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14. ABSTRACT Strategies aimed at promoting the formation of close-pack assemblies of fluoroalkyl helices on the surface of PDMS networks will be described and compared. Fluoroalkyl moieties were incorporated into Pt-catalyzed hydrosilylation networks <i>in situ</i> by using vinyl additives possessing either a single fluoroalkyl substituent, CH ₂ =CH-(CF ₂) ₇ CF ₃ (F8-vinyl), or eight ((methyl, vinyl)D ₁ (F8H ₂) ₈ T ₈ POSS or vinyl fluorodecyl POSS). Post-cure methods involving the incorporation of surface thiol groups and subsequent thiolene addition reactions were also explored for the facile production of PDMS networks with oleophobic surface properties. Synthetic routes and characterization of intermediates will be presented in addition to dynamic wettability analysis of modified PDMS networks.					
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a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code) 661-275-5857



In-situ and post-cure surface modification of PDMS elastomers for low surface energy applications

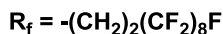
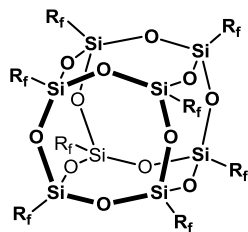
Raymond Campos,* Sean M. Ramirez, James F. Ruether,*
Kevin R. Lamison,** Joseph M. Mabry,*** and Bruce M. Novak***

***The University of Texas at Dallas, Department of Chemistry and
The Alan G. MacDiarmid Nano Tech Institute, 800 W Campbell Rd.,
Richardson, TX 75252**

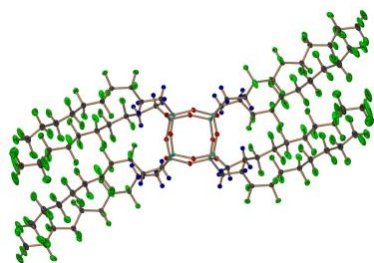
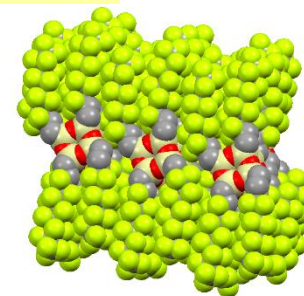
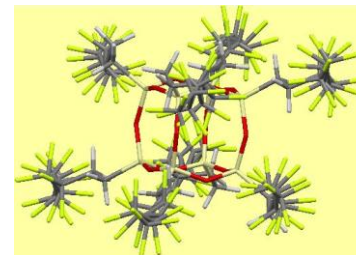
****ERC, Inc., Air Force Research Laboratory, Space & Missile
Propulsion Division, Edwards Air Force Base, CA 93524**

***** Air Force Research Laboratory, Space & Missile Propulsion
Division, Edwards Air Force Base, CA 93524**

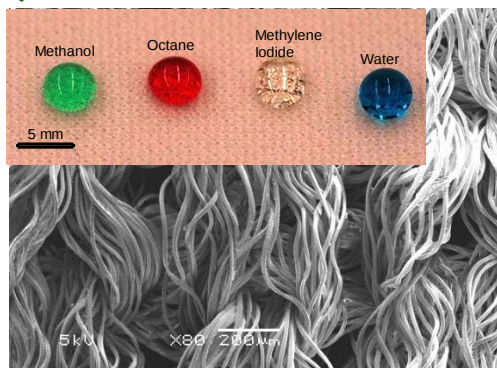
Properties of Fluorodecyl₈T₈ POSS



- Extremely low surface energy
- Surface migration in polymers
- Surface responsive behavior

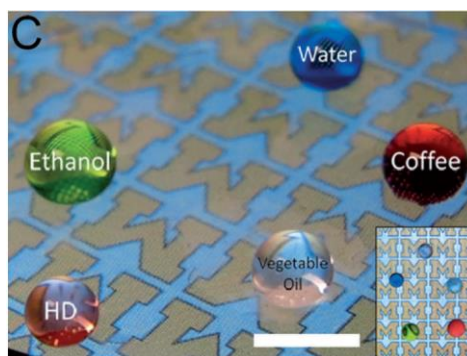


Enabling....



**Superomniphobic fabrics
via dip-coating**

Choi *et al.*, *Ang. Chem.*, 2009



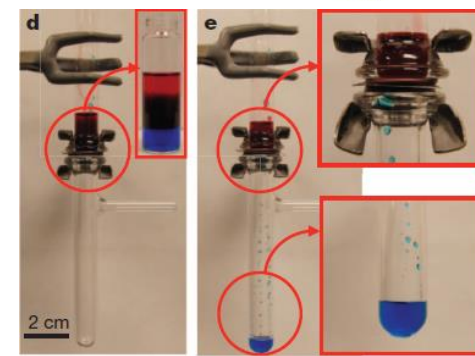
**Transparent
Omniphobicity**

Golovin *et al.*, *Ang. Chem.*, 2013



**Extreme
Omniphobicity**

Pan *et al.*, *JACS.*, 2012

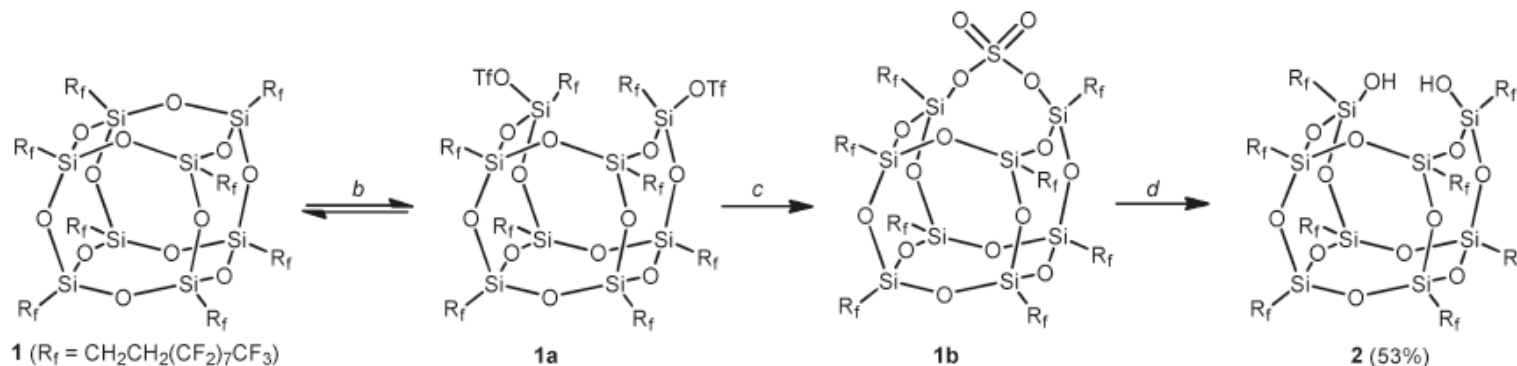


**Oil/water emulsion
gravity separation**

Kota *et al.*, *JACS.*, 2012

Functional Fluorodecyl POSS Compounds Enabled by Incompletely Condensed Intermediate

Scheme 1. Synthesis of Incompletely Condensed Fluoroalkyl Silsesquioxane^a

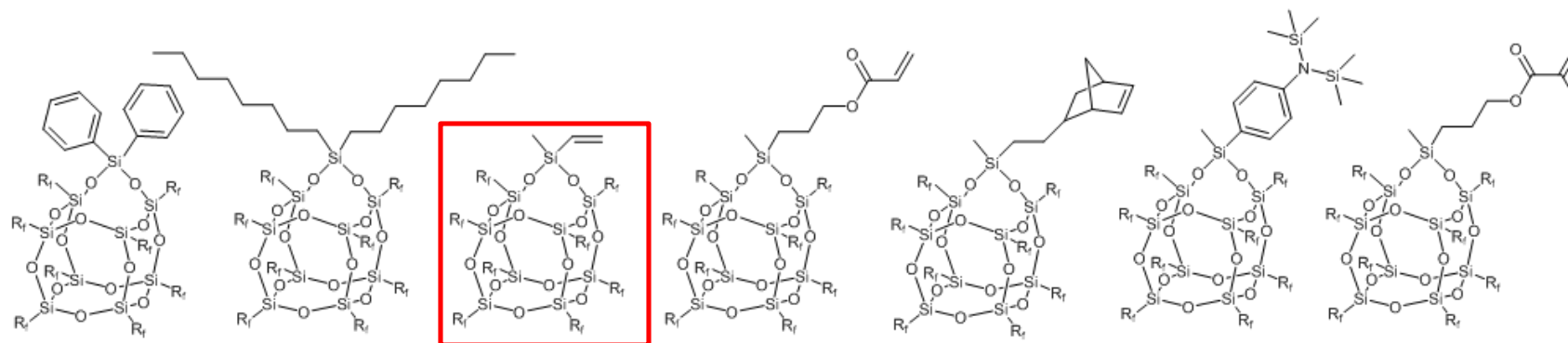
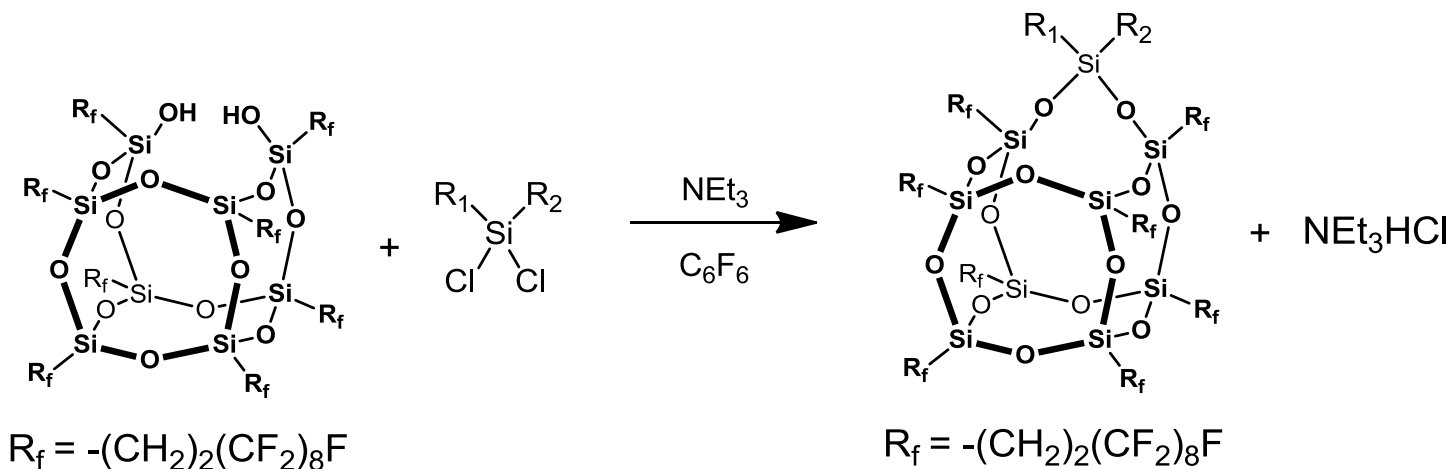


^a Conditions: All reactions were performed in C_6F_6 at 25 °C. ^b $\text{CF}_3\text{SO}_3\text{H}$, 75 min; ^c $\text{NBut}_4\text{HSO}_4$, 30 min; ^d $(\text{CF}_3)_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (10:1), 12 h.



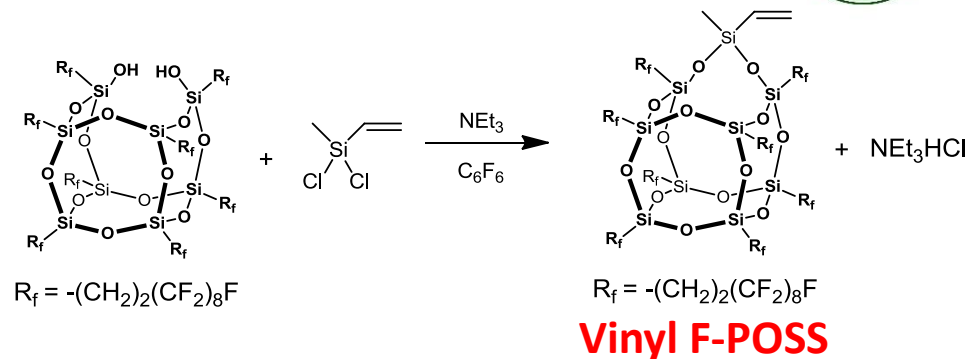
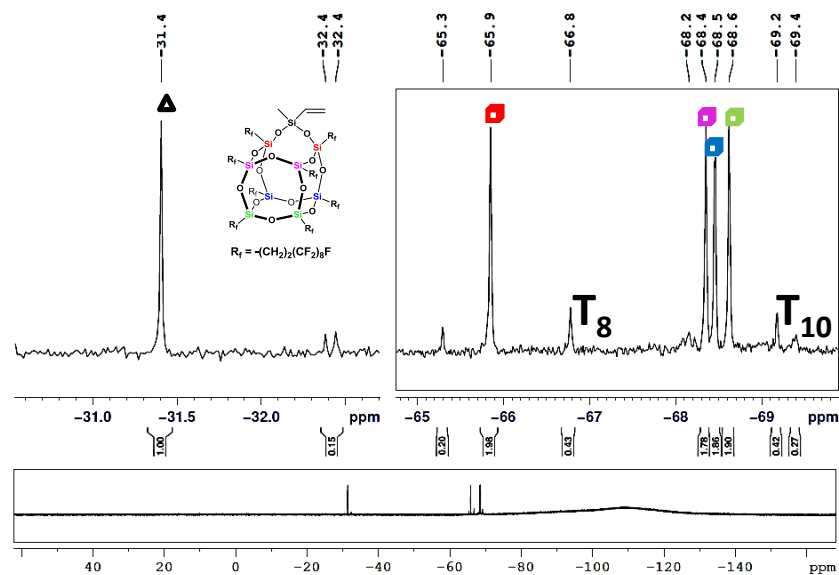
Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS*, **2011**, 133, 20084.

Functional Fluorodecyl POSS Synthesis from Incompletely Condensed Fluorodecyl POSS

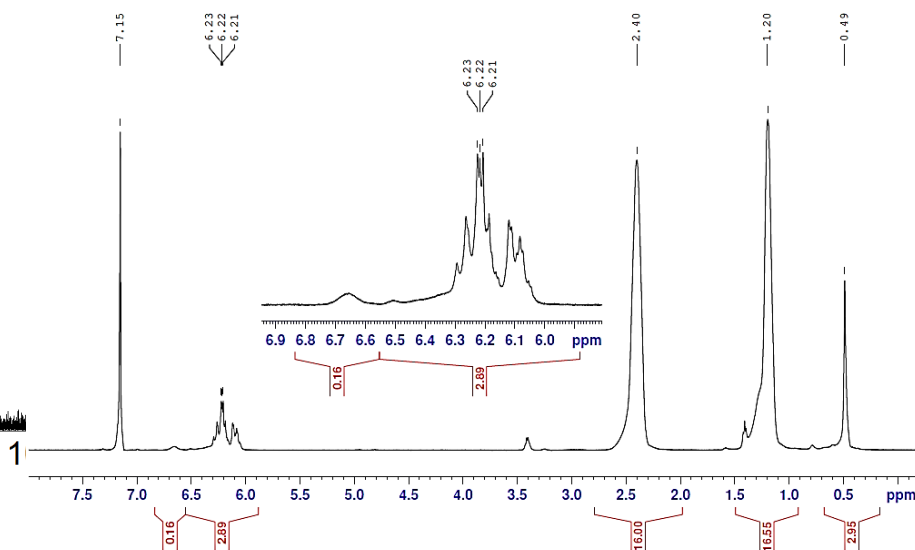
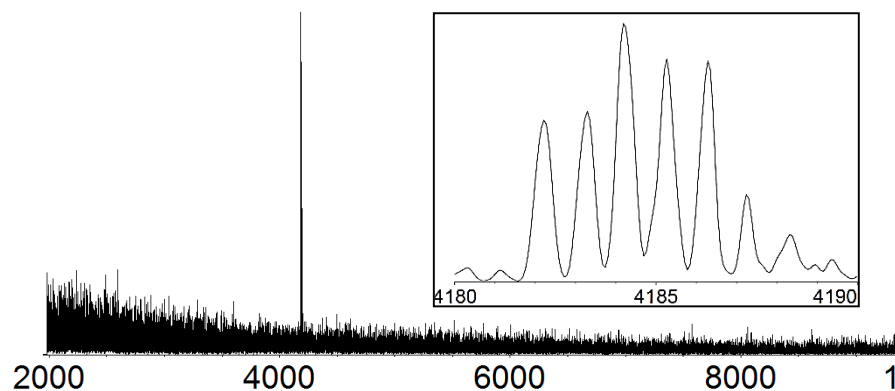


Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS*, **2011**, 133, 20084.

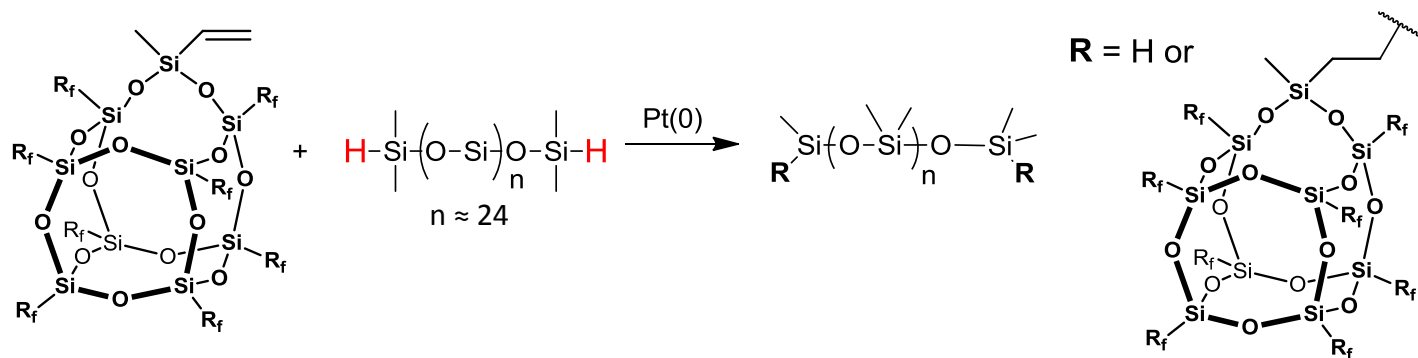
Fluorodecyl₈T₈D₁(methyl, vinyl) POSS



Theoretical $[M \cdot Ag]^+ = 4185.71$ Da

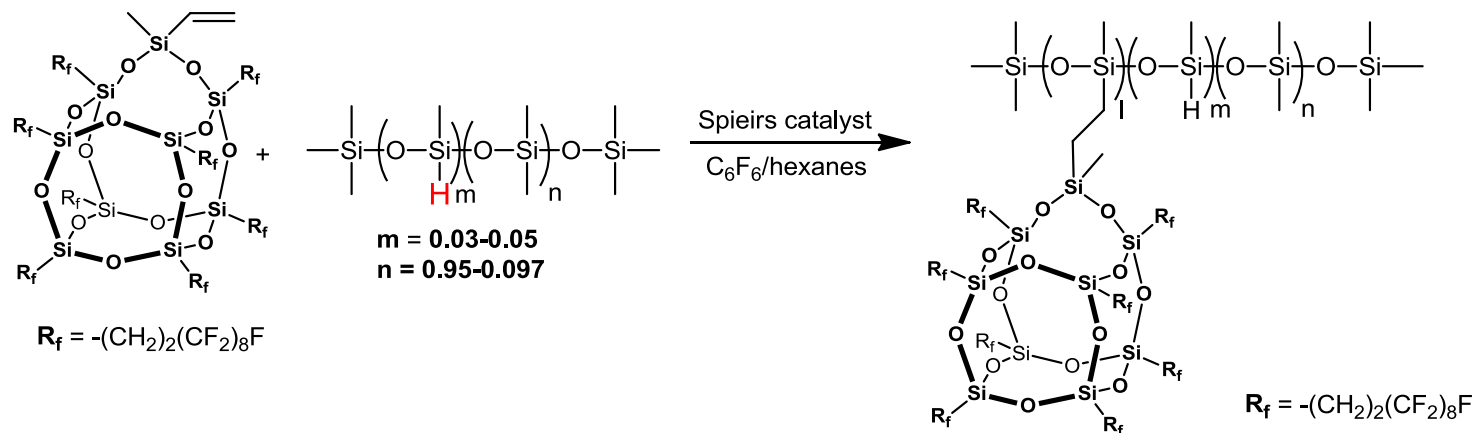


Facile F-POSS Grafting to PDMS via Hydrosilylation



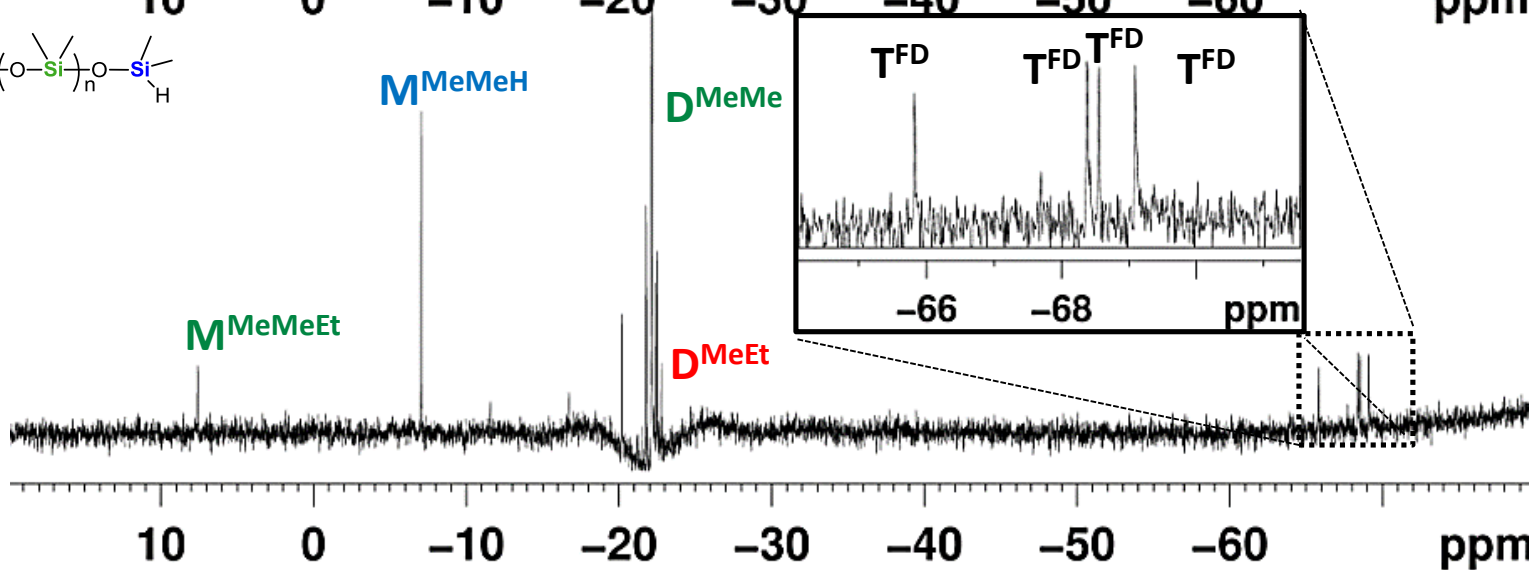
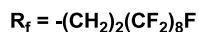
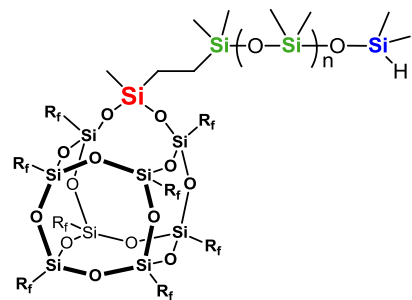
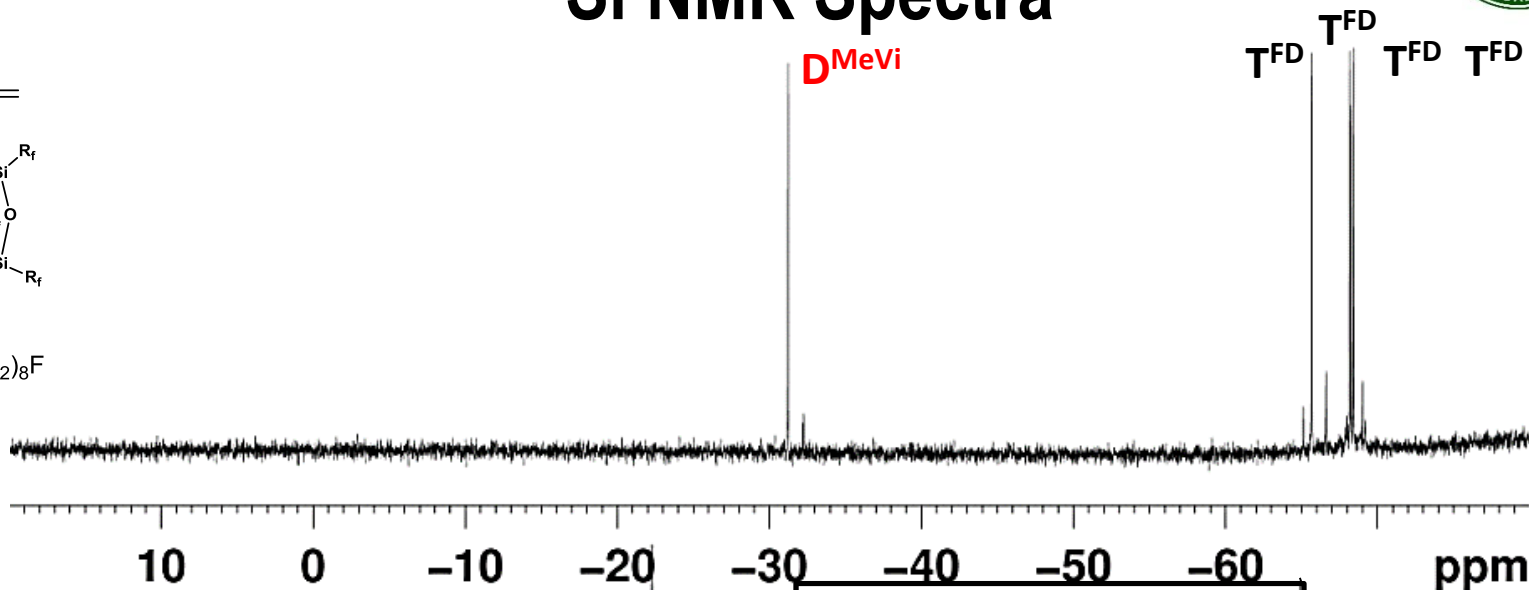
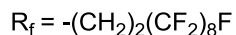
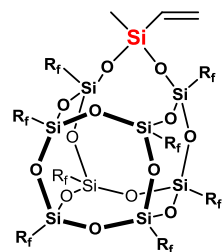
1, 5, 10, 20, 44 wt%

Vinyl: silane, 1:32, 1:8, 1:4, 1:2, 1:1

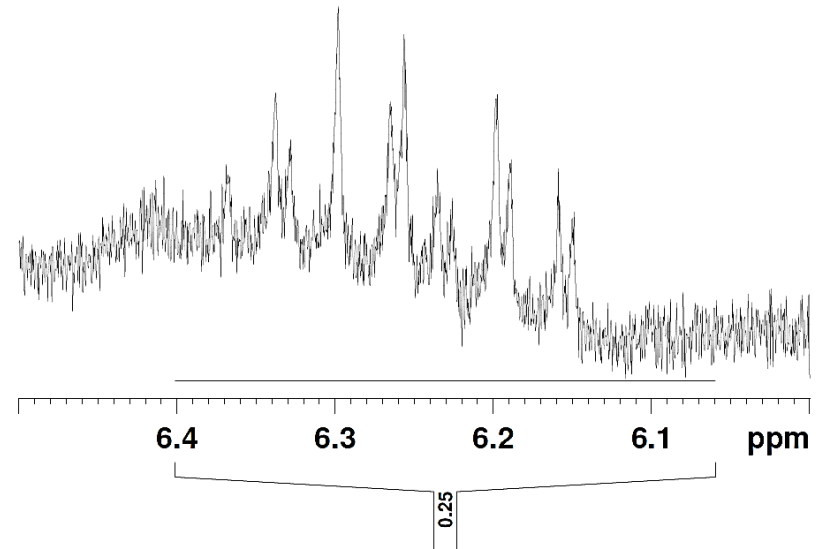
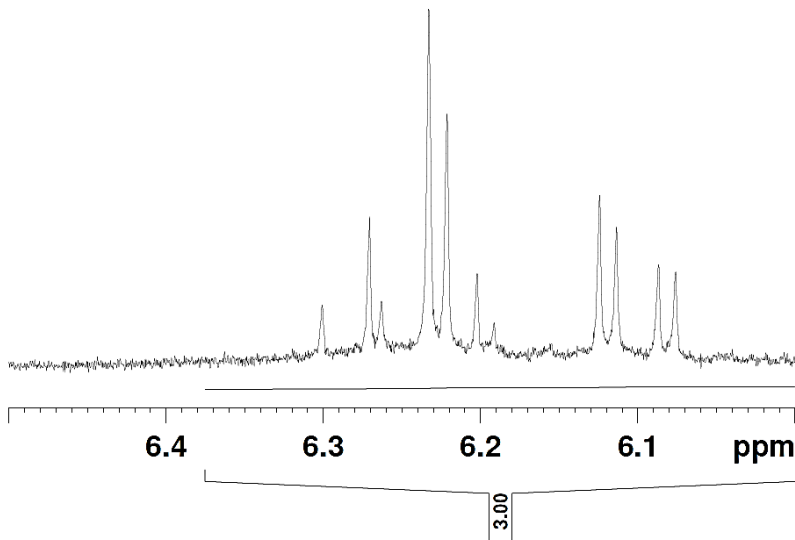
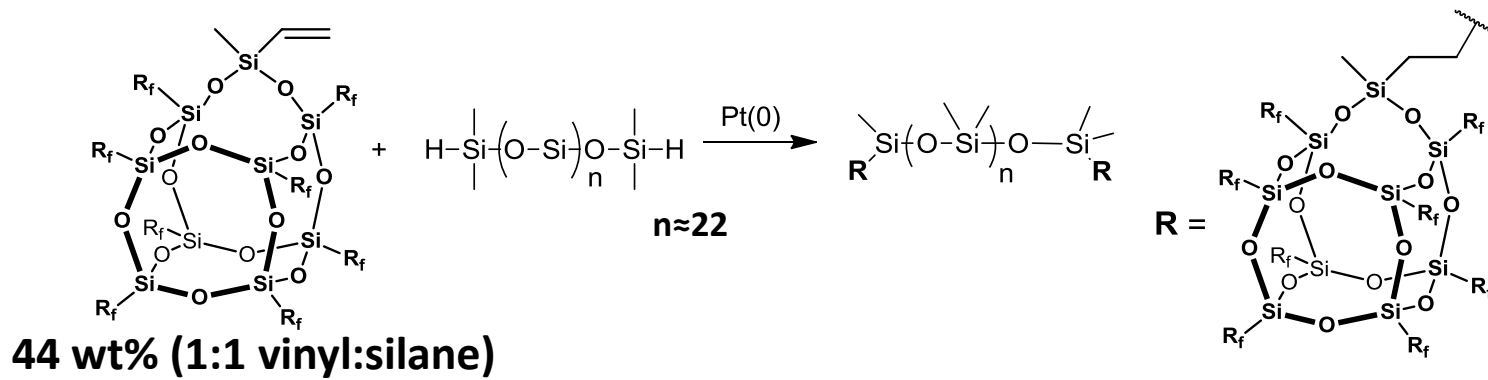


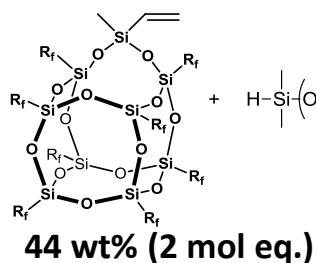
Complete Conversion at 10 wt% F-POSS:

^{29}Si NMR Spectra

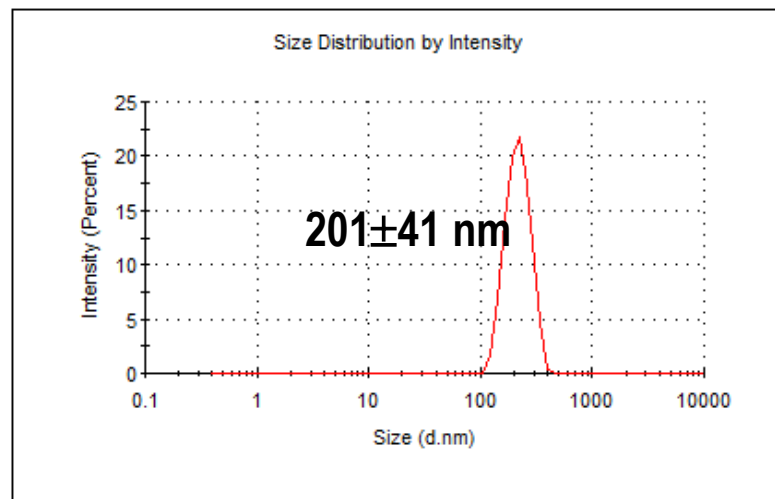
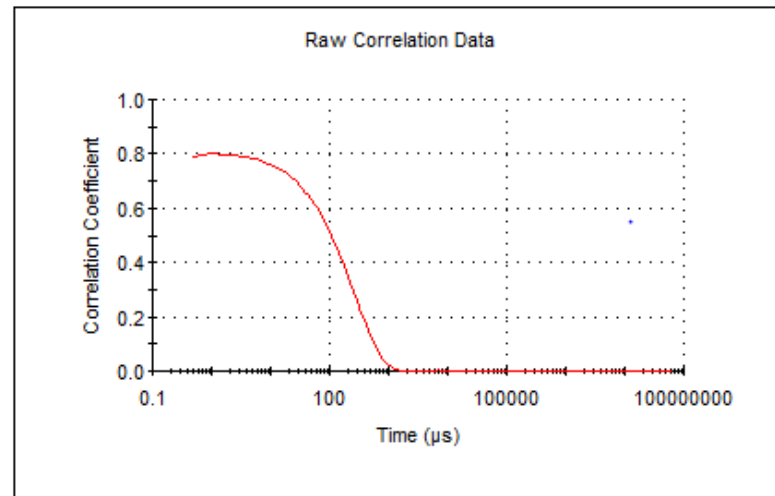
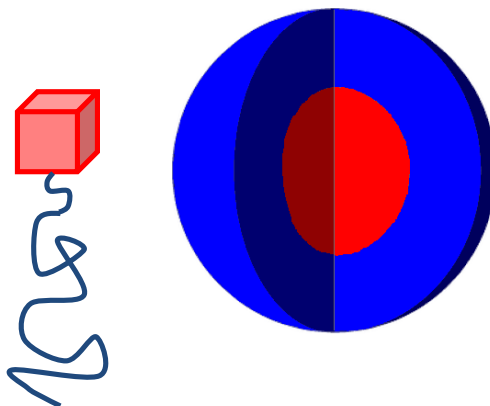
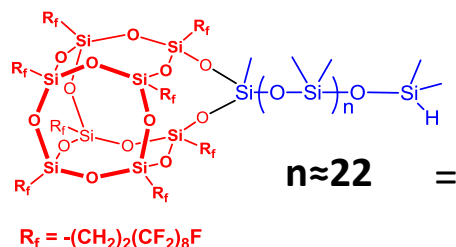
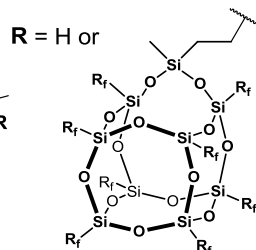


Incomplete Conversion at ≥ 20 wt% F-POSS: ^1H NMR Spectra

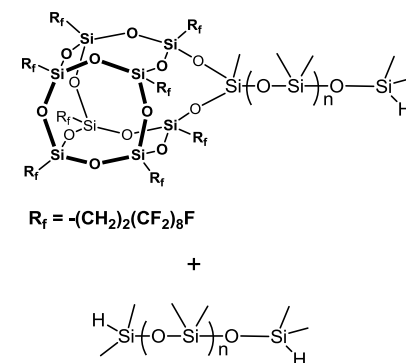
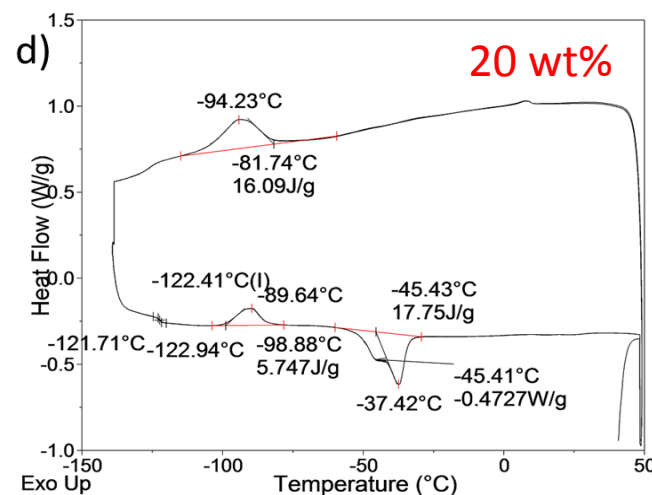
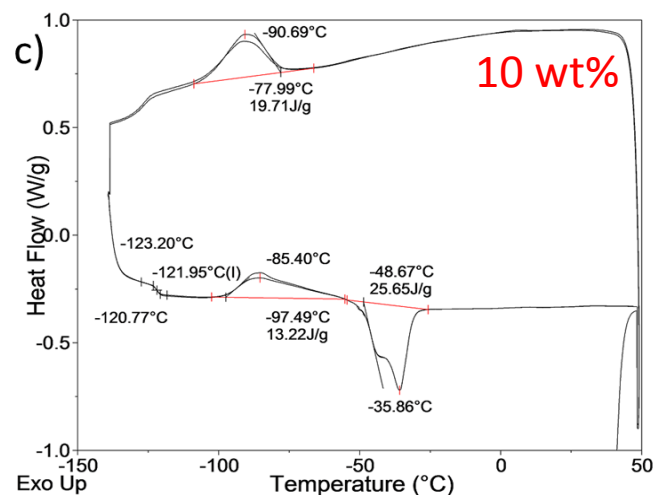
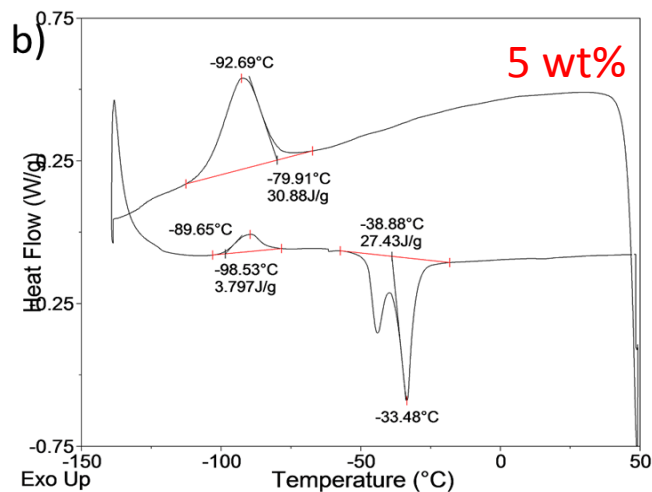
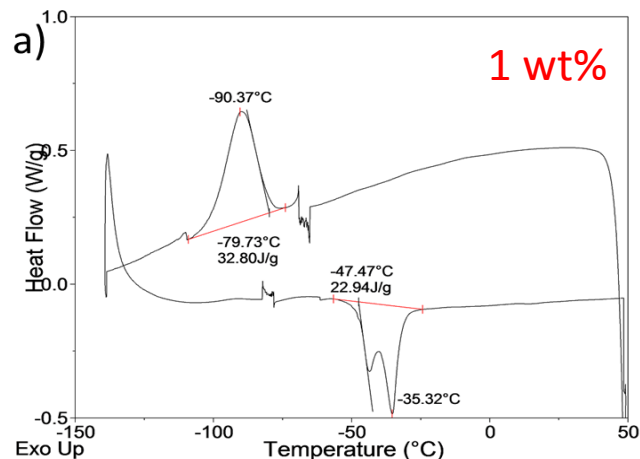


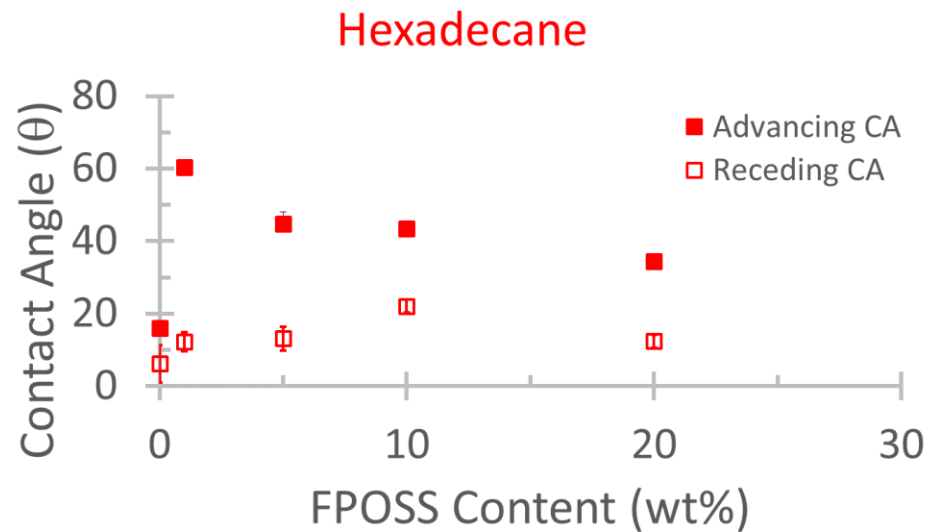
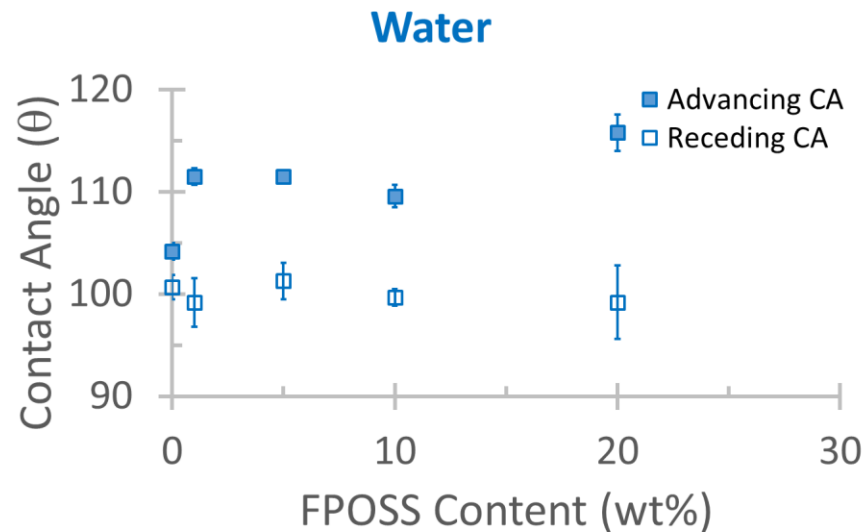
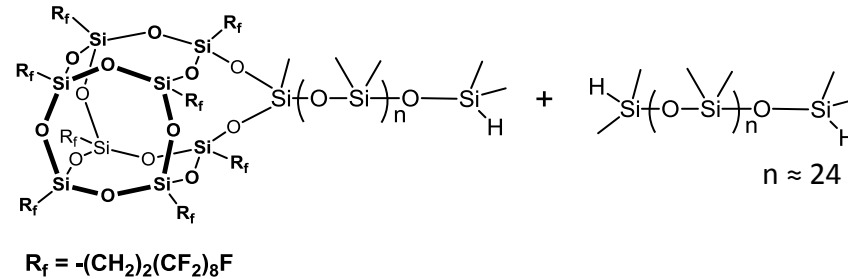


Crude rxn. mix.
4:1 C₆F₆:hexanes



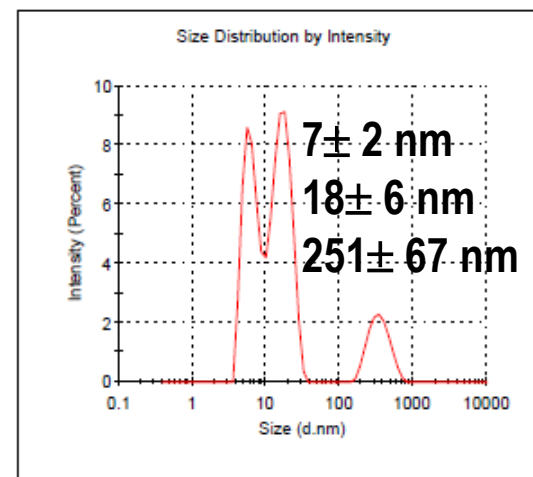
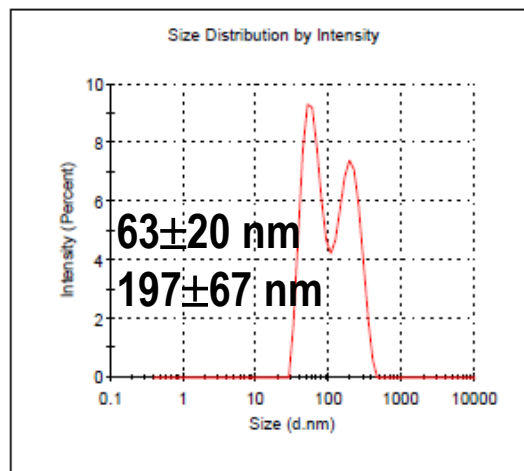
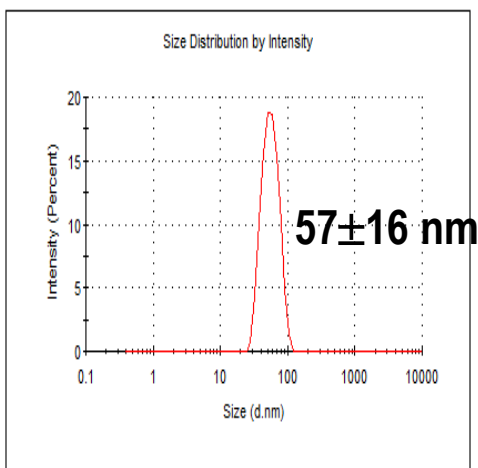
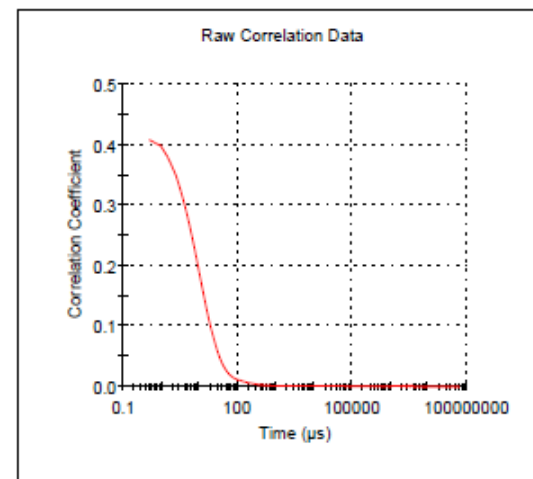
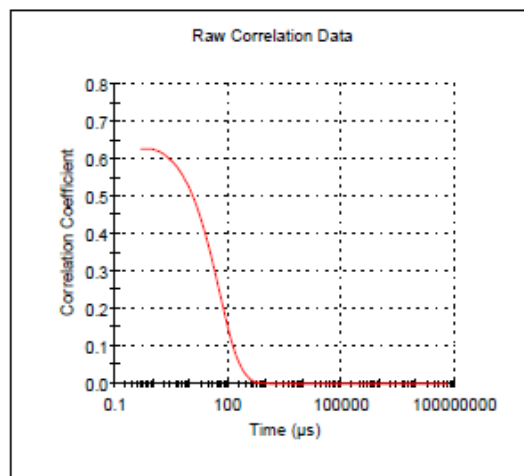
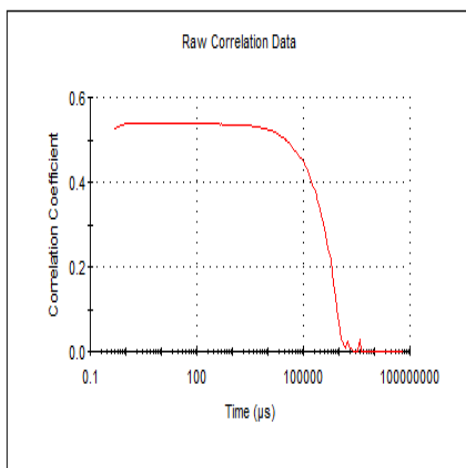
F-POSS Enchainment does not Change the T_g of PDMS





Pure fluorodecyl₈T₈ POSS: Water $\theta_{adv}/\theta_{rec} = 124^\circ/116^\circ$
Hexadecane $\theta_{adv}/\theta_{rec} = 80^\circ/61^\circ$

F-POSS PDMS Amphiphile Aggregation: Dynamic Light Scattering

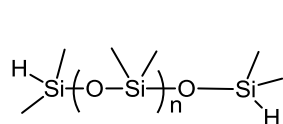


PDMS (1000 cSt)
0.001 M, 25 C

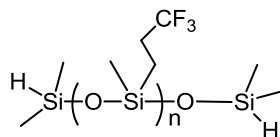
CDCI3
0.001 M, 25 C

AK225
0.001 M, 25 C

Thermal Stability of FPOSS-PDMS Micelles

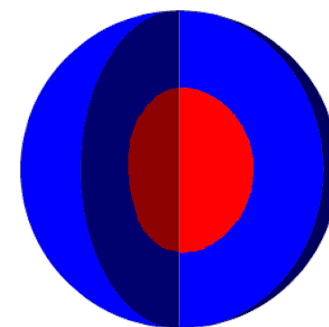
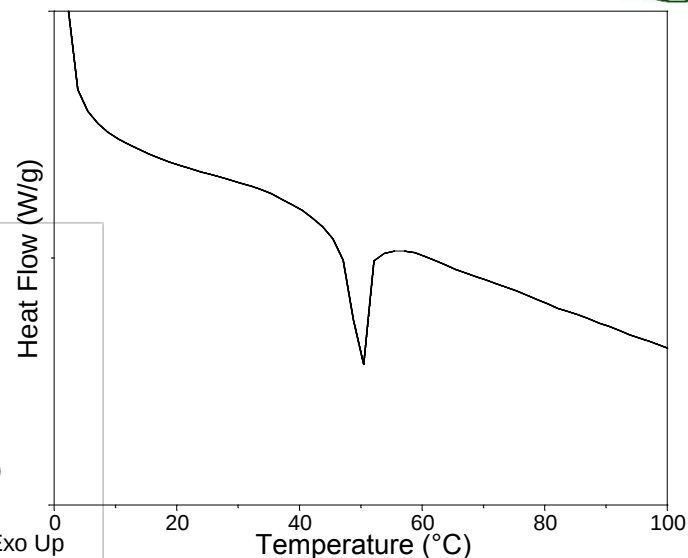
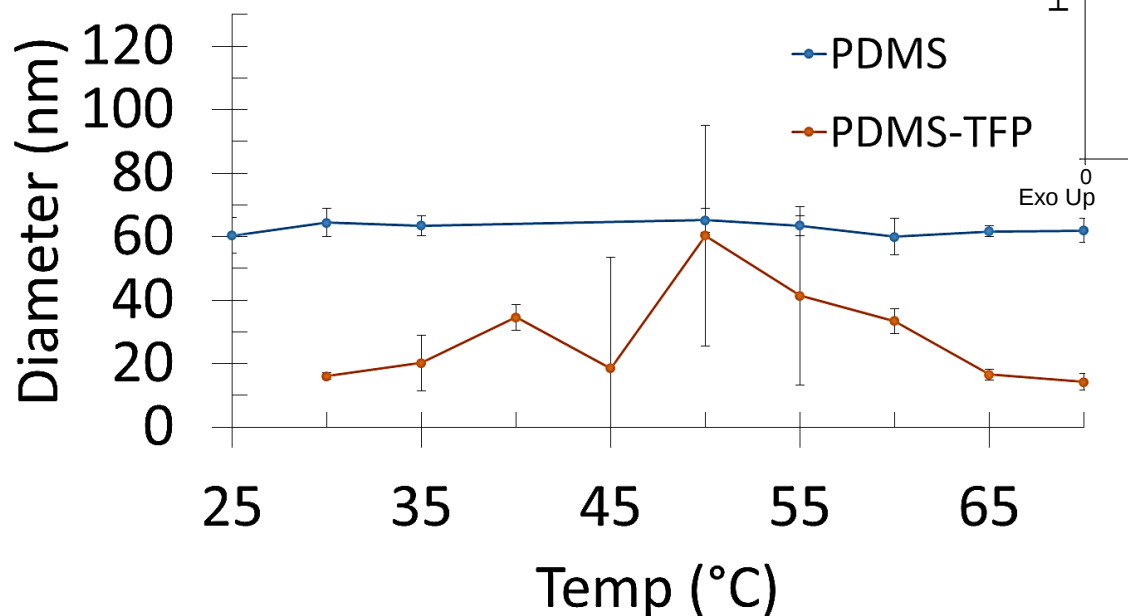


PDMS



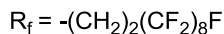
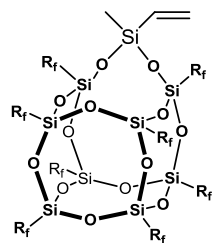
PDMS-TFP

5 wt% FPOSS-PDMS



In fluorinated matrix

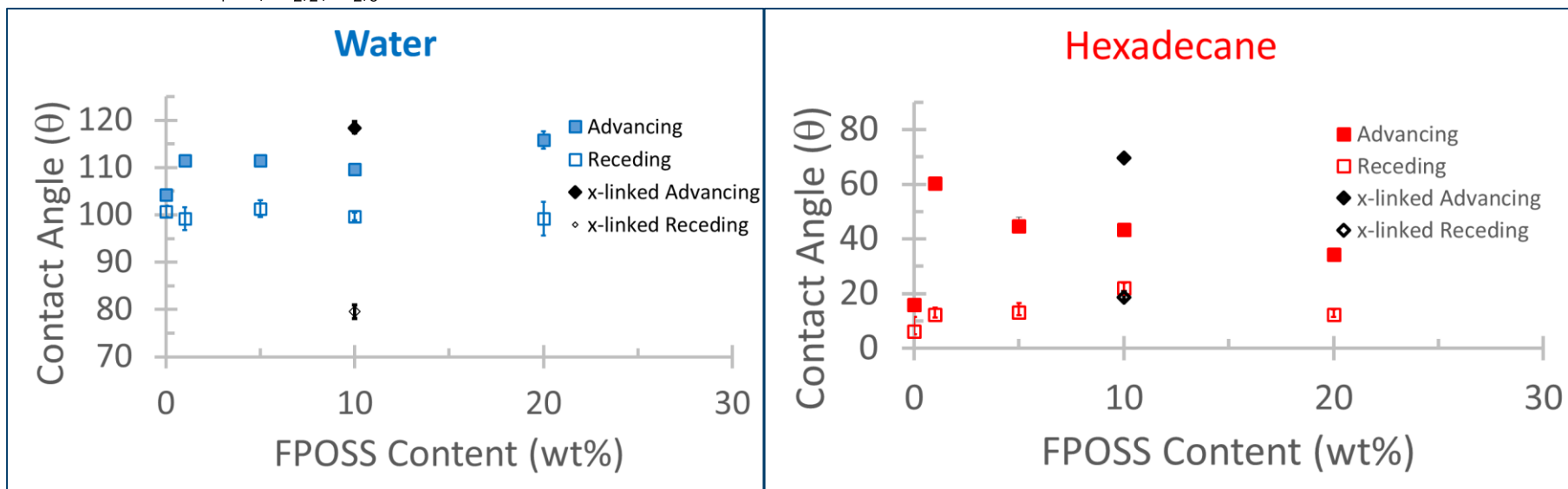
Surface Wetting of Fluorodecyl POSS-Enchained PDMS Elastomers



Sylgard 184
10:1 base:curative

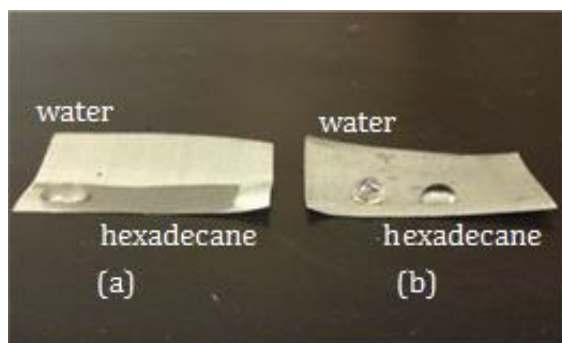
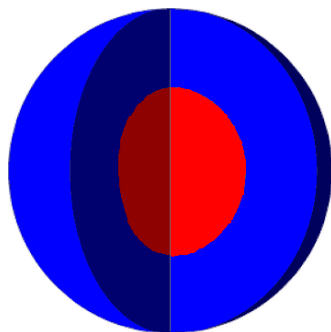
70 °C/4 hrs,
45 °C/17 hrs

F-POSS enchained PDMS Elastomer
(Black diamonds in figures)



Pure fluorodecyl₈T₈ POSS: Water $\theta_{adv}/\theta_{rec} = 124^\circ/116^\circ$

Hexadecane $\theta_{adv}/\theta_{rec} = 80^\circ/61^\circ$



Stainless steel mesh (325)

$$\text{H}_2\text{O } \theta_{\text{adv}} / \theta_{\text{rec}} = 132.6^\circ \pm 0.9 / 25.8^\circ \pm 9.2$$

$$\text{C}_{16}\text{H}_{34} \theta_{\text{adv}} / \theta_{\text{rec}} = 0^\circ / 0^\circ$$

➤ FPOSS enchainment enhances mechanical robustness accompanied by a reduction in liquid repellence

➤ F-POSS end-capped PDMS amphiphiles strongly favor the formation of micelles

➤ Aggregation plays a large role in the synthesis, assembly, and function of F-POSS PDMS amphiphiles

**Stainless steel mesh (325) dip-coated
44 wt% FPOSS x-linked PDMS**

$$\text{H}_2\text{O } \theta_{\text{adv}} / \theta_{\text{rec}} = 154.7 \pm 3.5^\circ / 147.8 \pm 1.7^\circ$$

$$\text{C}_{16}\text{H}_{34} \theta_{\text{adv}} / \theta_{\text{rec}} = 128.1 \pm 1.1^\circ / 84.0 \pm 20.7^\circ$$

Acknowledgments

