REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
October 2012	Briefing Charts	October 2012- December 2012

4. TITLE AND SUBTITLE
Polymerization of Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers

5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Sean M. Ramirez, Yvonne Diaz, Timothy S. Haddad, and Joseph M. Mabry

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
Q0AD

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQRC
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2012-433

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited. PA#13011

13. SUPPLEMENTARY NOTES
Briefing Charts for the Silicon and Silicon Containing Composites, San Diego, California in 12 December 2012.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Joseph Mabry
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	34	**19b. TELEPHONE NO** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			661-275-5857

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

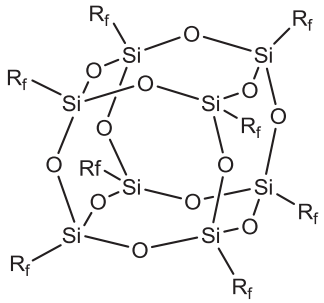
Polymerization of Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers

Sean M. Ramirez,[1] Yvonne Diaz,[2] Timothy S. Haddad,[1] and Joseph M. Mabry[2]

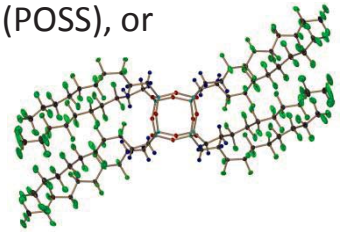
[1]ERC Inc., Air Force Research Laboratory, Rocket Propulsion Division, Edwards AFB, CA 93524-7680 U.S.A.
Phone: (661) 275-5769, sean.ramirez.ctr@edwards.af.mil

[2]Air Force Research Laboratory, Rocket Propulsion Division, Edwards AFB, CA 93524-7680 U.S.A.

Introduction to F-POSS



(1,1,2,2-tetrahydroperfluorodecyl)$_8$Si$_8$O$_{12}$ Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS



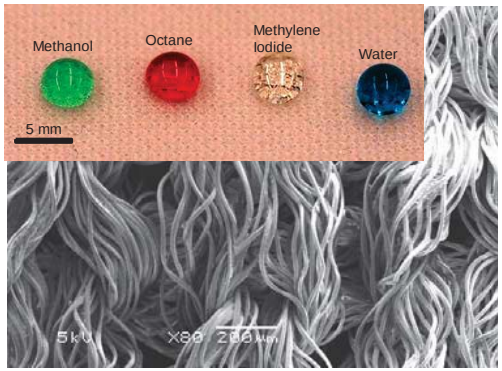
- hybrid organic-inorganic structure
- well-defined polyhedral architecture
- long-chain fluoroalkyl substituents on periphery of cage

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

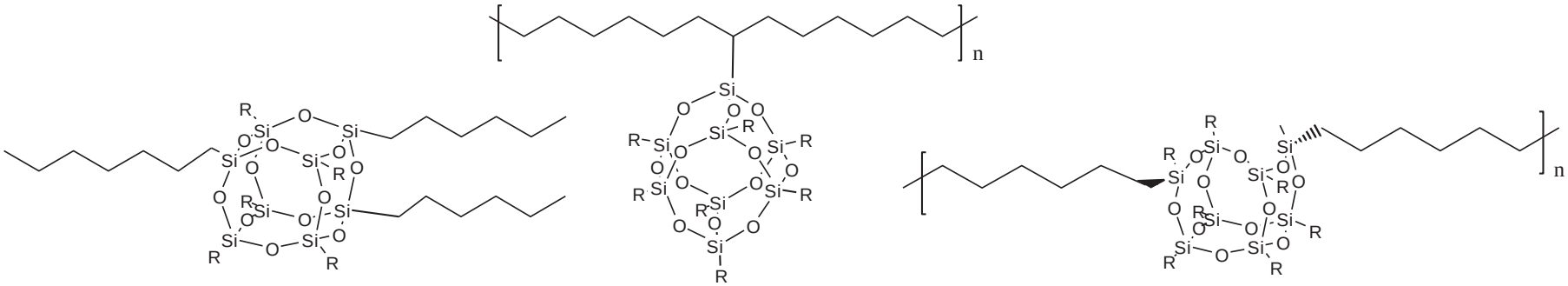
Superhydrophobic/oleophilic dip-coated fabric
Tuteja *et al*, Science, **2007**, 318, 1618



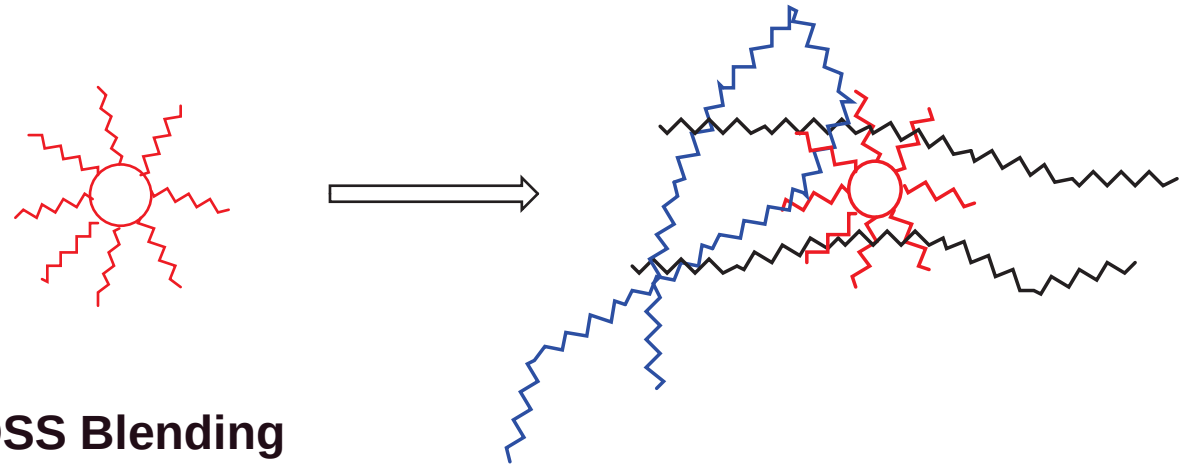
Superamphiphobic dip-coated fabric
Choi *et al*, Adv Mater, **2009**, 21, 2190

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

POSS Incorporation in Polymers



Cross-linker **Pendant Polymer** **Bead Copolymer**

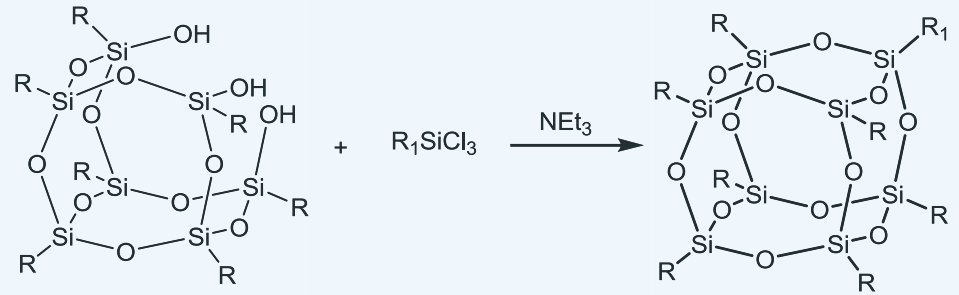


POSS Blending

Cordes, D. B.; Lickiss, P. D.; Rataboul, F., *Chem. Rev.* 2010, *110* (4), 2081-2173. Phillips, S. H.; Haddad, T. S.; Tomczak, S. J., *Curr. Opin. Solid State Mater. Sci.* 2004, *8*, 21-29 Iacono, S. T.; Buddy, S. M.; Mabry, J. M.; Jr., D. W. S., *Polymer* 2007, *48*, 4637-4645. Koh, K; et. al., *Macromolecules* 2005, *38*, 1264-1270.

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

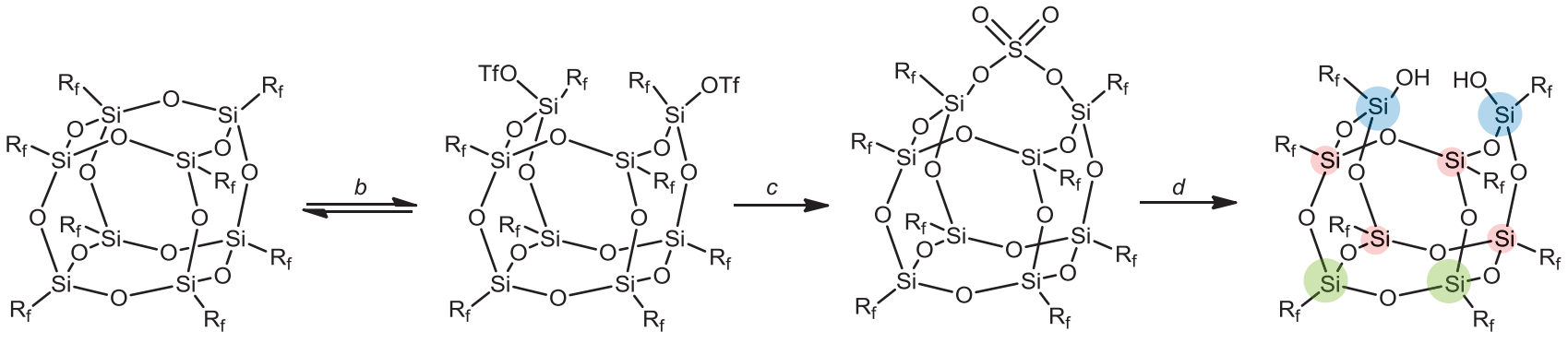
Methods to Produce Incompletely Condensed Silsesquioxanes

- 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 long-chain 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.

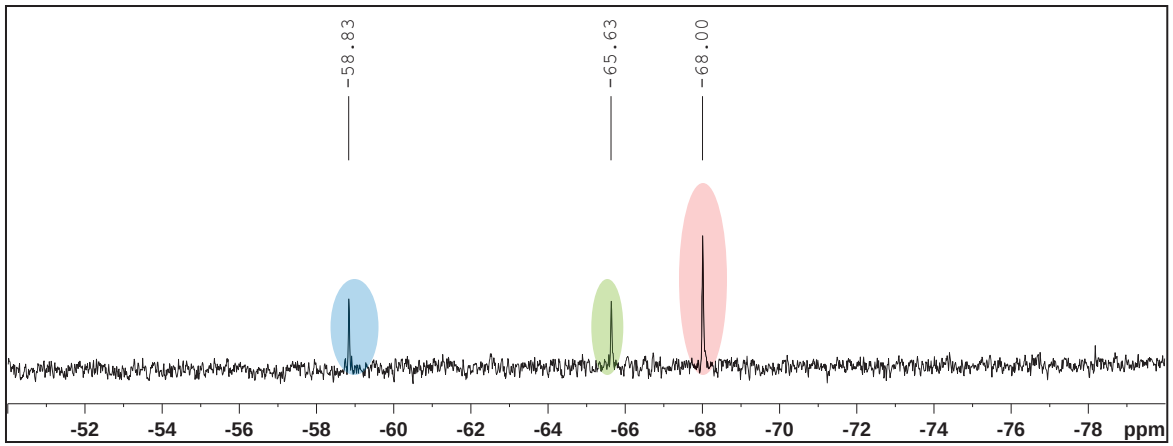
Incompletely Condensed Silsesquioxane



[a]Conditions: All reactions were performed in C_6F_6 at 25 °C. [b]CF_3SO_3H, 75 mins. [c]$NBut_4HSO_4$, 30 mins, [d]$(CF_3)_2CH_2OH/H_2O$ (10:1), 12 hrs.

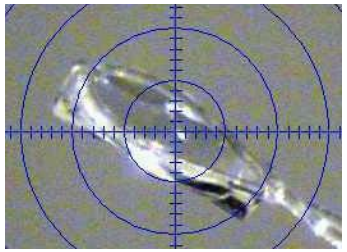
- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.

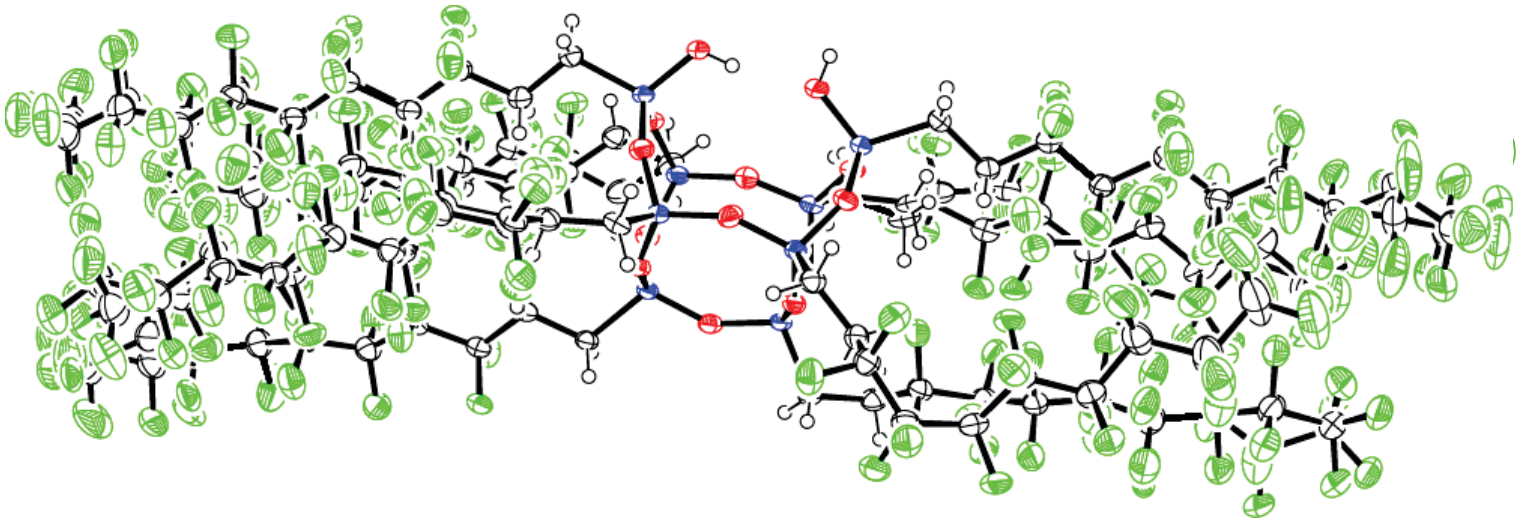
^{29}Si NMR in C_6F_6 of disilanol F-POSS

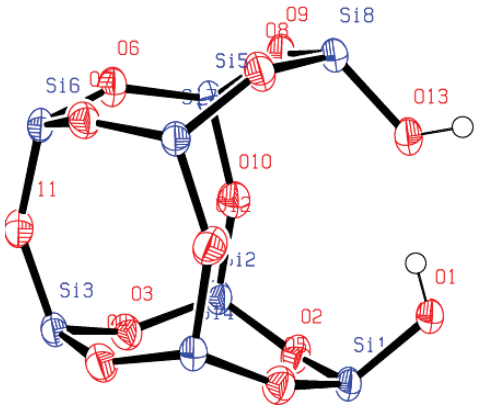


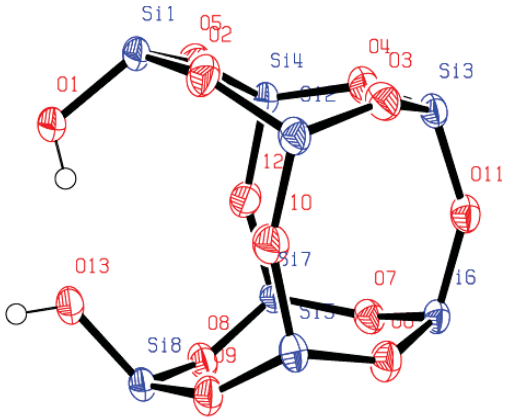
Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Haddad, T. S.; Mabry, J. M. ACS Symposium Series" Advances in Fluorine Containing Polymers 2012 1106, 95-109.
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* 2011, *133*, 20084.

X-Ray Crystal Structure of Disilanol





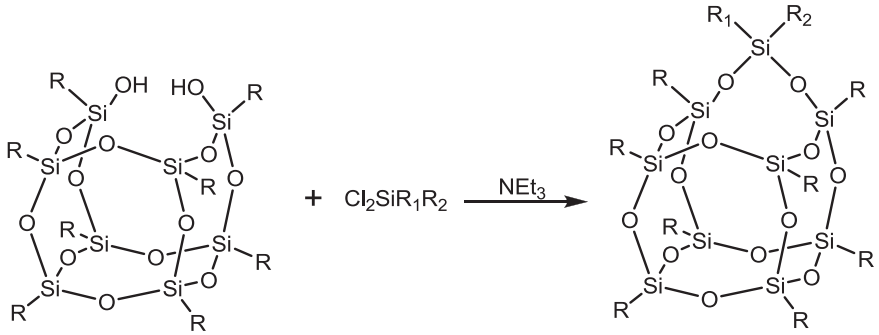




- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- M_r=,monoclinic, space group P2(1)/c , a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, α= 90.00°, β=92.21(10) °, γ=90.00 °, V= 12878(2) Å^3

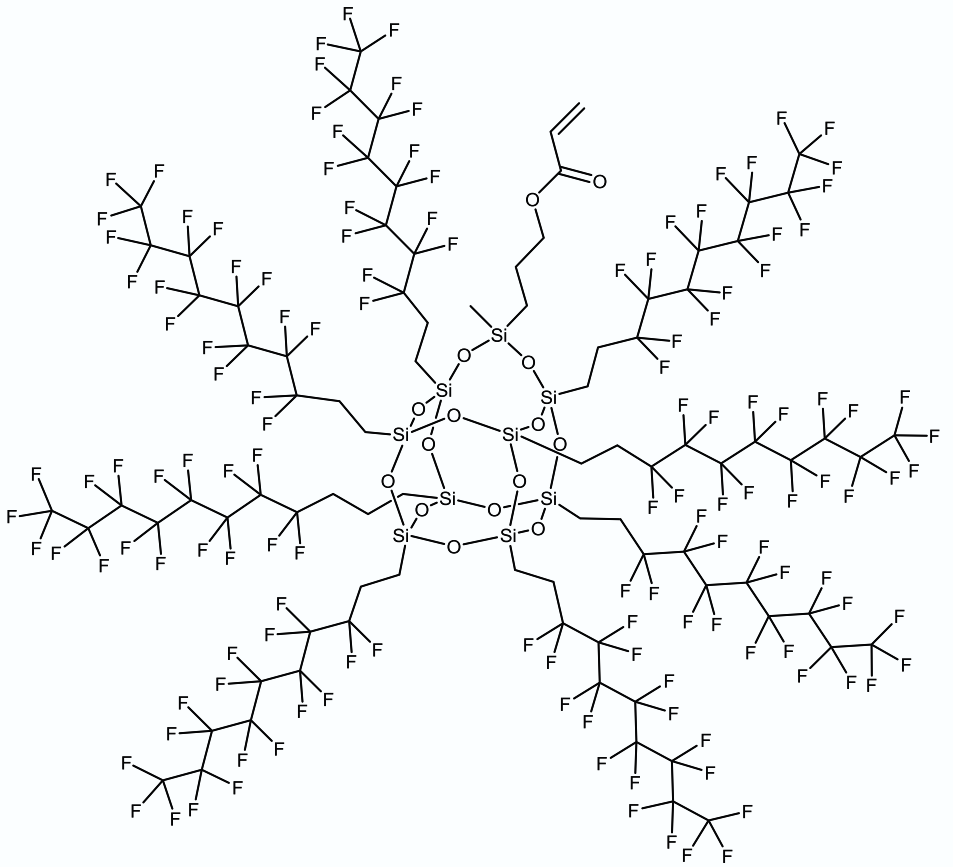
Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Haddad, T. S.; Mabry, J. M. ACS Symposium Series" Advances in Fluorine Containing Polymers 2012 1106, 95-109.
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* 2011, *133*, 20084.

Edge Capping Reactions



R = $CH_2CH_2(CF_2)_7CF_3$
R_1 = alkyl or aromatic
R_2 = 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

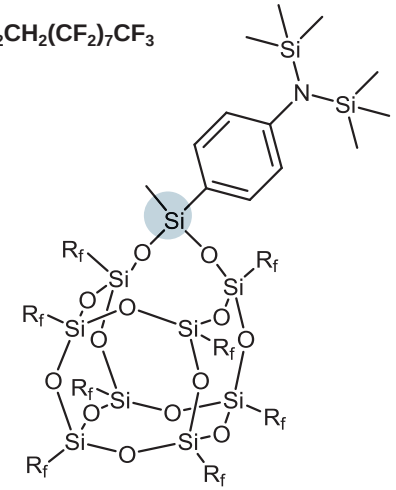


Macromer/RBM = 4178 g/mol

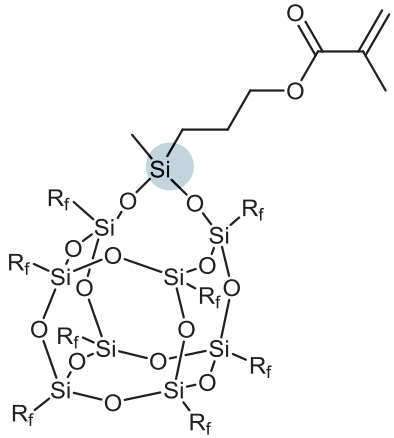
Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Haddad, T. S.; Mabry, J. M. ACS Symposium Series" Advances in Fluorine Containing Polymers 2012 1106, 95-109.
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* 2011, *133*, 20084.

^{29}Si NMR of F-POSS Structures

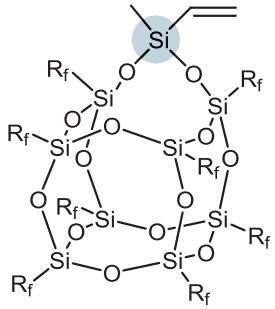
R = $CH_2CH_2(CF_2)_7CF_3$



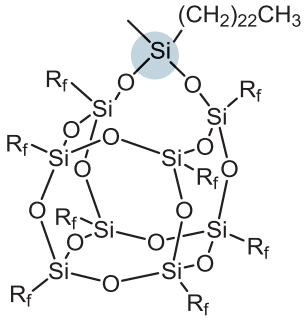
-29.5 ppm



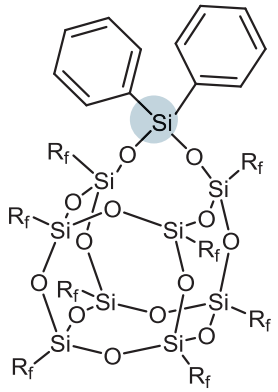
-17.8ppm



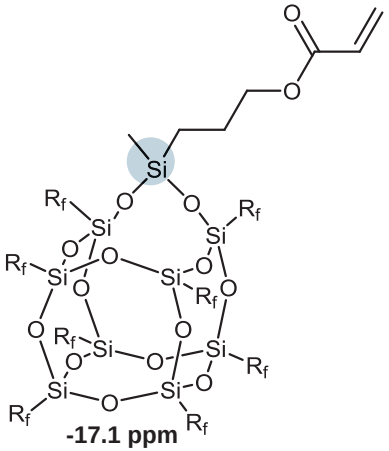
-32.1 ppm



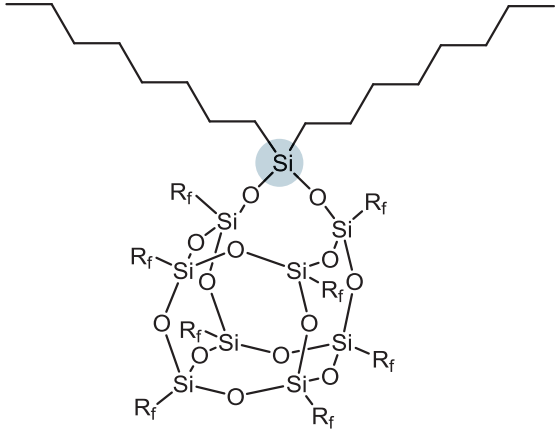
-17.8 ppm



-45.5 ppm



-17.1 ppm

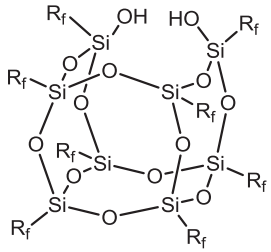


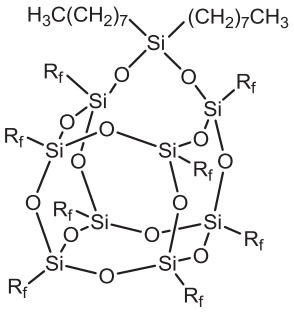
-17.9 ppm

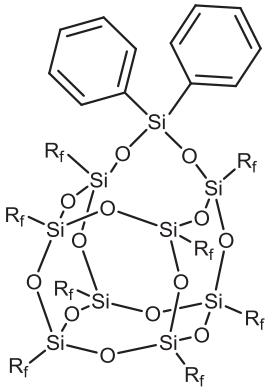
Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Haddad, T. S.; Mabry, J. M. *ACS Symposium Series" Advances in Fluorine Containing Polymers* 2012 1106, 95-109.
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* 2011, *133*, 20084.

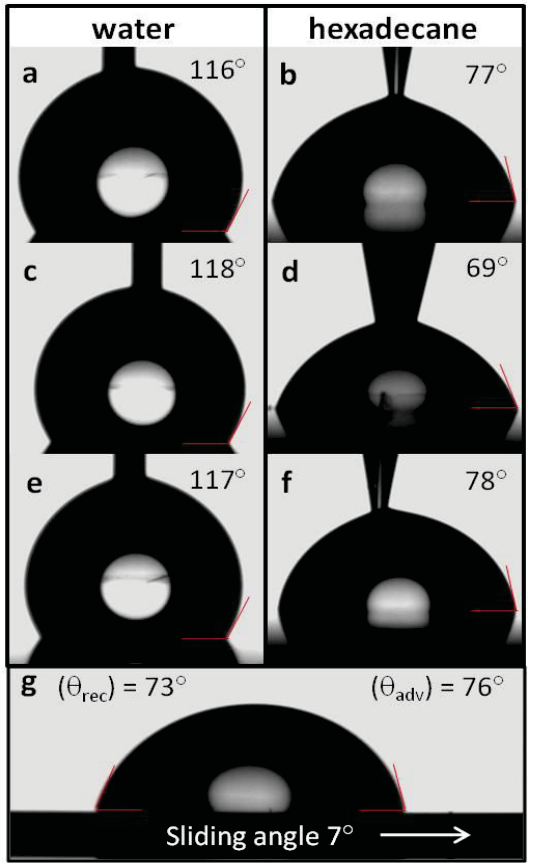
Contact Angle Measurements

- 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?*





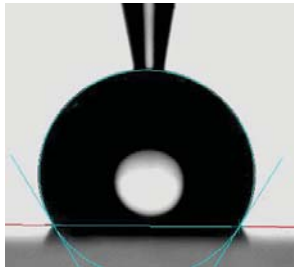




Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10μL) rolling off surface coated with compound **diphenyl** (g).

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.

Dynamic Contact Angle Measurements

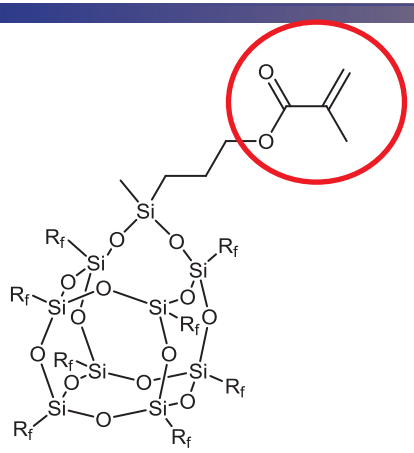


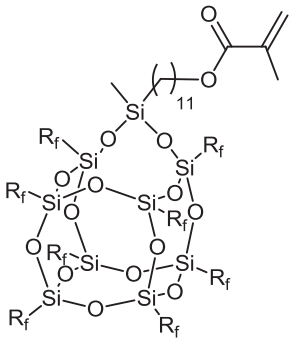
Functional Group on F-POSS	*water*		*hexadecane*	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS*	124 ± 0.5°	109.6 ± 0.7°	79.1 ± 0.4°	65.1 ± 0.5°
Si-$(OH)_2$	116.8 ± 0.4°	111 ± 0.6°	77.4 ± 0.4°	74.4 ± 0.8°
Si-$(CH_3)(CH{=}CH_2)$	116.2 ± 0.4°	100.6 ± 0.8°	78.4 ± 0.3°	70.6 ± 2.3°
Si$((CH_3)((CH_2)_3OC(O)CCH{=}CH_2)$	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°

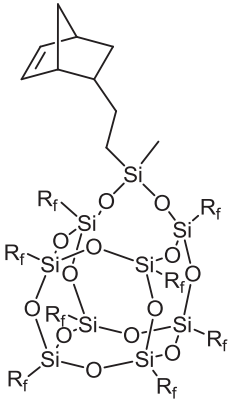
Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).

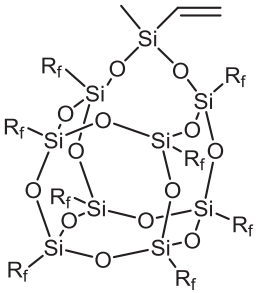
*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544.

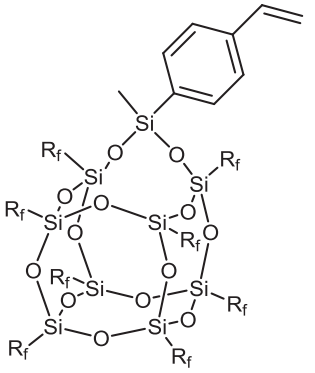
F-POSS Structures Synthesized

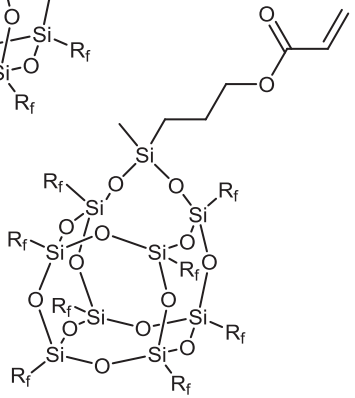


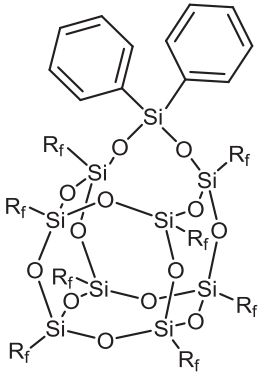




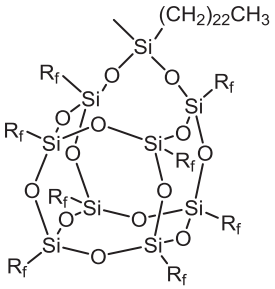


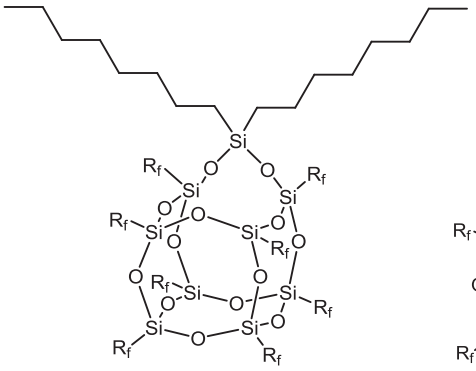


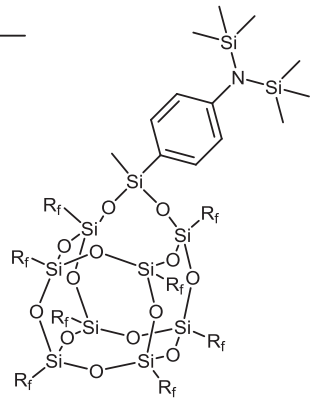


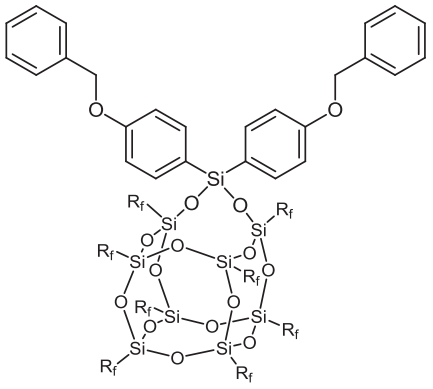


R_f = $CH_2CH_2(CF_2)_7CF_3$

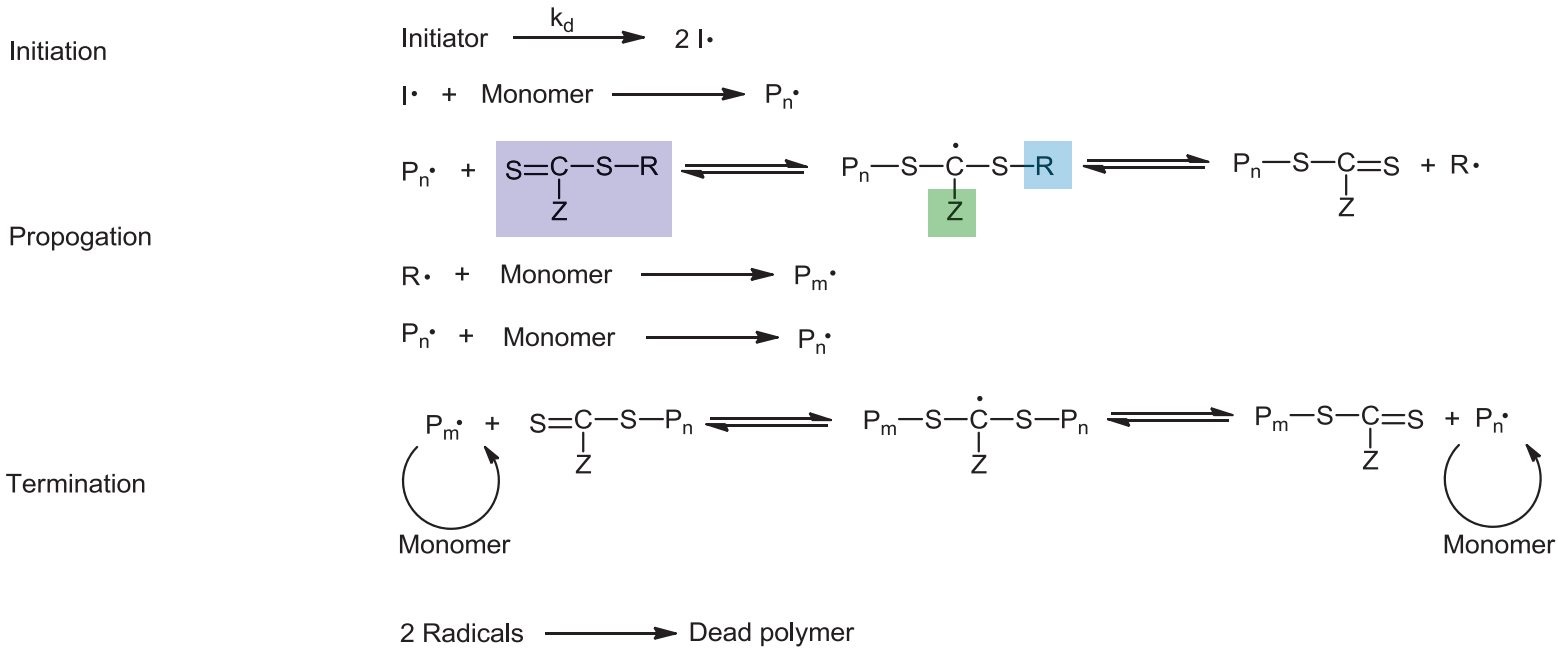




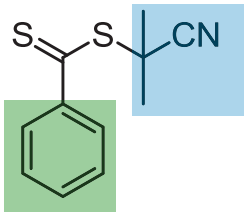




Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization



Chain Transfer Agent

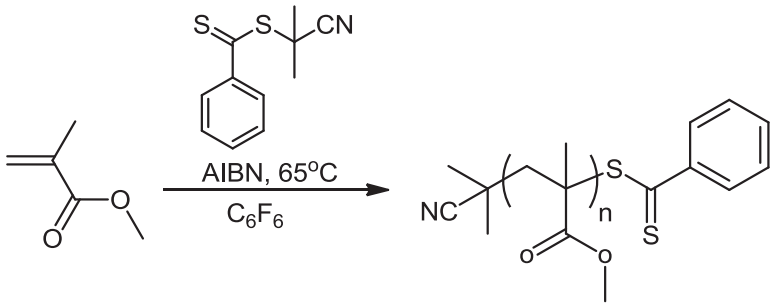


RAFT Polymerization

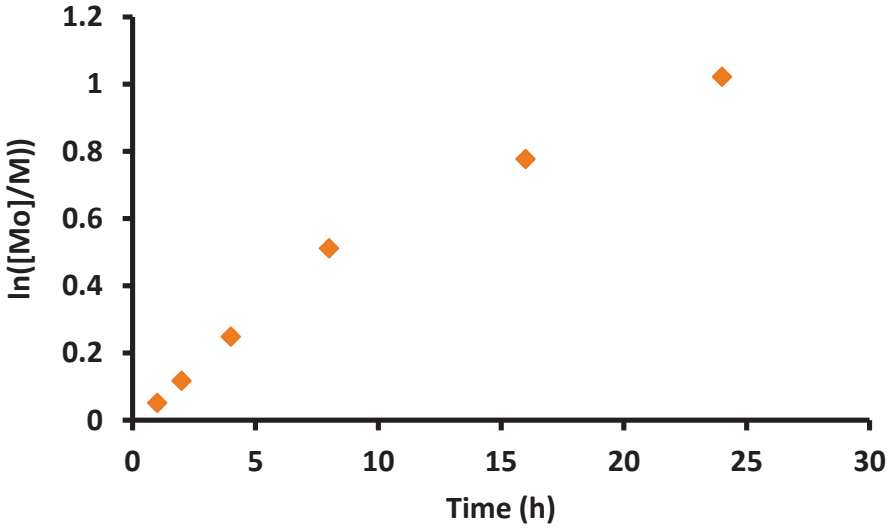
- Controlled polymerization
- Allows for block copolymers
- Tune molecular weight

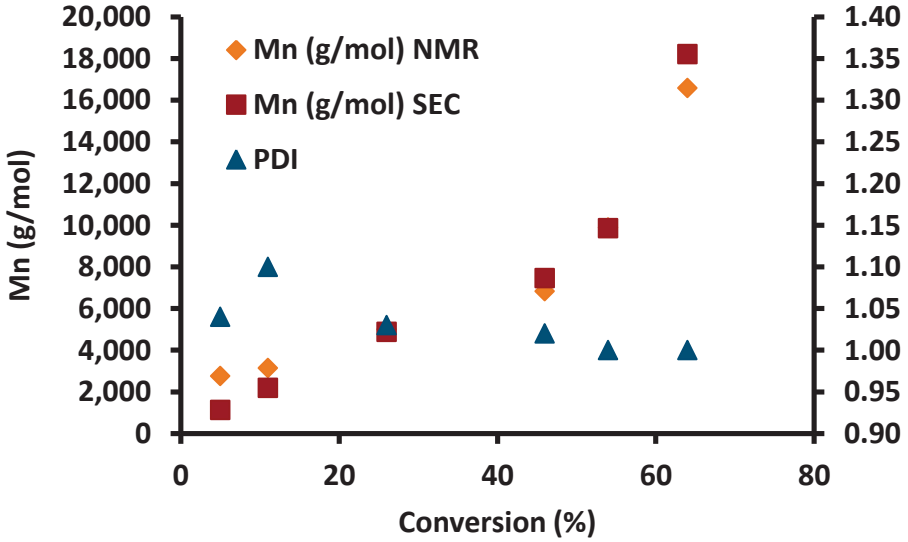
Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H., *Macromolecules* 1998, *31*, 5559−5562.
Moad, G.; Bicciocchi, E.; Chen, M.; Chiefari, J.; Guerrero-Sanchez, C.; Haeussler, M.; Houshyar, S.; Keddie, D.; Rizzardo, E.; Thang, S. H.; Tsanaktsidis, J., *ACS Symp. Ser.* 2012, *1100*, 243-258.

RAFT polymerization of MMA in C_6F_6



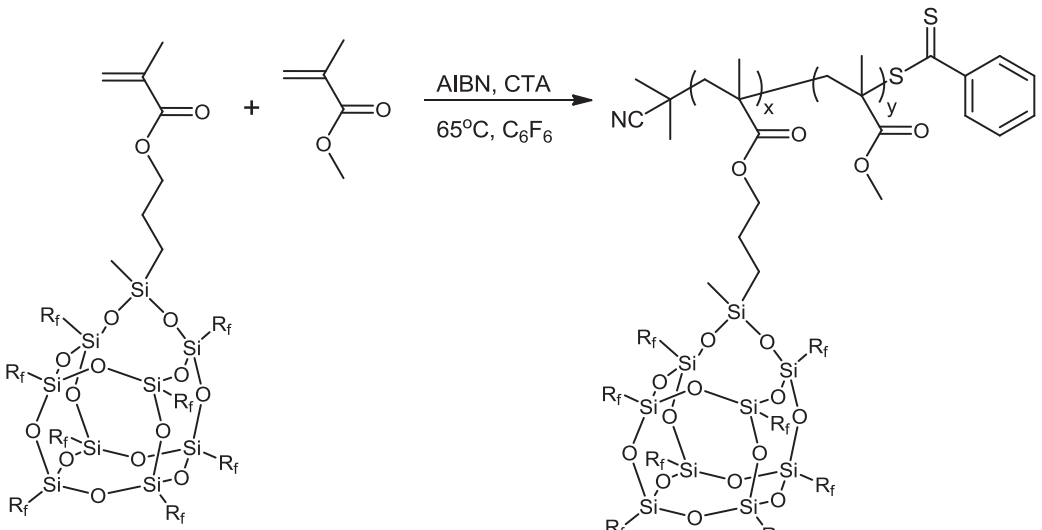
- Testing RAFT in fluorinated solvent
- RAFT polymerization proceeds in C_6F_6
- Best control in first 10 hours

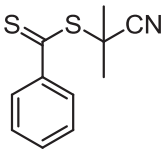


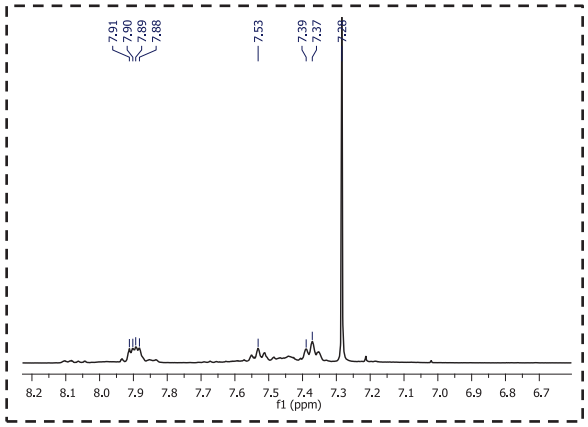


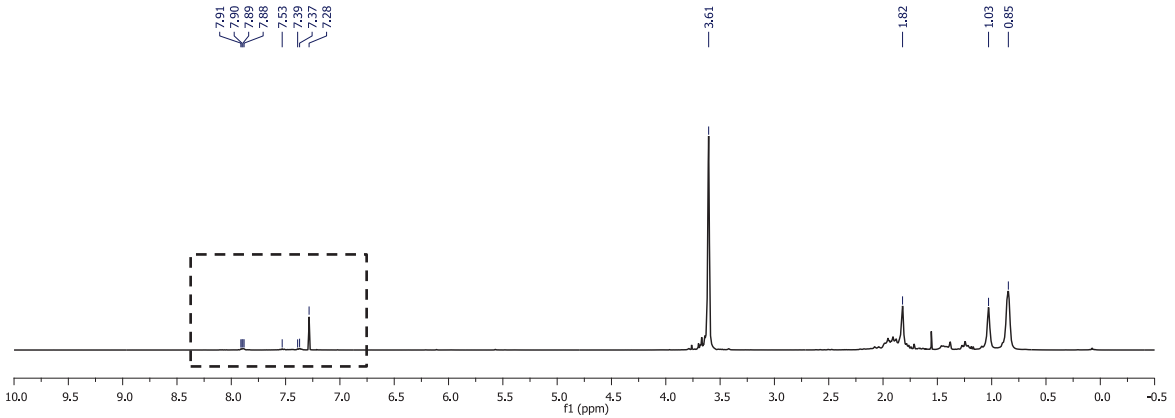
SEC MALLS: RI and LS detector (Wyatt), 1.0 mL/min, 30 min, THF.

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



CTA = 





$R_f = CH_2CH_2(CF_2)_7CF_3$

^1H NMR in $CDCl_3$

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

F-POSS	M_w		Conv.	water		hexadecane	
wt %	(g/mol)	PDI	%	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
	F-POSS-MMA			117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°
0	58,100	1.05	73	77.8 ± 1.3°	57.8 ± 2.5°	wetted	wetted
1	58,700	1.08	72	109.2 ± 2.4°	61.5 ± 1.9°	67.8° ± 1.4	wetted
5	23,000	1.01	30	117.8 ±1.6°	95.7 ± 5.9°	76.7 ± 1.1°	68.8 ± 1.9°
10	26,600	1.01	29	118.2 ± 1.4°	101.1 ±2.5°	77.2 ± 0.4°	69.5 ± 2.1°
25	37,700	1.03	41	120.8 ± 97.0°	97.0 ± 2.4°	82.9 ± 0.4°	74.6 ± 2.0°

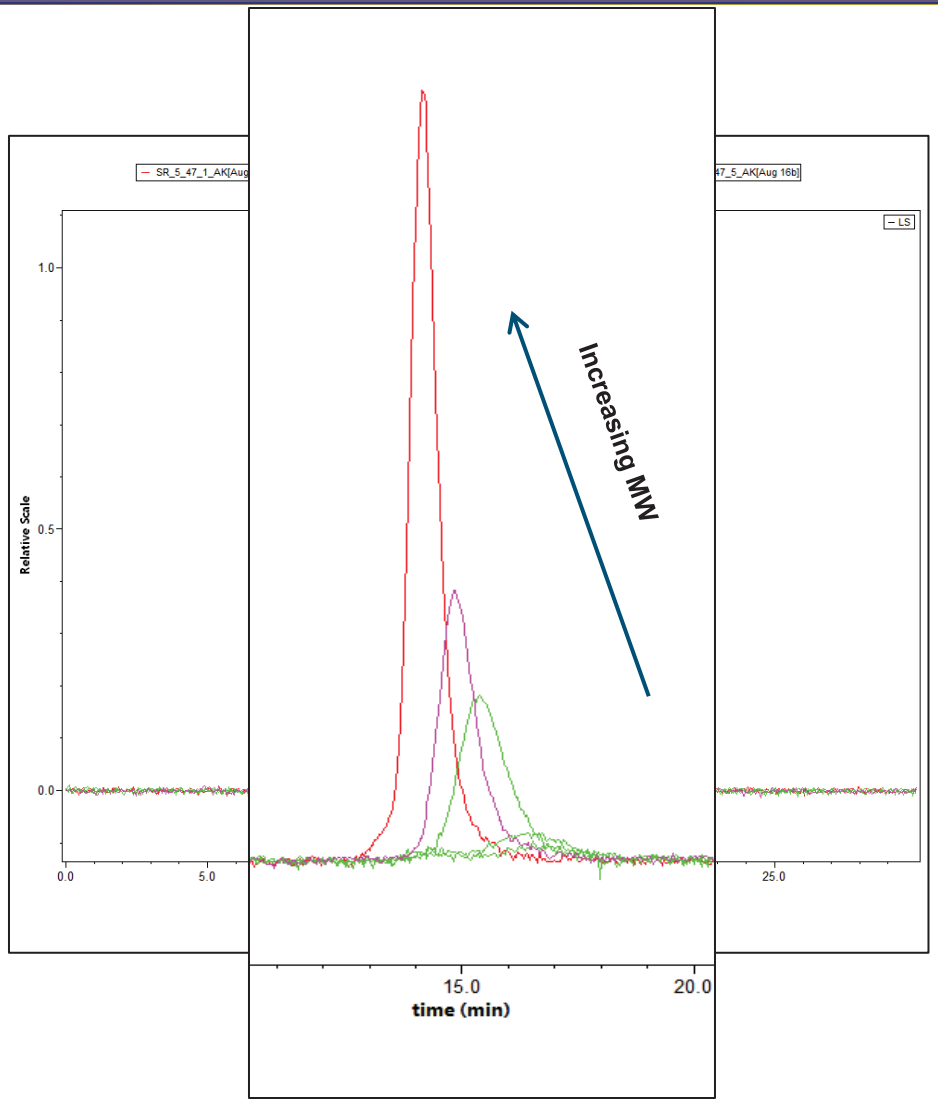
SEC-MALLS conditions: 25°C, flow rate (1 mL/min), solvent (Asahiklin-225 [mixture of dichloropentafluoropropanes]), concentration measured with RI detector. Contact angle conditions: polymer solutions (20 mg/mL) were spun cast on SiO_2 wafers at 900 rpm.

Isemura, T.; Kakita, R.; Kawahara, K., *Journal of Chromatography A* 2004, *1026*, 109-1196.
Wesdemiotis, C.; Pingitore, F.; Polce, M. J.; Russell, V. M.; Kim, Y.; Kausch, C. M.; Connors, T. H.; Medsker, R. E.; Thomas, R. R., *Macromolecules* 2006, *39*, 8369-8378.

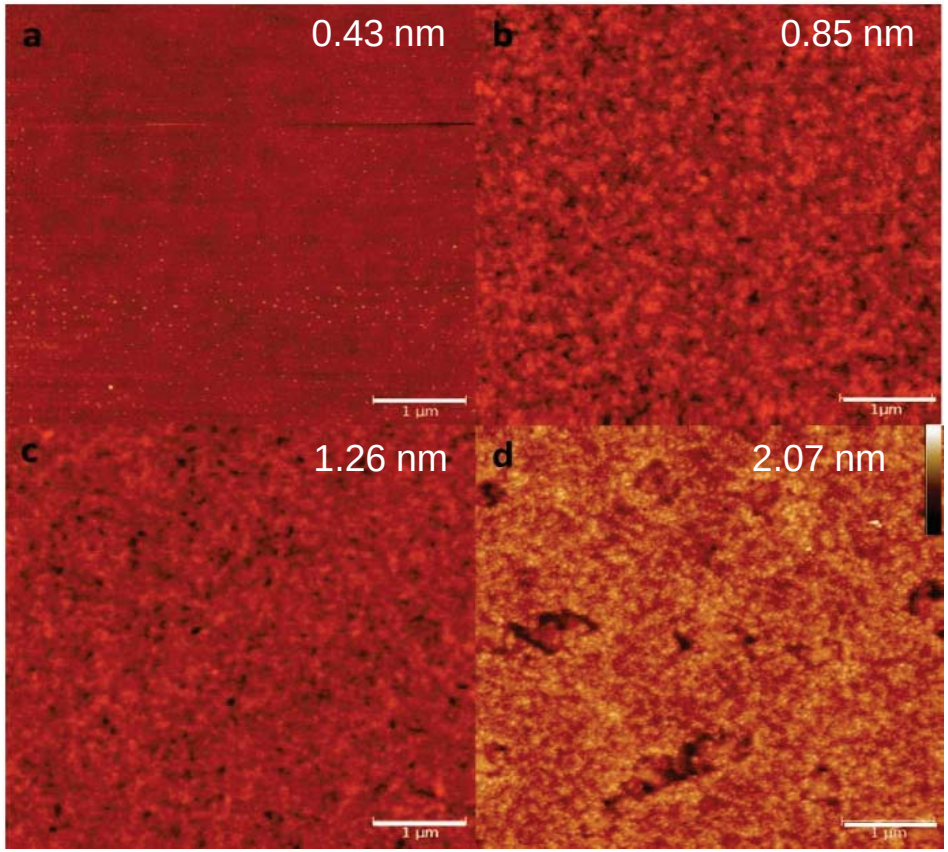
RAFT copolymerization of P(F-POSS-MA)-co-PMMA

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
  - Polymerization difficult above 50 wt % F-POSS-MMA loading



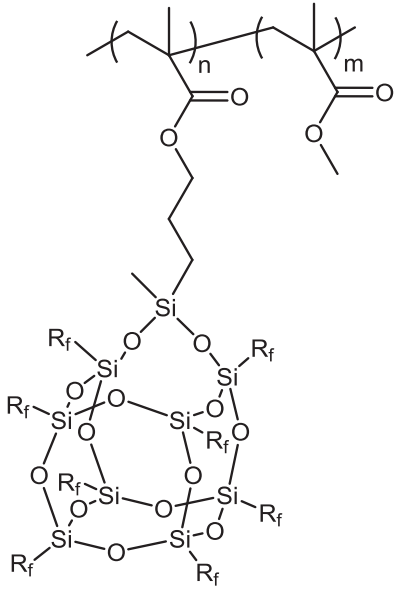
AFM of P(F-POSS-MA)-co-PMMA

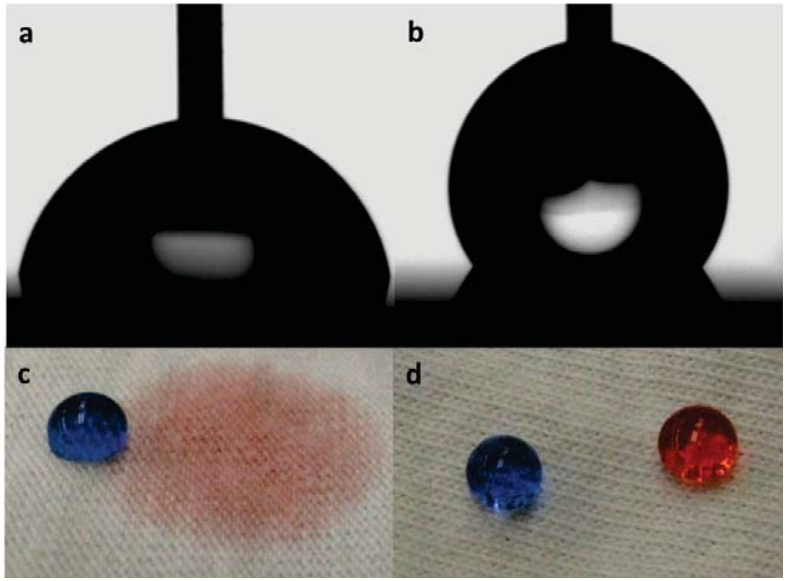


AFM image of spun cast films of a) 1 wt. % b) 5 wt. %. c) 10 wt. % and d) 25 wt.% F-POSS copolymer on SiO_2 from a 10 mg/mL concentrated solution in Asahiklin-225 at 900 rpm. Each image is shown with a z-scale of 0–10 nm. Top corner of each image root mean squared (rms) surface roughness.

PMMA Copolymerization Summary

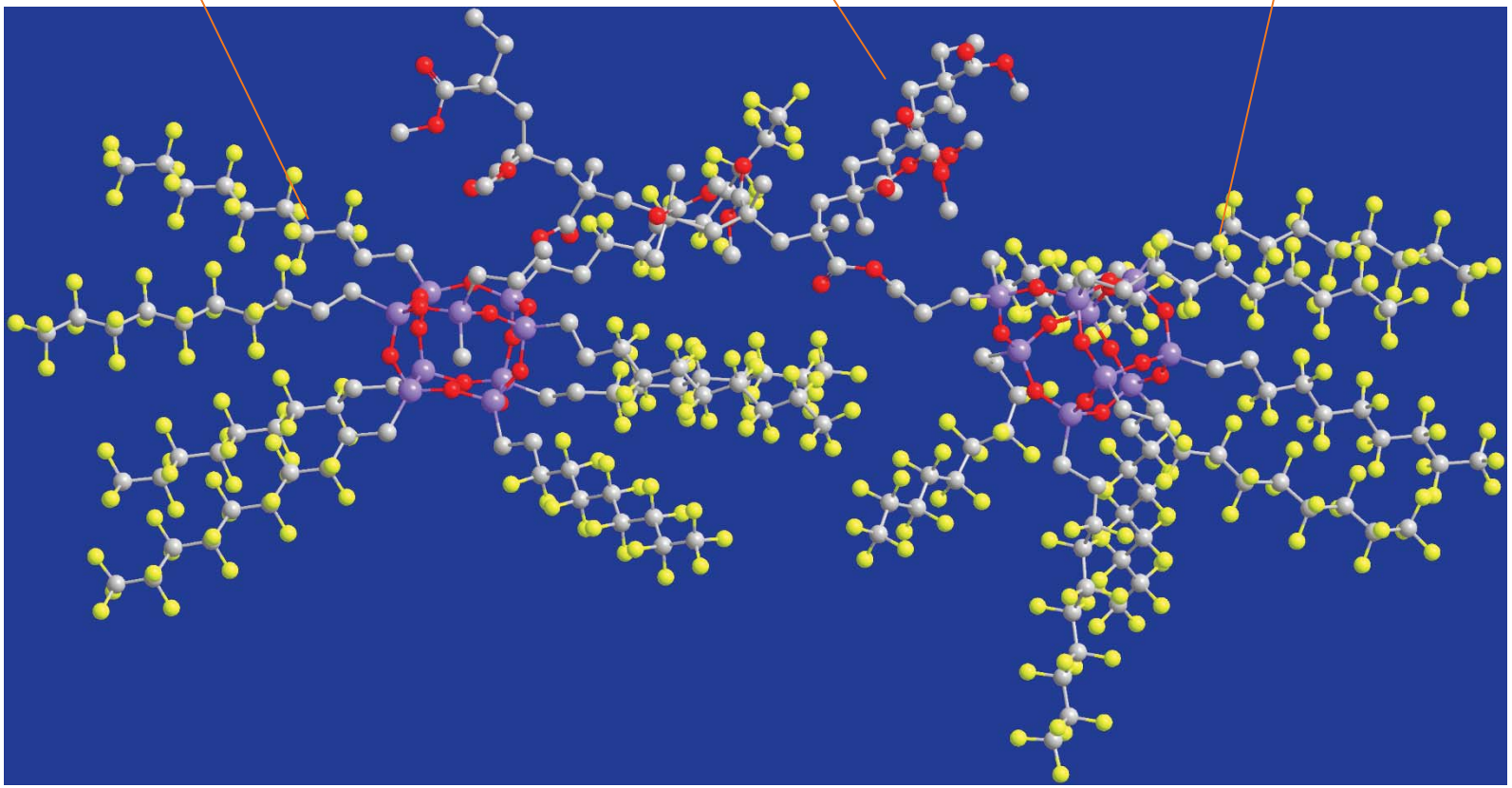
- Copolymerizations produced F-POSS based copolymers.
- Polymerization have trouble at higher F-POSS monomer feed ratios and are more controlled at lower conversion with RAFT initiator.
- Can we make homopolymer?



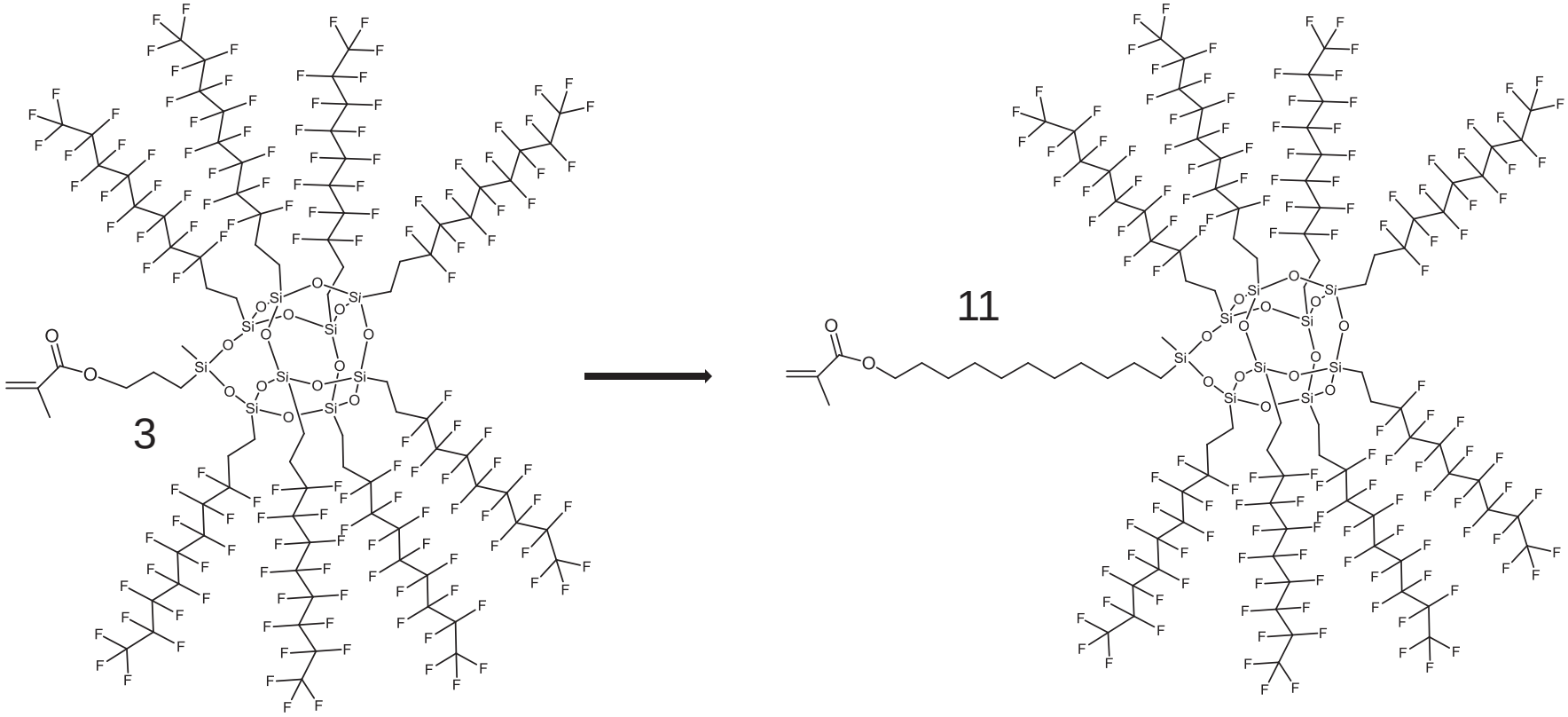


Static contact angle of a water droplet on a) 0 wt.% F-POSS copolymer or b) 25 wt.% F-POSS copolymer. Water (blue) and hexadecane (red) droplets on cotton fabric coated with c) 0 wt.% F-POSS copolymer and d) 25 wt. % F-POSS copolymer from 1% solution in Asahiklin-225.

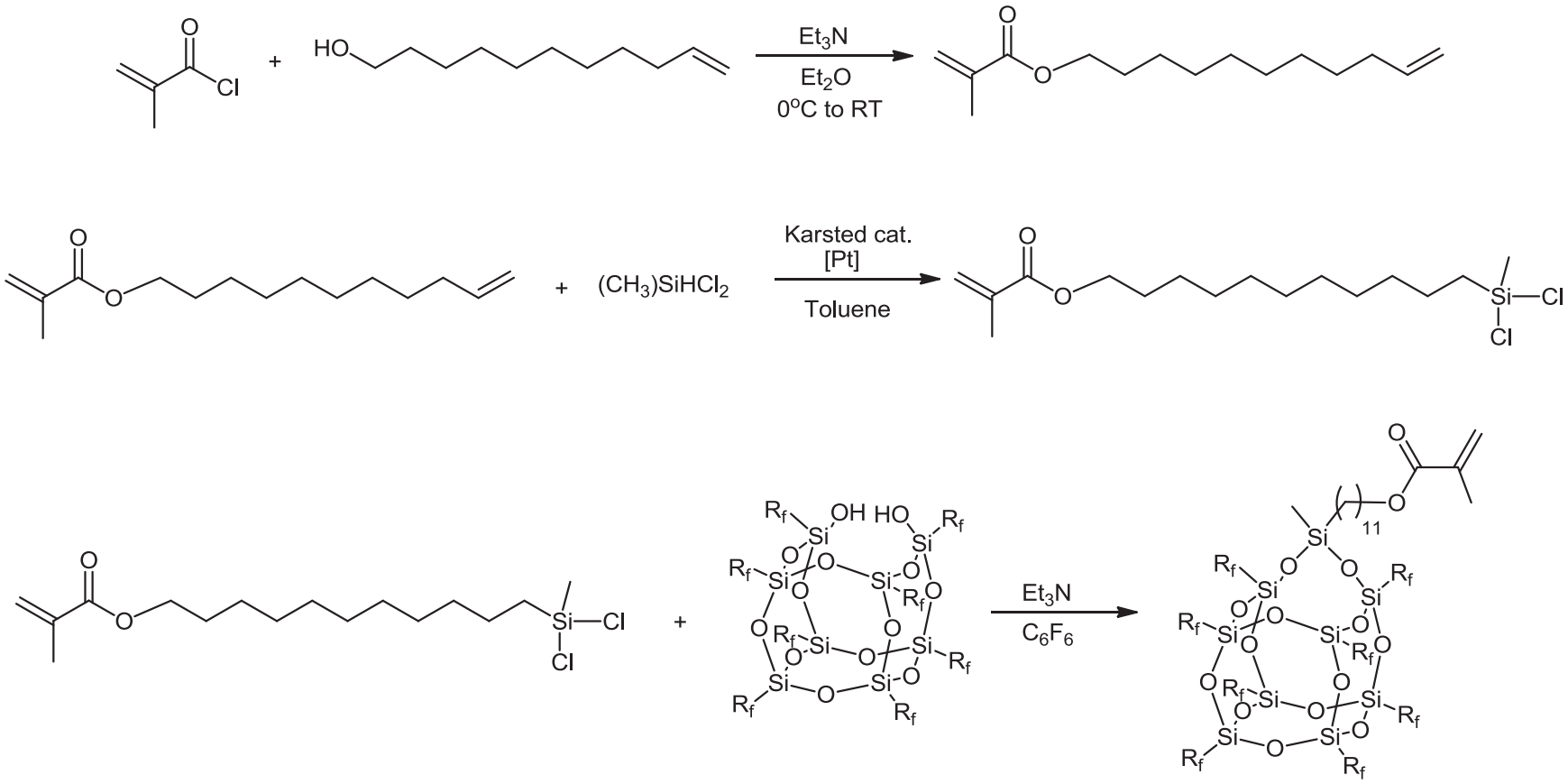
Is it crowded in here?



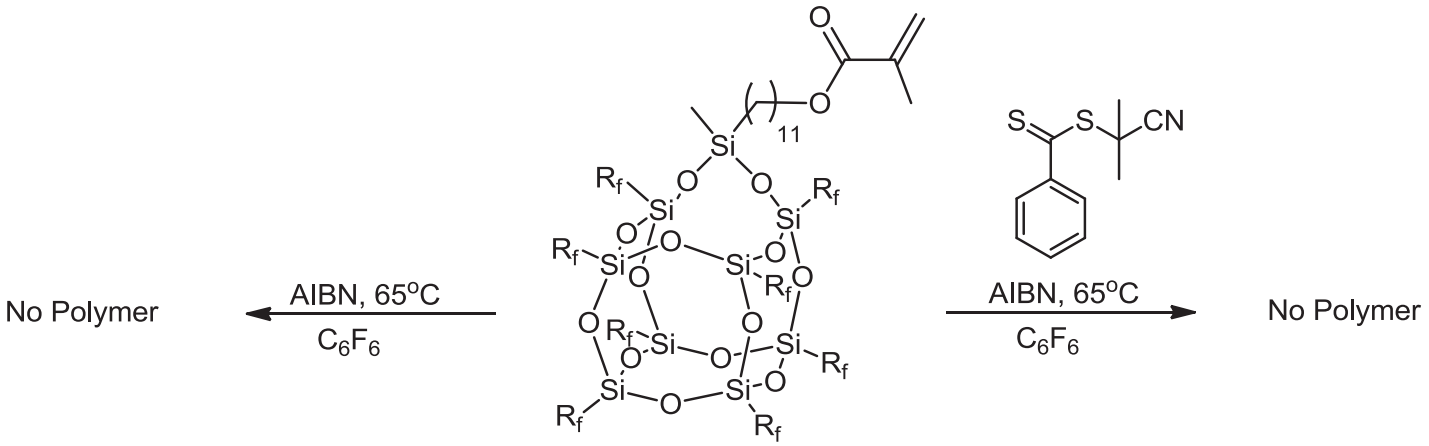
Extend the Chain



Long Chain Monomer Synthesis

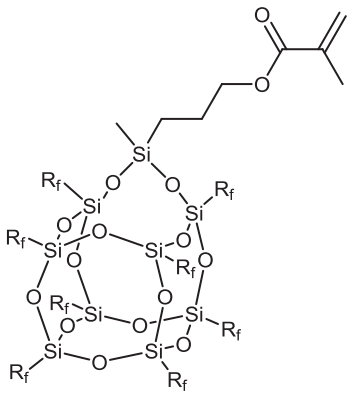


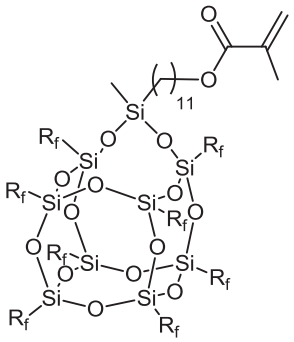
Free Radical Polymerization

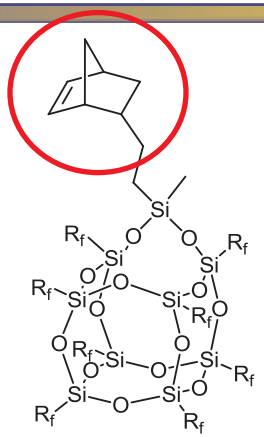


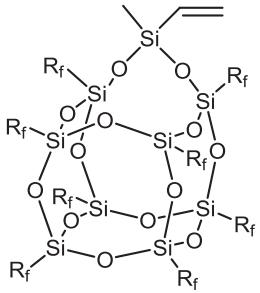
- No polymerization

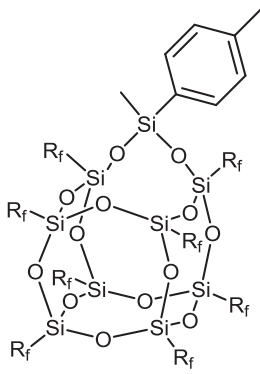
F-POSS Structures Synthesized

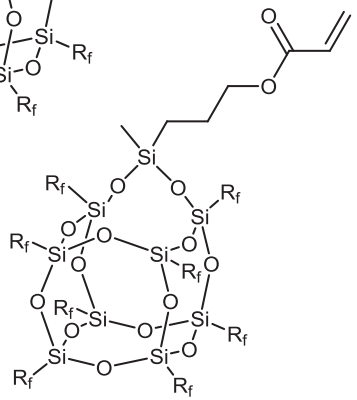


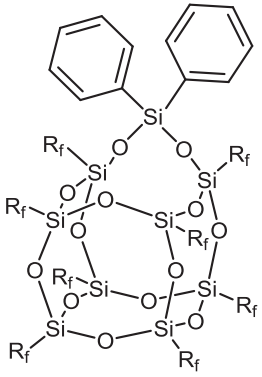




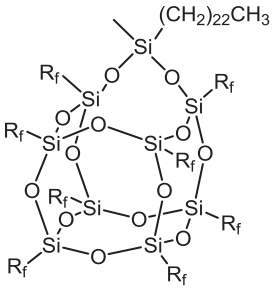


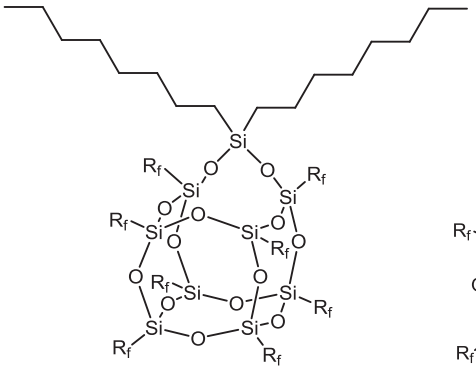


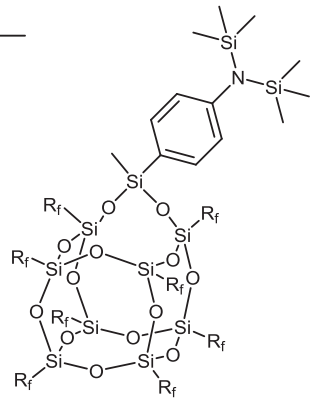


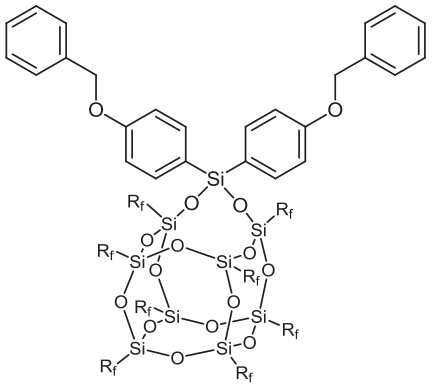


R = $CH_2CH_2(CF_2)_7CF_3$

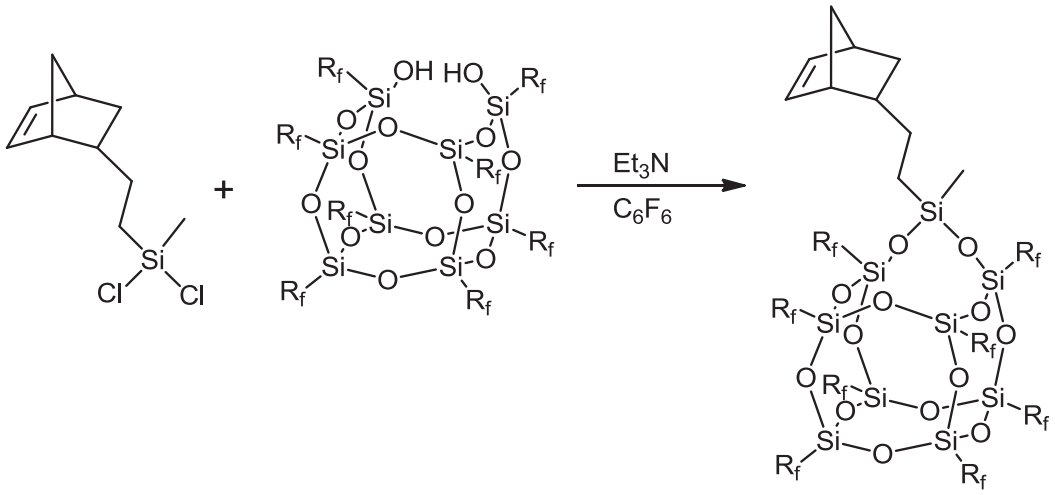






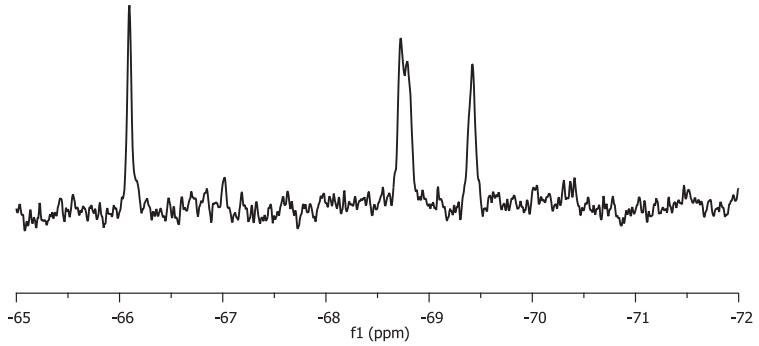


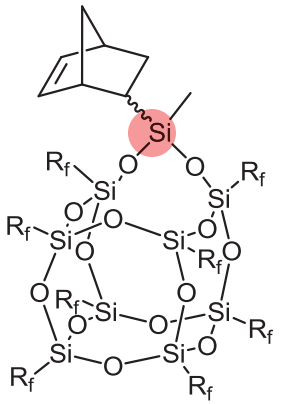
Norbornene Synthesis

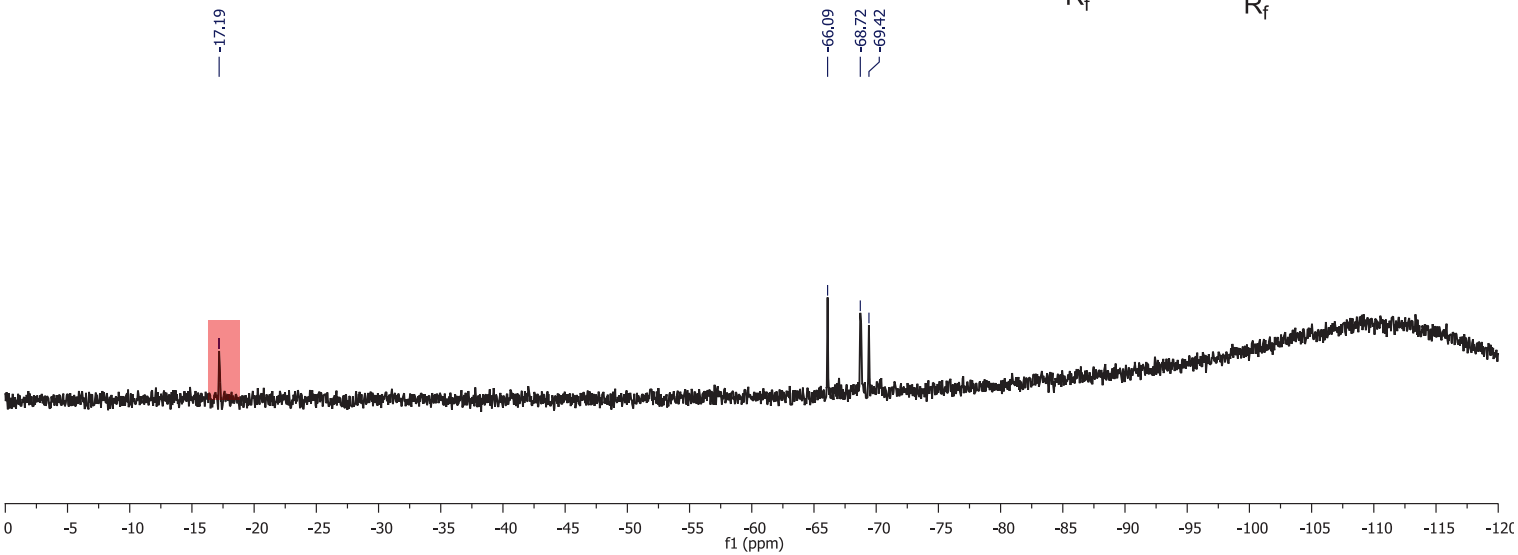


- Edge capping reactions typically have 52% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Norbornene functionalized F-POSS for ring opening metathesis polymerization (ROMP)

^{29}Si NMR

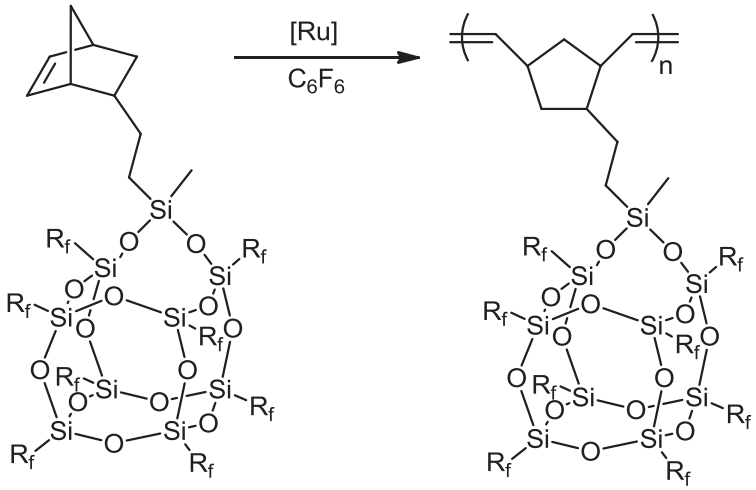


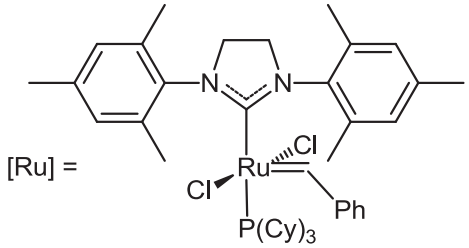




NMR: $CDCl_3/C_6F_6$

ROMP (Norbornene)





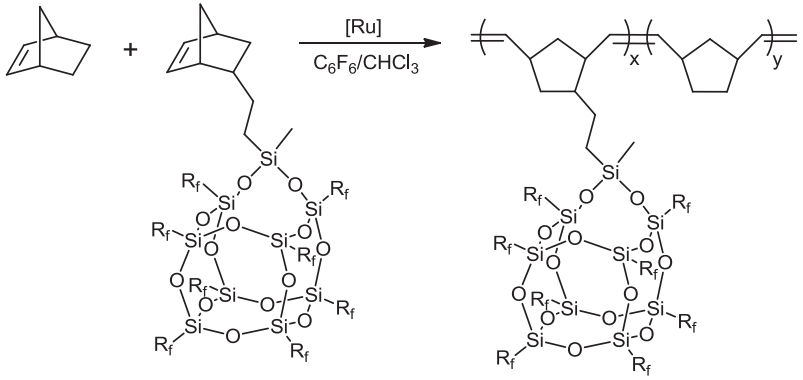
Grubb's 2nd generation catalyst
(soluble in hexafluorobenzene)

- Polymerization
  - Multiple polymerization in hexafluorobenzene
  - 100:1, 50:1, 25:1 [monomer:catalyst]
  - Reaction of 30 minutes (monitored by NMR)
  - Higher monomer:catalyst ratios yield insoluble polymers
  - Low T_g polymers (~5°C at 10°C/min ramp rate) [polynorbornene ~ 35-60°C]
  - Need a method to determine molecular weight

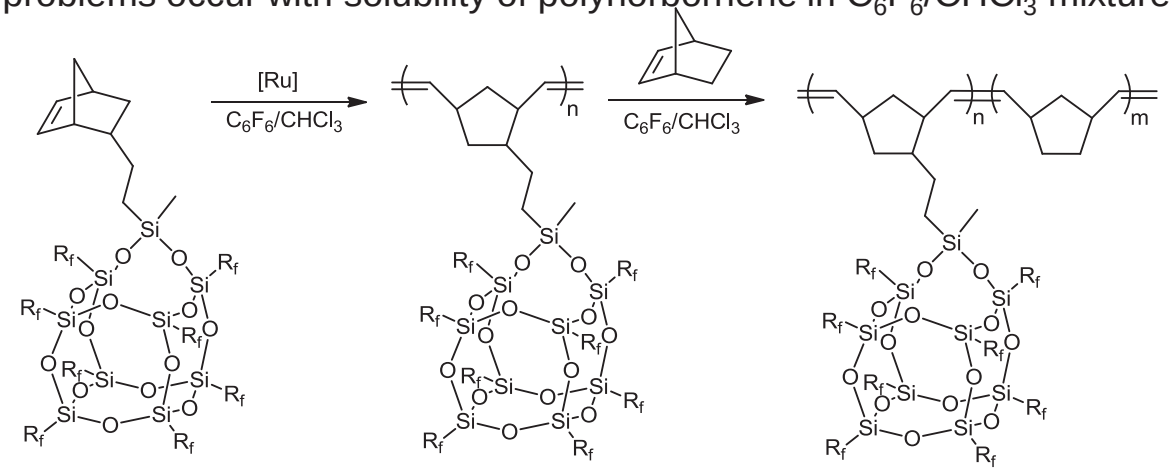
Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W., *J. Amer. Chem. Soc.* 1992, *114* (10), 3974-3975. Maughon, B. R.; Grubbs, R. H., *Macromolecules* 1996, *29* (18), 5765-5769.

ROMP (Copolymerization)

Two Approaches

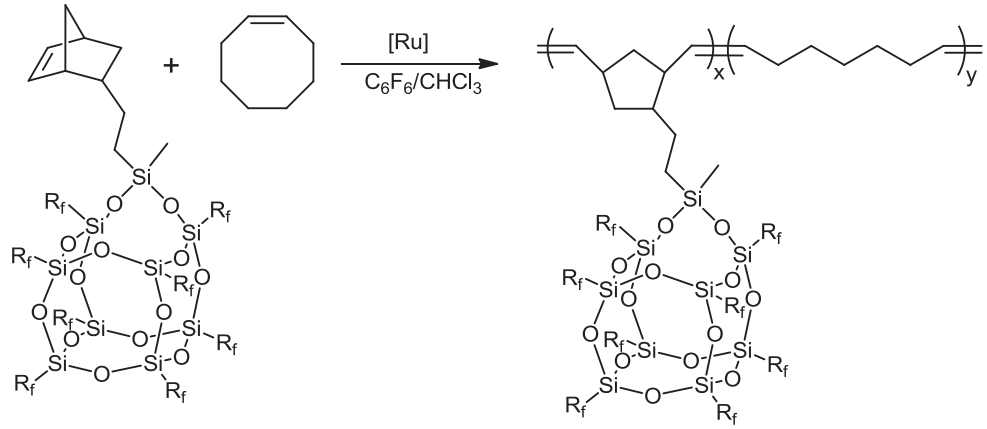


Random copolymer –problems occur with solubility of polynorbornene in $C_6F_6/CHCl_3$ mixture.

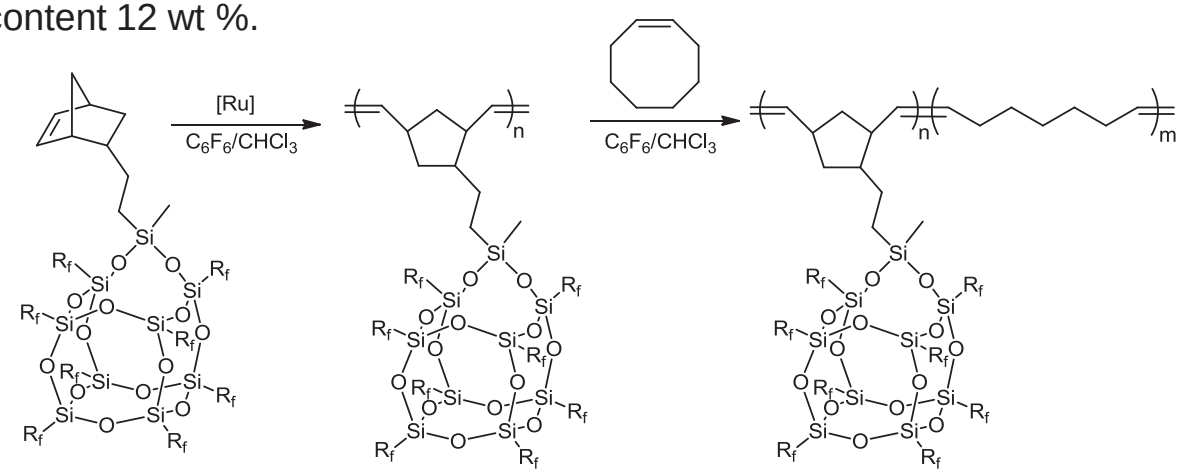


Block copolymers – keeping everything soluble remains a challenge here as well.

ROMP (Cyclooctene)



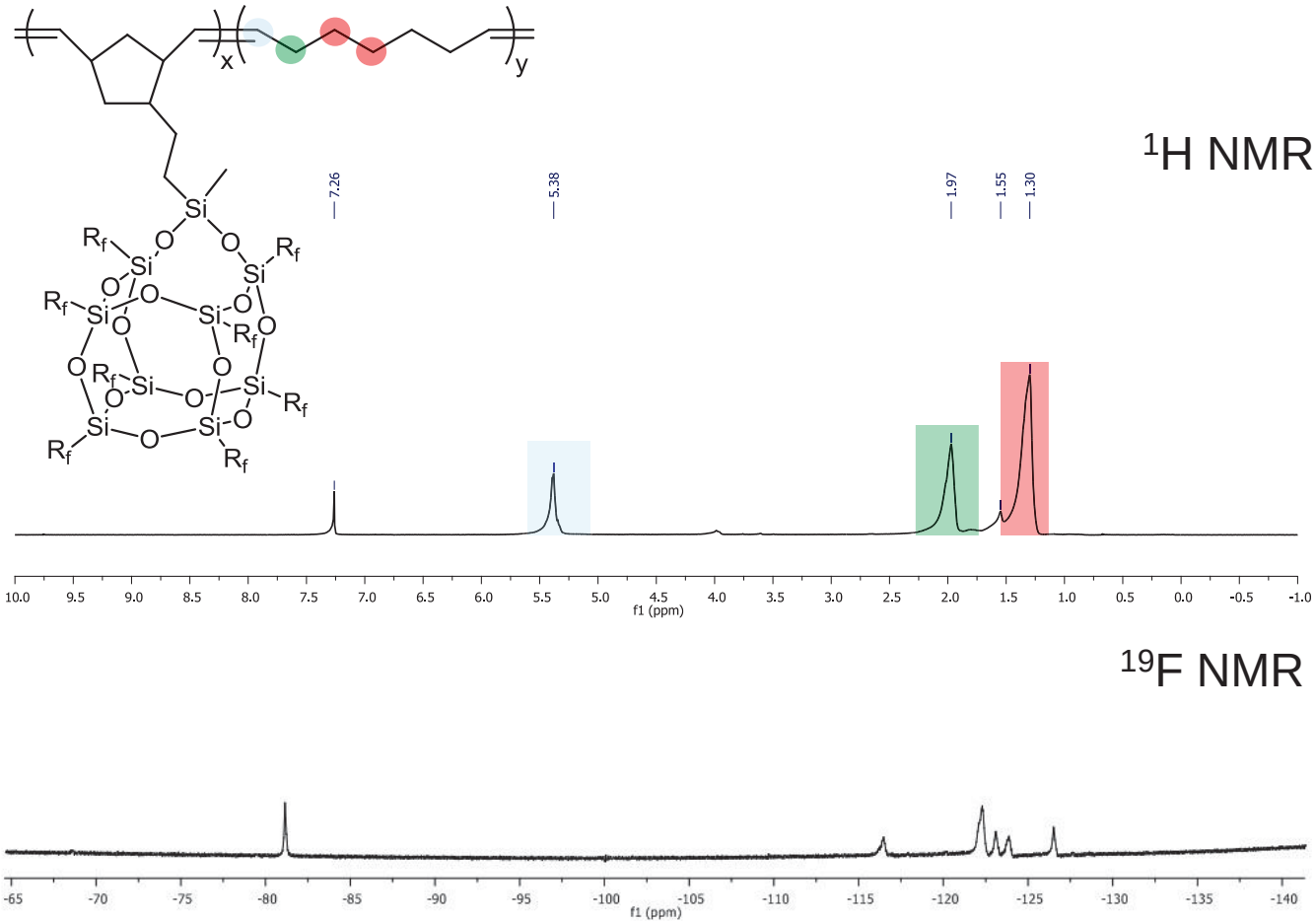
Random copolymer – resulting polymers are soluble cyclooctene solvents (chloroform, THF, etc…) F-POSS content 12 wt %.



Block copolymers – resulting polymer is insoluble, possibly due to high molecular weight conversion F-POSS content 12 wt %.

Liu, C.; Chun, S. B.; Zheng, L.; Haley, E.; Coughlin, E. B.; Mather, P. T., *Macromolecules* 2002, *35*, 9868-9874. Alonso-Villanueva, J.; Cuevas, J. M.; Laza, J. M.; Vilas, J. L.; Leon, L. M., *Journal of Applied Polymer Science* 2010, *115*, 2440-2447. Alonso-Villanueva, J.; Rodriguez, M.; Vilas, J. L.; Laza, J. M.; Leon, L. M., *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* **2010,** *47*, 1130-1134.

NMR of Copolymer



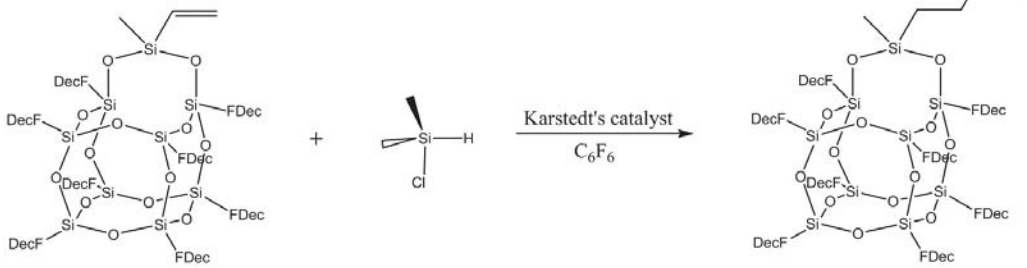
Polymer was precipitated in methanol, dissolved, and precipitated into asahiklin-225 before NMR.

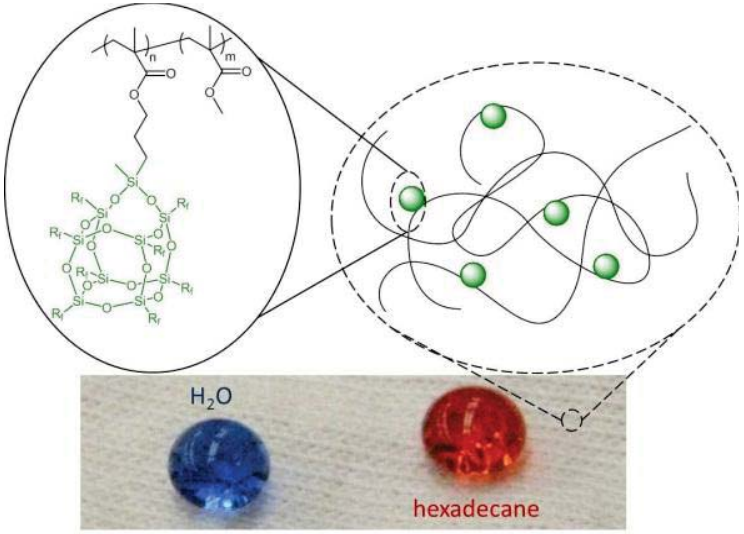
$R_f = CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$

$CDCl_3$

Summary

- RAFT copolymerizations were shown to be controlled and highly reproducible.
- ROMP polymerization works well. Work needs to be done with catalyst choice, solvent, and other reaction condition.
- 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….





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[ξ]
Mr. Brian Moore*
Mr. Kevin Lamison
Dr. Timothy Haddad
Dr. Andrew Guenthner
Ms. Dana Pinson
Dr. Christopher Sahagun
Cpt. Rebecca Stone*

United States Air Force Academy:

Dr. Scott Iacono
Olawale Lawal[ξ]
Michael Duff[ξ]

UT Dallas:

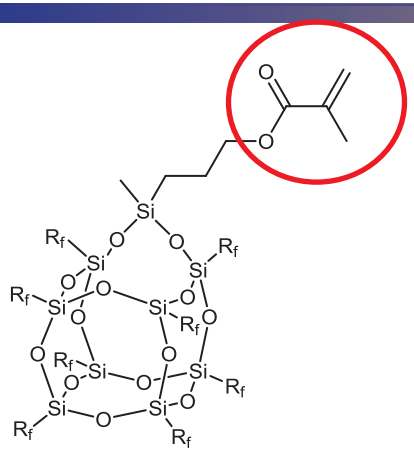
Dr. Dennis Smith
Mr. Raymond Compos*

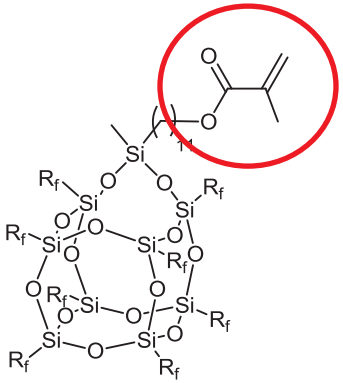
Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

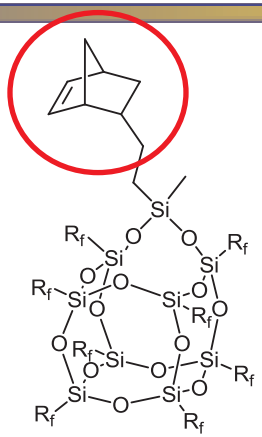
We thank Peter Müller at the Massachusetts Institute of Technology (MIT) and the American Crystallography Association (ACA) summer course for their assistance with small molecule X-ray crystal structure determination and refinement.

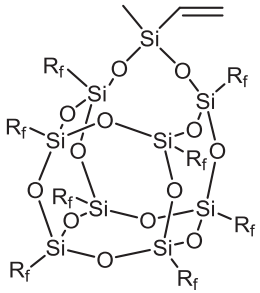
[ξ]Summer coop/student (undergraduate)
*Former group member

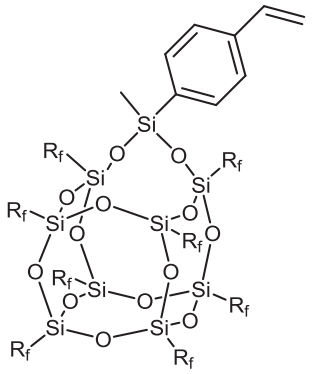
F-POSS Structures Synthesized

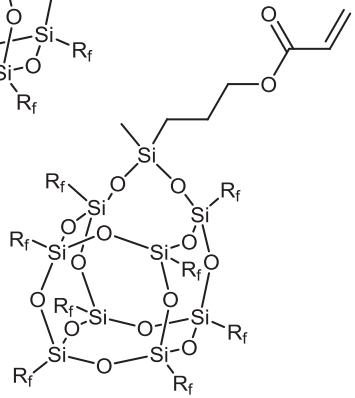


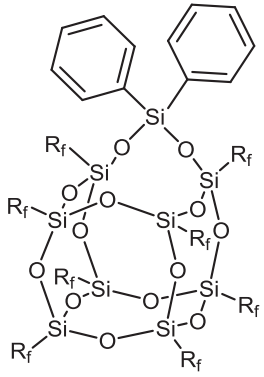












R = $CH_2CH_2(CF_2)_7CF_3$