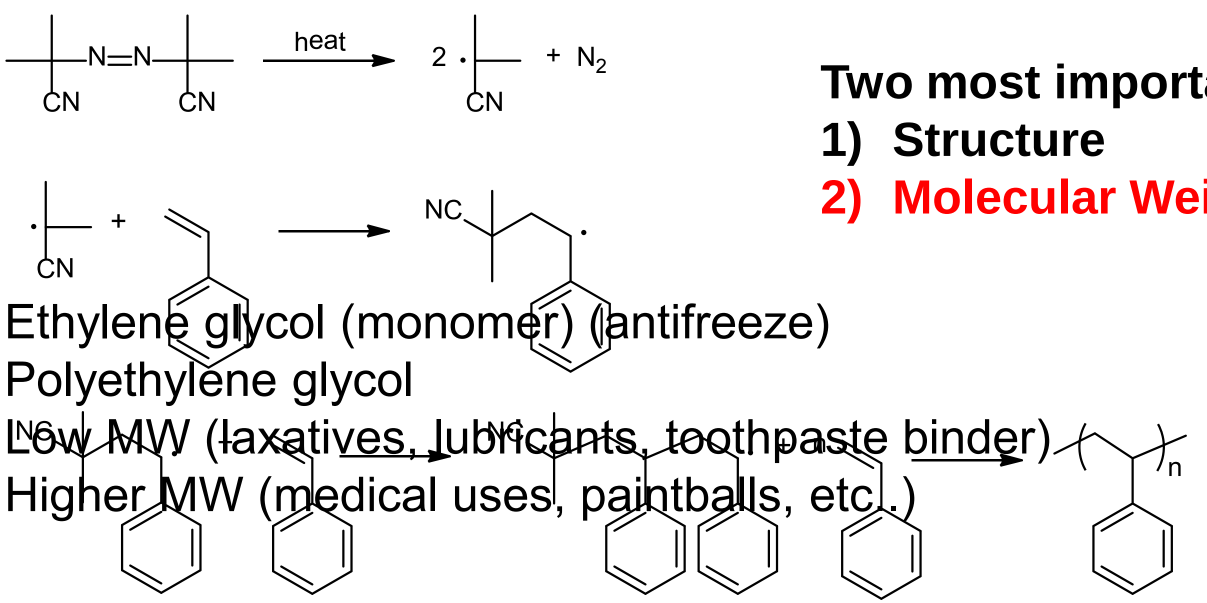
# Free Radical Polymerization

Initiation
Initiator $\xrightarrow{k_d}$ 2 I•
I• + Monomer $\xrightarrow{k_i}$ $P_n$•

Propogation
$P_n$• + Monomer $\xrightarrow{k_p}$ $P_n$•

Termination
2 Radicals $\xrightarrow{k_t}$ Polymer

Example: Polystyrene




Ethylene glycol (monomer) (antifreeze)
Polyethylene glycol
Low MW (laxatives, lubricants, toothpaste binder)
Higher MW (medical uses, paintballs, etc.)

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

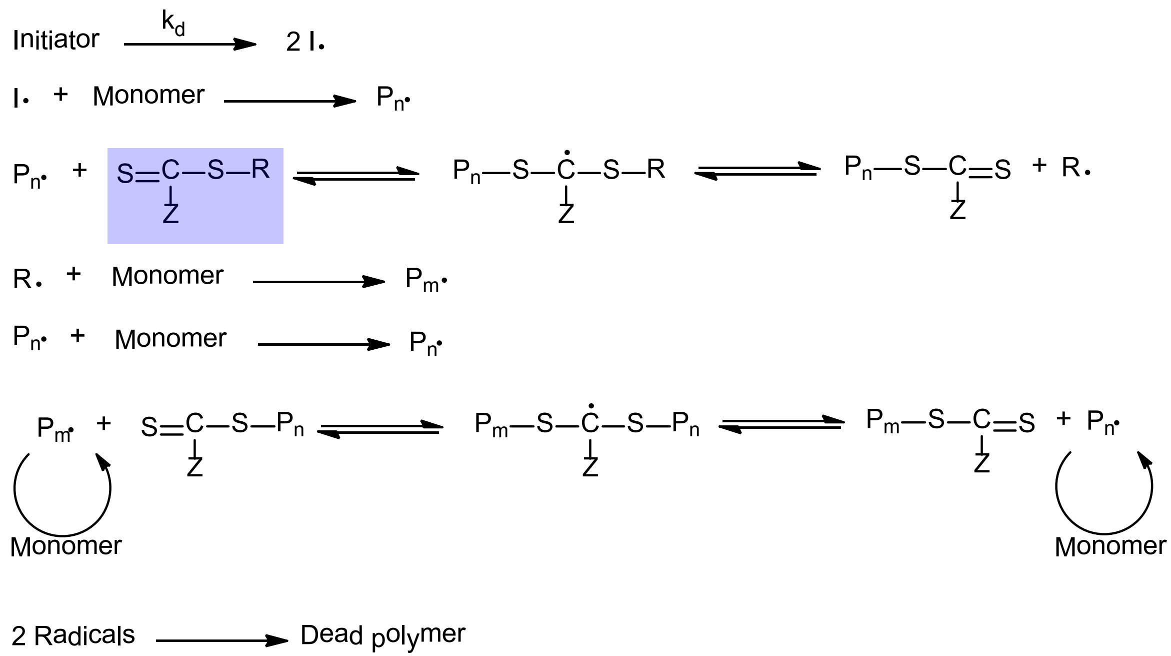
**Two most important factors for polymers:**
1) **Structure**
2) **Molecular Weight**

# Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization

Initiation

Propogation

Termination



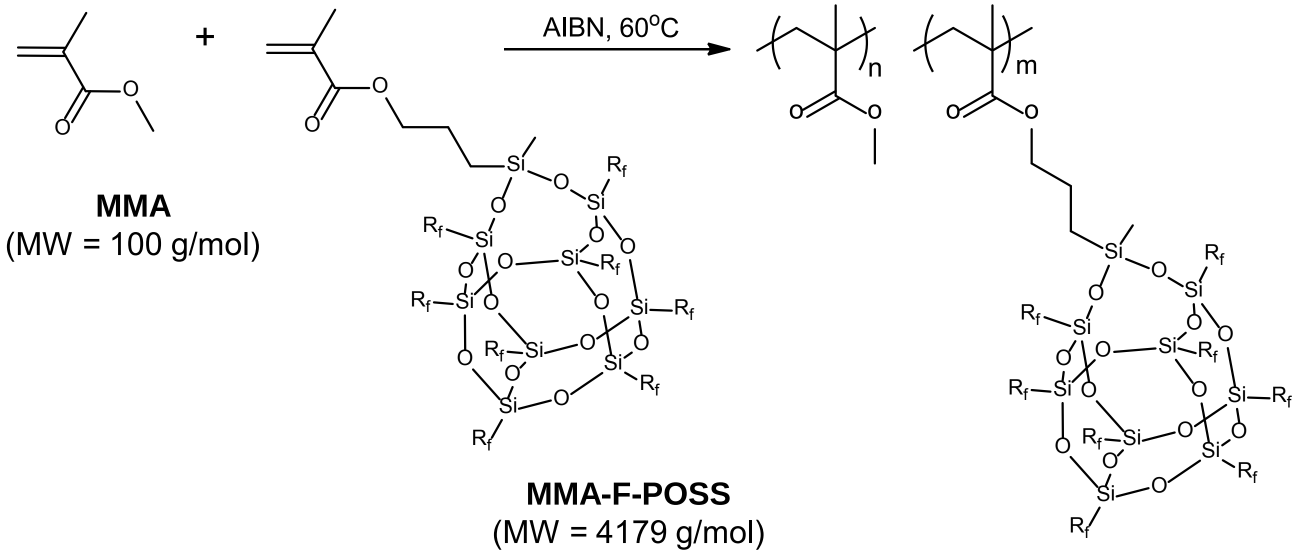

Chain Transfer Agent

RAFT Polymerization

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

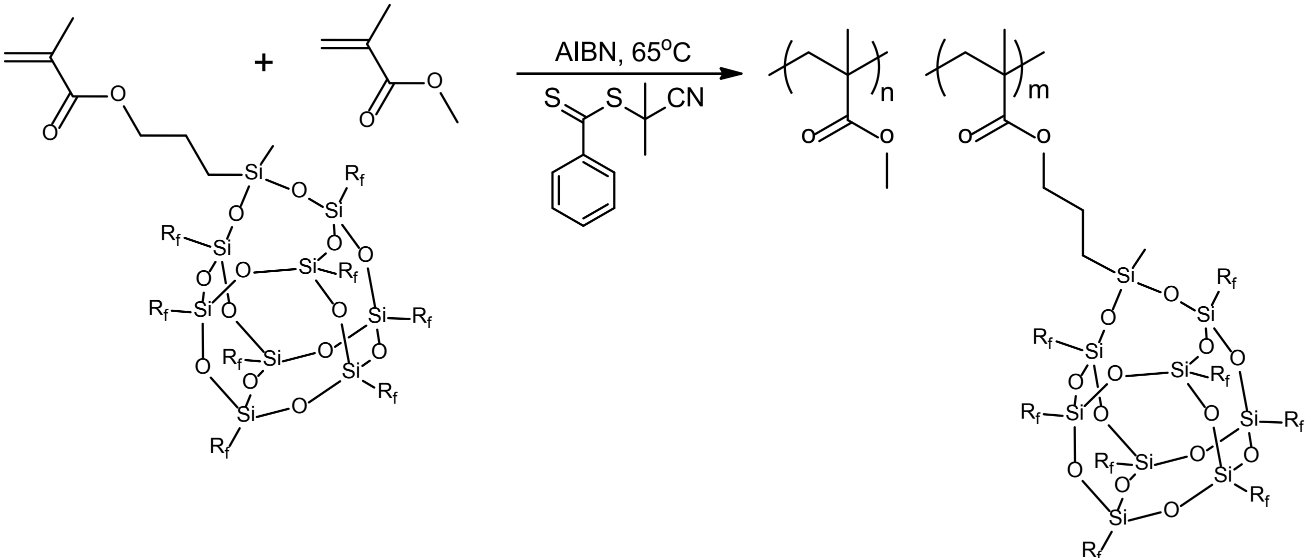

Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living Free Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules* 1998, *31*, 5559−5562

# Free Radical Copolymerizations




- 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 ominiphobic polymer composites.
  - Reaction mechanisms, polymer composites, block copolymers, etc….

# Acknowlegdements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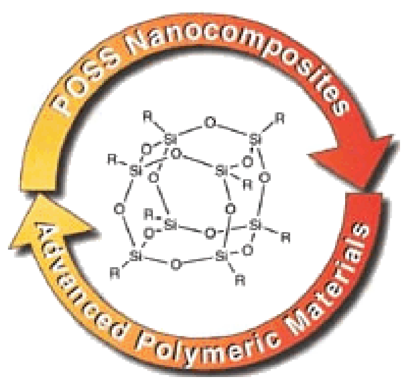
Dr. Greg Yandek
Dr. Josiah Reams
Ms. Yvonne Diaz
Mr. Raymond Compos

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Ms. Dana Pinson
Capt. Rebecca Stone

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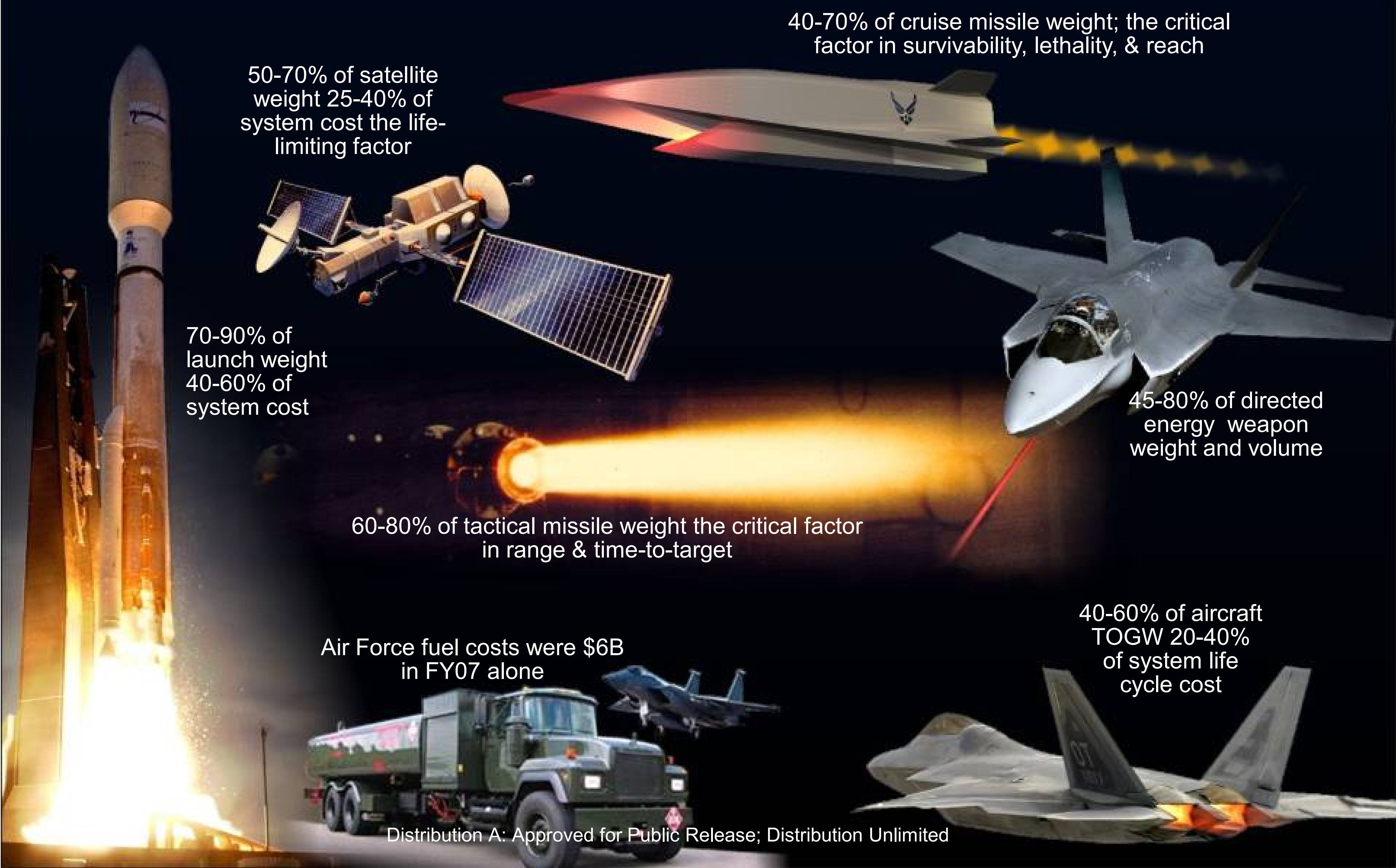
Air Force Office of Scientific Research

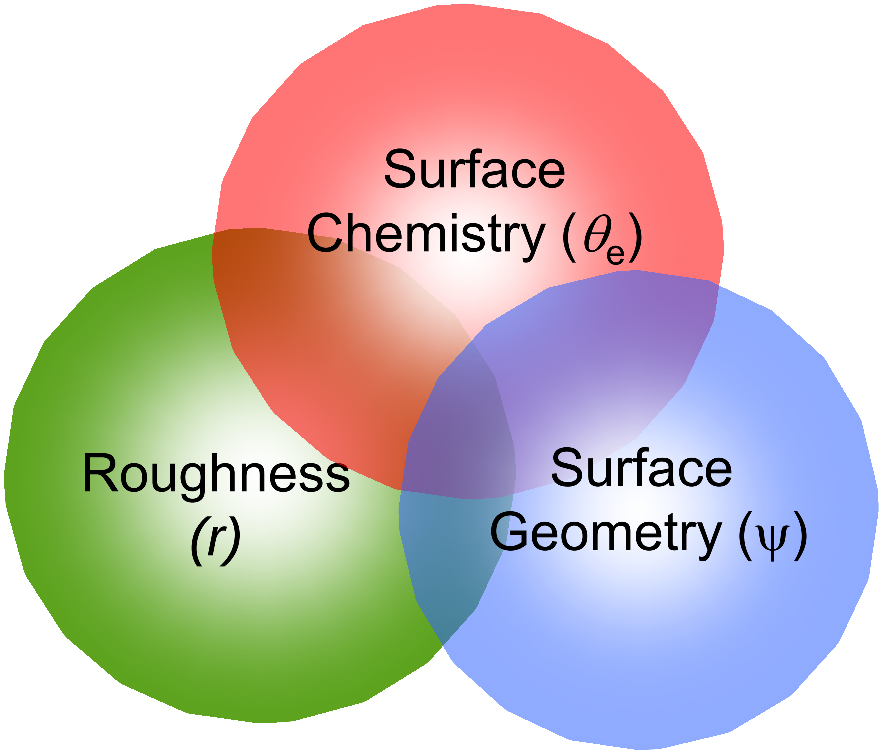
Air Force Research Laboratory, Propulsion Directorate

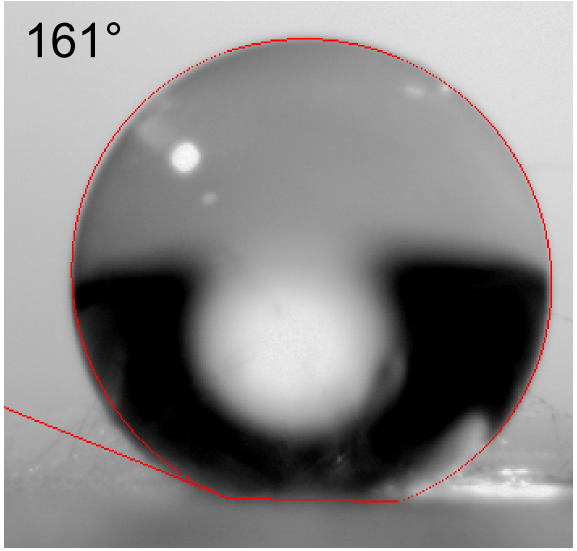
# Propulsion & Power are Important!



# Designing Superoleophobic Surfaces

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




Superhydrophobic
$\theta > 150°$

PMMA + 44 wt% POSS

electrospun coating (beads on a string) morphology

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