

REPORT DOCUMENTATION PAGE

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	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S) Joseph M. Mabry, Patrick N. Ruth ¹	 Rusty L. Blanski, Rene Gonzalez	5d. PROJECT NUMBER 4847
		5e. TASK NUMBER 0249
		5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ¹ ERC, Inc. 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680	 ² Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680	8. PERFORMING ORGANIZATION REPORT NUMBER
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11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-VG-2003-049	

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Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20031003 093

15. SUBJECT TERMS

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FILE

MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO)

28 Feb 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: ~~AFRL-PR-ED-VG-2003-049~~
~~Joseph M. Mabry~~ (ERC); Rusty L. Blanski; Patrick N. Ruth; Capt. ~~Rene I. Gonzalez~~, "Fluorinated
POSS"

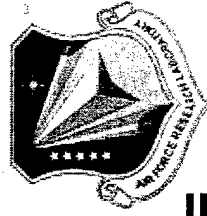
American Chemical Society Conference
(New Orleans, LA, 23-27 Mar 2003) (Deadline: 21 Mar 2003)

(Statement A)





Fluorinated POSS



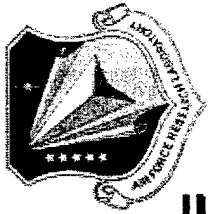
Joseph M. Mabry,^{1*} Rusty L. Blanski,²
Patrick N. Ruth,¹ and Rene I. Gonzalez²

¹ERC Inc., Air Force Research Laboratory

²Air Force Research Laboratory

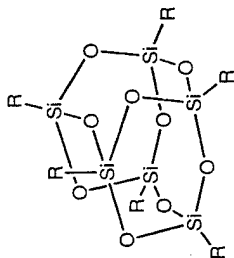
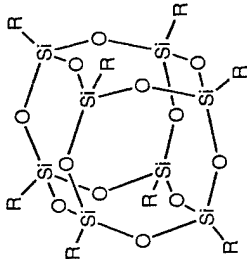
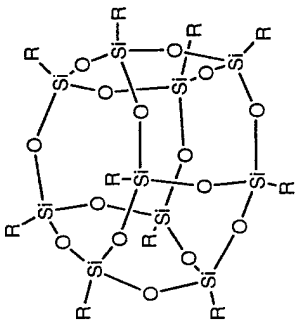
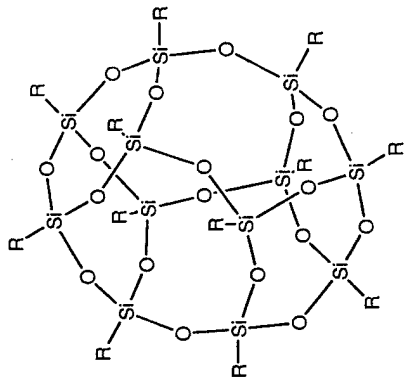
Edwards Air Force Base, CA 93524

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

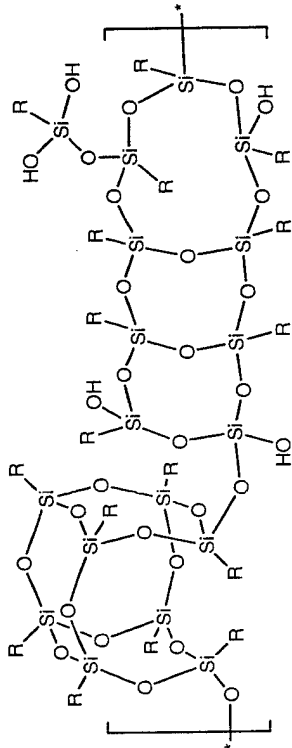


POSS Synthesis

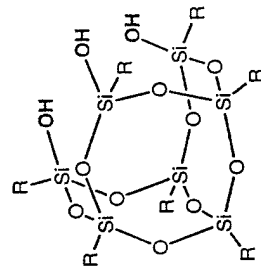
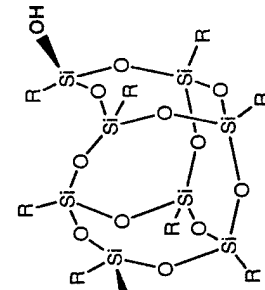
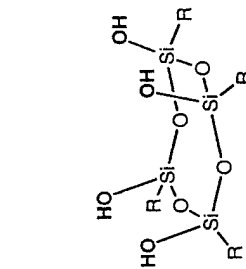
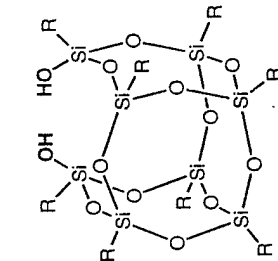
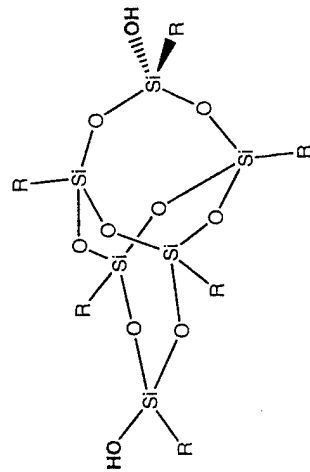
$RSiX_3$ acid or base hydrolysis



Completely condensed



Resin

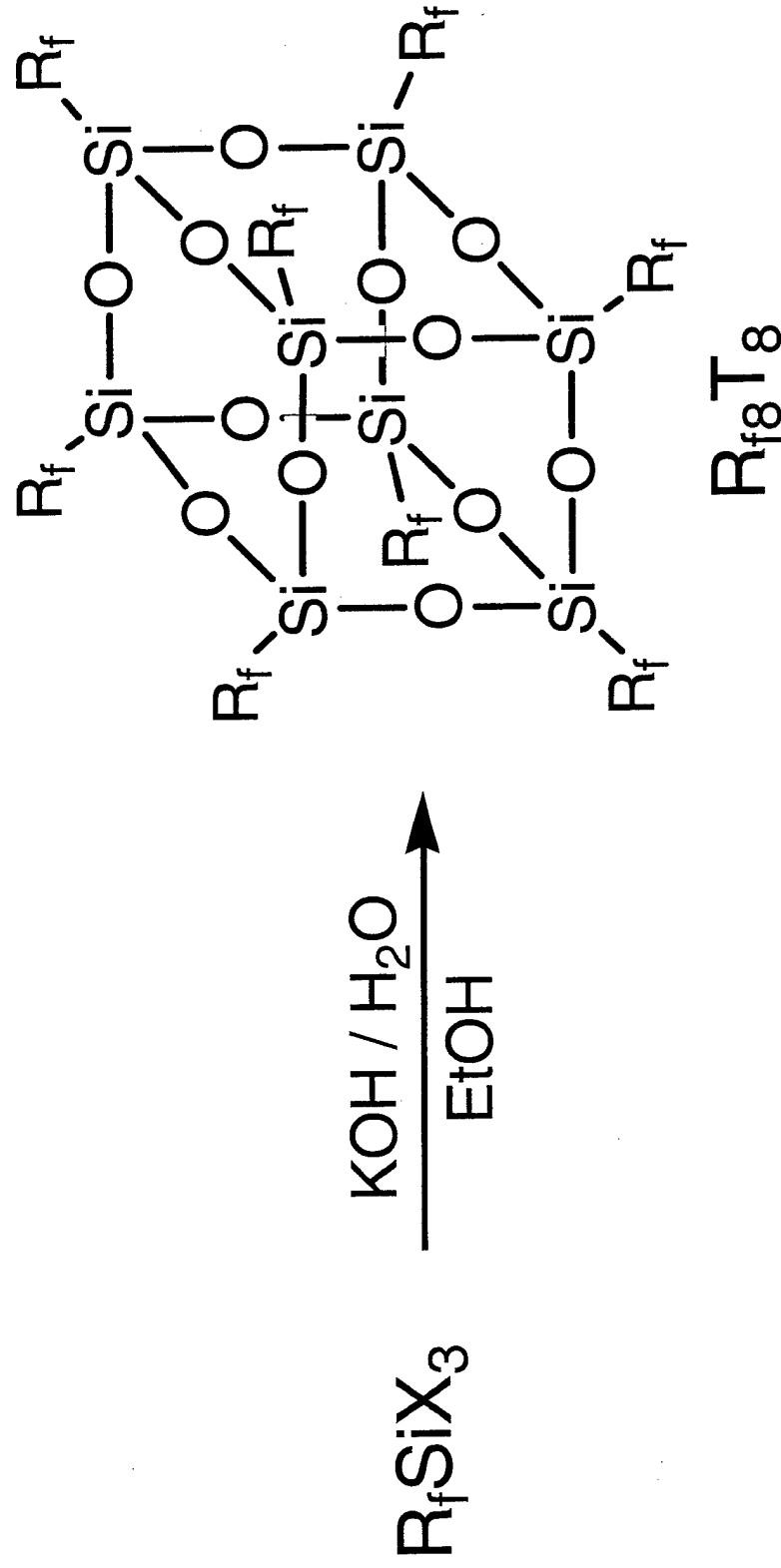
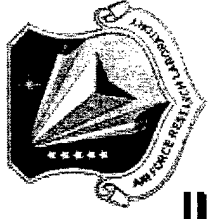


Incompletely condensed

Brown, Feher, AFRL, Hybrid Plastics 2



Synthesis

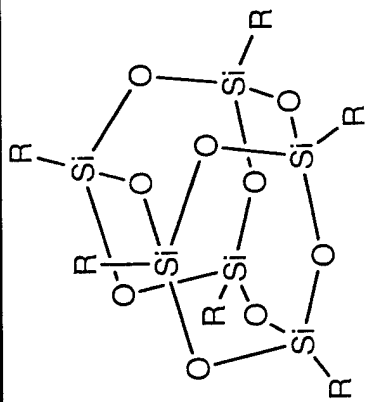
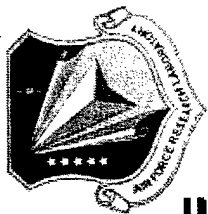


X = -OMe, -OEt

$\text{R}_f = -\text{CH}_2\text{CH}_2\text{CF}_3, -\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3, -\text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$

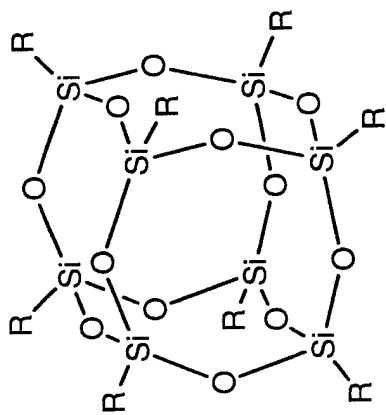


Fluorodecyl_nT_n



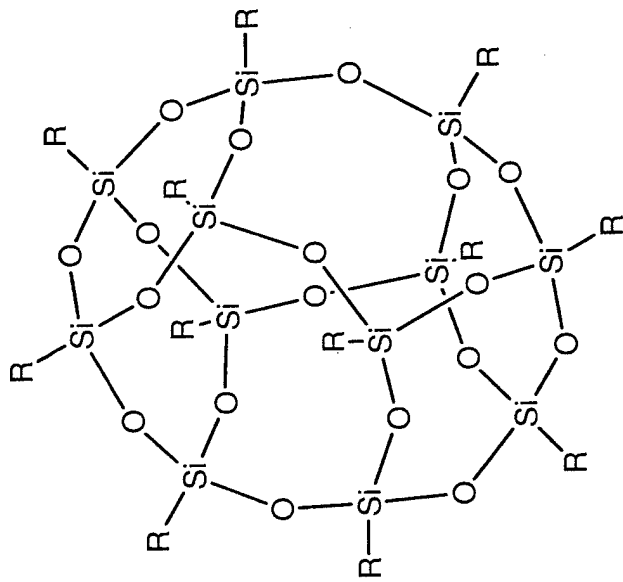
T₆ (~5%)

R = -CH₂CH₂(CF₂)₇CF₃

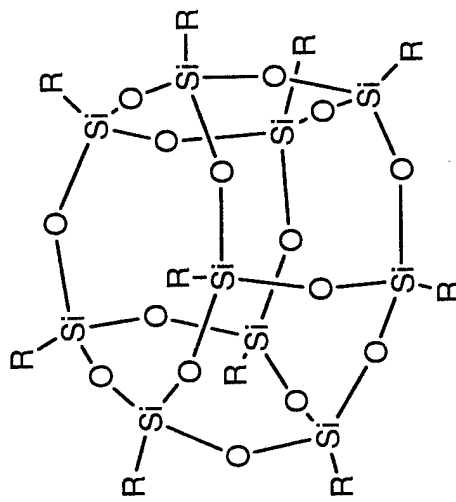


T₈ (~91%)

MW = 3993.54



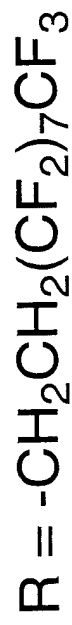
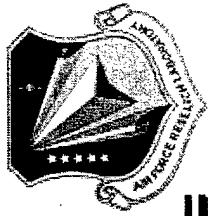
T₁₂ (~3%)



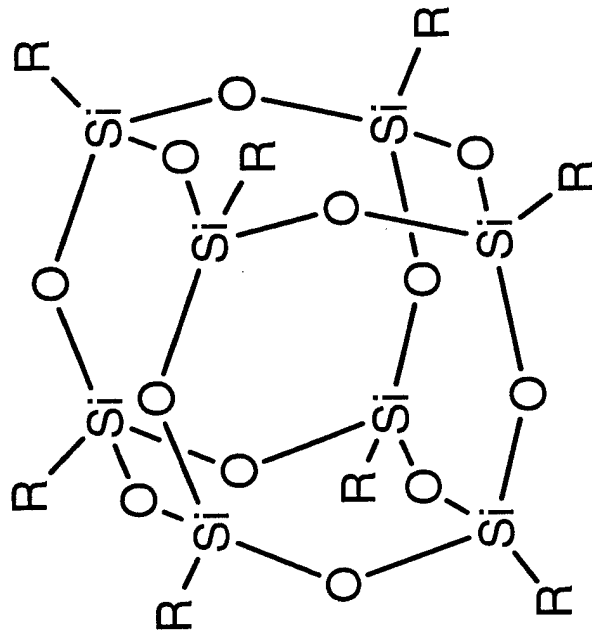
T₁₀ (~1%)



100% Fluorodecyl₈T₈



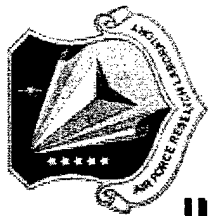
MW = 3993.54



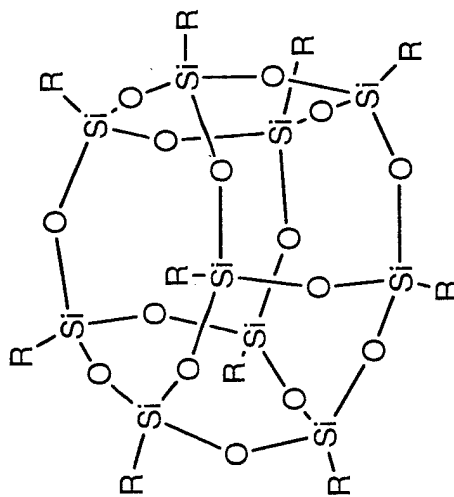
T₈



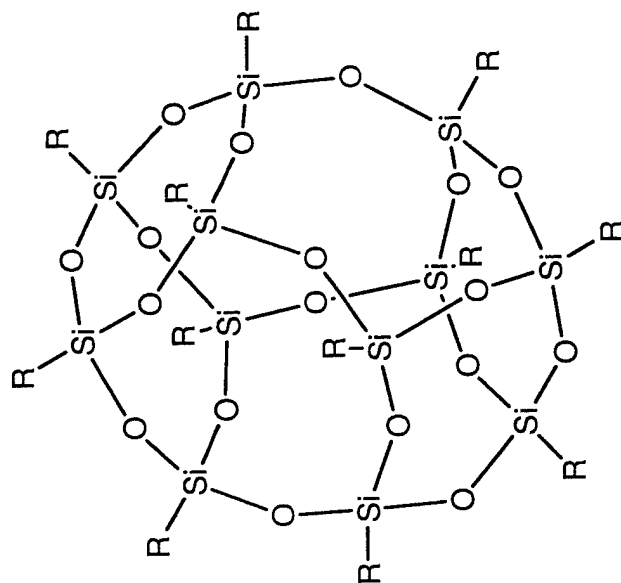
3,3,3-Trifluoropropyl T_n



R = -CH₂CH₂CF₃



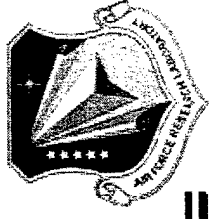
T₁₀ (~11%)



T₁₂ (~89%)



Why Fluorinated POSS?

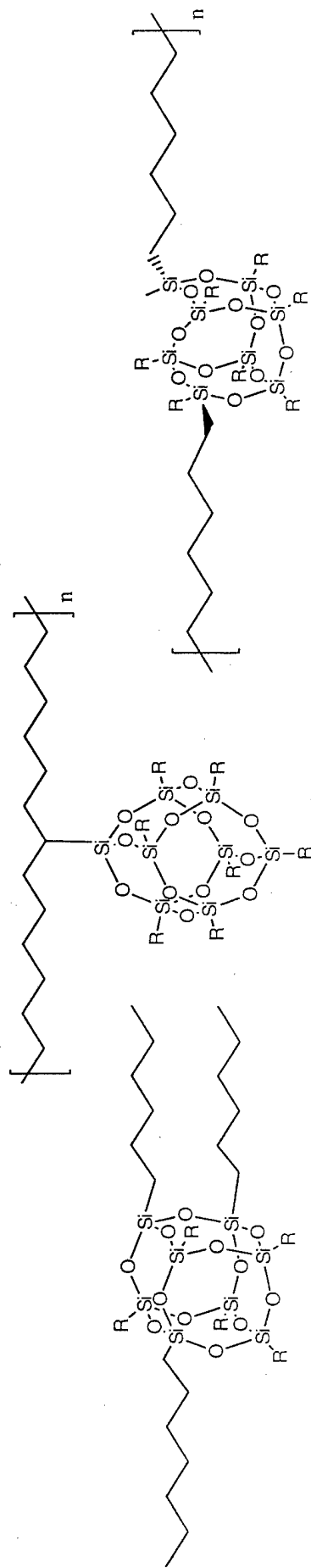
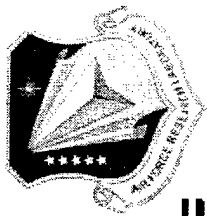


Fluorinated POSS may be useful:

- To make spacecraft coatings resistant to atomic oxygen
- In creep-resistant fluoropolymer seals and gaskets
- In hydrophobic surfaces



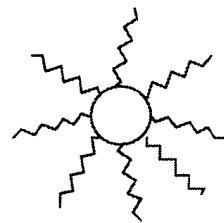
POSS Polymer Incorporation



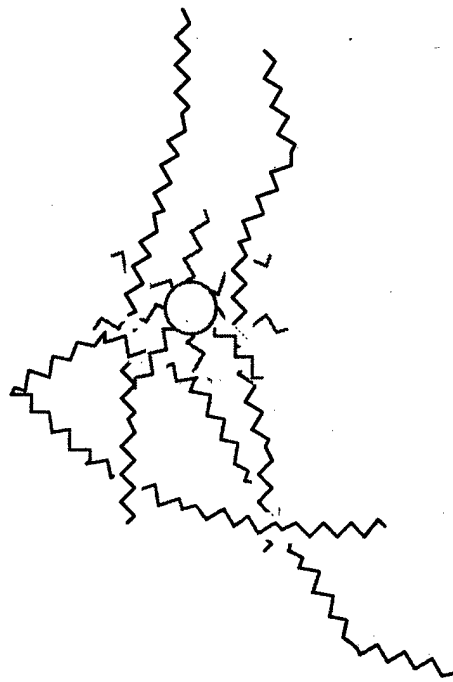
Cross-linker

POSS Pendant

Bead Copolymer

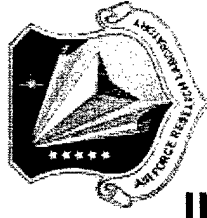


POSS Blending

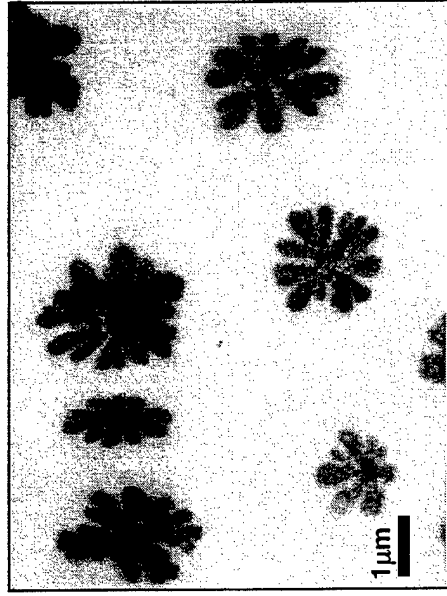




Importance of R groups: Affect compatibility with polymer matrix



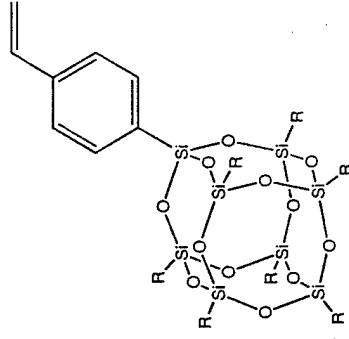
50 Wt % POSS Blends in 2 Million MW PS



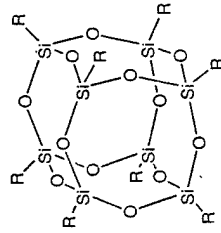
Domain Formation



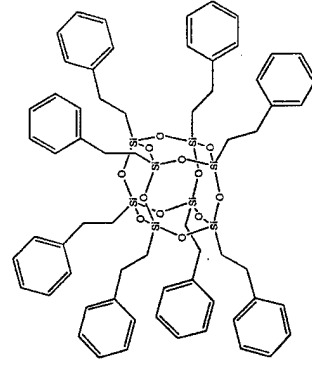
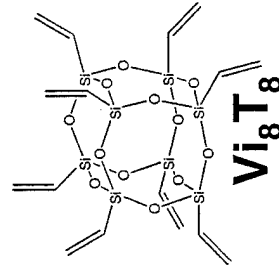
Partial Compatibility



Cp₇T₈Styryl



Cp₈T₈



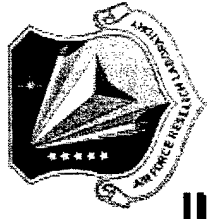
Phenethyl₈T₈

Complete Compatibility-
POSS Nanodispersion/Transparent

Immiscible POSS Crystallites



Space Applications



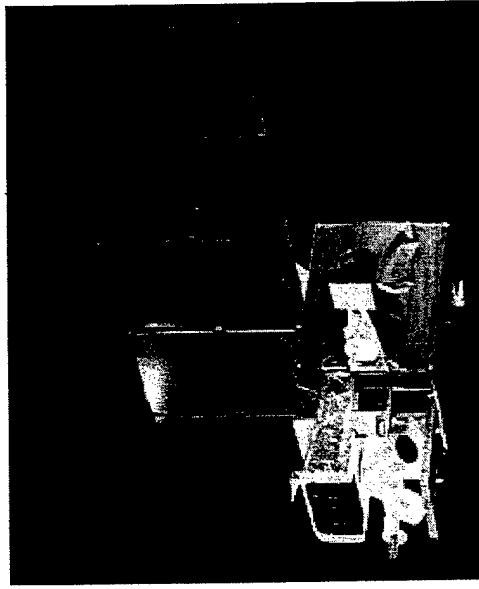
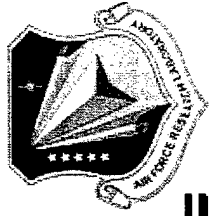
LEO Environment

(Altitudes of 200 to 1500 km)

- Atomic Oxygen
 - Formed from photo-dissociation of O_2 in atmosphere.
 - Actual flux on spacecraft traveling at 8 to 12 km/s $\sim 10^{15}$ atoms/cm²•s
 - collision energy ~ 5 eV (C-C ~ 4 eV, C-N ~ 3 eV)
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar UV and VUV radiation
 - VUV wavelengths in LEO extend below 290nm.
 - Bond scission and radical formation can lead to embrittlement.



Goal: Develop Multi-Functional, Space-Survivable Materials



Satellites & Space Systems

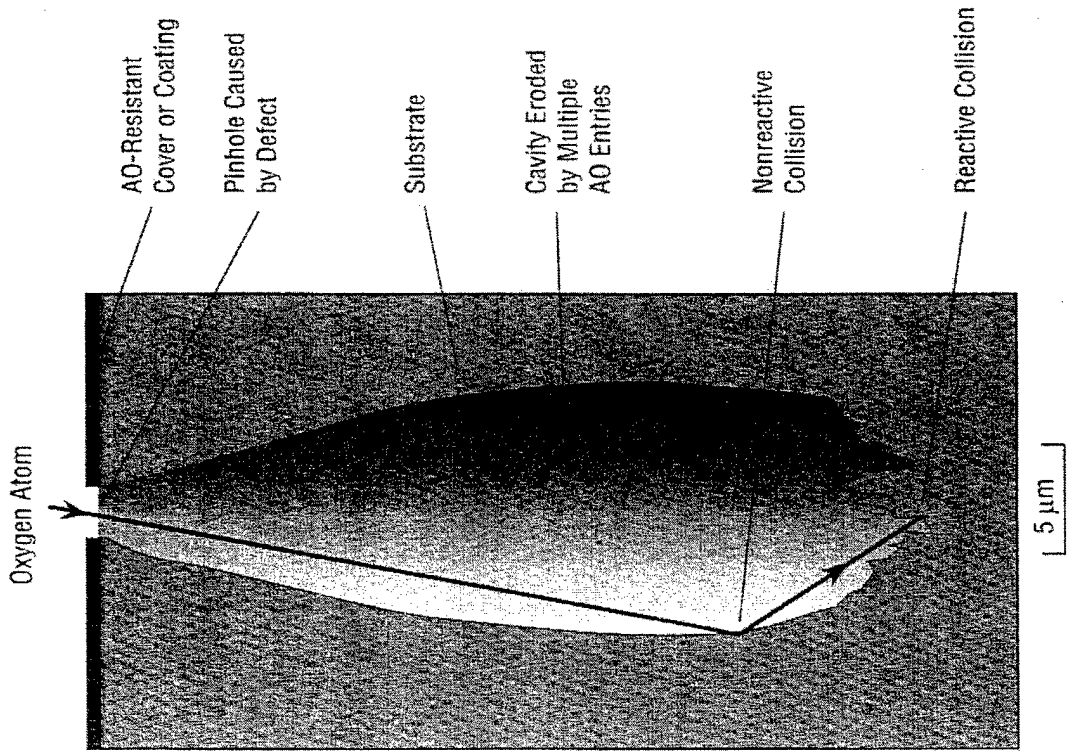
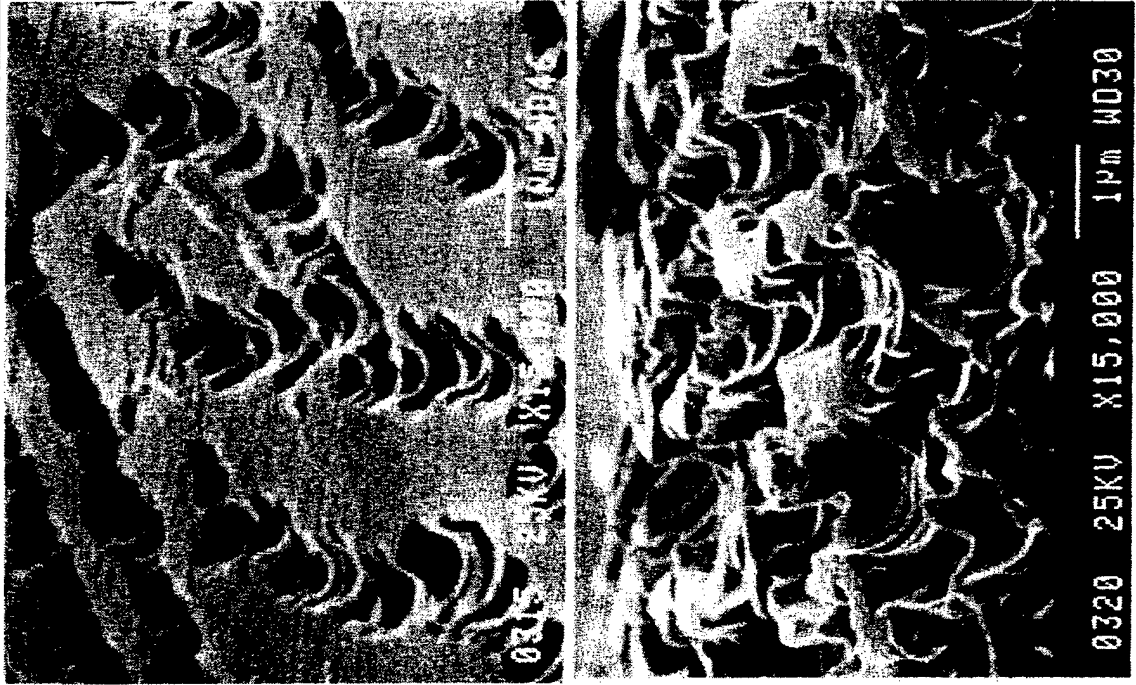
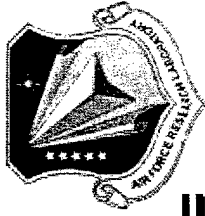
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-\text{C}_6\text{H}_4-\text{C}(=\text{O})-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

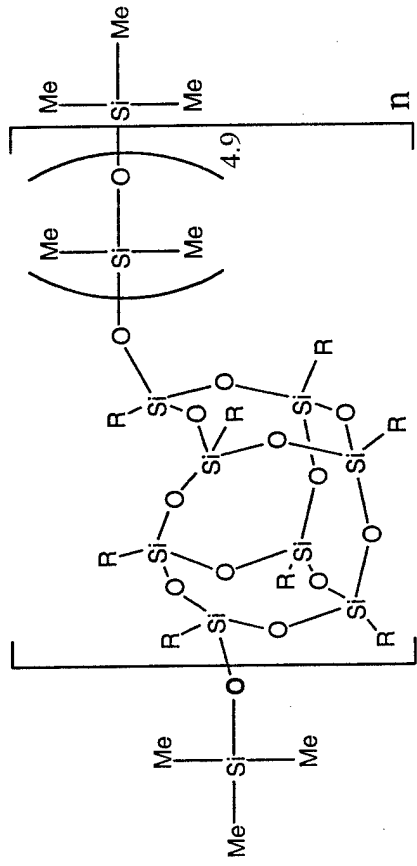
- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation



AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation



POSS Siloxane

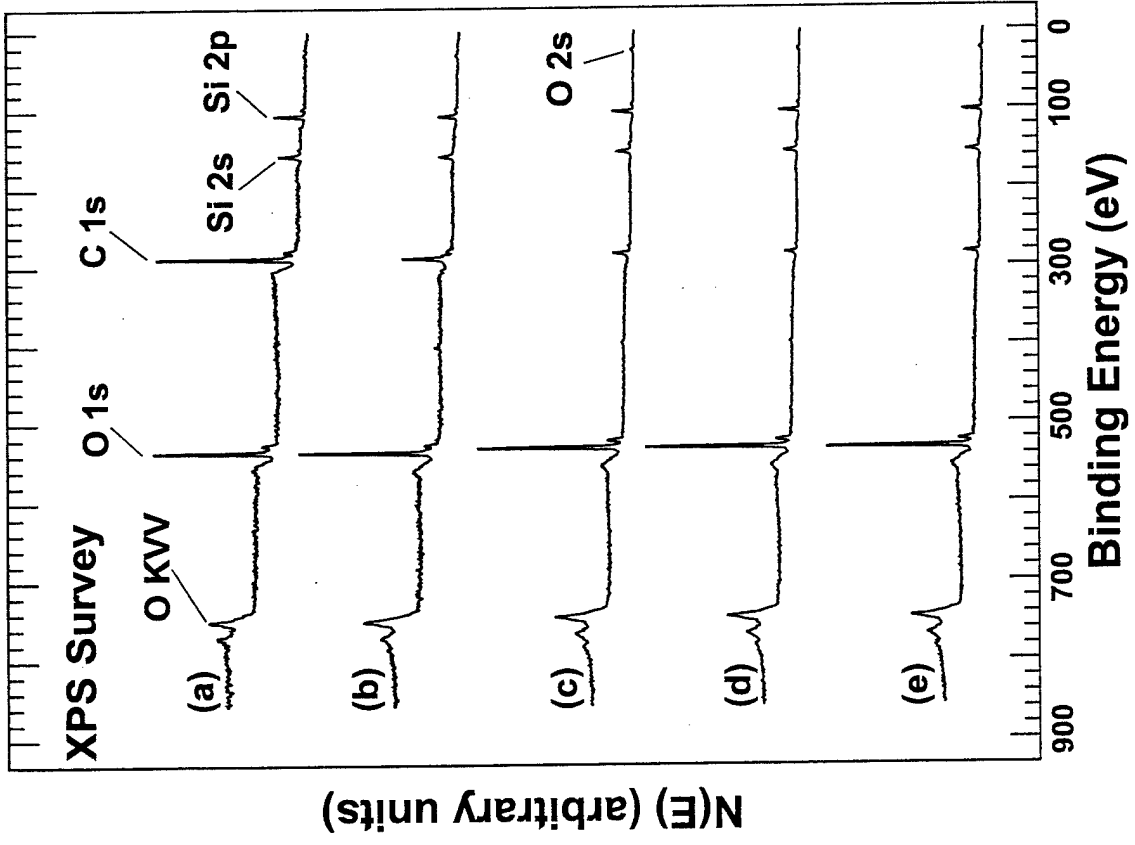


Composition, at %

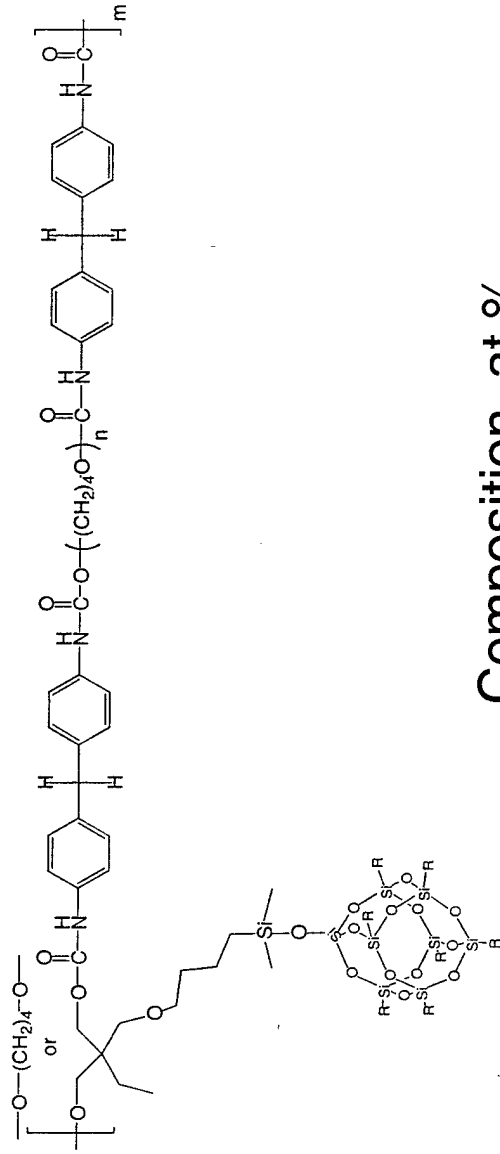
Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

Gonzalez, R. I., Phillips, S. H., Hoflund, G. B., *J. of Spacecraft and Rockets*, Vol 37, No. 4, 2000, pp. 463-467.

XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.



60 wt % POSS-Polyurethane

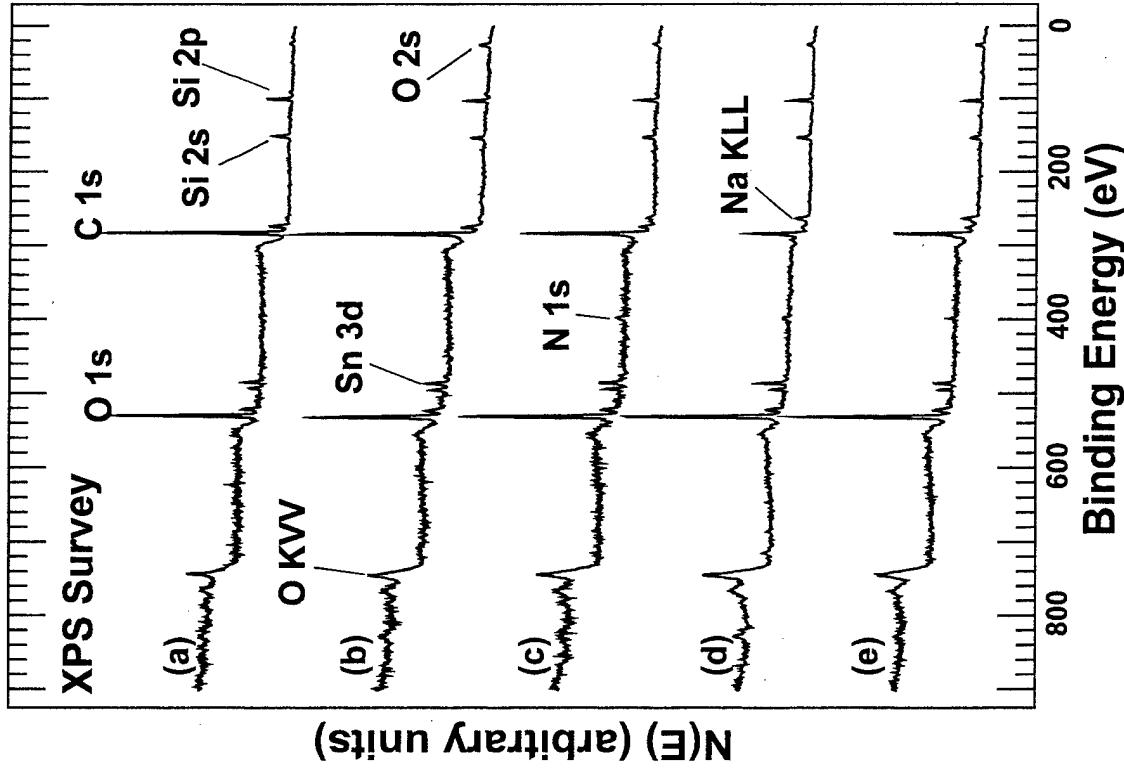


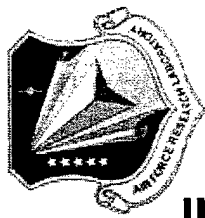
Composition, at %

Sample Treatment	O	C	Si	Sn	Na	N
As entered	18.2	70.1	11.3	0.4	-	-
2.0-hr	17.5	70.2	11.2	0.7	0.4	-
24.0-hr	23.7	58.2	13.2	0.9	1.4	2.6
63.0-hr	35.3	37.3	20.4	1.3	3.0	2.7
3.3-h air	31.6	48.5	14.6	1.0	2.7	1.6

Phillips, S. H., Hoflund, G. B., Gonzalez, R. I., 45th International SAMPE Symposium, 2000, Vol. 45, No. 2, pp. 1921-1931.

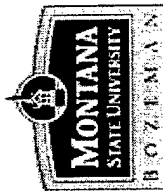
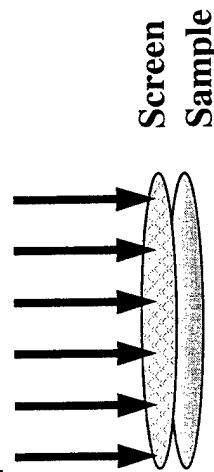
XPS Survey Spectra from a 60 wt % POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.





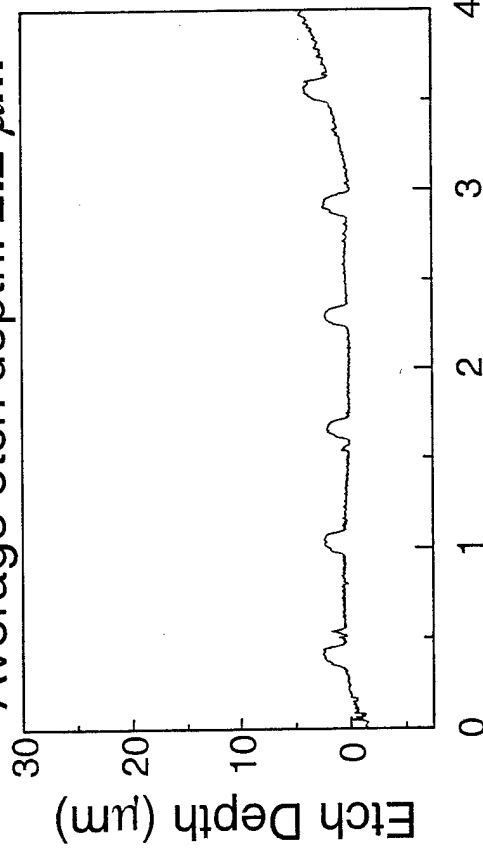
O-Atom Etching Experiment (~10 DAYS IN LEO)
Total AO fluence of 8.47×10^{20} atoms cm^{-2} (100,000 pulses)

Hyperthermal AO Beam



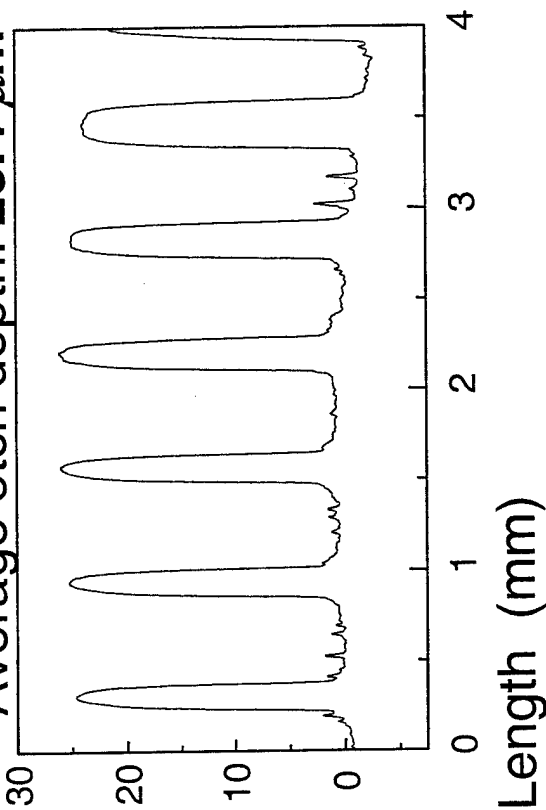
Kapton 10 wt % POSS

Average etch depth: $2.2 \mu\text{m}$

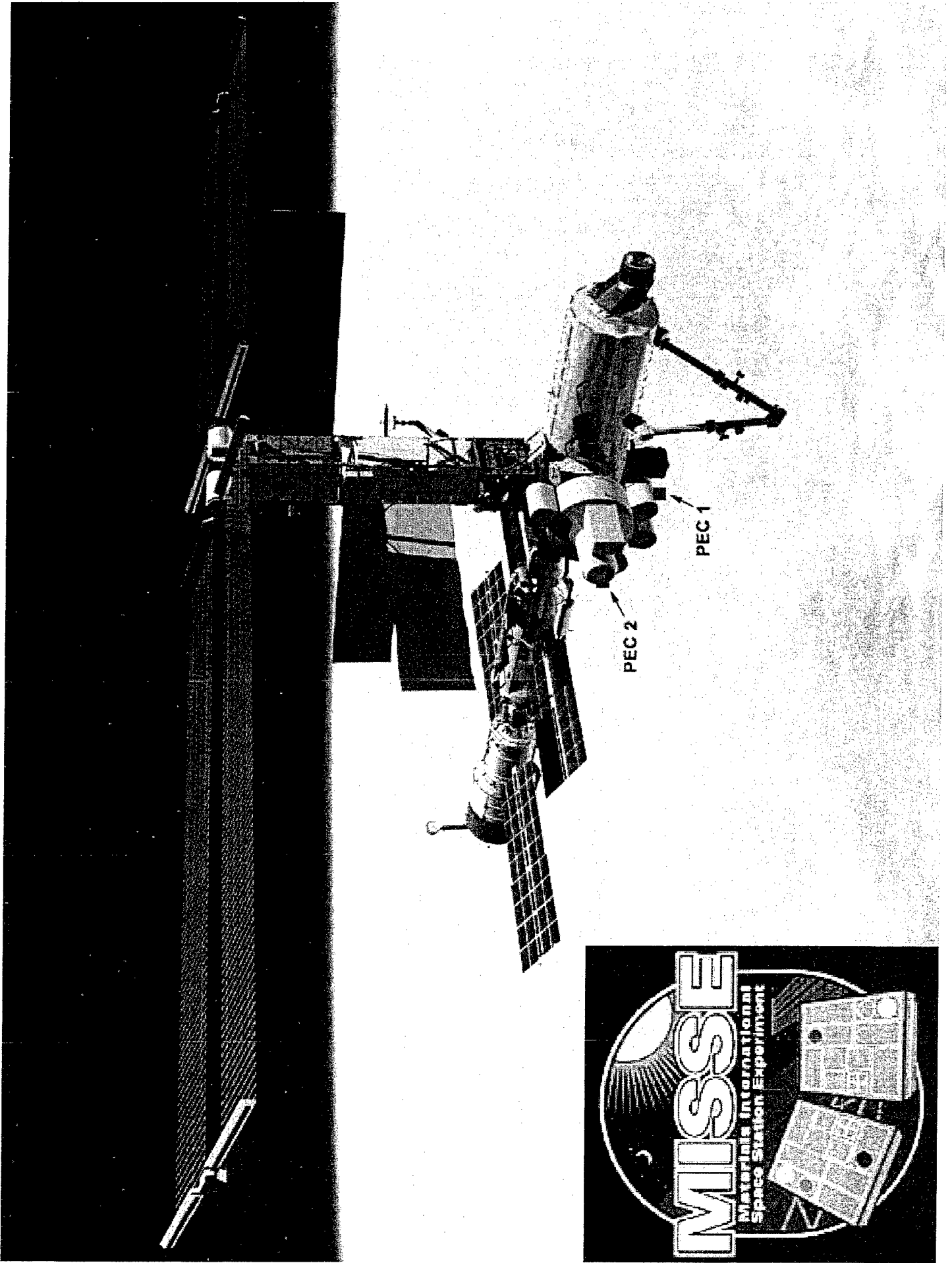


Kapton H Standard

Average etch depth: $25.4 \mu\text{m}$



Significantly improved oxidation resistance due to a rapidly formed ceramic-like, passivating and **self-healing** silica layer preventing further degradation of underlying virgin polymer.



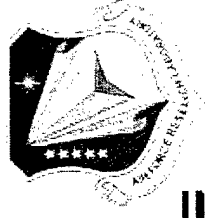
PEC 2

PEC 1





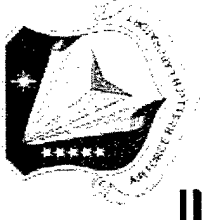
Creep Resistant Seals and Gaskets



- Fluoropolymers are resistant to organic fuels and fluids.
- Creep is the change in dimensions of a molded part resulting from cold flow incurred by continual loading.
- Creep can cause a press-fit to loosen or even fail.
- PTFE has a low tensile strength (2500–3000 psi at break).
- Tensile strength is a very important factor.
- POSS may reduce the amount of creep as well as enhance thermal and mechanical properties.
- POSS can be blended with most fluoropolymers.
- Supercritical methods may allow fluorinated POSS to be incorporated into PTFE.



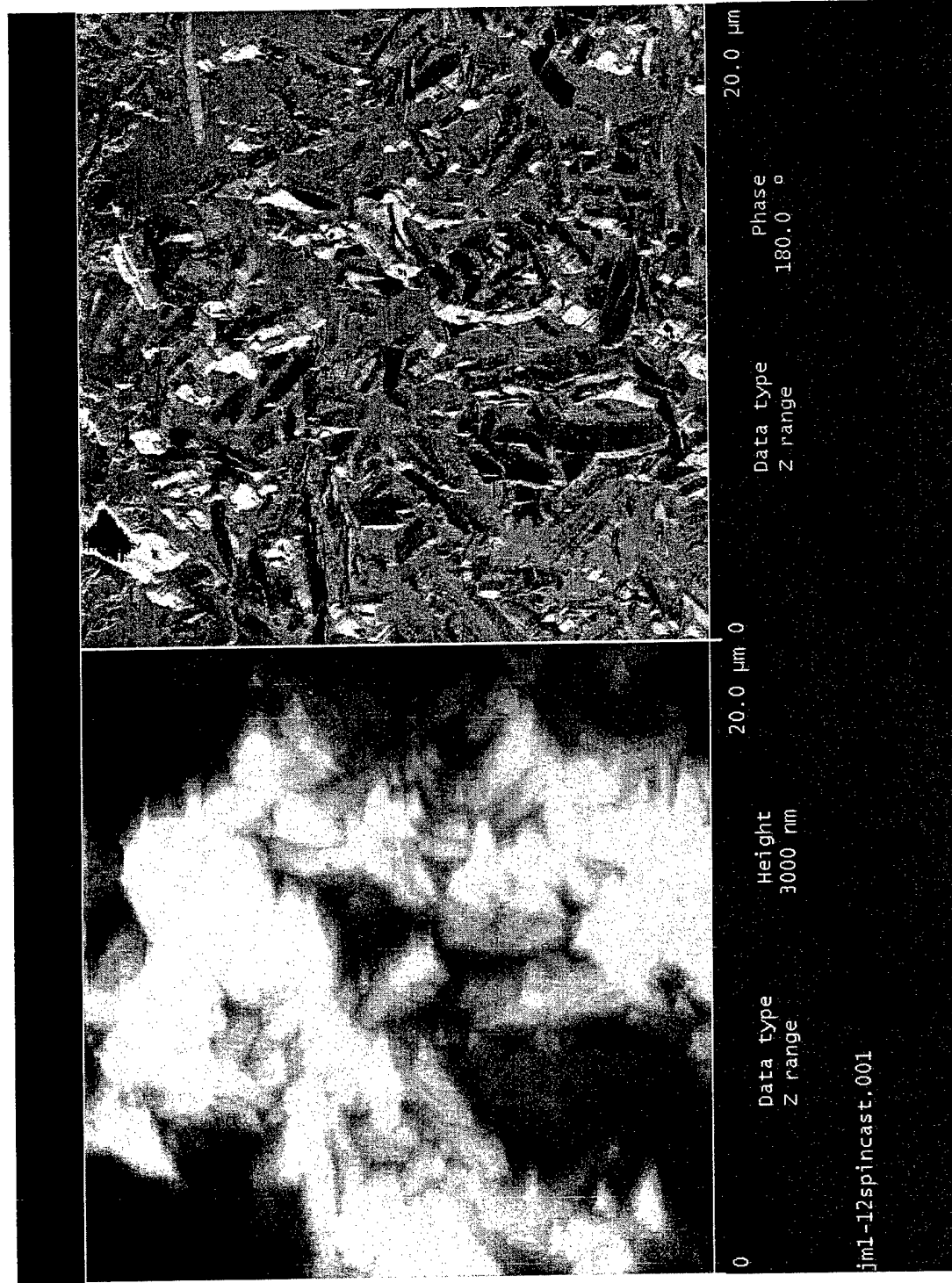
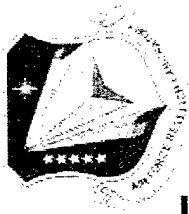
Surface Properties



- Fluorinated polymers are used for non-stick coatings and hydrophobic surfaces.
- Blended POSS may further decrease the surface energy of fluorinated polymers.
- One way to measure surface energy is to measure the contact angle of a drop of water on the surface.
- These low surface energy polymers may lead to anti-icing or non-wetting applications.



AFM Image of Spin-Cast Fluorodecyl_nT_n Surface



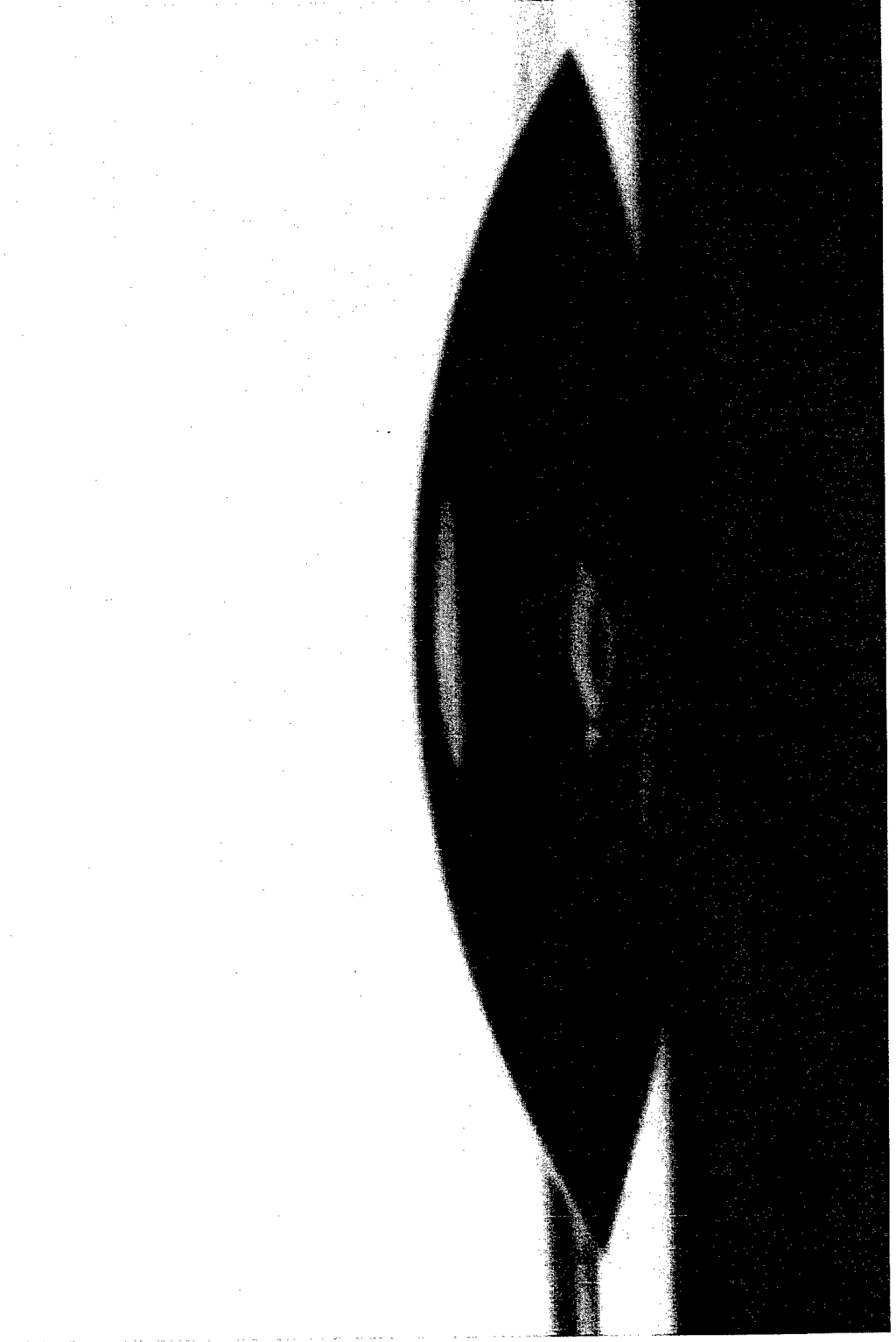


Contact Angle of Water on Mica $\sim 32^\circ$



12/12/02

a drop of water on a freshly cleaved mica surface in air and at room temperature.
Contact angle ~ 32 deg.



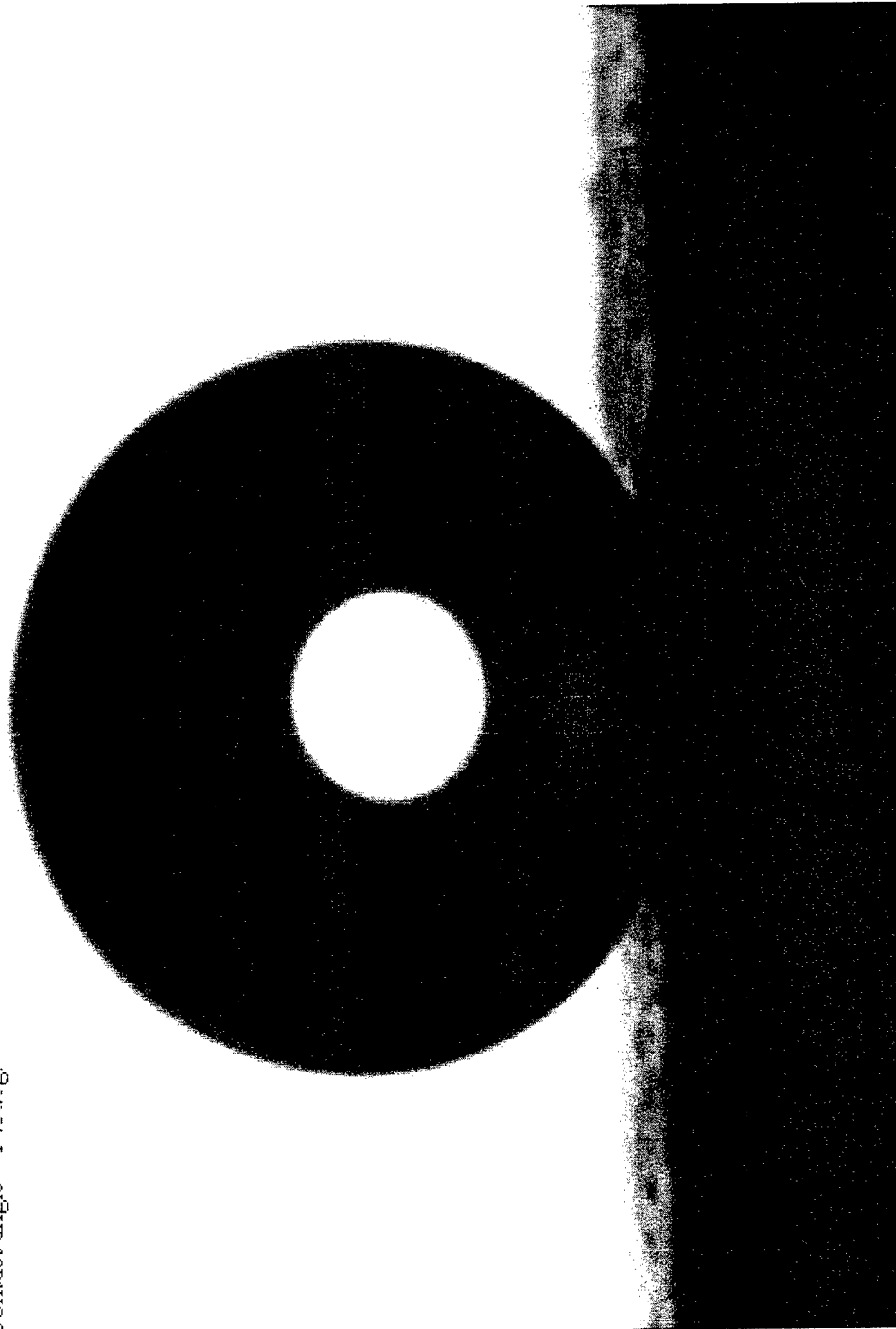


Contact Angle of Water on Fluorodecyl POSS film ~140°



12/12/02

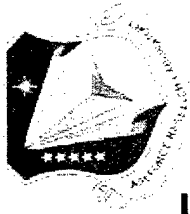
a drop of water on a fluorinated mica surface in air and at room temperature.
Contact angle ~ 140deg.



30° Higher than PTFE



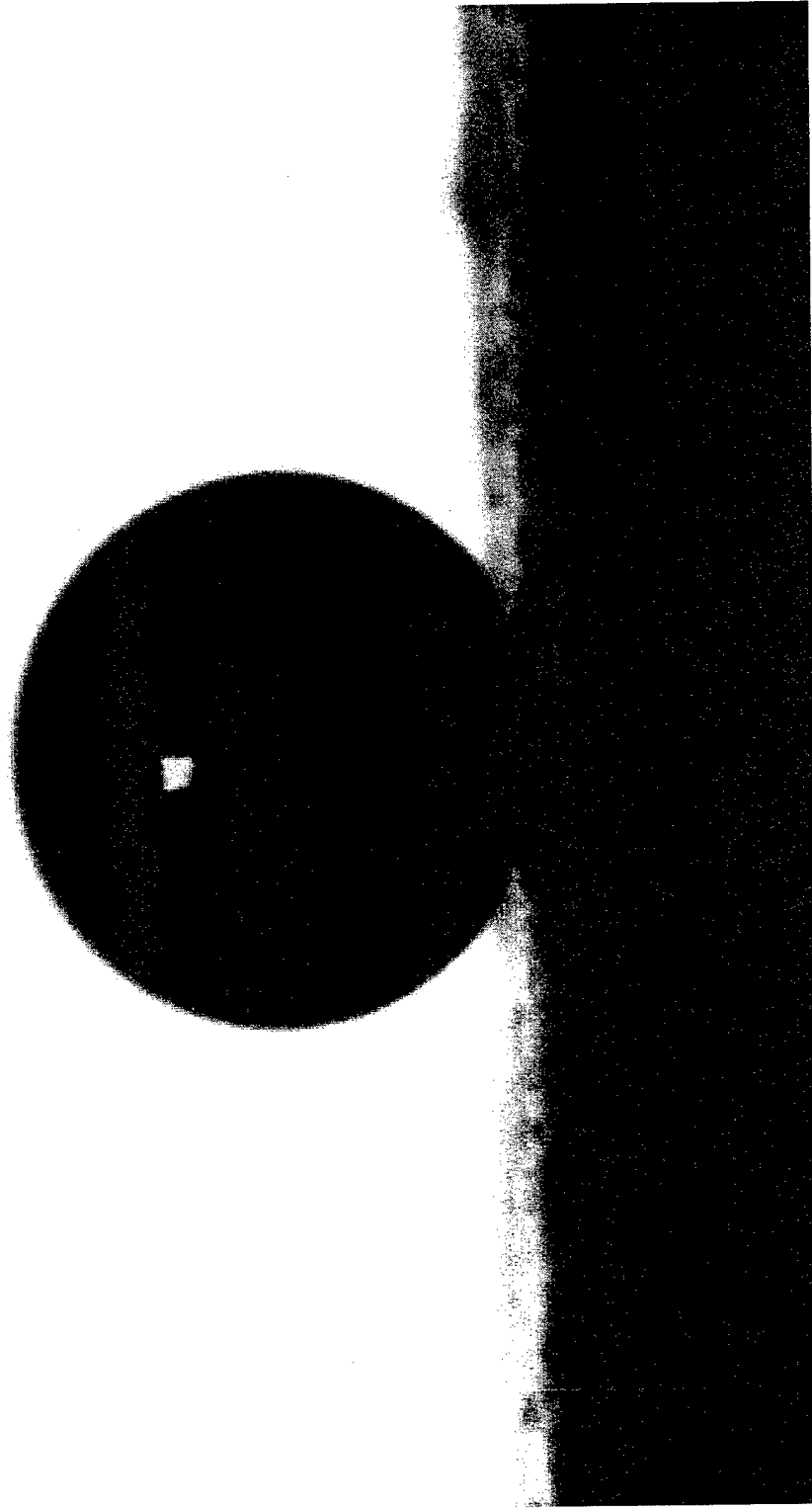
Contact Angle of Mercury on Fluorodecyl POSS film $\sim 145^\circ$



12/12/02

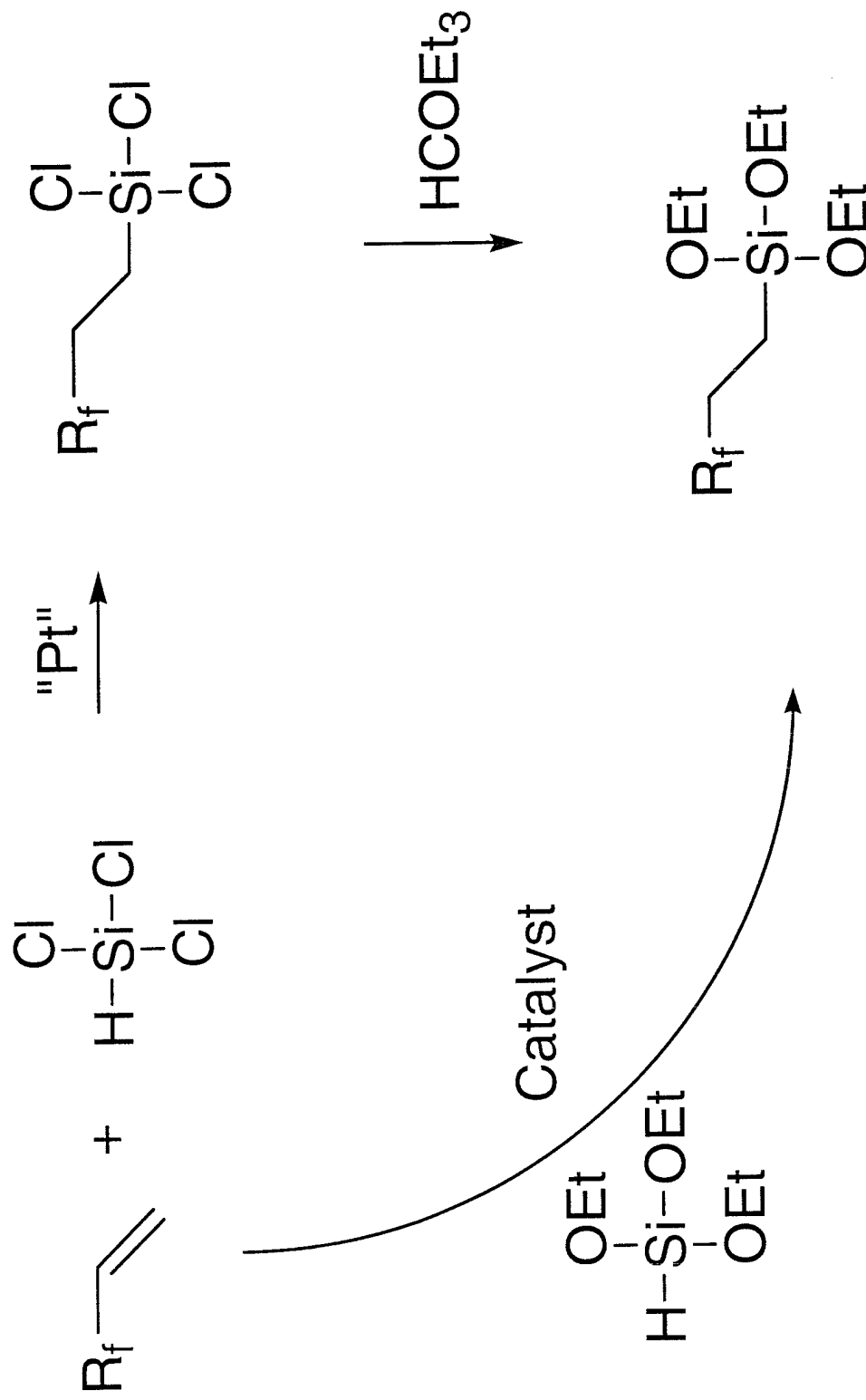
A drop of mercury on fluorinated mica surface in air and at room temperature.

Contact angle- 145deg.



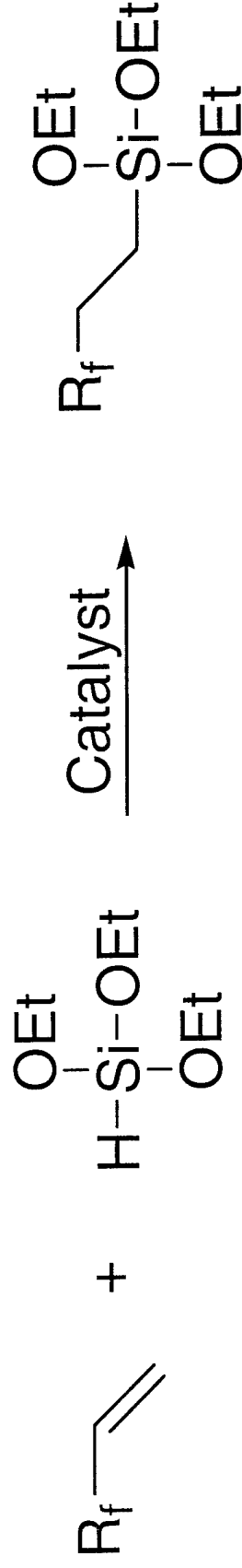


Hydrosilylation





Hydrosilylation

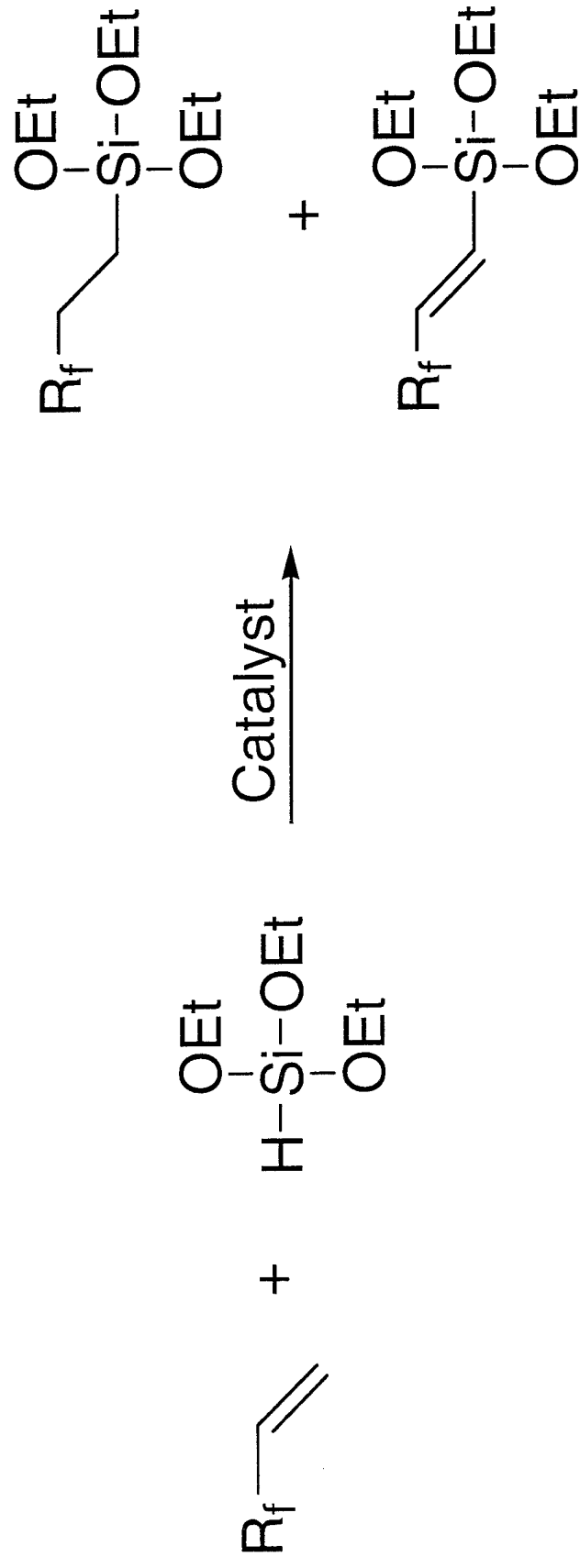


<u>Catalyst</u>	<u>Result</u>
Karstedt (Pt)	No Reaction
H ₂ PtCl ₆ (Pt)	No Reaction
RuH ₂ (CO)(PPh ₃) ₃	< 50% Yield
RhCl(PPh ₃) ₃	~ 50% Yield
Co ₂ (CO) ₈	Underway

Yield based on methylene to vinyl proton ratio in ¹H NMR.



Side Reaction



Problem:

Dehydrogenative silylation product also gives vinyl peaks in ^1H NMR spectra



Summary



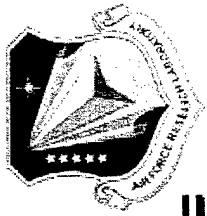
Fluorinated POSS may be useful to make spacecraft coatings resistant to atomic oxygen by forming a silica-like passivating layer.

Fluorinated POSS may be useful in fluoropolymer seals and gaskets to increase mechanical strength and improve creep characteristics.

Fluorinated POSS may also be useful to decrease surface energy in hydrophobic surfaces.

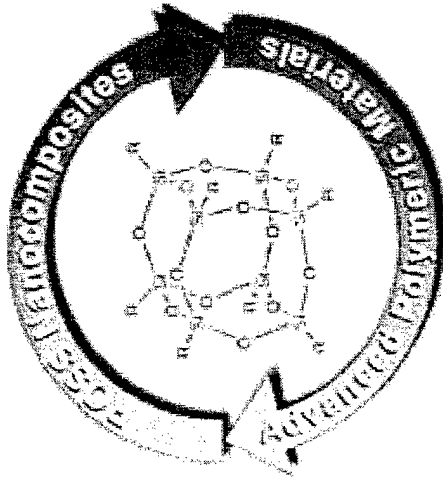


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The Polymer Working Group at Edwards Air Force Base is:

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Mr. Pat Ruth
Dr. Sandra Tomczak
Mr. Brian Moore
Dr. Brent Viers
Dr. Darrell Marchant

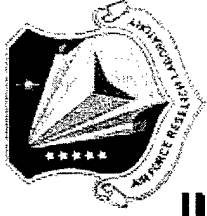


Dr. Shawn Phillips
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Dr. Joe Mabry
Mrs. Sherly Largo
Dr. Tim Haddad

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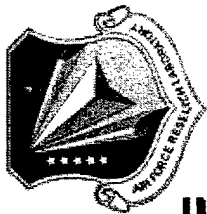


Backup Slides





100% Fluorodecyl₈T₈



4jm1-32 Fluorodecyl₈T₈ after extraction Mabry 12-27-02

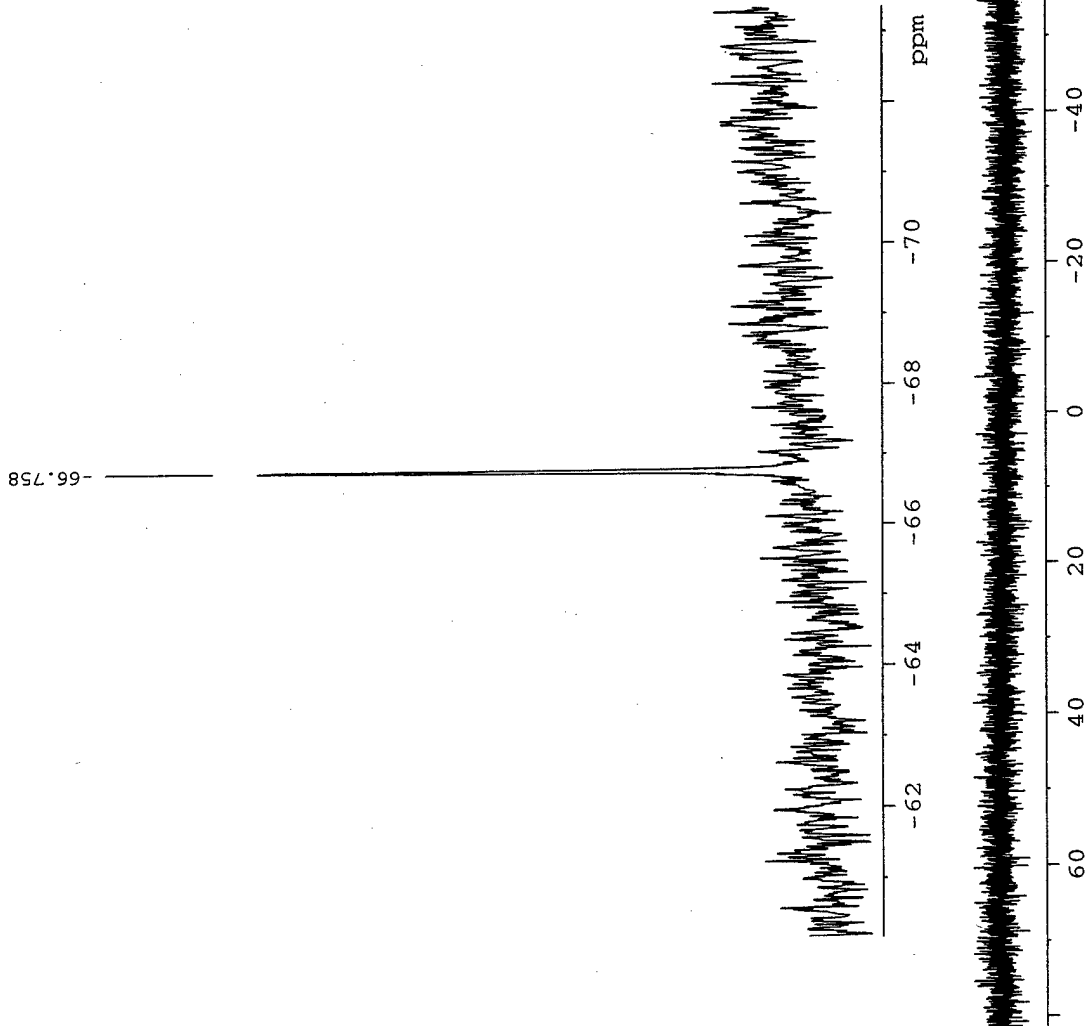
Current Data Parameters
NAME FdN1n1.226
EXPNO 29
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021227
Time 6.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 6066
DS 4
SWH 31847.133 Hz
FIDRES 0.485949 Hz
AQ 1.0289652 sec
RG 8192
DQ 1.00 usec
DE 6.00 usec
TE 300.0 K
TD 8.00000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 29Si
P1 8.40 usec
PL1 -5.00 dB
SFO1 79.466059 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 18.50 dB
PL12 18.00 dB
SFO2 400.1316005 MHz

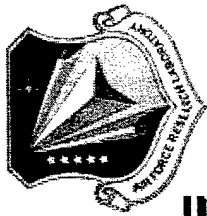
F2 - Processing parameters
SI 32768
SF 79.4945550 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





3,3,3-Trifluoropropyl_nT_n

3jm1-43 TFPnTn Mabry 01-30-03



Current Data Parameters
Date_ 20001124
Time_ 12:32
EXPNO 19
PROCNO 1

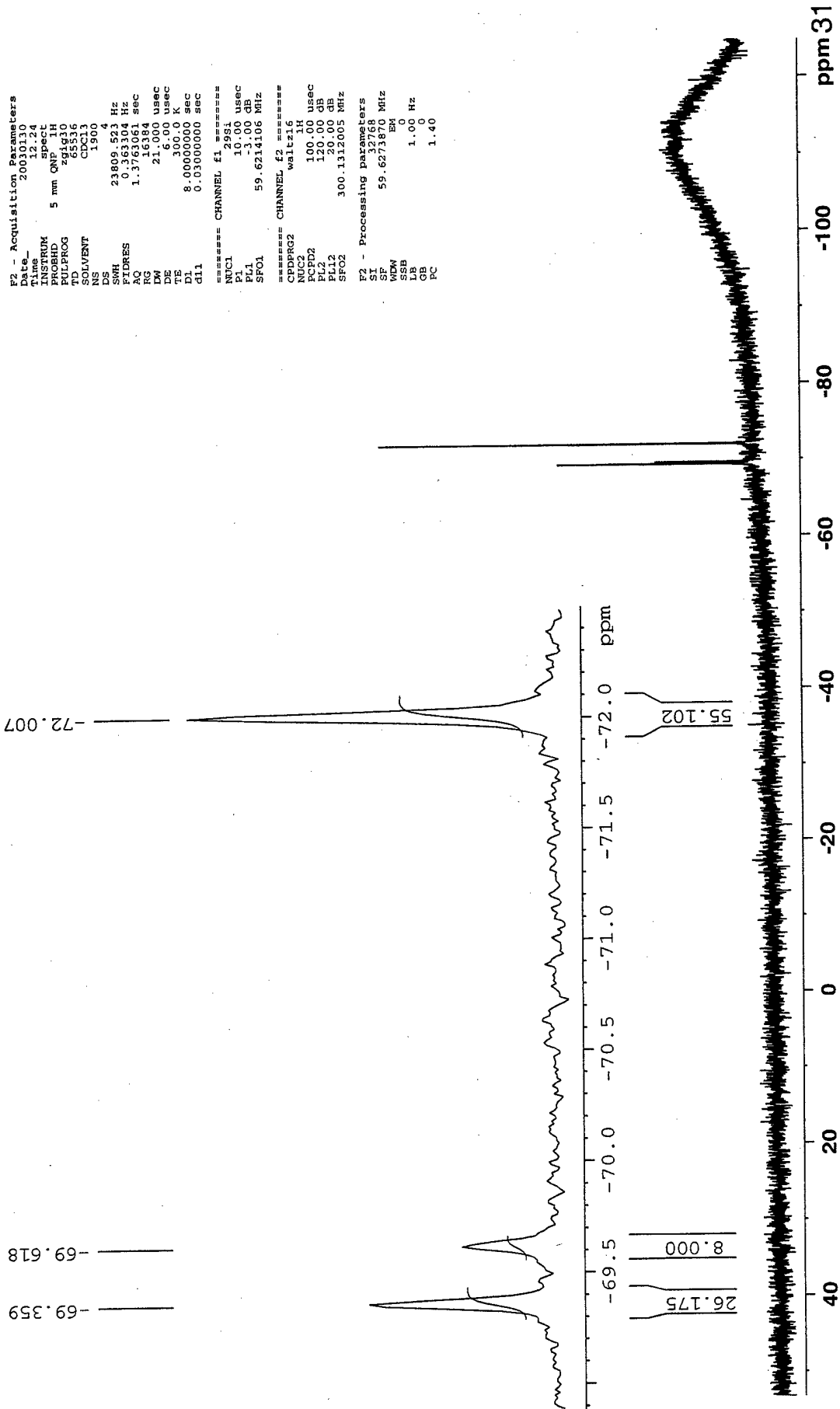
F2 - Acquisition Parameters

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INSTRUM spect
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TD 65536
SOLVENT CDCl₃
NS 1900
DS 4
SWH 23809.523 Hz
FIDRES 0.363304 Hz
AQ 1.3763084 sec
RG 0.0000000
EM 21.000 usec
DE 6.000 usec
TE 300.0 K
D1 8.00000000 sec
d11 0.03000000 sec

==== CHANNEL f1 =====
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P1 10.00 usec
PL1 -3.00 dB
SFO1 59.6214106 MHz

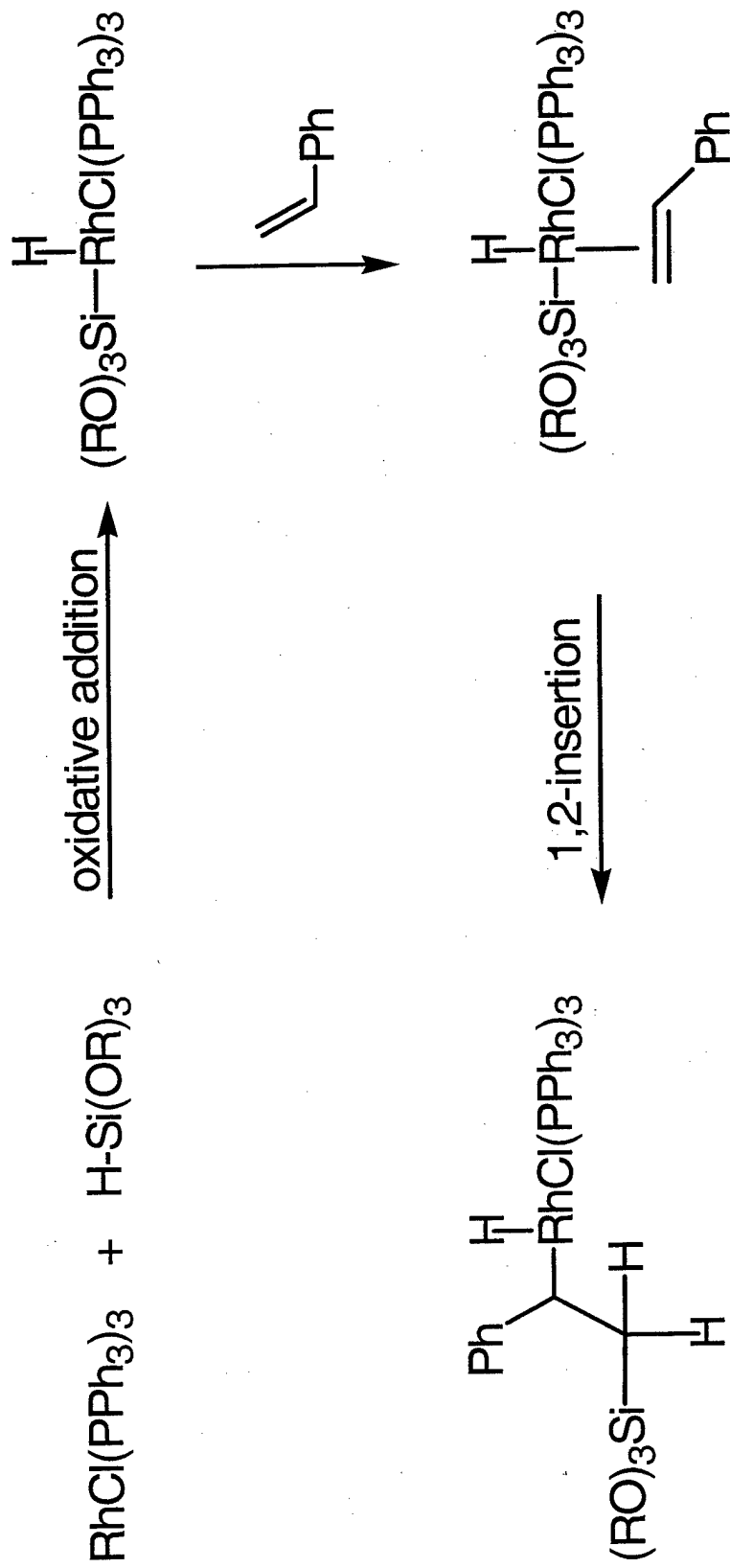
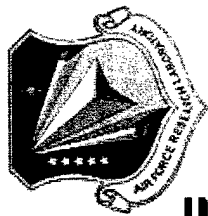
==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL3 20.00 dB
SFO2 300.1312005 MHz

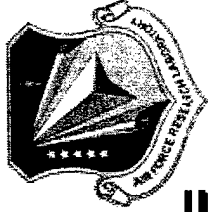
F2 - Processing parameters
SI 32768
SF 59.6273684 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



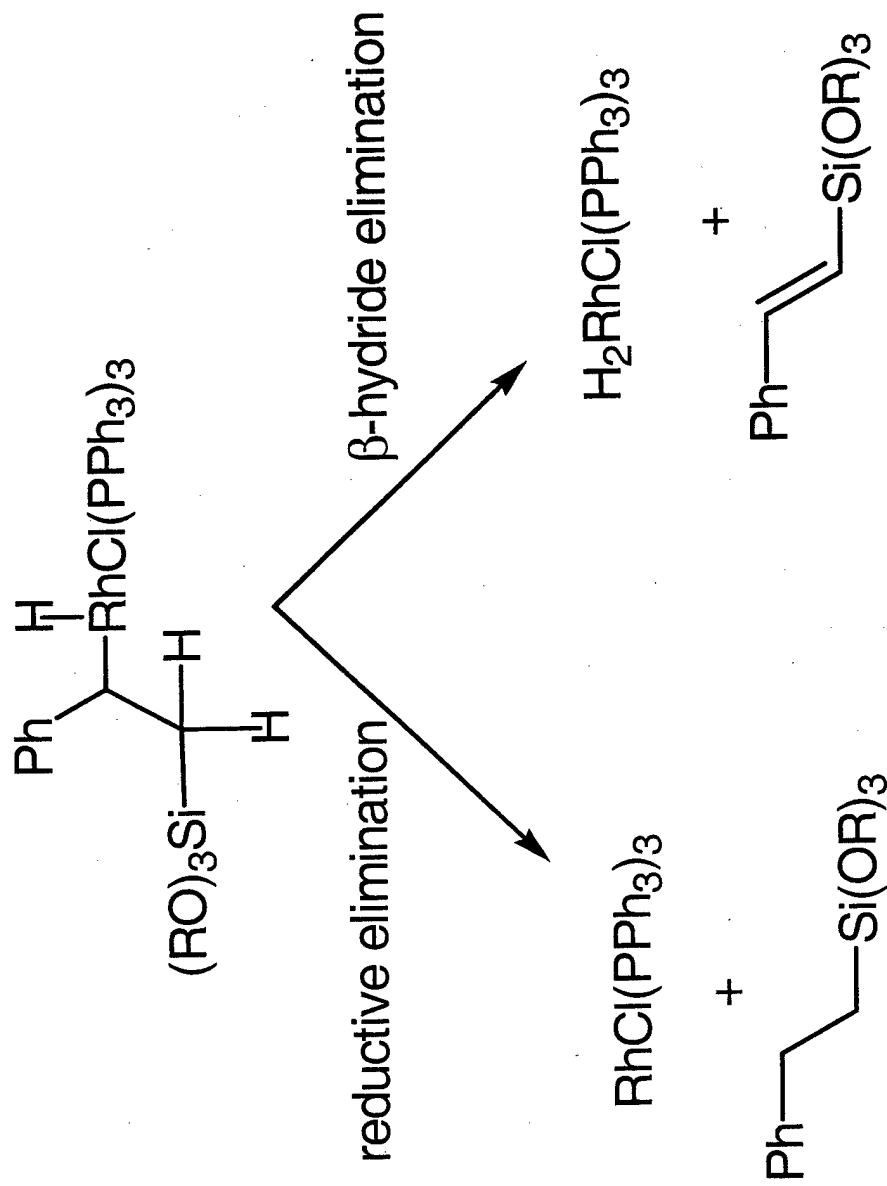


Mechanism





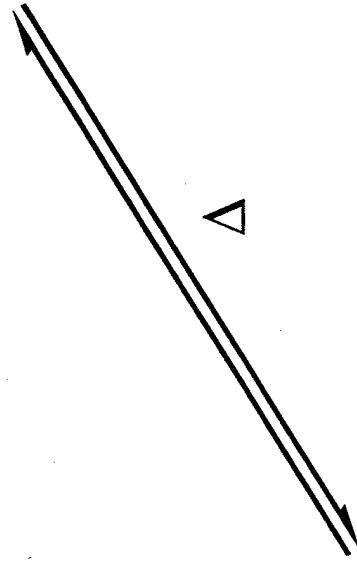
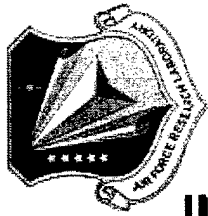
Mechanism



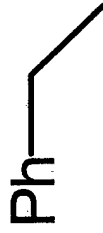
Hydrosilylation competes with dehydrogenative silylation.



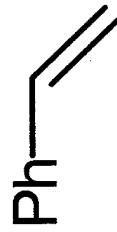
Mechanism



+



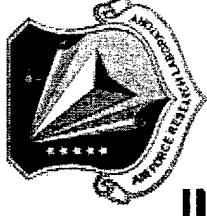
+



Rh species produced by β -hydride elimination hydrogenates unreacted alkene.



Surface Energy of Fluorosiloxanes



<u>Polymer</u>	<u>Surface Energy (mJ/m²)</u>
Poly(methylheptadecafluorodecylsiloxane)	7.0
Poly(methylnonafluorohexylsiloxane)	9.5
Poly(methyltrifluoropropylsiloxane)	13.6
Poly(dimethylsiloxane) (PDMS)	22.8
Poly(tetrafluoroethylene) (PTFE)	19.1