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FLUOROALKYL POLYHEDRAL OLIGOMERIC SILSESQUOXANE (F- POSS) BASED MONOMERS AND POLYMERS

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ACS Meeting 2011

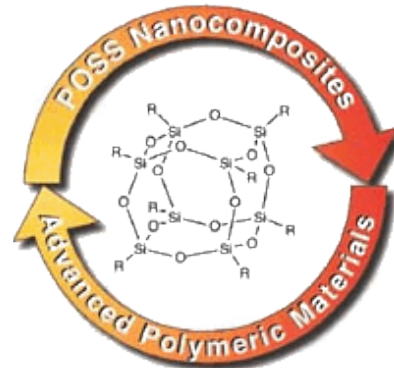


Polymer Working Group



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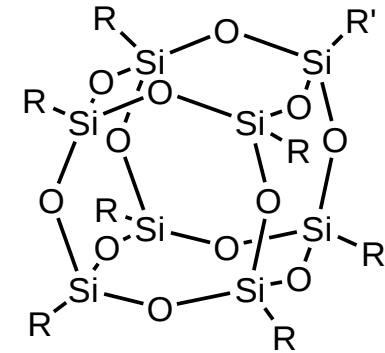
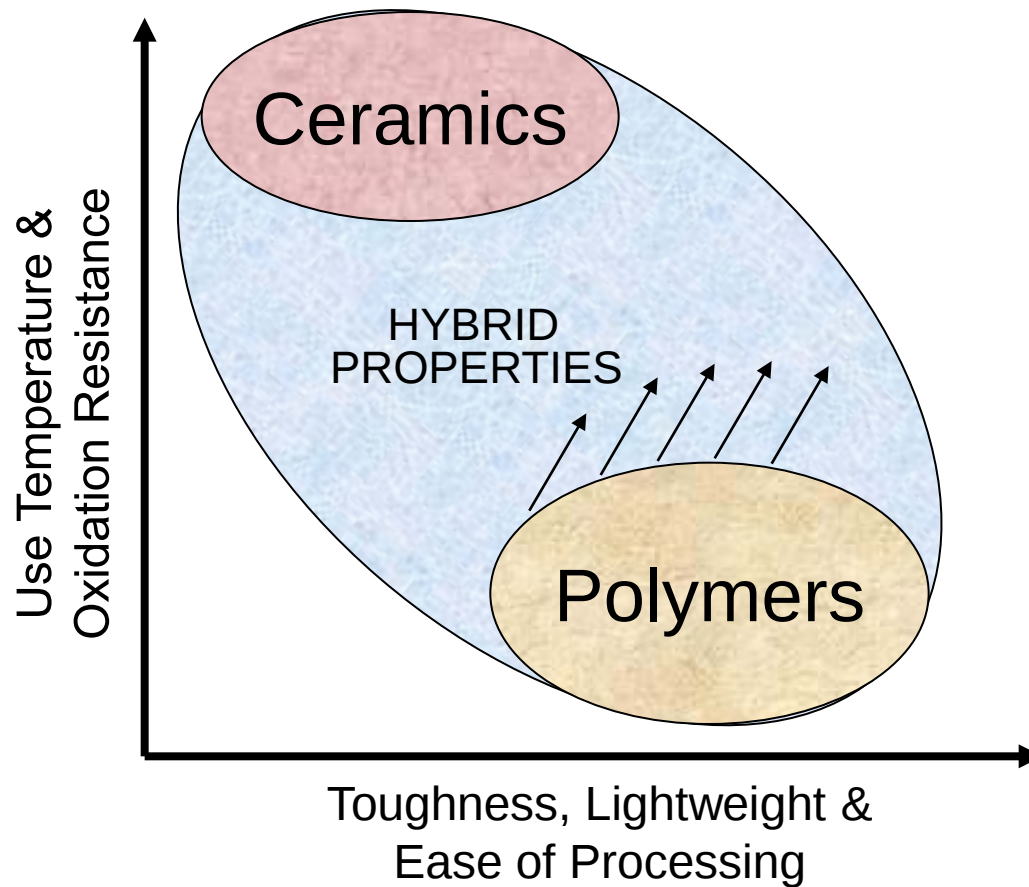


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Dr. Tim Haddad
Dr. Andy Guenthner
Dana Pinson

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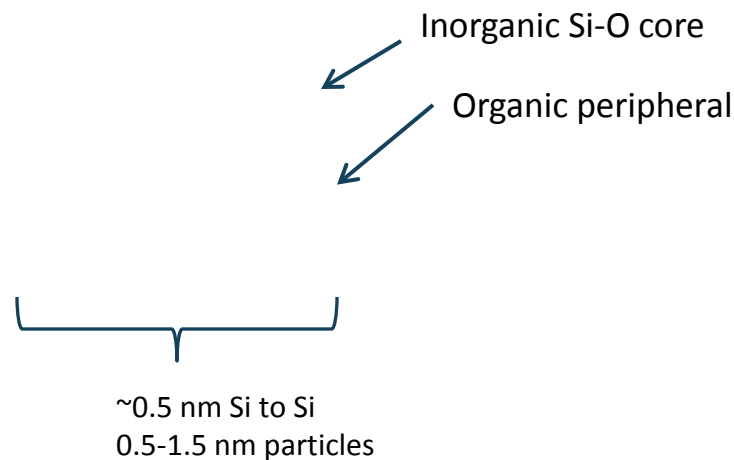
Hybrid Inorganic/Organic Polymers





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





Fluorinated polyhedral oligomeric silsesquioxane (F-POSS)



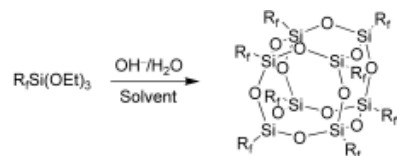
F-POSS, a subclass of POSS which consists of a silicon-oxide core $[\text{SiO}_{1.5}]$ with a periphery of long-chain fluorinated alkyl groups.

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

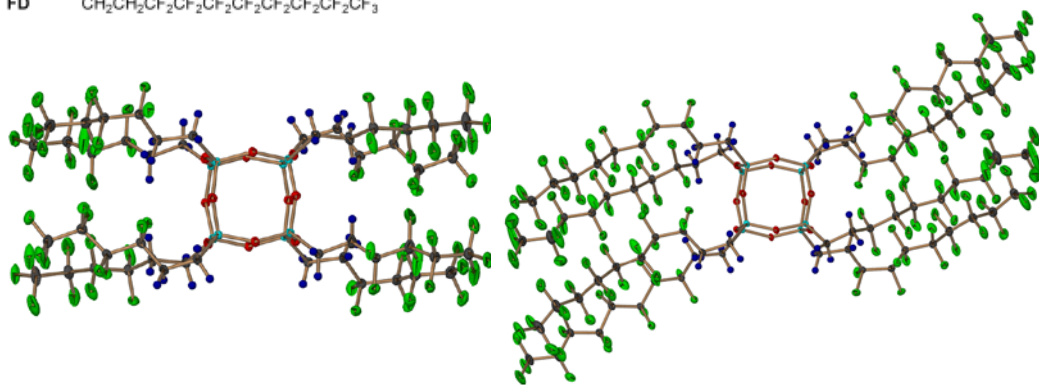
(a) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D., *Angew. Chem., Int. Ed.* **2008**, 47, 4137-4140; (b) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr., *Macromolecules* **2007**, 40, 9517-9522; (c) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M., *Chem. Commun.* **2007**, 4992-4994. (d) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H., *Adv. Mater.* **2009**, 21, 2190-2195; (e) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., *Proc. Natl. Acad. Sci. U. S. A.* **2008**, 105, 18200-18205; (c) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., *Science* **2007**, 318, 1618-1622; (f) 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, 3544-3554.



Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS)

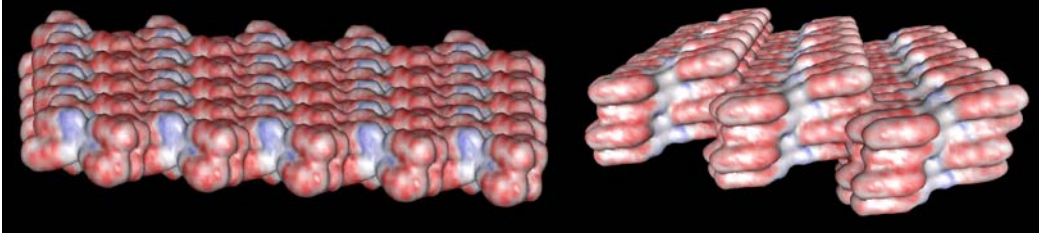


FH $R_f = \text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$
 FO $\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$
 FD $\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$



Fluorohexyl₈T₈

Fluorodecyl₈T₈



PMMA + 44 wt% POSS

electrospun coating (beads on a string)
morphology

Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* **2008**, 47, 4137. (left)

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)

Distribution A: Approved for public release; distribution unlimited



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

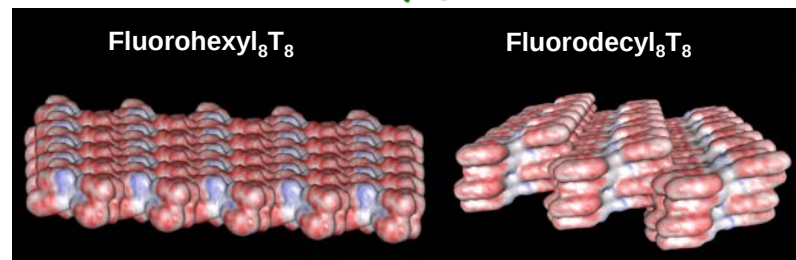
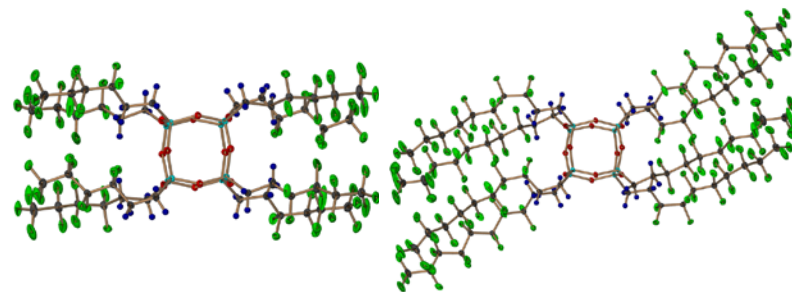
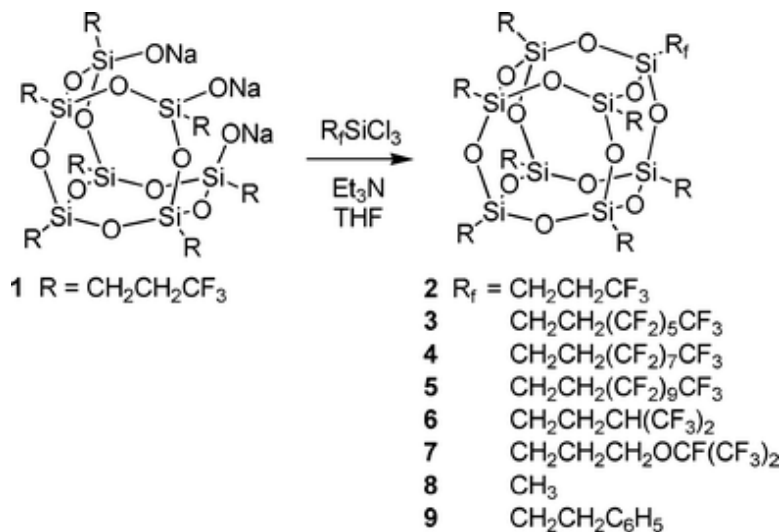
Which method can be applied to F-POSS?

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.



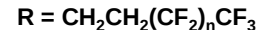
Trifluoropropyl Example

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





Synthesis of F-POSS-(OH)₃



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

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

*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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Which method can be applied to F-POSS?

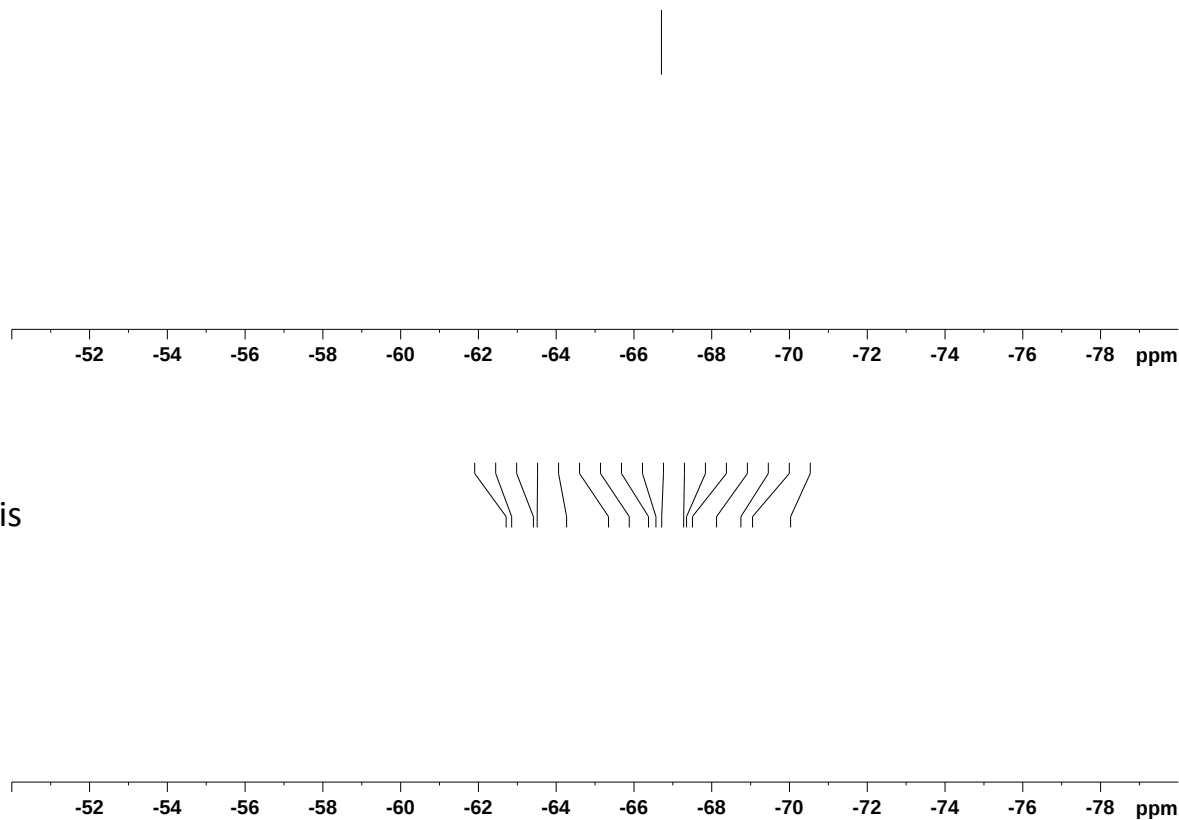
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Initial Reactions with Triflic Acid



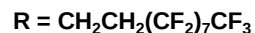
- Fluorodecyl T₈
- Reacted with triflic acid to open cage structure
- Structures analyzed with ²⁹Si NMR
- Equivalents of triflic acid to POSS cage is important to success of reaction
- Disappointing results



²⁹Si NMR taken in fluorinated solvent

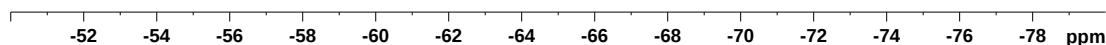
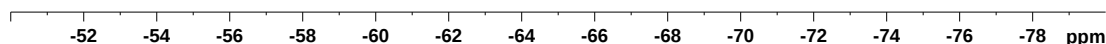


Synthesis of F-POSS-(OTf)₂



Mixture of unknown incompletely caged silsesquioxanes and resin

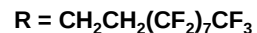
- After a little bit of refining
- An open cage structure is partially visible
- Starting material is still present
- Reaction not very clean
- Si ratio (1:1:2)



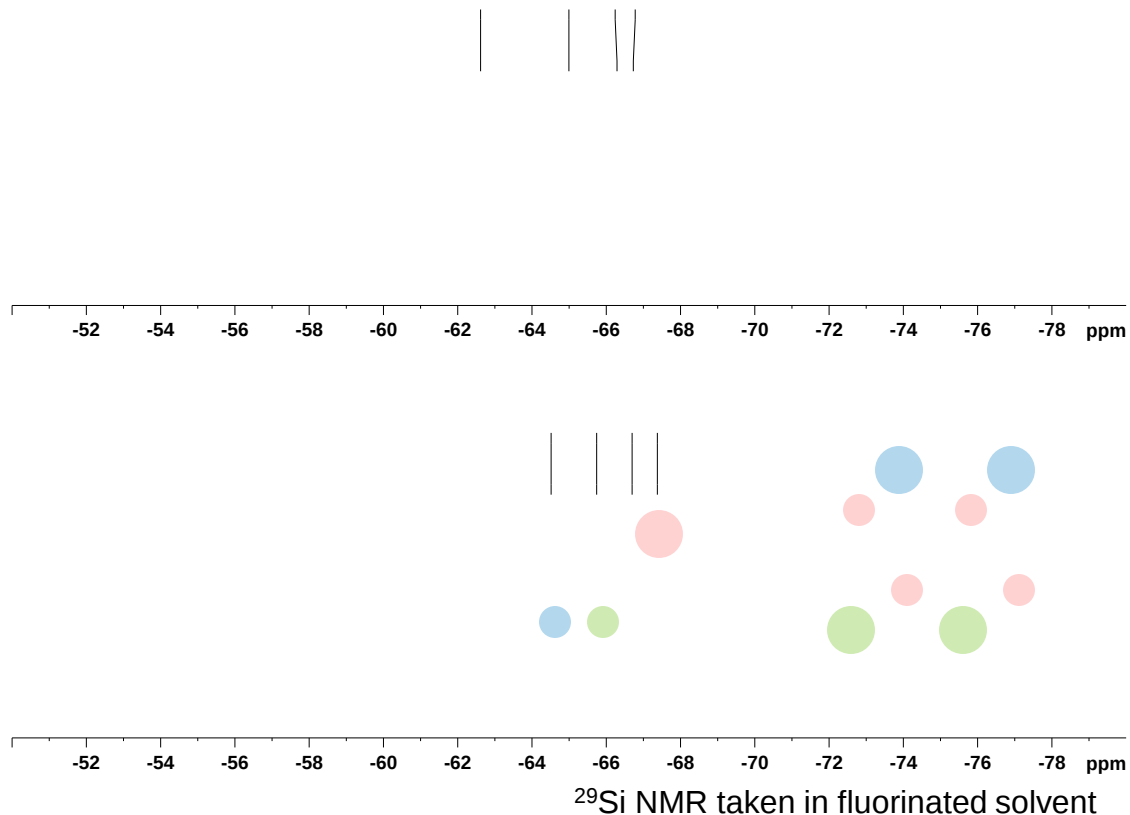
²⁹Si NMR taken in fluorinated solvent



Synthesis of F-POSS-SO₂

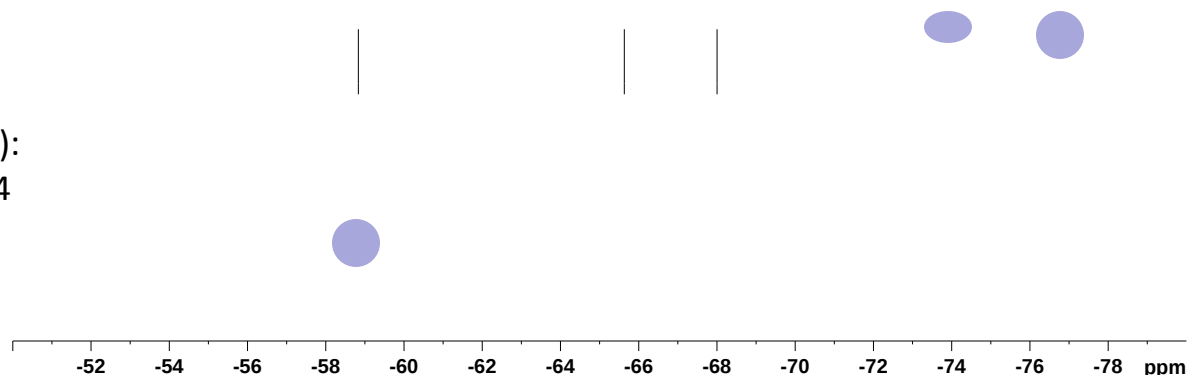
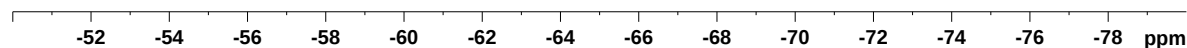
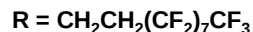


- Bridge sulfate cleans up reaction
- Structure significantly more stable than F-POSS-(OTf)₂, however still difficult to isolate
- Removal of starting material extremely difficult
- Si ratio (1:1:2)





Synthesis of F-POSS-(OH)₂



²⁹Si NMR taken in fluorinated solvent

- 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-SO₂
- Anal. Calcd. for C₈₀H₃₄F₁₃₆O₁₃Si₈ (found): C, 23.94 (23.99), H, 0.85 (0.75), F, 64.44 (64.72)
- Dehydration of disilanol leads to T₈ formation
- Si ratio (1:1:2)



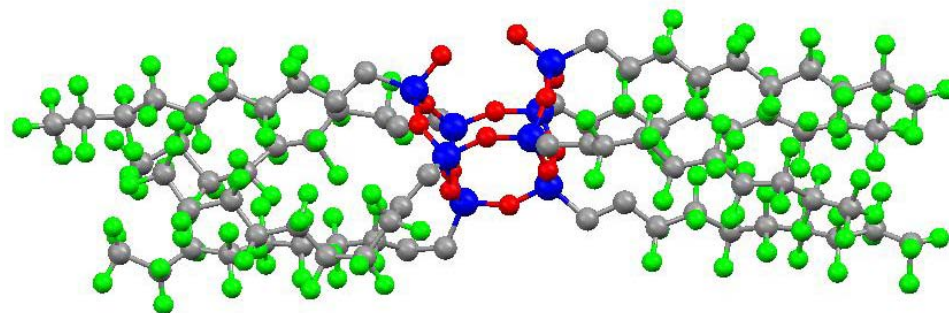
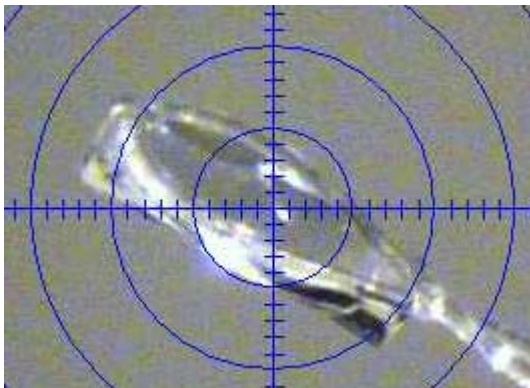
Overall Synthesis



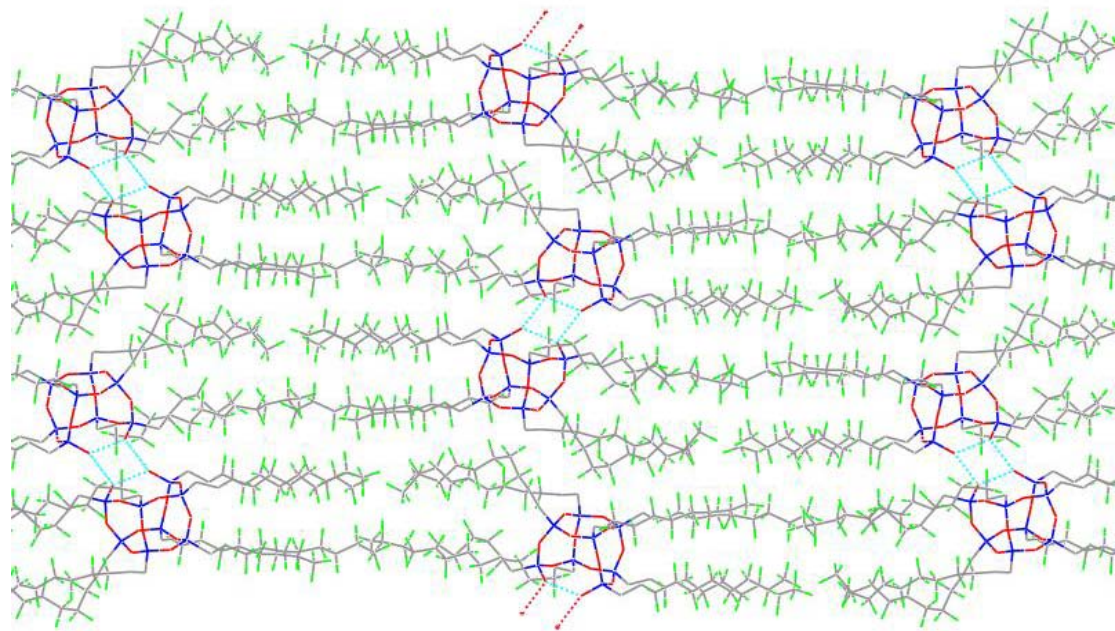
- Isolated yield for F-POSS-(Si(OH)₂) is ~40-52% over the three step reaction process
- Reaction Intermediates difficult to isolate (work in progress)
- scalable
- Major side product is unreacted starting material
 - Typically this is completely recovered at the final step and recycled, starting the process all over again



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, $\alpha=90.00^\circ$, $\beta=92.21(10)^\circ$, $\gamma=90.00^\circ$, $V=12878(2)$ Å³





Edge Capping Reactions

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

$R_1 = \text{CH}_3$

$R_2 = \text{CH}_2\text{CH}_2\text{CH}_2 \text{OC}(\text{O})\text{CHCH}_2$

- 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



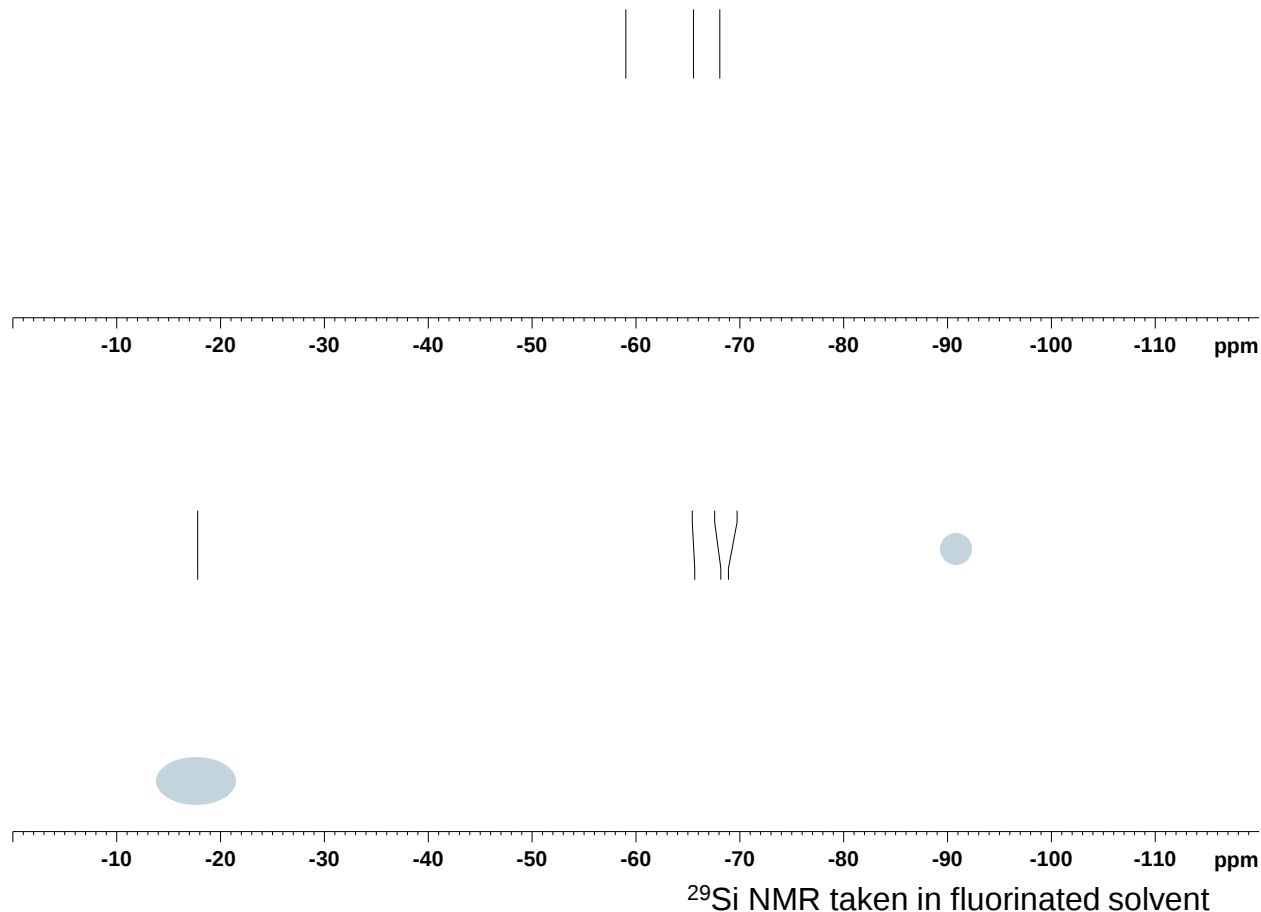
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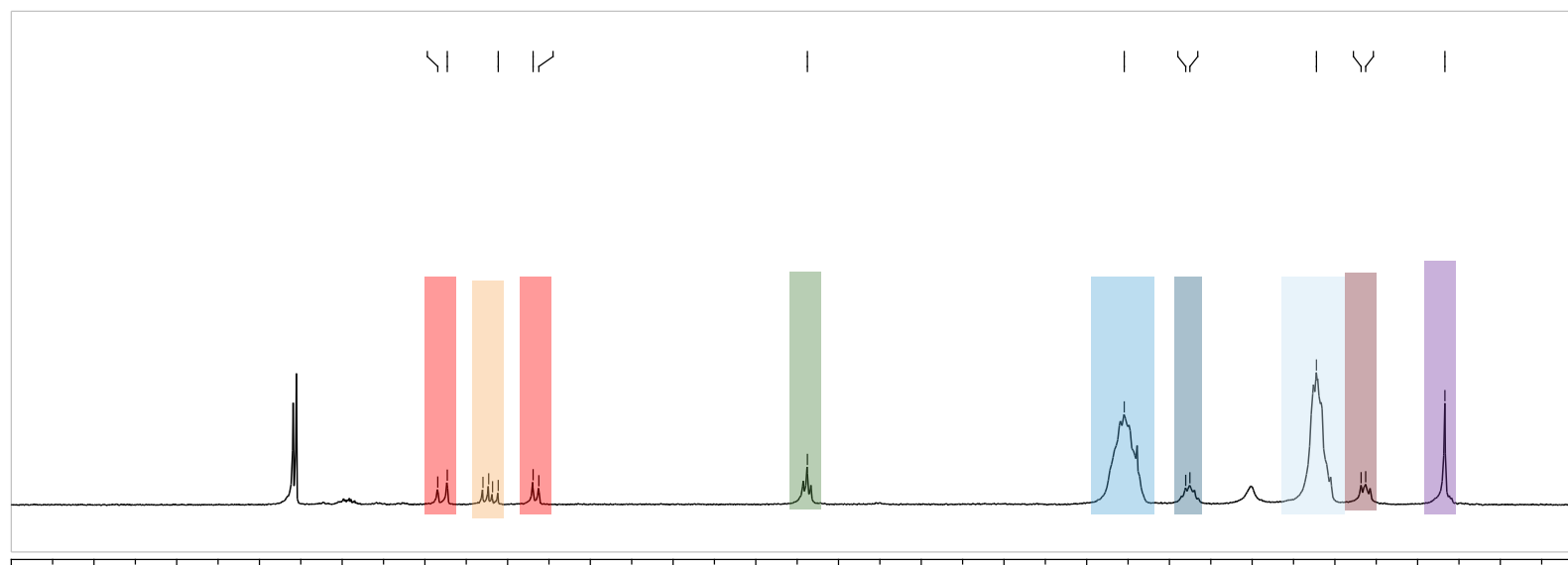
$R_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)CHCH}_2$

- 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!**



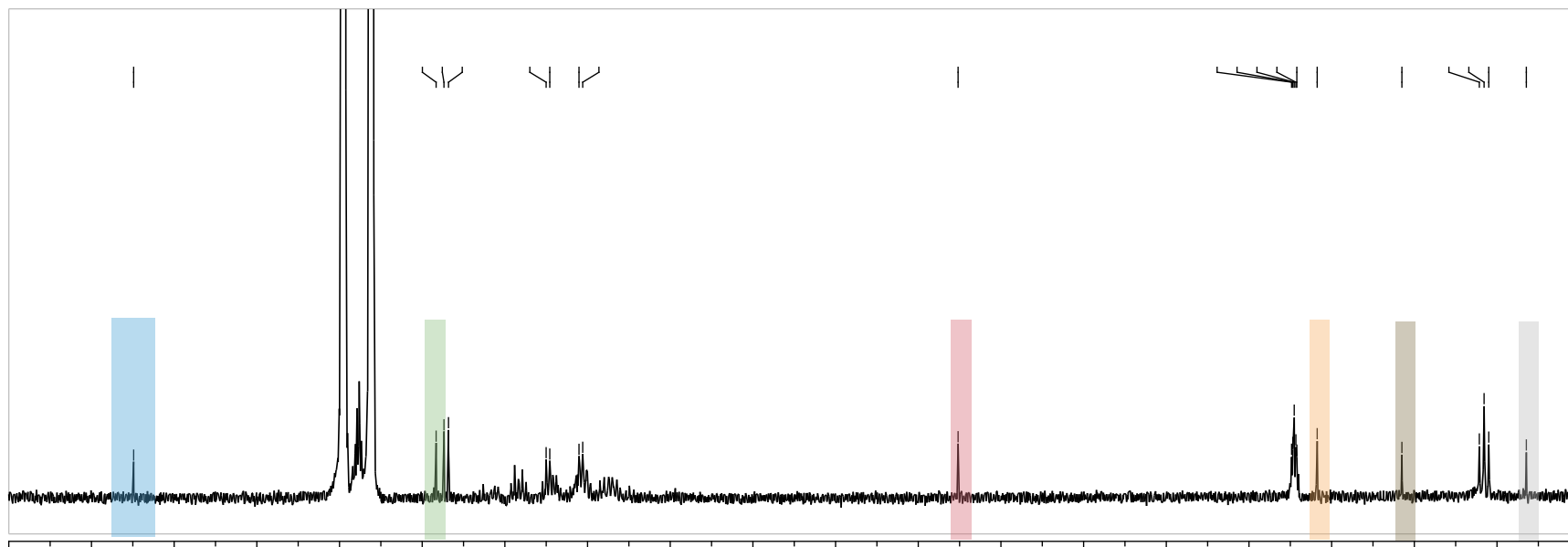


^1H NMR Characterization of Compounds



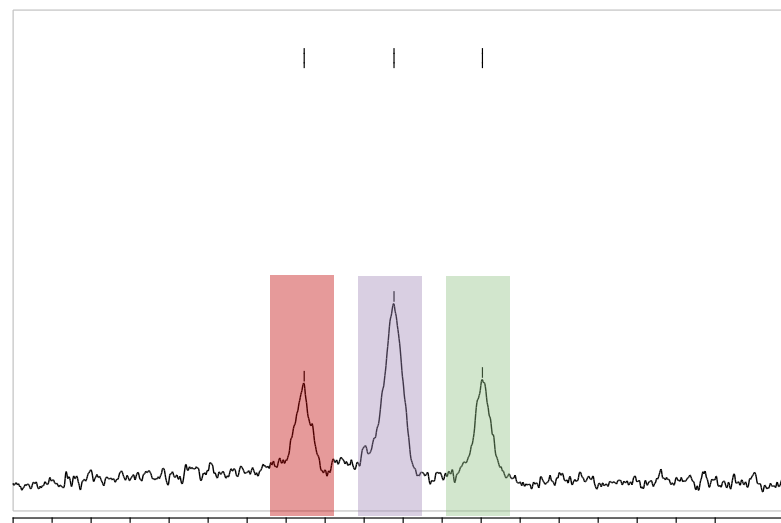
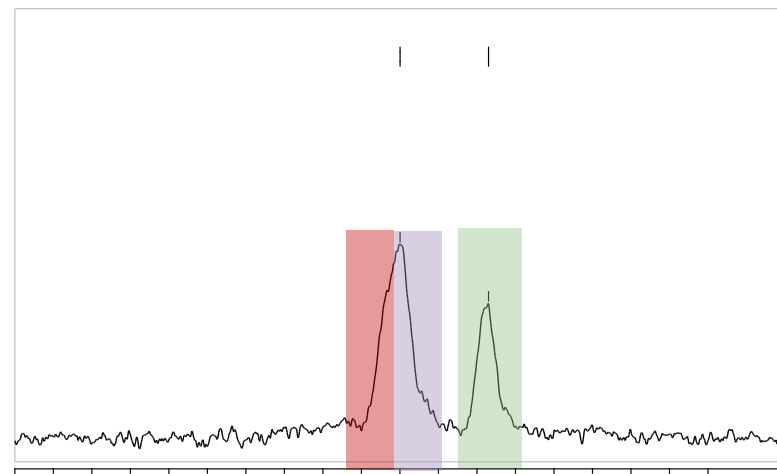
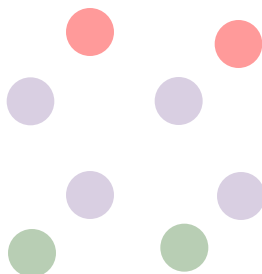
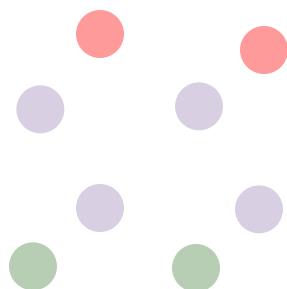
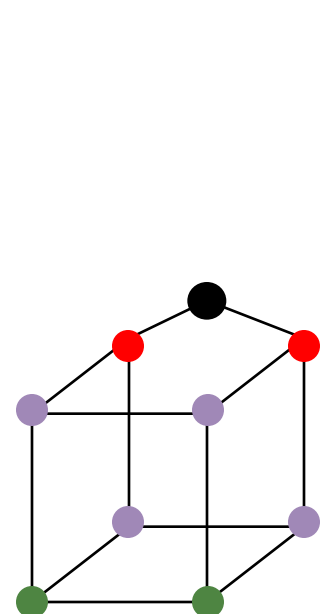


^{13}C NMR Characterization of Compounds



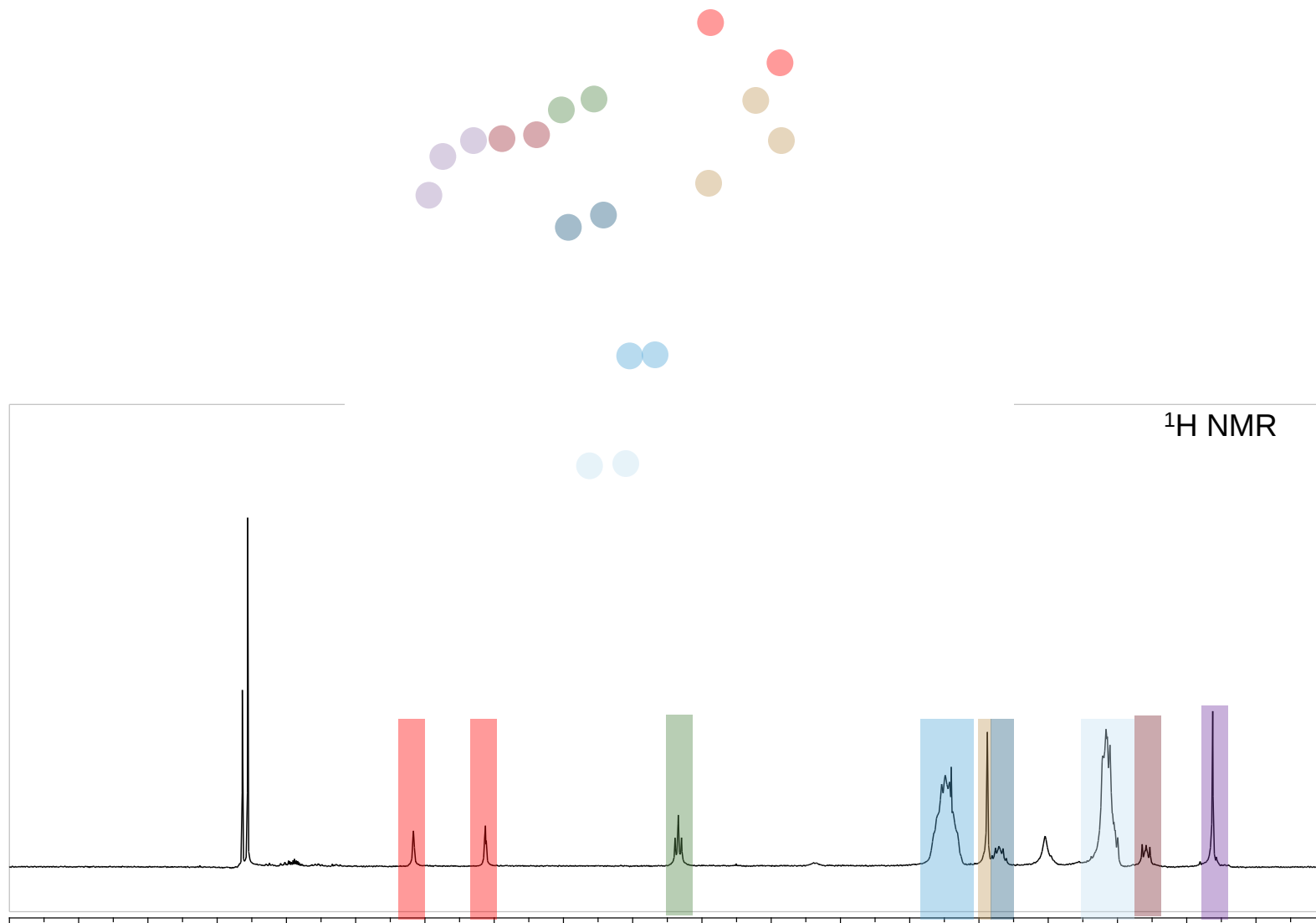


^{13}C NMR Characterization of Compounds





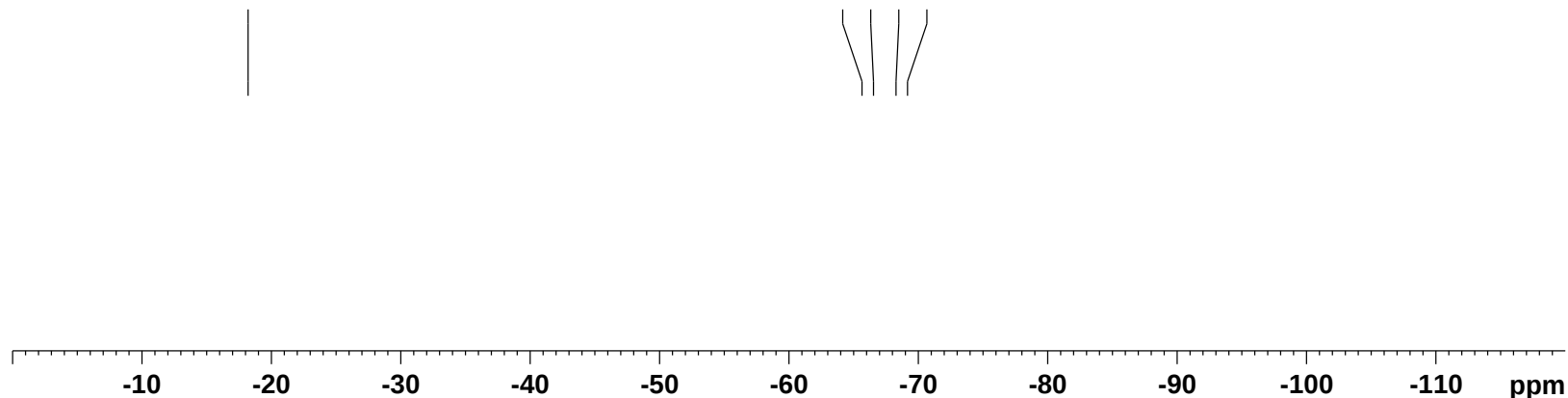
^1H NMR Characterization of Compounds





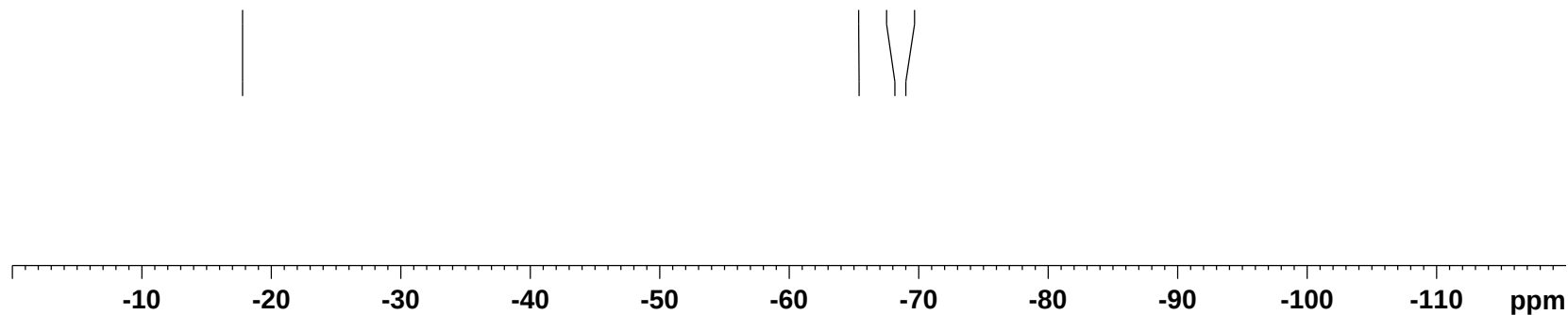
Separation of T_g from Product

Before



²⁹Si NMR taken in fluorinated solvent

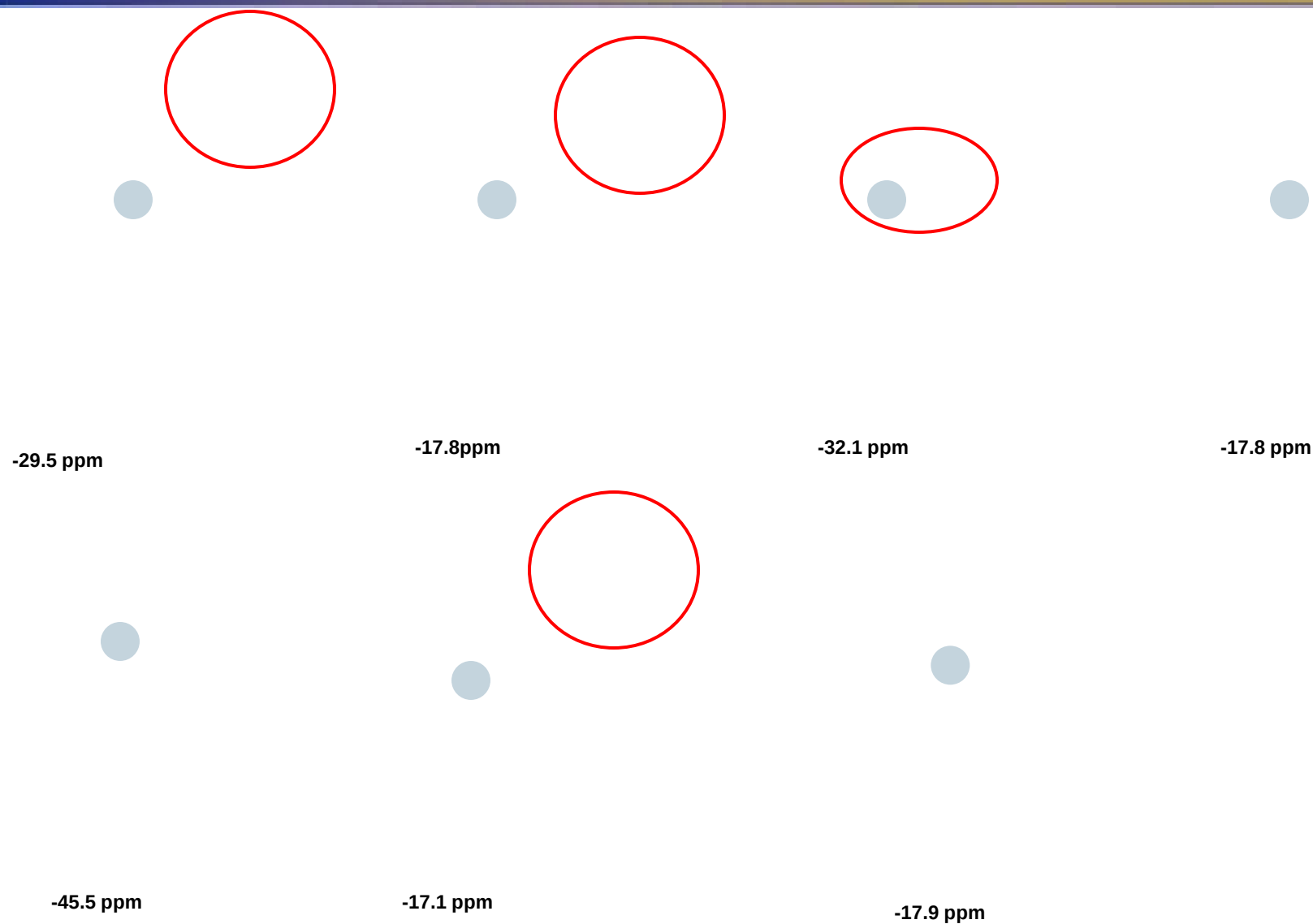
After



²⁹Si NMR taken in **diethyl ether-d₁₀**



F-POSS Structures Synthesized



R = CH₂CH₂(CF₂)₇CF₃

Distribution A: Approved for public release; distribution unlimited



Contact Angle Measurements

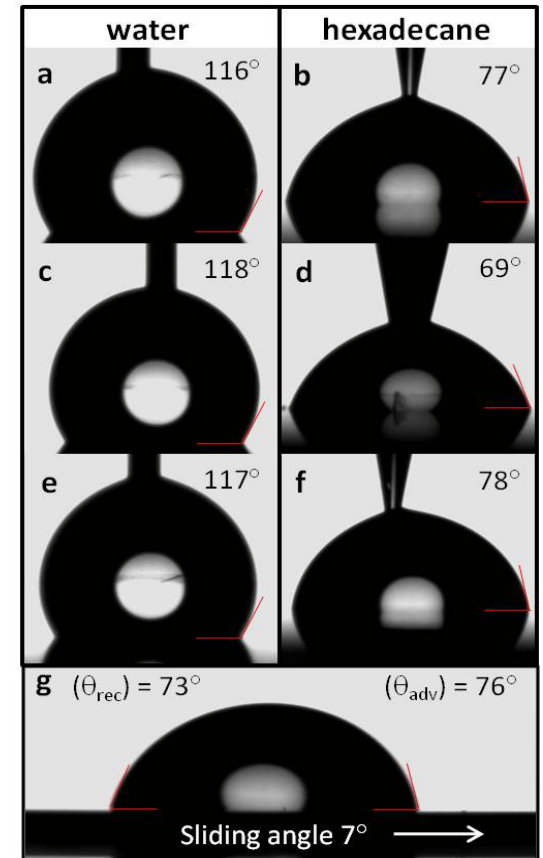


- Non-wetting surfaces can be developed by a combination of three parameters
 - Chemical functionality (high fluorine content)
 - Roughness (micro- and nanoscale)
 - Surface Geometry (re-entrant curvature)
- *What type of influence will functional groups have on F-POSS surface properties?*
- *Solvent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



Contact Angle Measurements

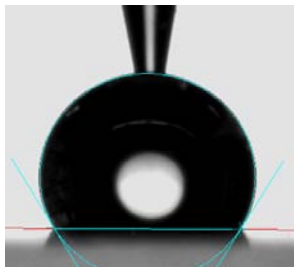
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Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10 μ L) rolling off surface coated with compound **diphenyl** (g).



Contact Angle Measurements



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

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).

*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.



Copolymerizations

MMA
(MW = 100 g/mol)

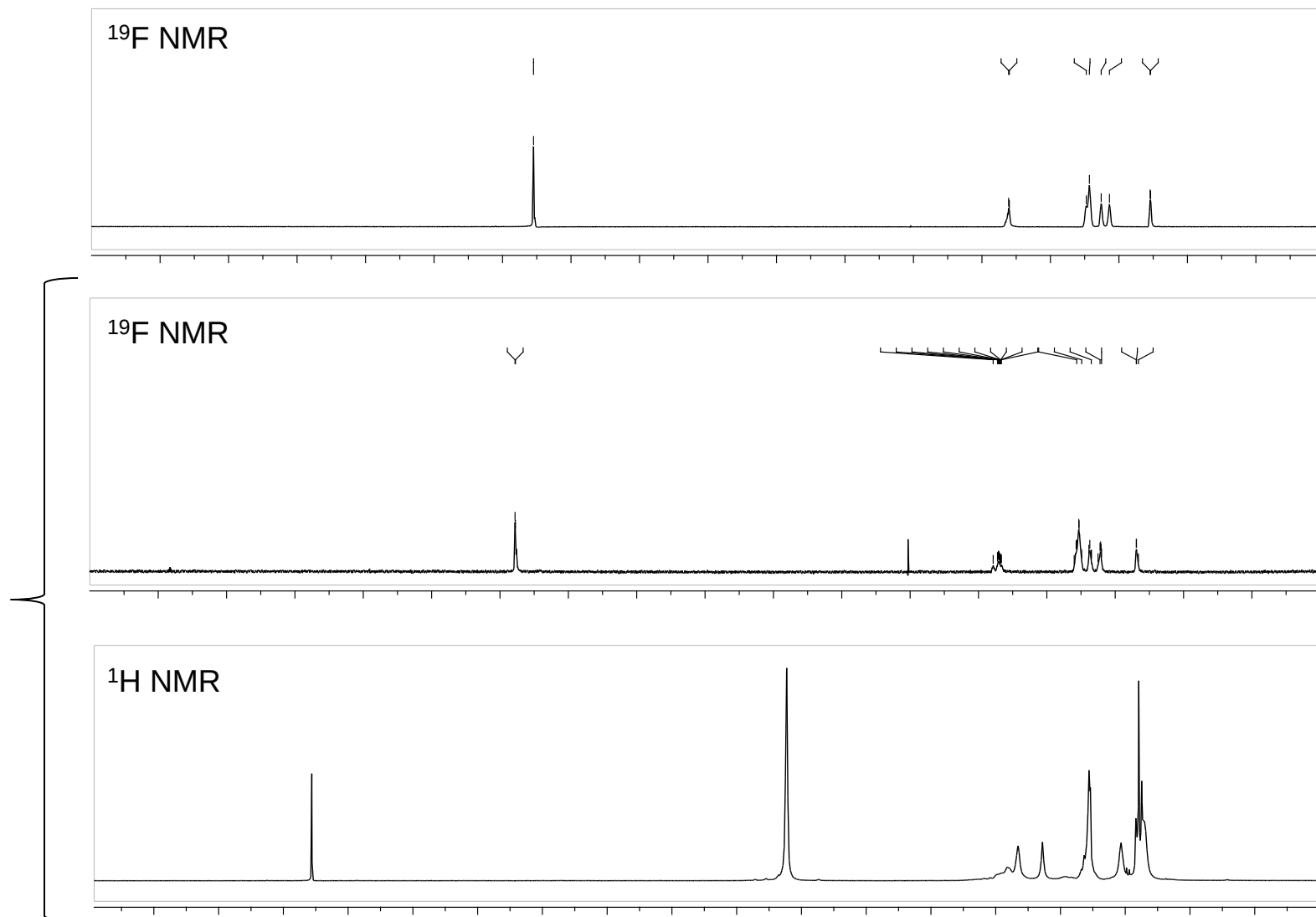
MMA-F-POSS
(MW = 4178 g/mol)

	<i>Weight (g)</i>		<i>Weight</i>	<i>Monomer (mmol)</i>		<i>Mol Ratio</i>	<i>Initiator</i>	<i>Conversion</i>
	<i>MMA-F-POSS</i>	<i>MMA</i>	<i>(%)</i>	<i>MMA-F-POSS</i>	<i>MMA</i>	<i>(MMA:MMA-F-POSS)</i>	<i>(mol %)</i>	<i>(%)</i>
SR-3-141	0.085	1.311	6.3	0.02	13.1	655	0.5	42
SR-3-145	0.362	1.31	21.6	0.09	13.1	145	0.2	71

Sampe 141 was run in pure C₆F₆.
Sample 145 was run in a THF/C₆F₆ mixture.



NMR Characterization of Copolymers





Future Directions

- Surface Functionalization

276 - FluoroPOSS monolayers covalently bound to a silica surface

Authors: **Raymond Campos**, Dr. Sean M Ramirez PhD, Dr. Timothy S Haddad PhD, Dr. Joseph M Mabry PhD

Division: POLY: Division of Polymer Chemistry

Date/Time: **Tuesday, March 29, 2011 - 02:30 PM**

Session Info: POLY/PMSE Poster Session (02:30 PM - 04:00 PM)

Location: Hilton Anaheim

Room: California Blrm D

- Polymerizations of monomers



Summary



- Synthesis of disilanol F-POSS from F-POSS was accomplished in a three step reaction process
- 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....

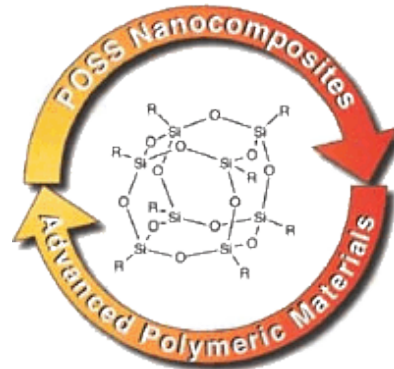


Polymer Working Group



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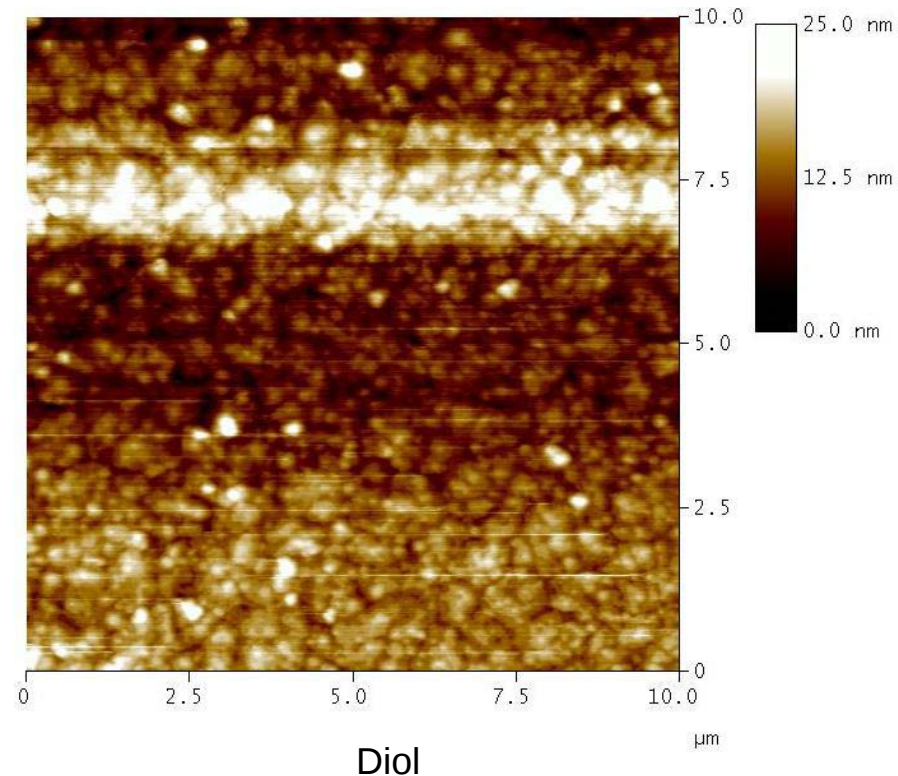
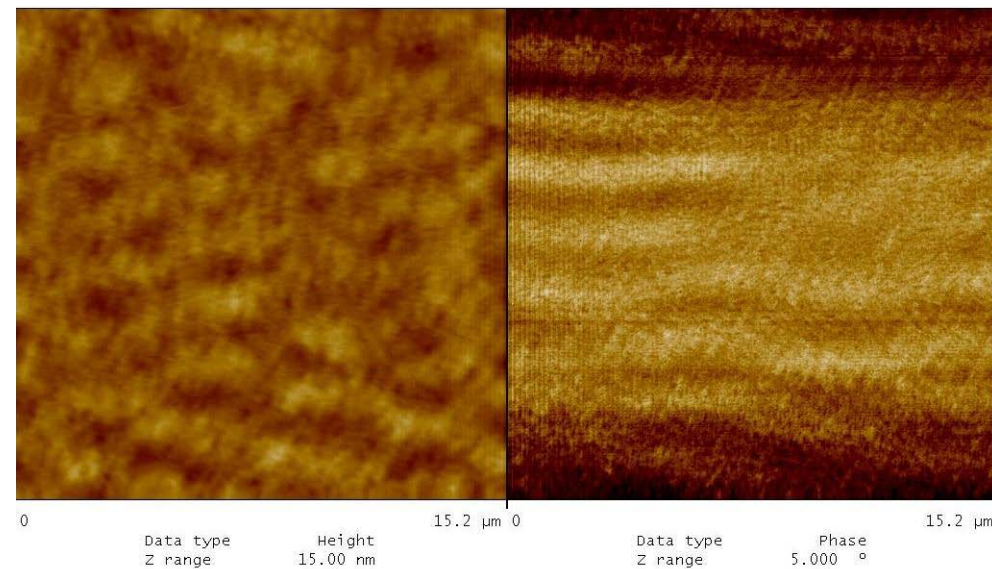


Optical Profilometry and (AFM) Measurements



- Diol – $R_a = 1.59$ nm (3.88 nm)
- Vinyl – $R_a = 1.25$ nm (1.22 nm)
- Acrylate - $R_a = 0.84$ nm (1.83 nm)
- Methacrylate – $R_a = 2.85$ nm (0.85 nm)

Acrylate



Raw AFM images shown