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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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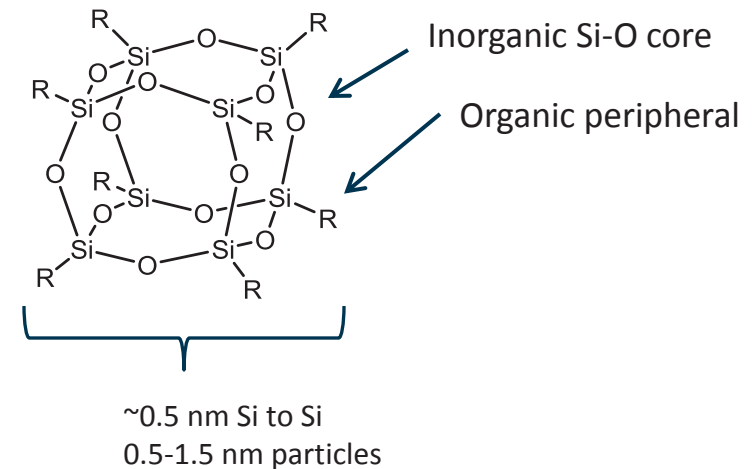
*FLUOROPOLYMER 2012*



# Polyhedral Oligomeric Silsesquioxane POSS (RSiO<sub>1.5</sub>)<sub>n</sub>



- 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



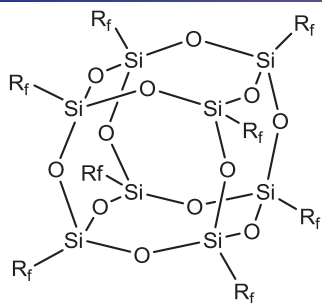
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Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110*, 2081.

Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* **2004**, *8*, 21.

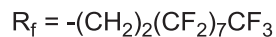
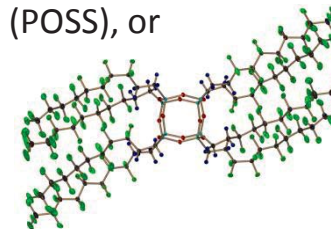


# Introduction to F-POSS



(1,1,2,2-tetrahydroperfluorodecyl)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS

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



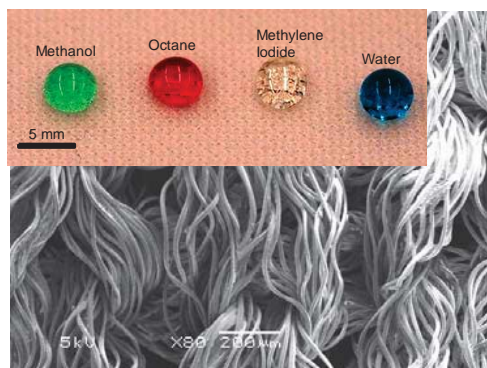
Due to its unique structure, fluorodecyl POSS has one of the lowest surface energies of any crystalline solid currently known

- |                             |            |
|-----------------------------|------------|
| - fluorodecyl POSS          | 9.3 mN/m   |
| - polytetrafluoroethylene   | 18-20 mN/m |
| - CF <sub>3</sub> monolayer | 6.7 mN/m   |

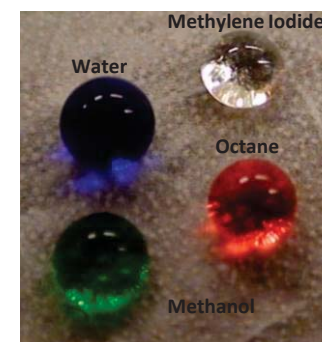
Low surface energy and other unique properties of fluorodecyl POSS has enabled the development of various types of tunable non-wetting polymeric surfaces



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



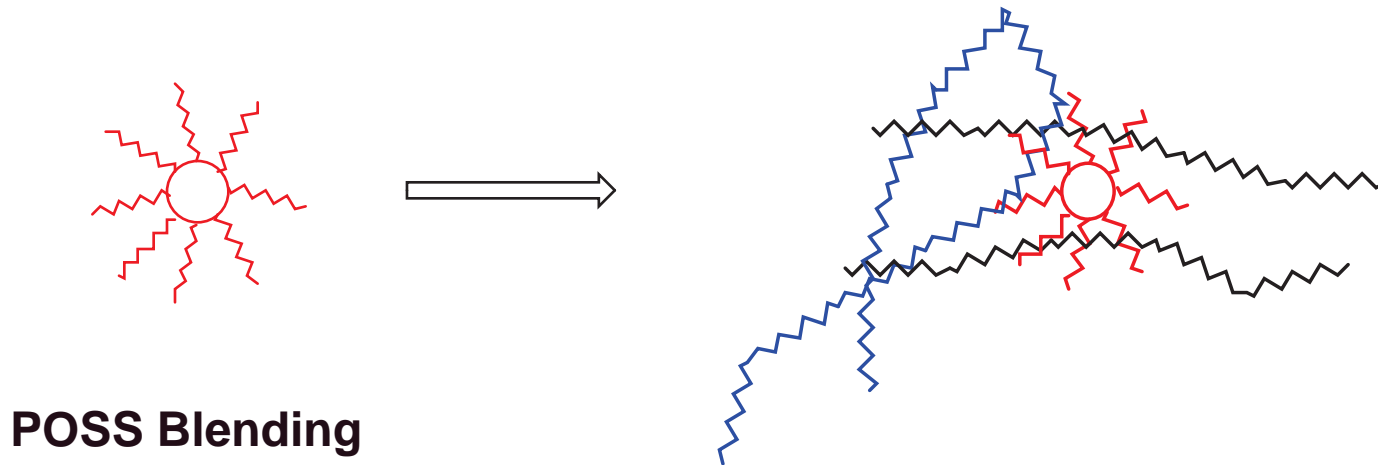
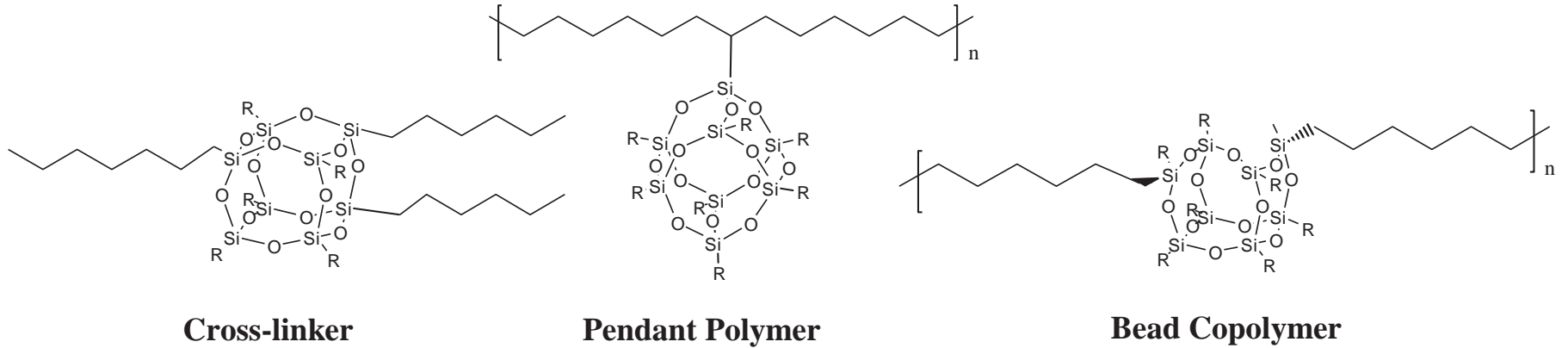
Superamphiphobic dip-coated fabric  
Choi *et al*, Adv Mater, **2009**, 21, 2190



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



# POSS Incorporation in Polymers

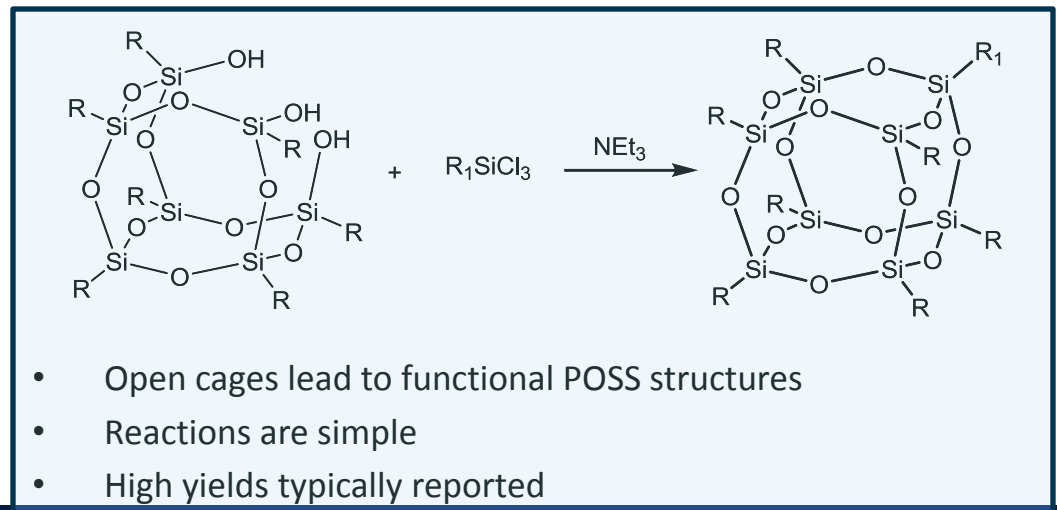




# Functional F-POSS (Open-Caged)

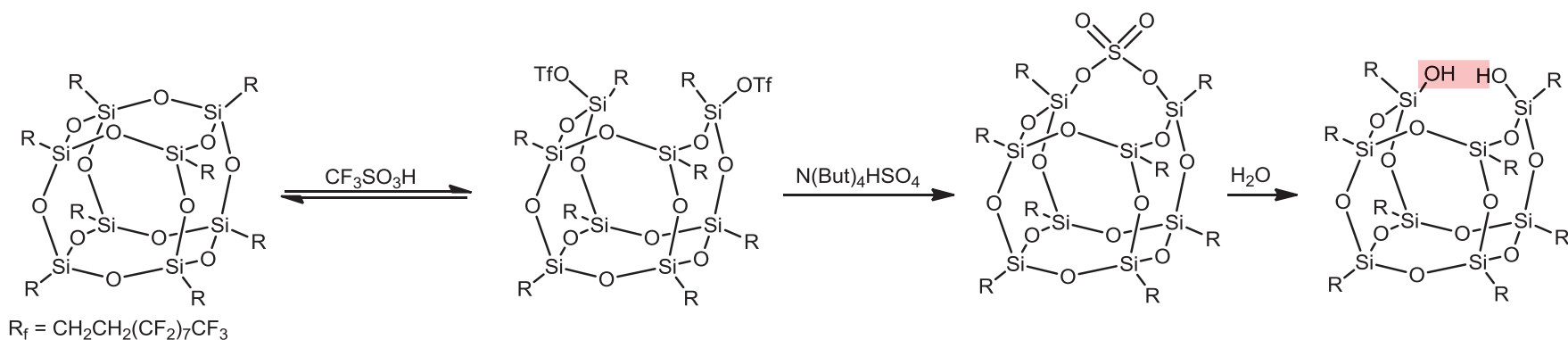


- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a *building block* material 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....



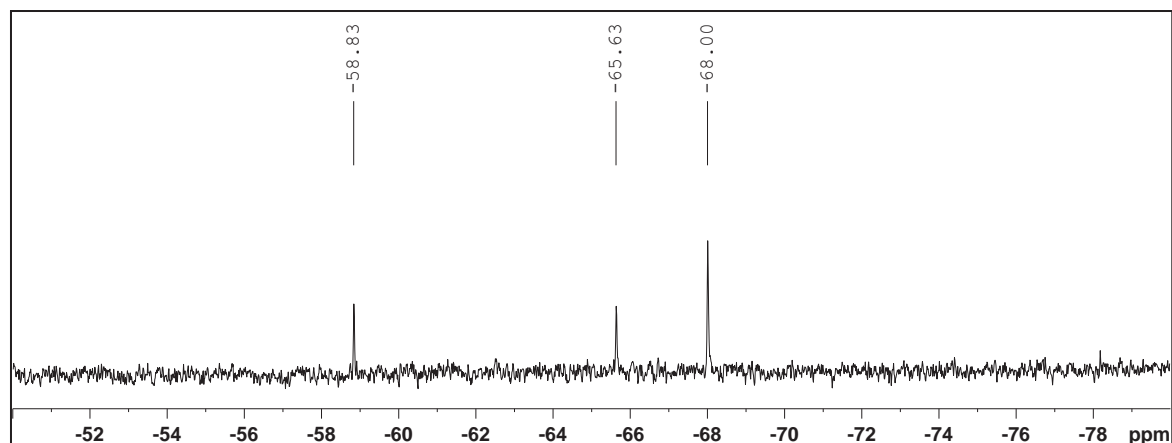


# Incompletely Condensed Silsesquioxane



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

$^{29}\text{Si}$  NMR in  $\text{C}_6\text{F}_6$  of disilanol F-POSS

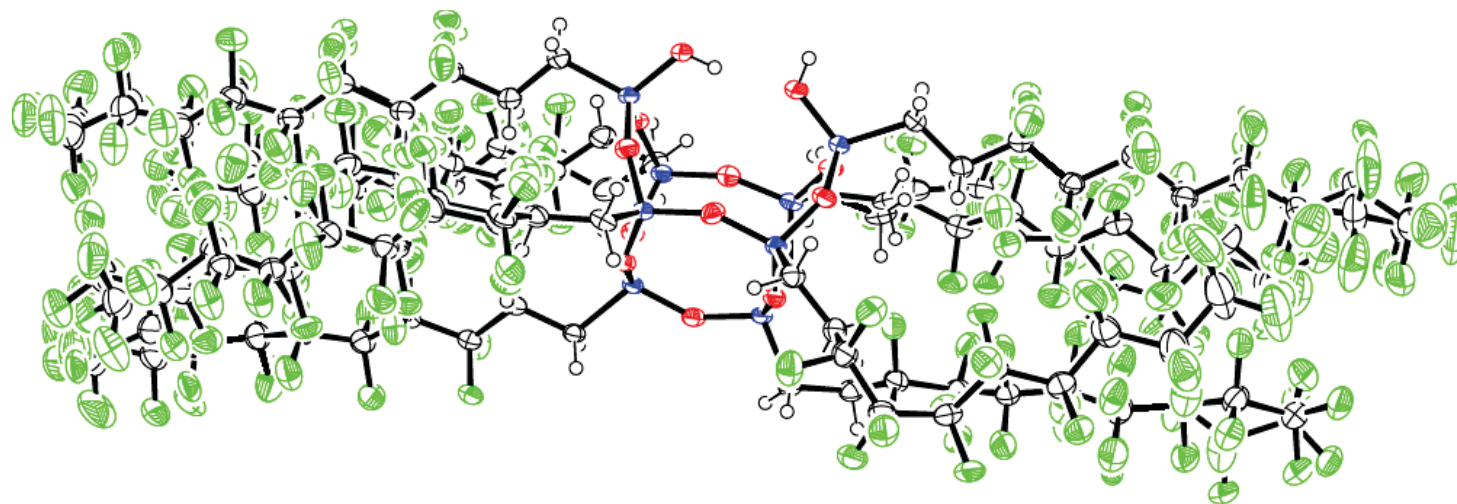
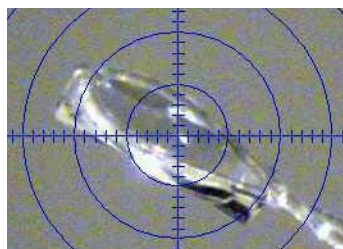


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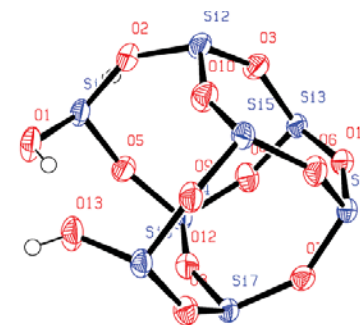
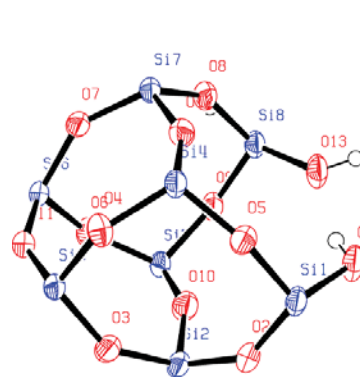
Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Haddad, T. S.; Mabry, J. M. ACS Symposium Series" Advances in Fluorine Containing Polymers 2012 1106, 95-109.  
Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, *133*, 20084.



# X-Ray Crystal Structure of Disilanol



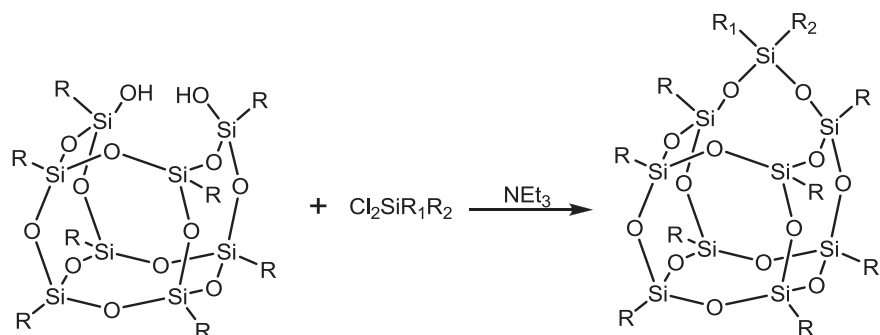
- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- $M_r$  = monoclinic, space group  $P2(1)/c$ ,  $a=11.84(10)$  Å,  $b=57.11(6)$  Å,  $c=19.06(2)$  Å,  $\alpha=90.00^\circ$ ,  $\beta=92.21(10)^\circ$ ,  $\gamma=90.00^\circ$ ,  $V=12878(2)$  Å<sup>3</sup>



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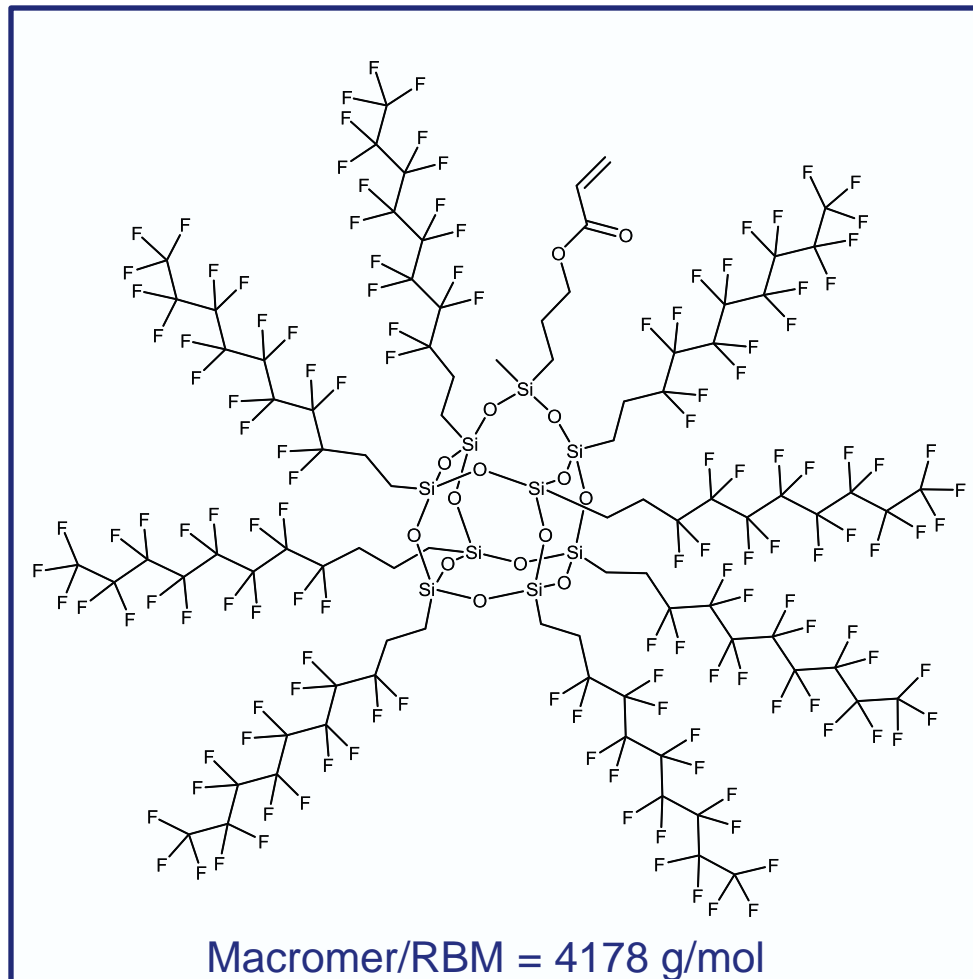


# Edge Capping Reactions



R = CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>CF<sub>3</sub>  
R<sub>1</sub> = alkyl or aromatic  
R<sub>2</sub> = alkyl or aromatic

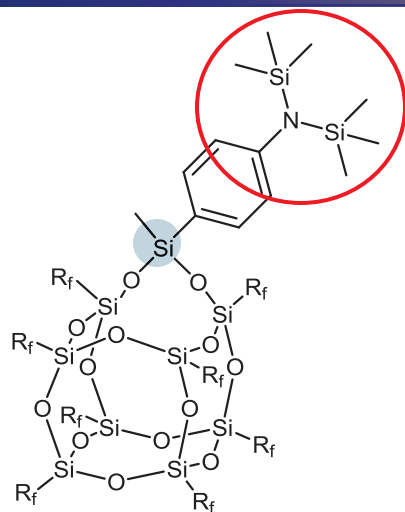
- Edge capping reactions typically have 40-90% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction



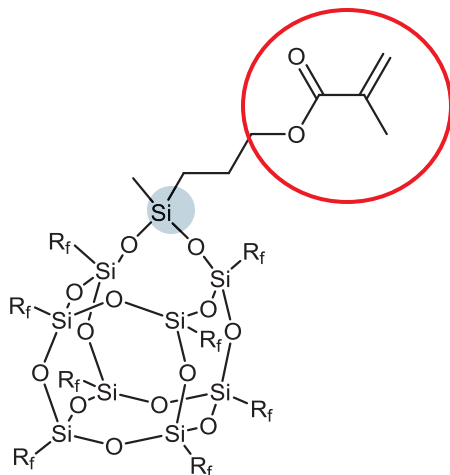
Macromer/RBM = 4178 g/mol



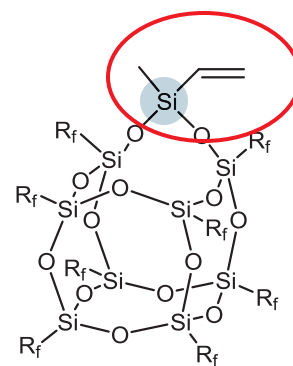
# F-POSS Structures Synthesized



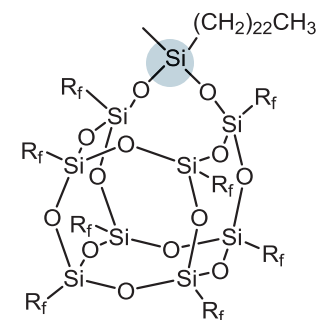
-29.5 ppm



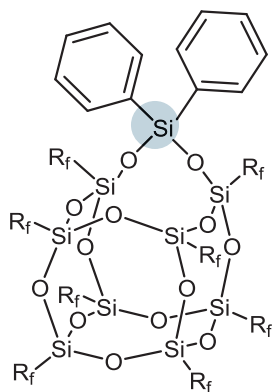
-17.8 ppm



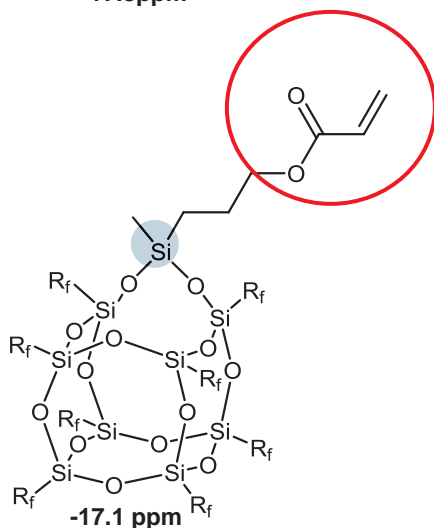
-32.1 ppm



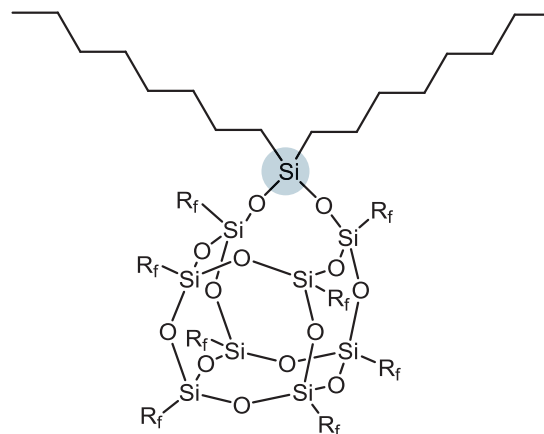
-17.8 ppm



-45.5 ppm



-17.1 ppm



-17.9 ppm

R = CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>CF<sub>3</sub>

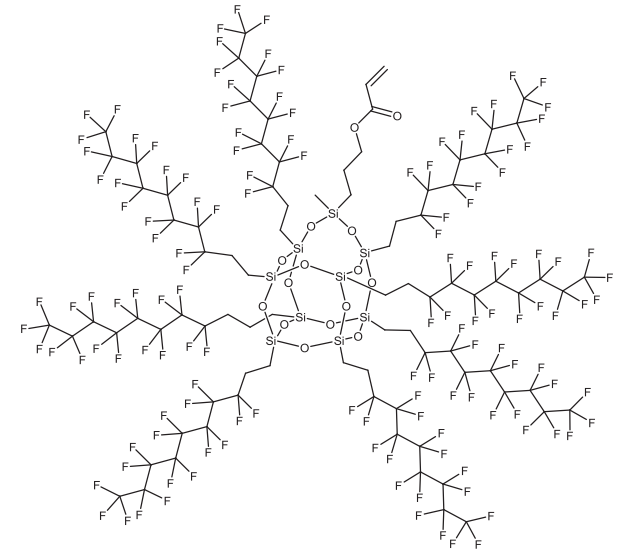
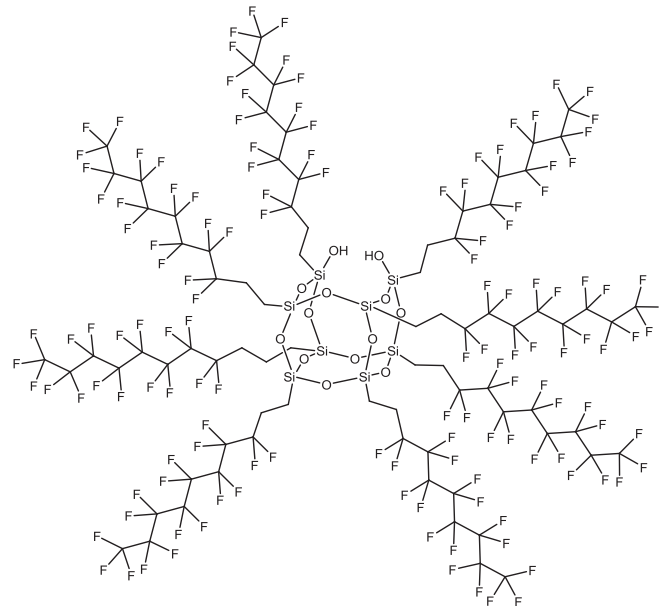
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# Contact Angle Measurements



- 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?*

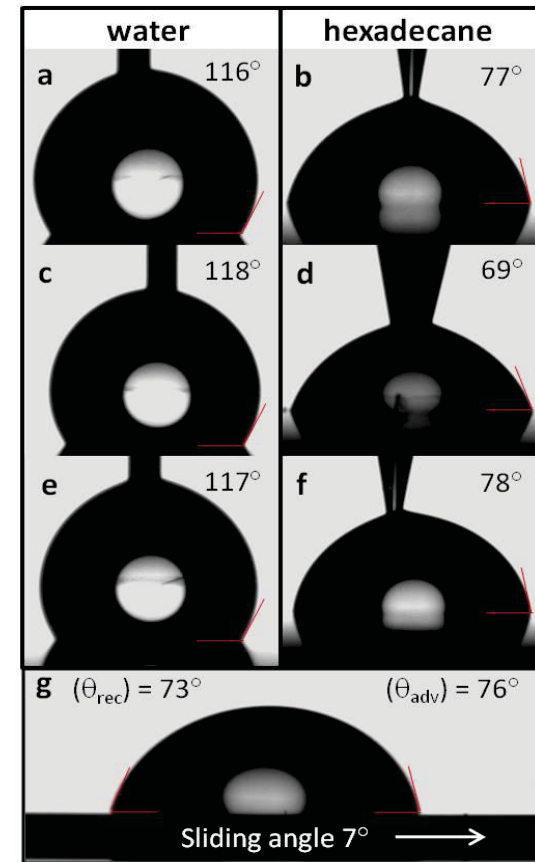
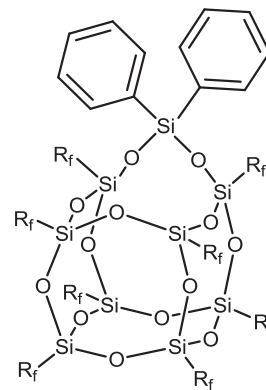
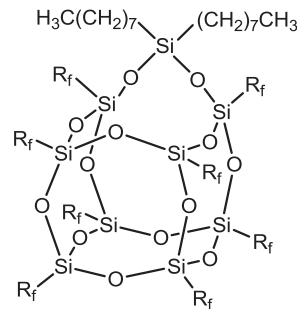
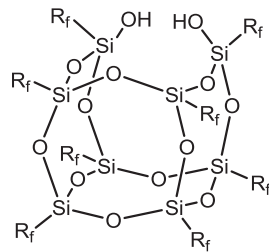




# Contact Angle Measurements



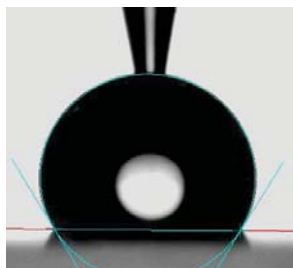
- Non-wetting surfaces can be developed by a combination of three parameters
  - Chemical functionality (high fluorine content)
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  - Surface Geometry (re-entrant curvature)
- *What type of influence will functional groups have on F-POSS surface properties?*
- *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



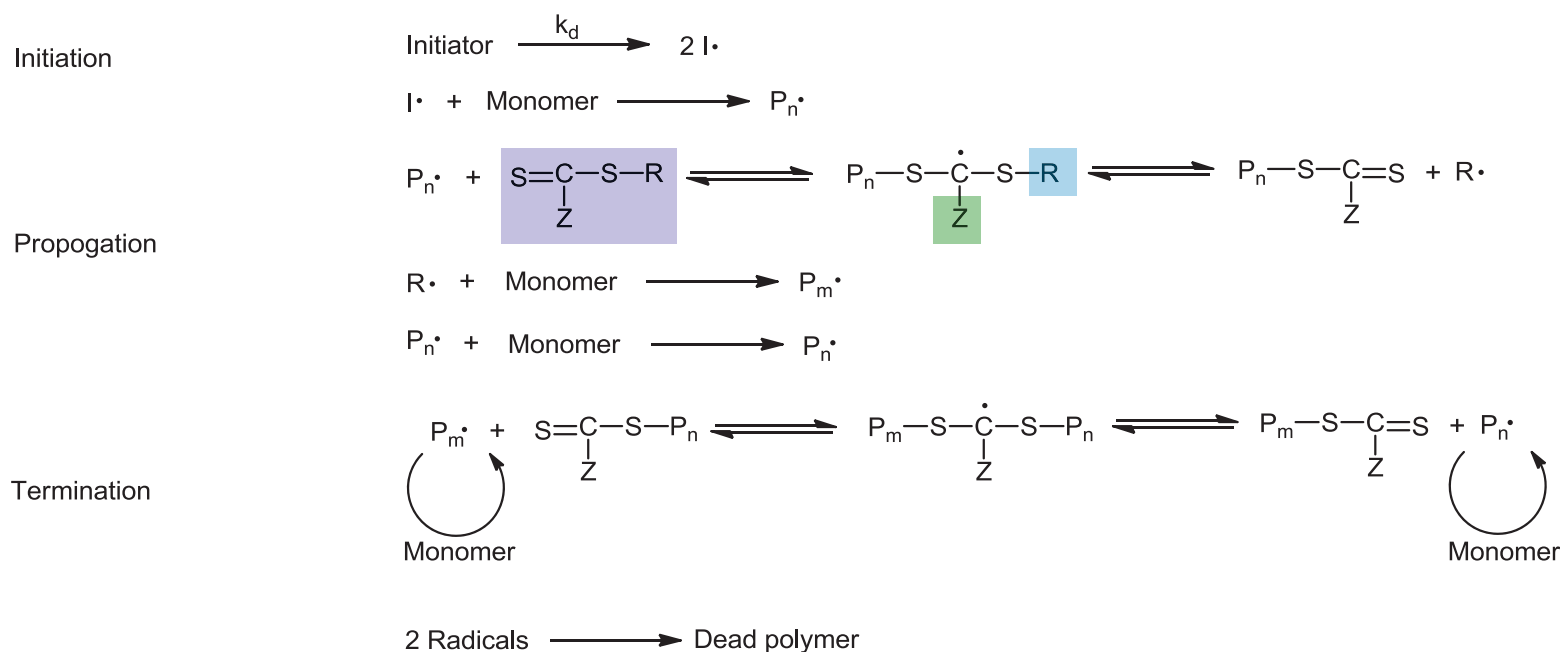
<i>Functional Group on F-POSS</i>	<i>water</i>		<i>hexadecane</i>	
	$(\theta_{adv})$	$(\theta_{rec})$	$(\theta_{adv})$	$(\theta_{rec})$
F-POSS*	$124 \pm 0.5^\circ$	$109.6 \pm 0.7^\circ$	$79.1 \pm 0.4^\circ$	$65.1 \pm 0.5^\circ$
Si-(OH) <sub>2</sub>	$116.8 \pm 0.4^\circ$	$111 \pm 0.6^\circ$	$77.4 \pm 0.4^\circ$	$74.4 \pm 0.8^\circ$
Si-(CH <sub>3</sub> )(CH=CH <sub>2</sub> )	$116.2 \pm 0.4^\circ$	$100.6 \pm 0.8^\circ$	$78.4 \pm 0.3^\circ$	$70.6 \pm 2.3^\circ$
Si((CH <sub>3</sub> )((CH <sub>2</sub> ) <sub>3</sub> OC(O)CCH=CH <sub>2</sub> ))	$118.2 \pm 1.0^\circ$	$90.6 \pm 1.0^\circ$	$76.8 \pm 0.3^\circ$	$64.8 \pm 1.0^\circ$
Si-(CH <sub>3</sub> )( (CH <sub>2</sub> ) <sub>3</sub> OC(O)C(CH <sub>3</sub> )=CH <sub>2</sub> )	$117.1 \pm 0.6^\circ$	$93.8 \pm 1.5^\circ$	$78.1 \pm 0.4^\circ$	$63.0 \pm 1.2^\circ$
Si-(CH <sub>3</sub> )((CH <sub>2</sub> ) <sub>22</sub> CH <sub>3</sub> )	$117.9 \pm 0.4^\circ$	$96.9 \pm 1.9^\circ$	$78.0 \pm 0.4^\circ$	$16.2 \pm 5.5^\circ$
Si-(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	$116.2 \pm 0.4^\circ$	$110.5 \pm 0.5^\circ$	$76.0 \pm 0.8^\circ$	$73.2 \pm 0.4^\circ$
Si-((CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> ) <sub>2</sub>	$117.9 \pm 0.5^\circ$	$95.5 \pm 0.4^\circ$	$69.1 \pm 1.2^\circ$	$23.1 \pm 1.2^\circ$

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).

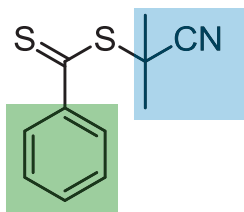
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# Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization



## Chain Transfer Agent



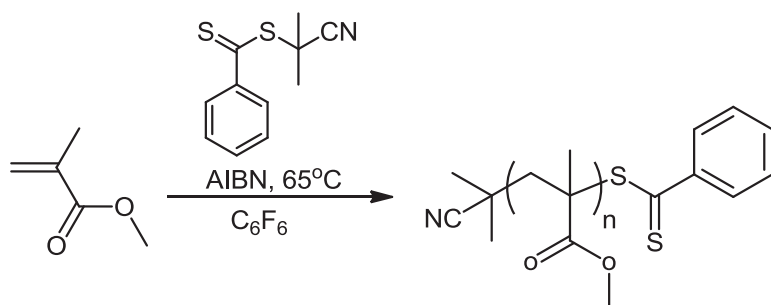
## RAFT Polymerization

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

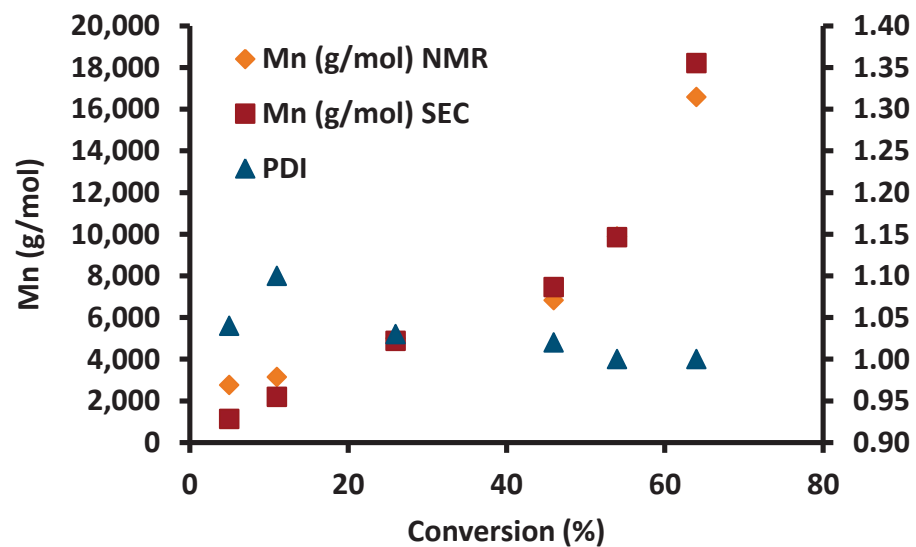
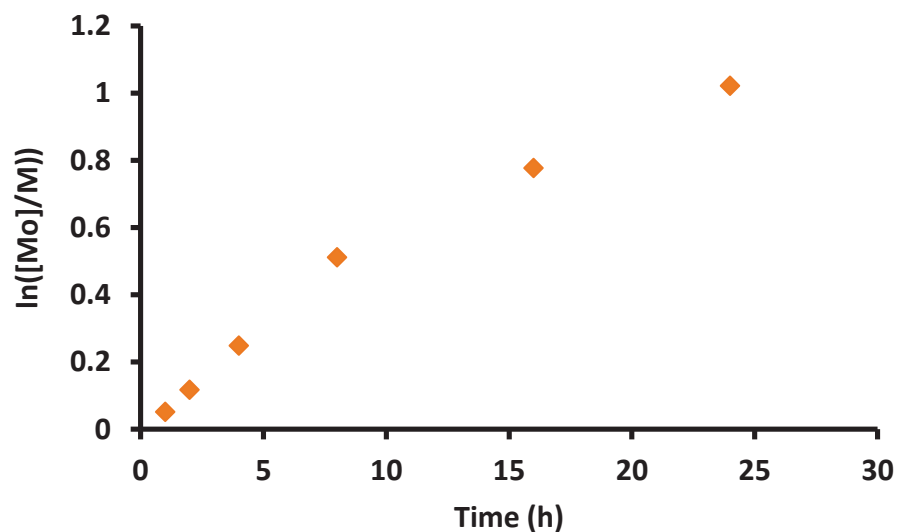
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# RAFT polymerization of MMA in $C_6F_6$



- Testing RAFT in fluorinated solvent
- RAFT polymerization proceeds in  $C_6F_6$
- Best control in first 10 hours

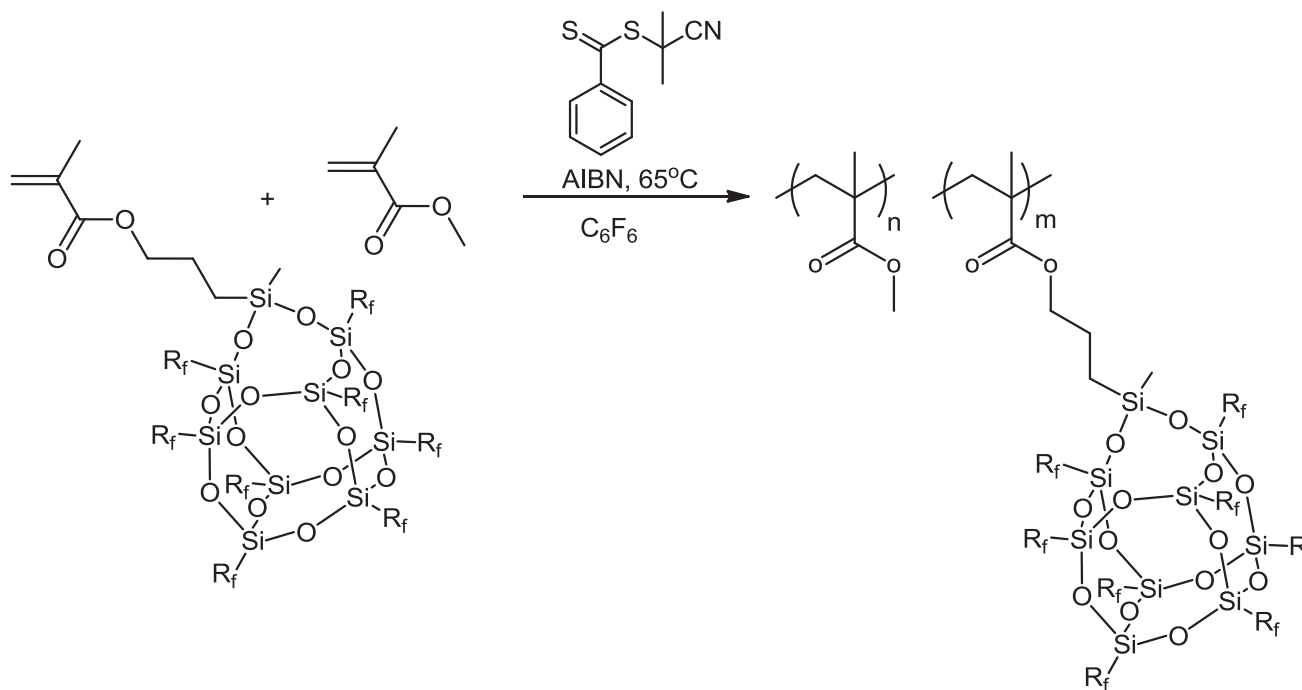


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SEC MALs: RI and LS detector (Wyatt), 1.0 mL/min, 30 min, THF.



# RAFT copolymerization of P(F-POSS-MA)- co-PMMA



RAFT polymerizations are performed in fluorinated solvent following methods developed for MMA.



# RAFT copolymerization of P(F-POSS-MA)- co-PMMA



F-POSS wt %	M <sub>n</sub>		Conv %	water		hexadecane	
	(g/mol)	PDI		(θ <sub>adv</sub> )	(θ <sub>rec</sub> )	(θ <sub>adv</sub> )	(θ <sub>rec</sub> )
<b>F-POSS-MMA</b>				117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°
<b>0</b>	45,000	1.05	80	77.8 ± 1.3°	57.8 ± 2.5°	wetted	wetted
<b>1</b>	53,700	1.08	72	109.2 ± 2.4°	61.5 ± 1.9°	67.8° ± 1.4	wetted
<b>5</b>	22,900	1.01	30	117.8 ± 1.6°	95.7 ± 5.9°	76.7 ± 1.1°	68.8 ± 1.9°
<b>10</b>	26,600	1.01	29	118.2 ± 1.4°	101.1 ± 2.5°	77.2 ± 0.4°	69.5 ± 2.1°
<b>25</b>	36,600	1.03	41	120.8 ± 97.0°	97.0 ± 2.4°	82.9 ± 0.4°	74.6 ± 2.0°

SEC-MALS conditions: 25°C, flow rate (1 mL/min), solvent (Asahiklin-225), concentration measured with RI detector. Contact angle conditions: polymer solutions (20 mg/mL) were spun cast on SiO<sub>2</sub> wafers at 900 rpm with a 30 second dwell time.

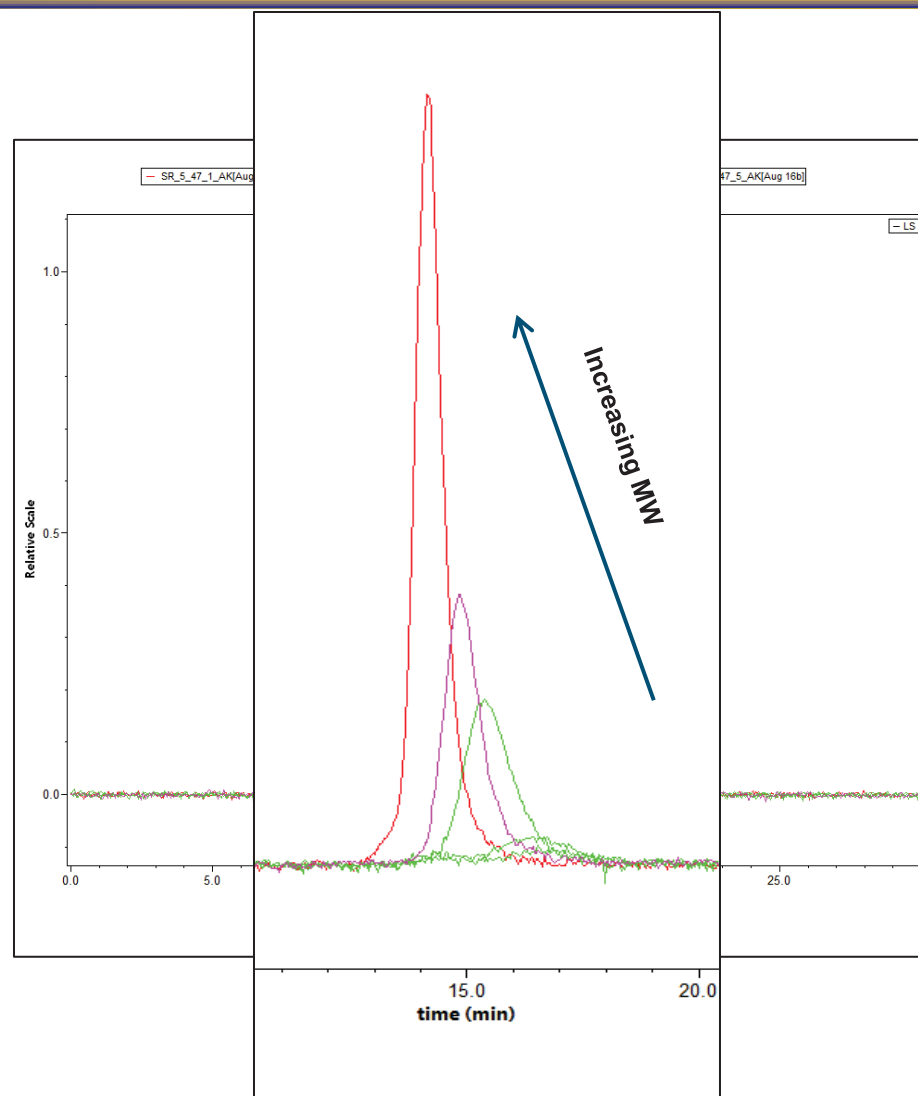


# RAFT copolymerization of P(F-POSS-MA)-co-PMMA



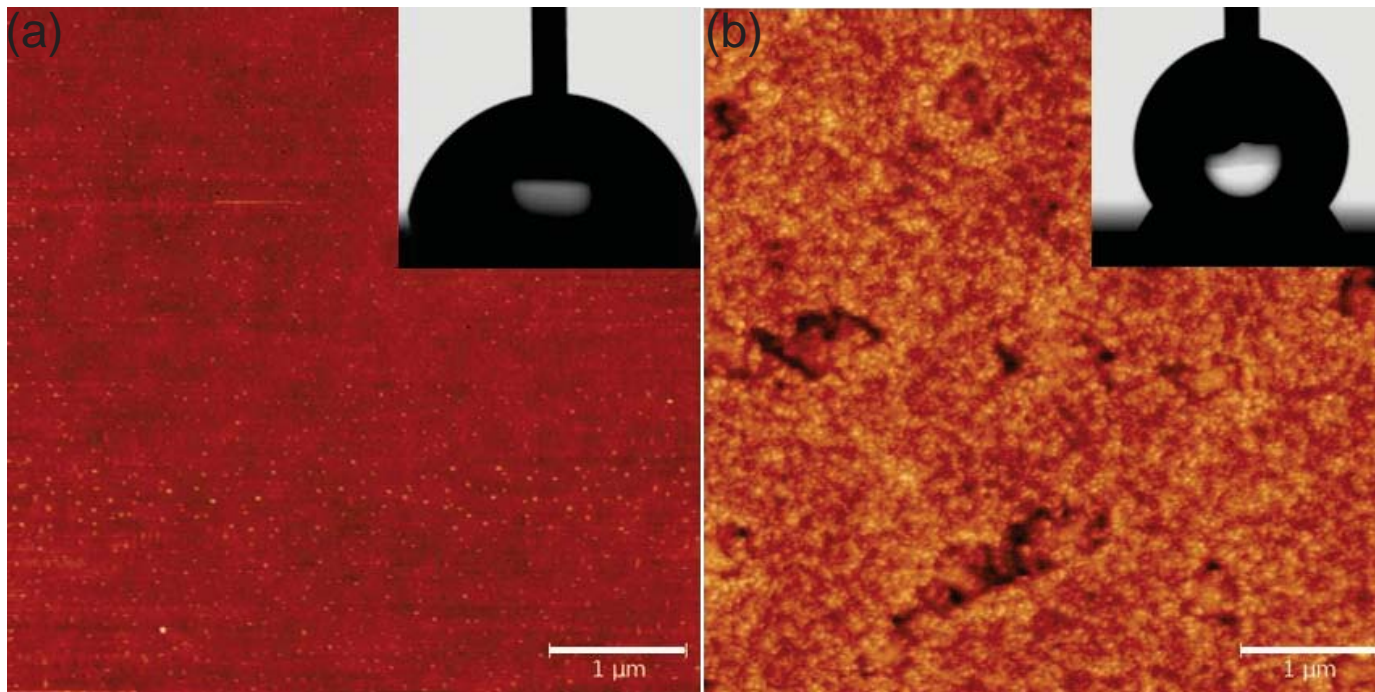
10% F-POSS	$M_n$	Conv	
Time (hr)	(g/mol)	PDI	%.
1*	4100	2.2	8
2	4,700	1.2	16
4	11,300	1.04	28
8	26,600	1.03	51

- **Determining impact of F-POSS on polymerization conditions**
  - No homopolymerization possible
  - Cannot polymerize well above 50 wt % F-POSS-MMA loading
  - Controlled at beginning of RAFT polymerization
  - \*NMR  $M_n$  value





# AFM of P(F-POSS-MA)-co-PMMA



AFM images of spun cast films of copolymers on  $\text{SiO}_2$ . Corner images are pictures of static contact angle measurements with hexadecane drops. a) 1 wt.% F-POSS copolymer b) 25 wt. % F-POSS copolymer. Z scale 0 – 15 nm

AFM: Chris Sahagan

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# Copolymerization Summary



- Copolymerizations produced F-POSS based copolymers.
- Polymerization have trouble at higher F-POSS monomer feed ratios and are more controlled at lower conversion with RAFT initiator.
- However, we really want the homopolymer!

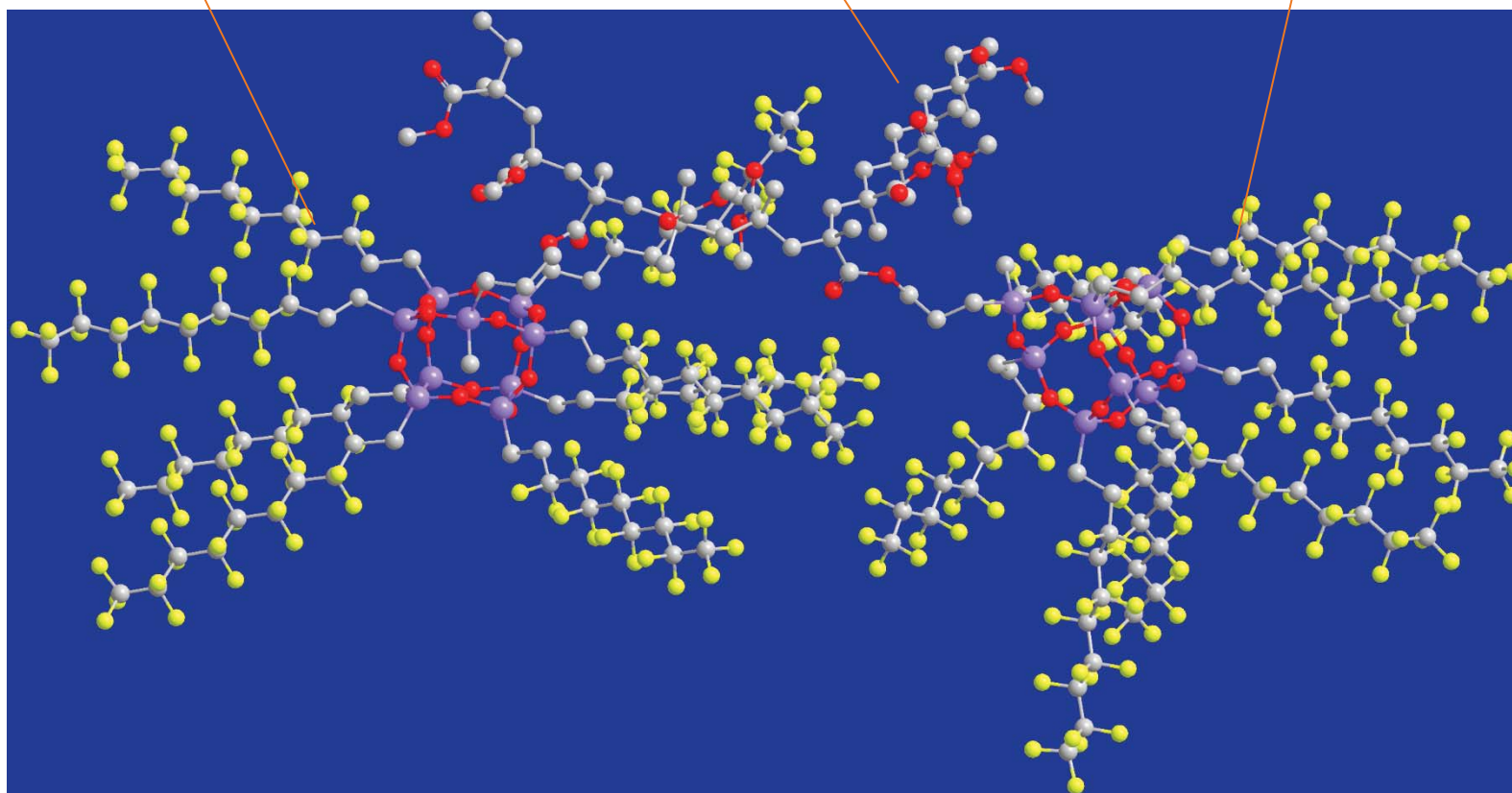


# Is it crowded in here?

F-POSS-MA

PMMA backbone (10 rpu)

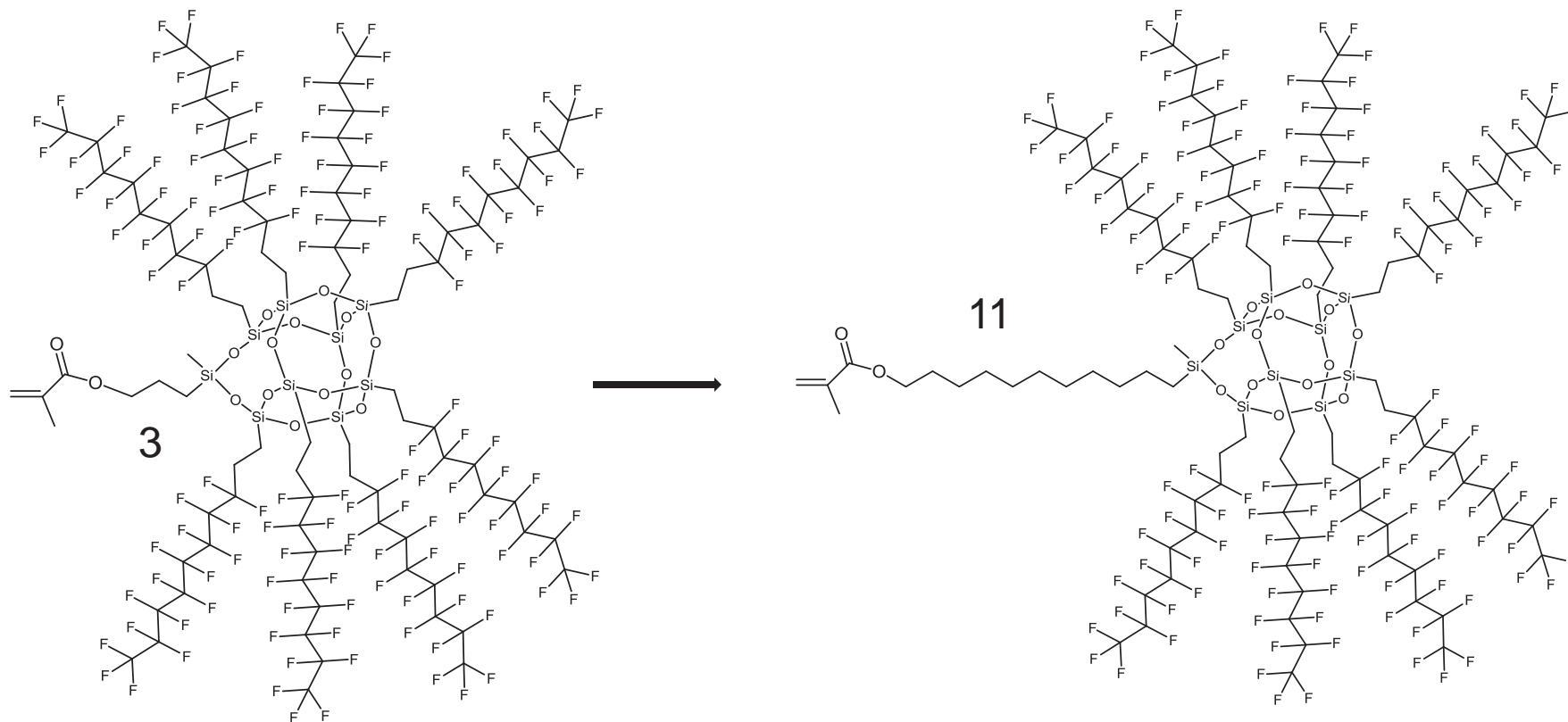
F-POSS-MA



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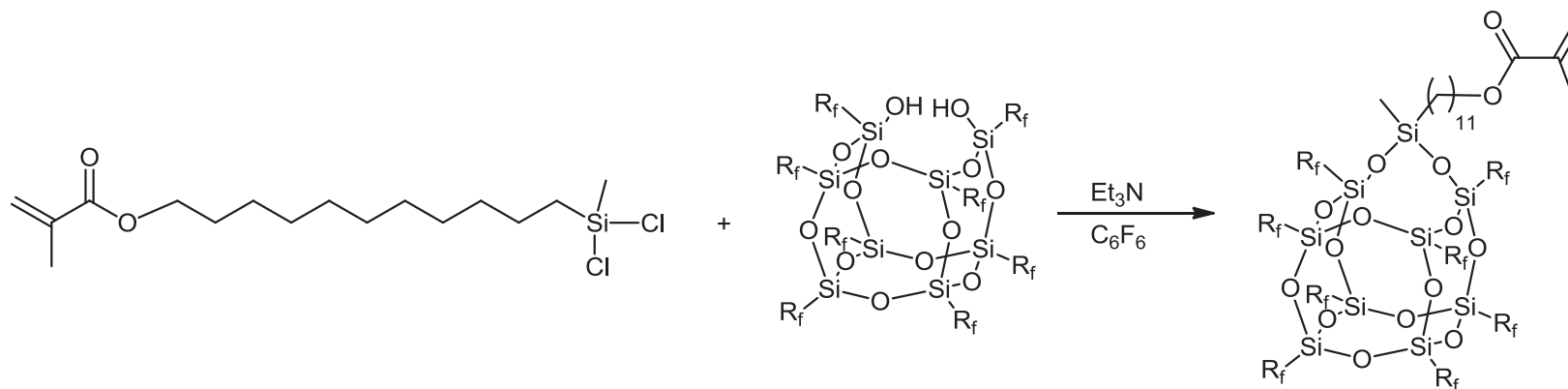
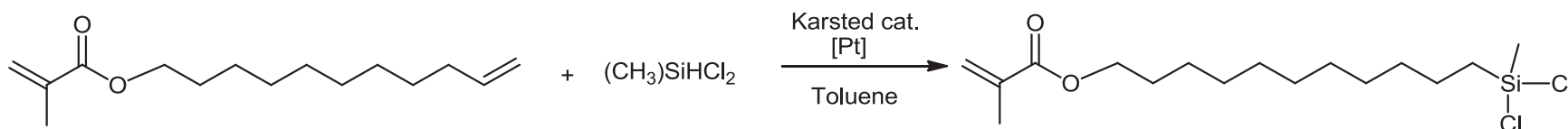
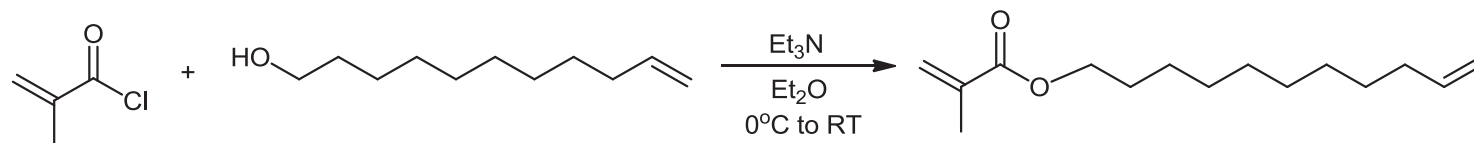
# Extend the Chain



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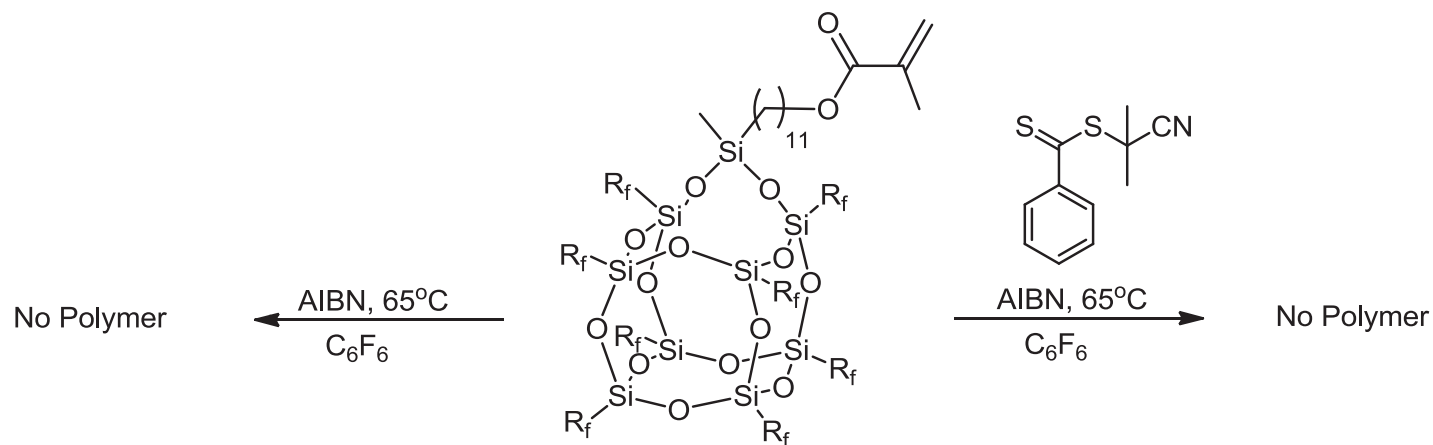


# Long Chain Monomer Synthesis





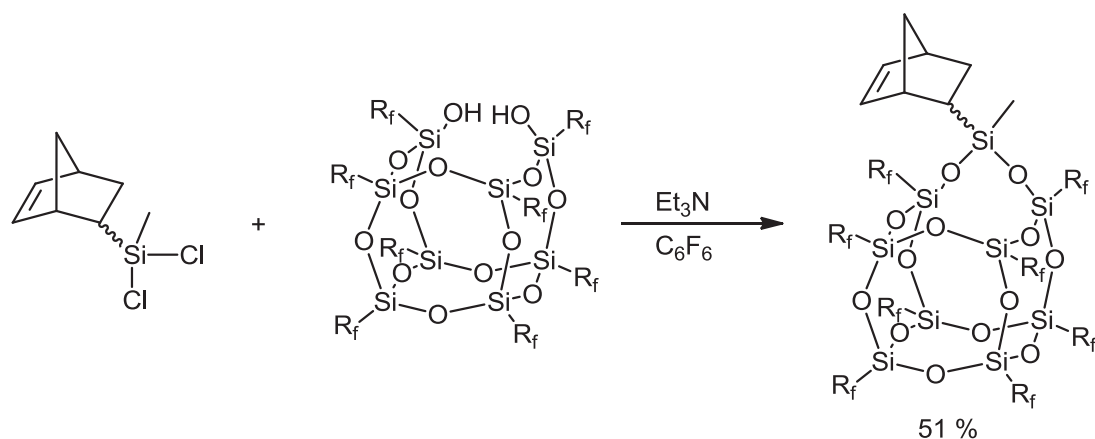
# Polymerization



- Still no sign of free radical homopolymerization
- Copolymerizations will be attempted next



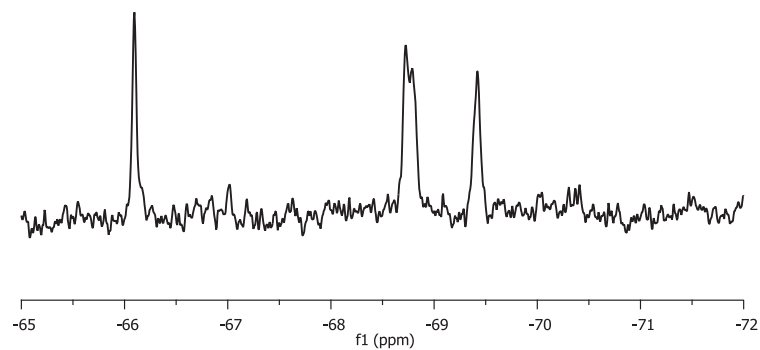
# Norbornene Synthesis



- Coupling reaction works well
  - Work-up is a bit tricky due to similar solubilities of disilanol, T8 side product, and product
  - Room for further improvement



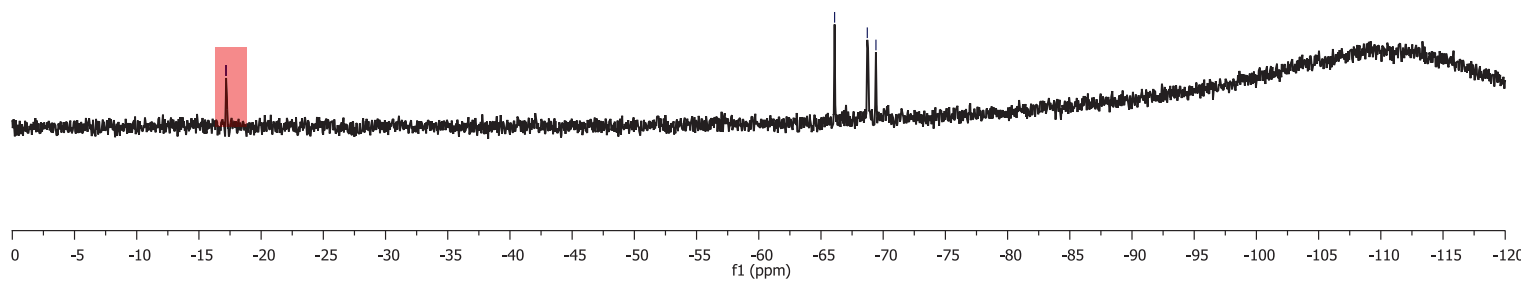
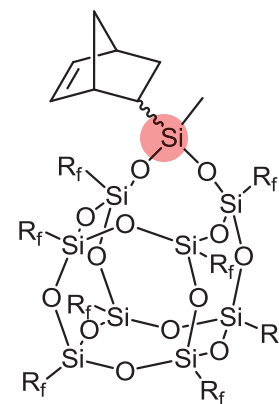
# $^{29}\text{Si}$ NMR



-66.09

-68.72

-69.42

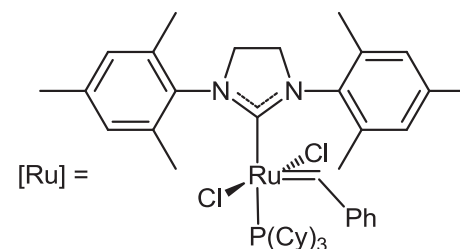
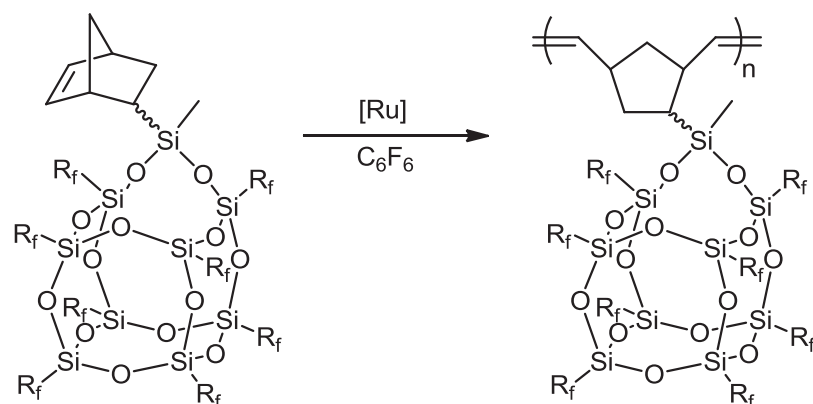


NMR:  $\text{CDCl}_3/\text{C}_6\text{F}_6$

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# ROMP



Grubb's 2<sup>nd</sup> generation catalyst  
(seems to be soluble in  
hexafluorobenzene)

- **Polymerization**

- Performed on 200 mg scale
- 50:1 monomer:cat
- Reaction of 30 minutes NMR run
- Initial signs point to polymerization success
- Further polymerizations will be pursued



# 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
- ROMP chemistry works well
- 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....



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