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MEMORANDUM FOR PRS (In-House Publication)

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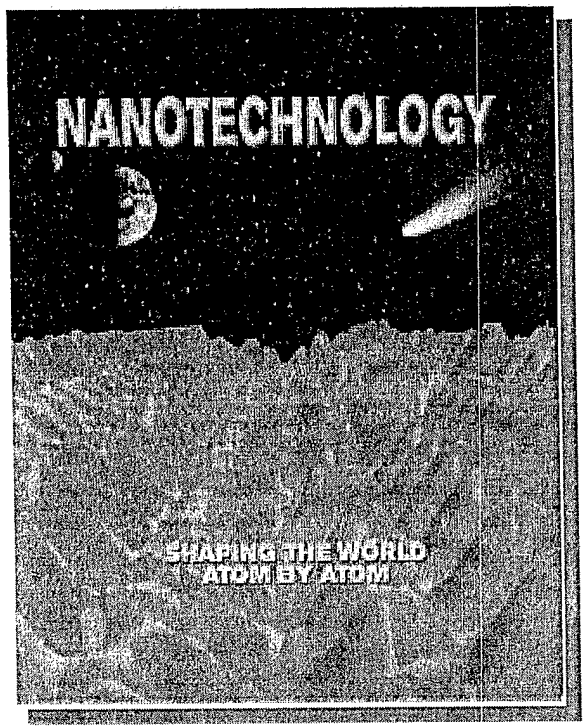
SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-087**
Brent Viers (PRSM), "Thin Film Properties of POSS"

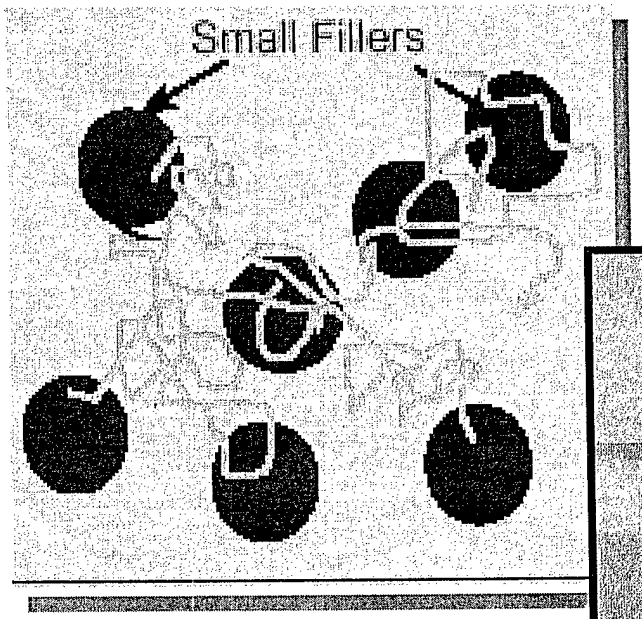
SAMPE Presentation **(Statement A)**
(Long Beach, CA, 10-16 May 2002) **(Deadline: 16 May 2002)**

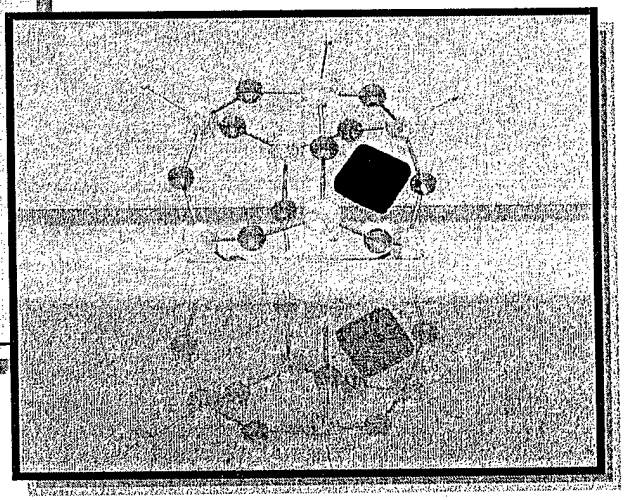
Thin Film Properties of POSS

Dr. Brent Viers
POSS Polymer Group Leader
Air Force Research Laboratory
Propulsion Materials (AFRL/PRSM)
Brent.viers@edwards.af.mil

Inorganic-Organic Hybrids = Nanotechnology







National Nanotechnology Initiative

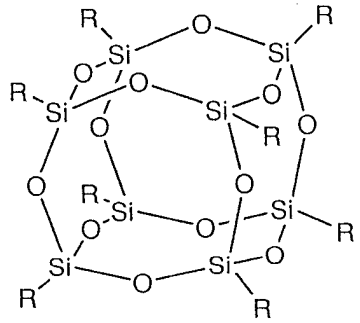
http://www.nano.gov

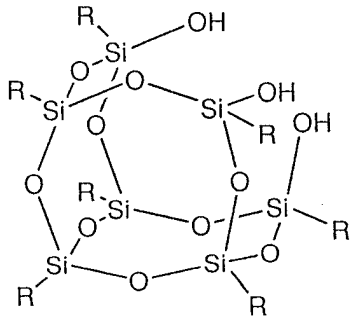
"Perpetual Plastics: By adorning the polymer structure of synthetic plastic with ceramic nanoparticles, researchers hope to develop new substances that will last far longer"

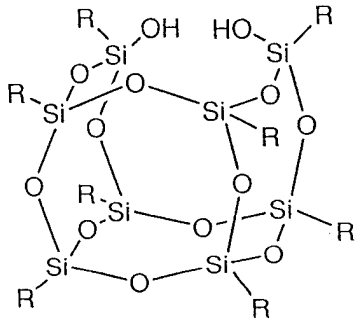
Mark Gordon, Iowa State U

What is POSS?

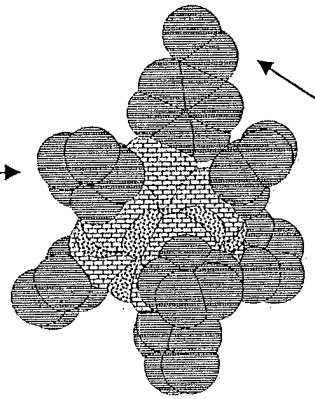
POSS=polyhedral oligomeric silsesquioxane







Nonreactive organic (R) groups for solubilization and compatibilization.



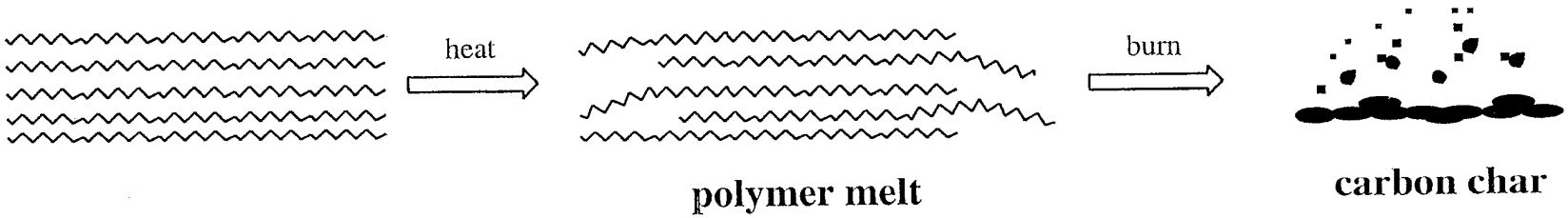
May possess one or more functional groups suitable for polymerization or grafting.

Si — Si = 5.4 Å

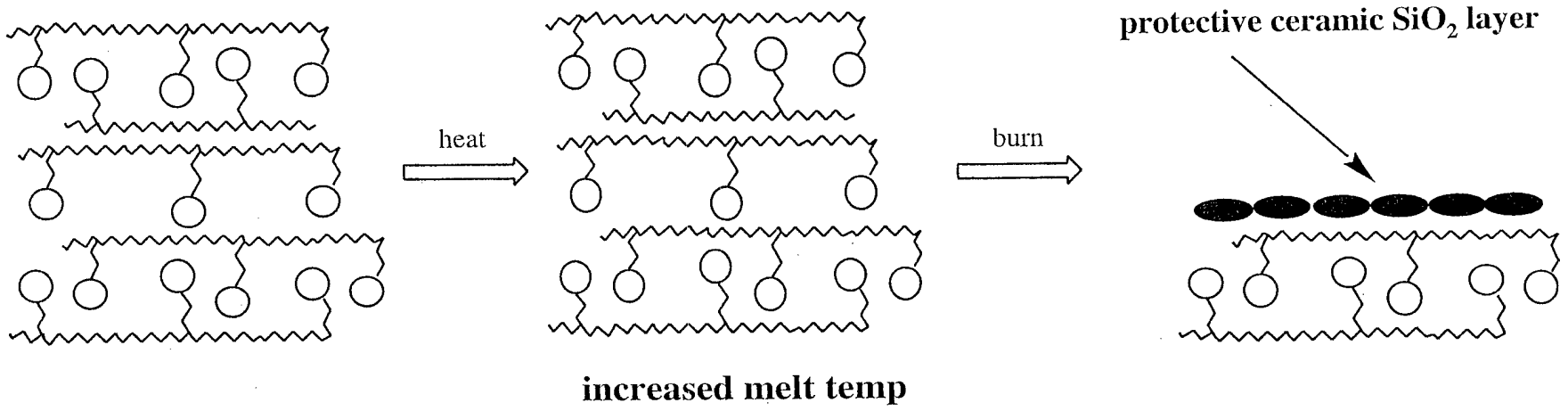
Cp — Cp = 15 Å

POSS for Low Ablation Materials

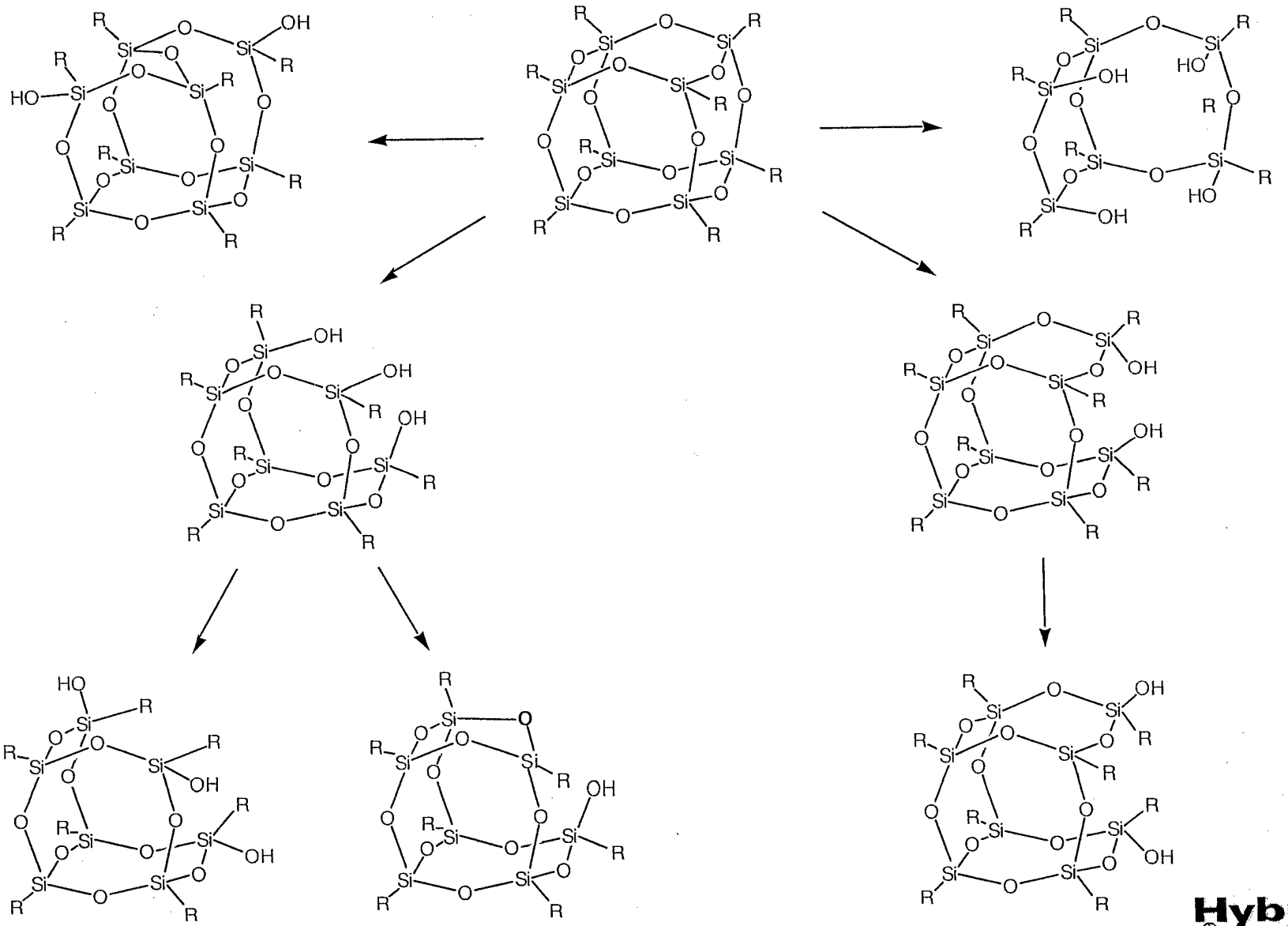
Traditional Polymer



POSS Polymer

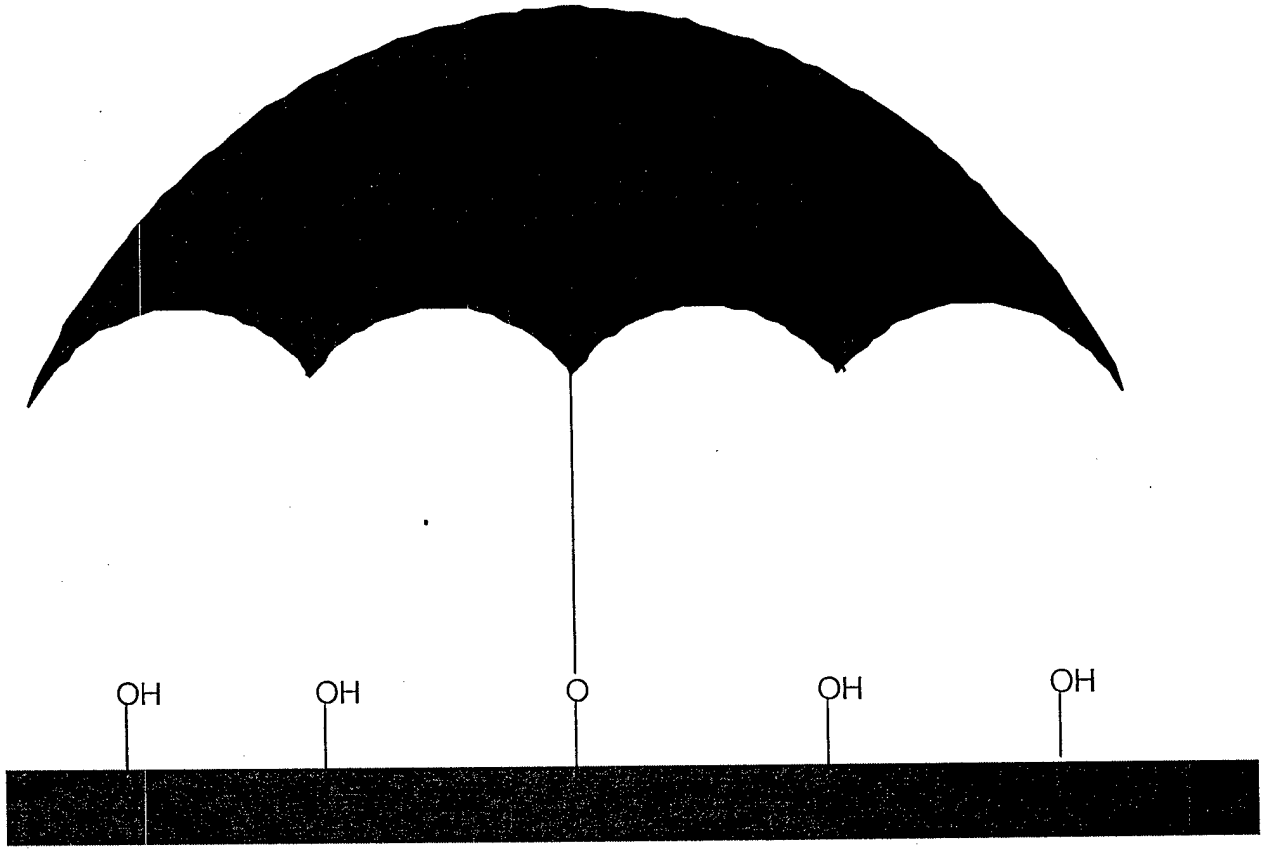


Stereochemical and Topological Control



Hybrid Plastics

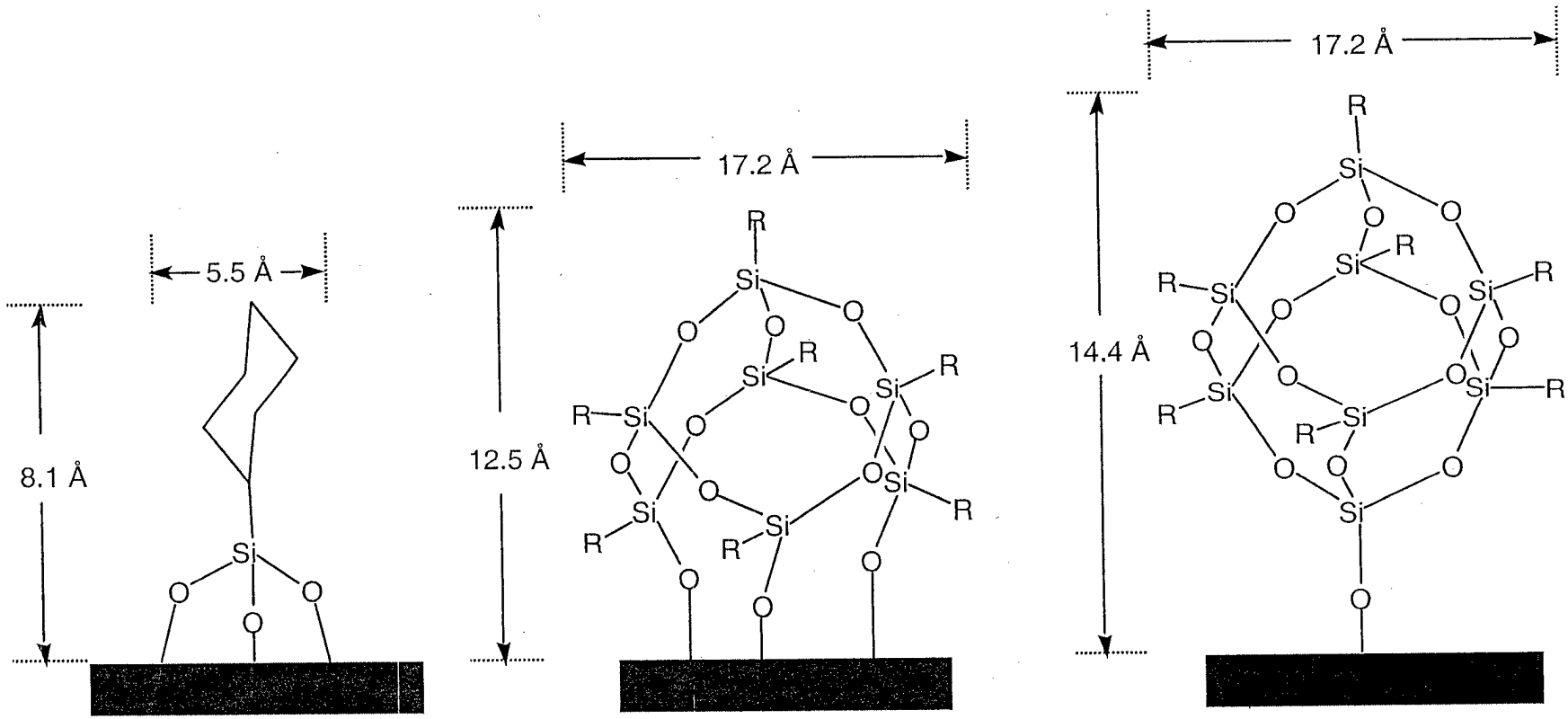
POSS™: The Hydrophobic "Umbrella"



- POSS™ acts a hydrophobic "umbrella" covering surface Si–OH groups (Approx. 10-12 Si–OH groups/POSS™ nanostructure)
- The surface coverage provided by a single POSS™ cage is approximately 8-10X that provided by a typical silane. (2.32 nm^2 vs. 0.24 nm^2)

Hybrid Plastics

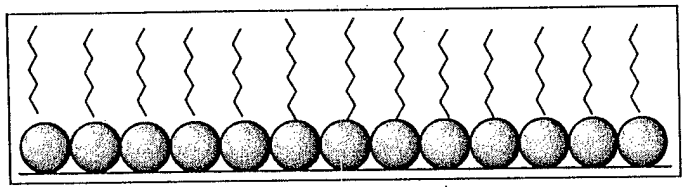
Silanes vs. POSS™: Monolayer Comparison



- The well-defined polyhedral structure leads to a more well-ordered, regular surface.
- POSS™ cages provide increased surface coverage leading to a more hydrophobic surface.

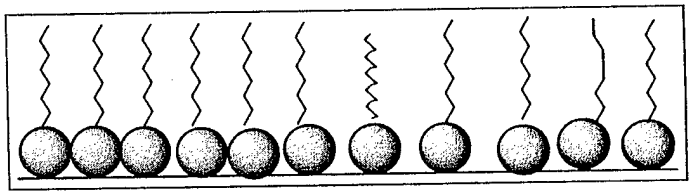
Hybrid Plastics

States of Monolayer Films



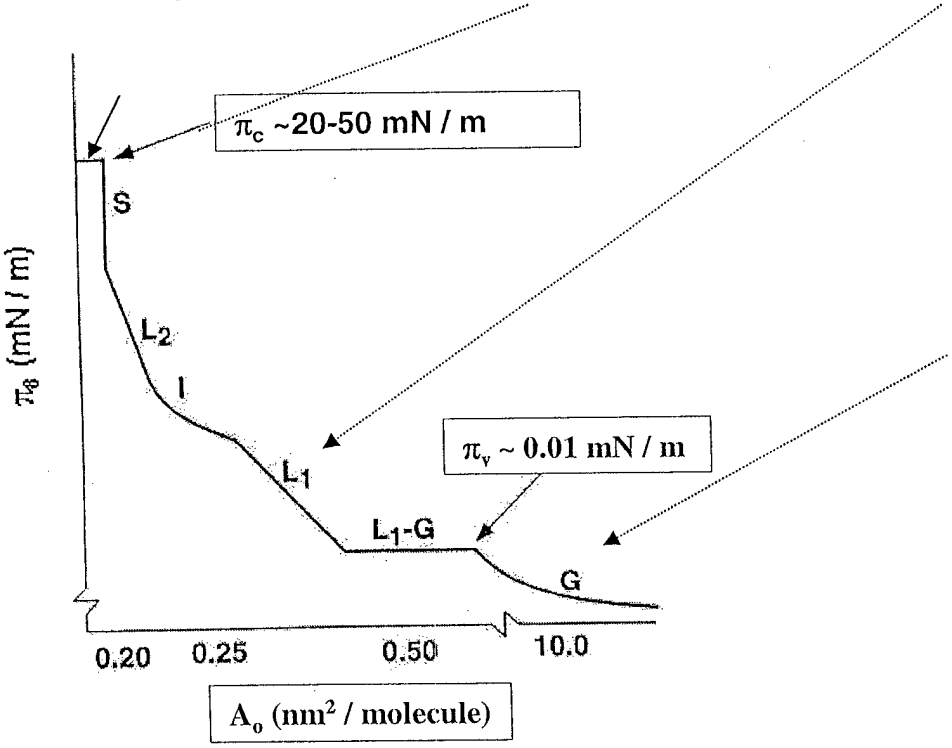
Solid Phase

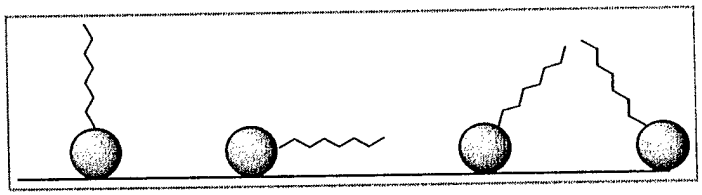
low compressibility (S), nearly linear plot



Liquid Phase

appear as liquid, some disorder in the structure, 2 types– liquid expanded (L_1) and liquid condensed (L_2)

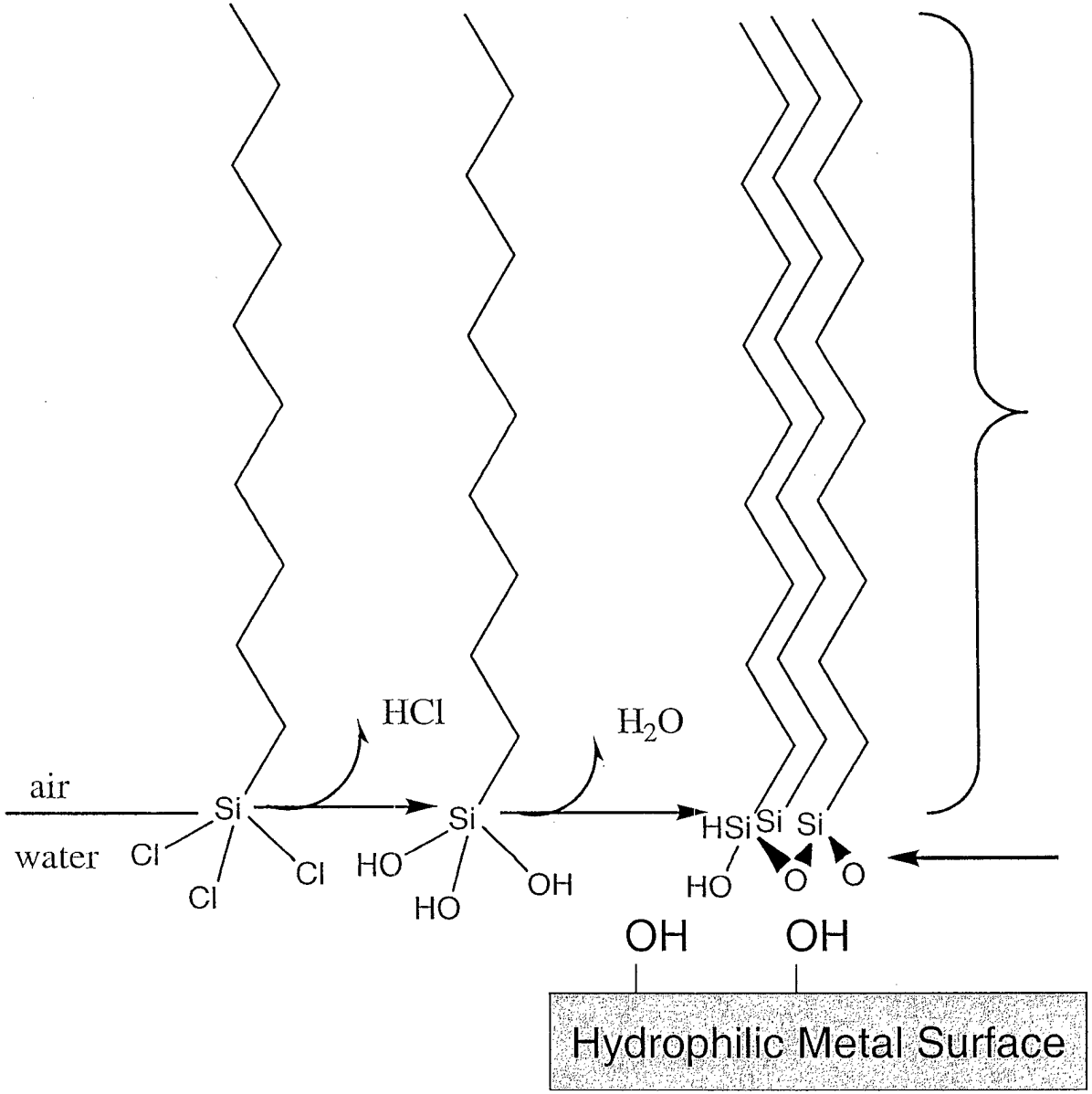




Gas Phase

obey an equation of state, area per molecule is large, Π as low as 0.001mN/m

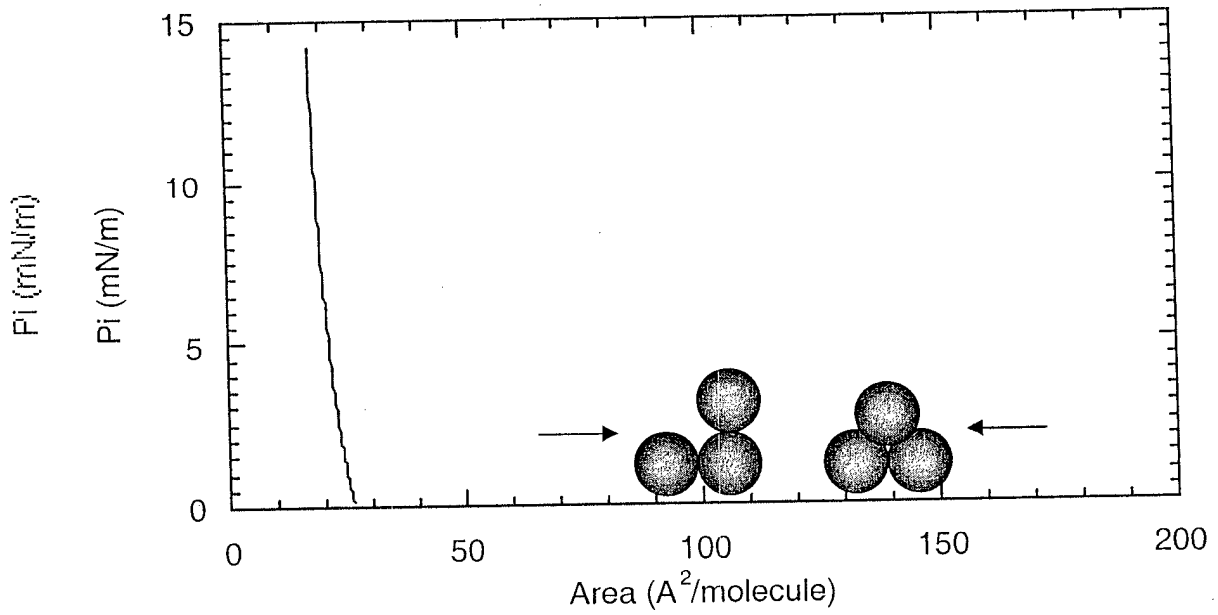
Chlorosilane Self Assembled Monolayers

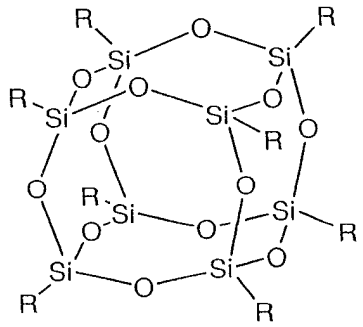


tightly packed alkyl chains=
strong hydrophobic interaction

covalently bonded bridging siloxane
and free hydrophilic silanol anchors

Fully Condensed POSS Cubes

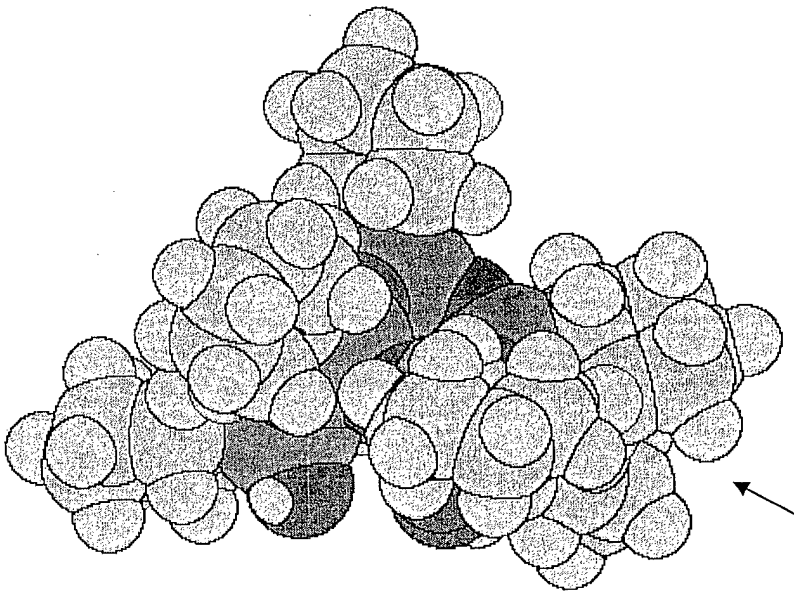




R = methyl
isobutyl, cyclopentyl

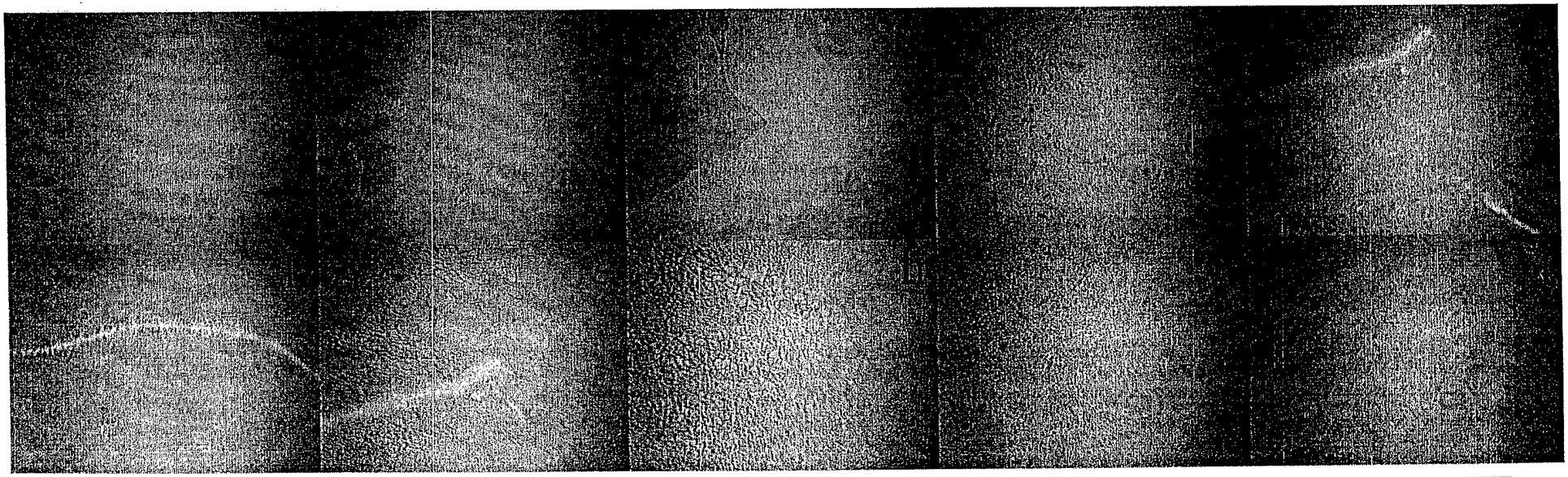
POSS likely exists as aggregates that agglomerate upon compression

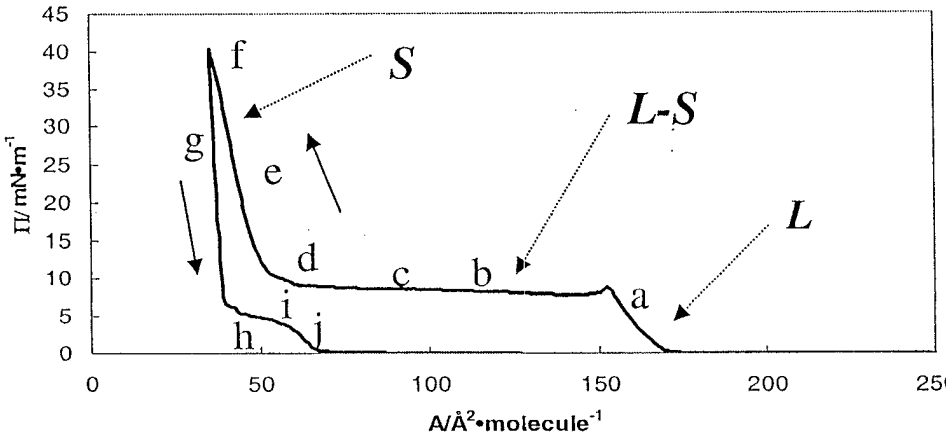
Steric Hindrance of POSS

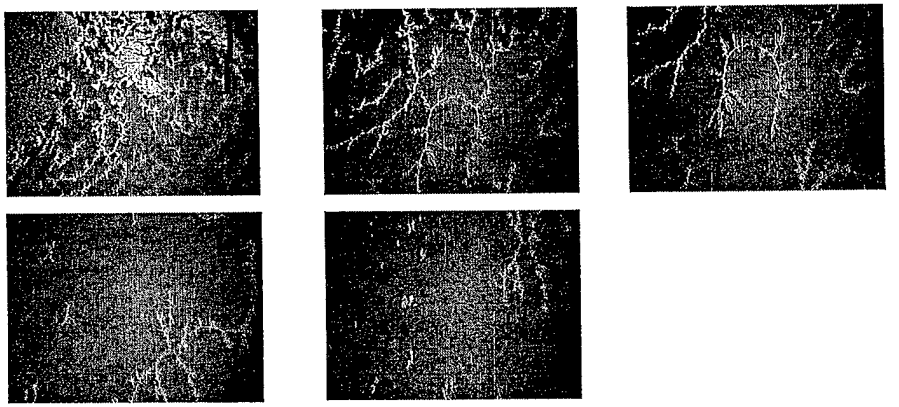


Hydrophobic
Organic groups
Extend past
Hydrophilic
Silanols!

Cyclopentyltrisilanol-POSS @ 22.5 °C

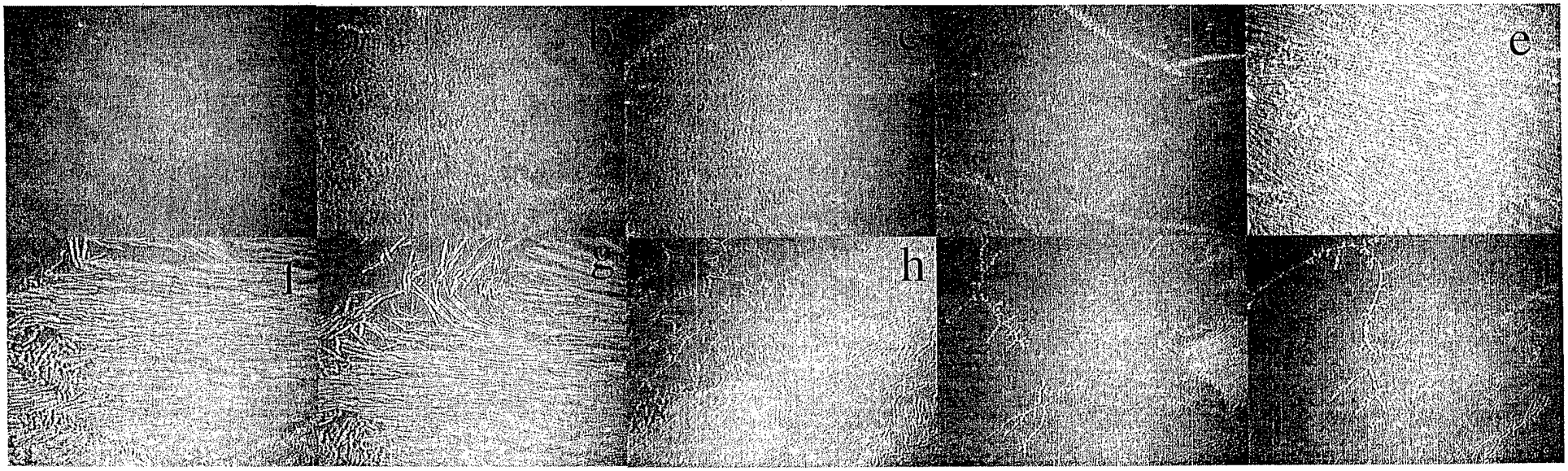


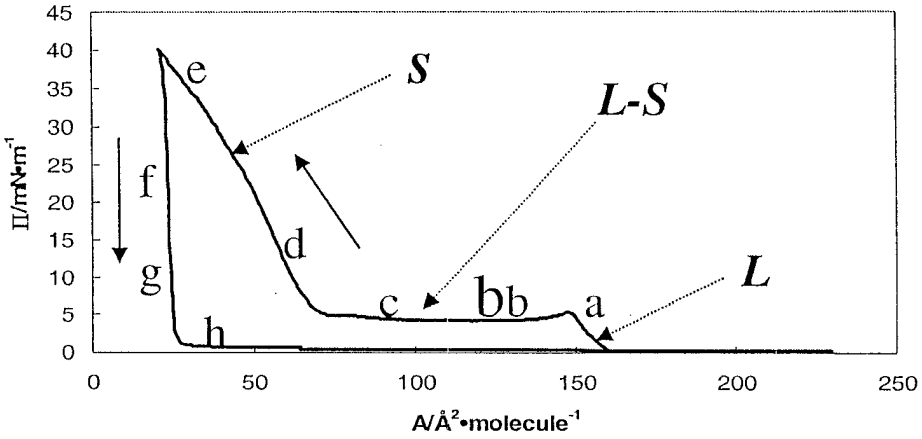


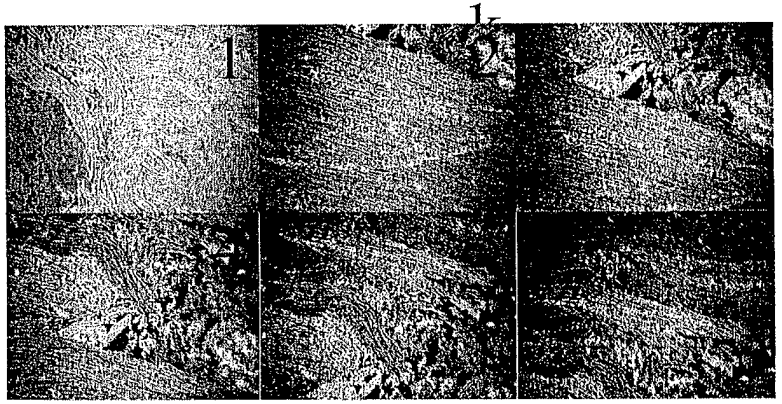


1-6 ,dendritic structures obtained during expansion in a second compression/expansion cycle

Cyclohexyltrisilanol-POSS @ 22.5°C

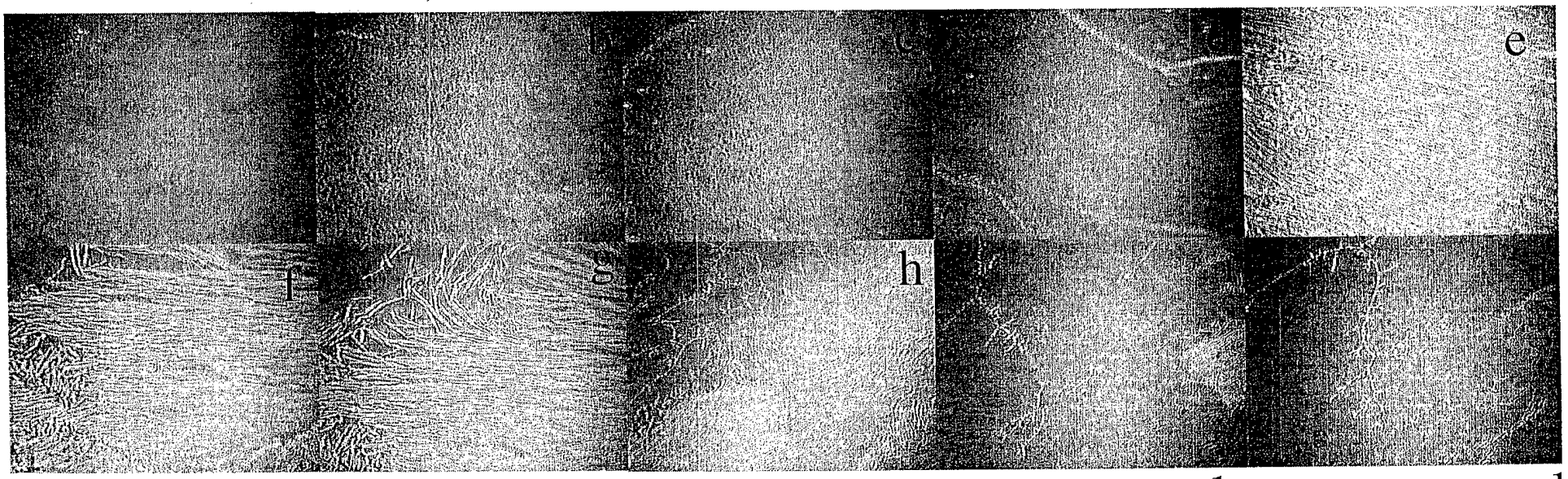


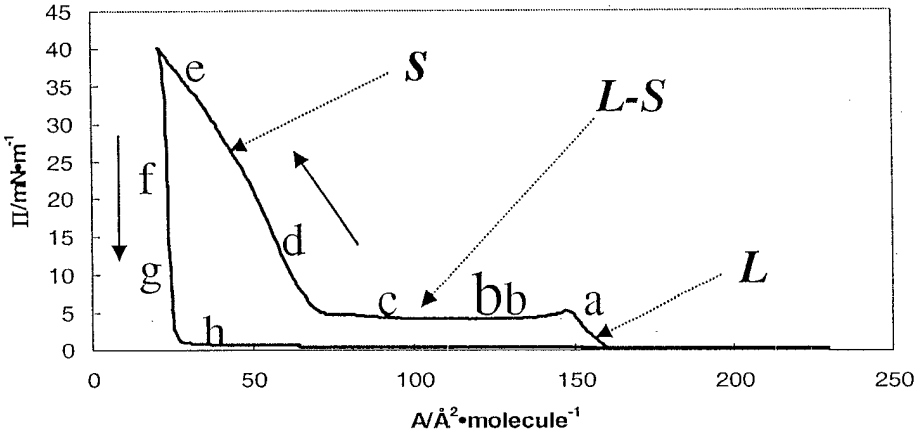


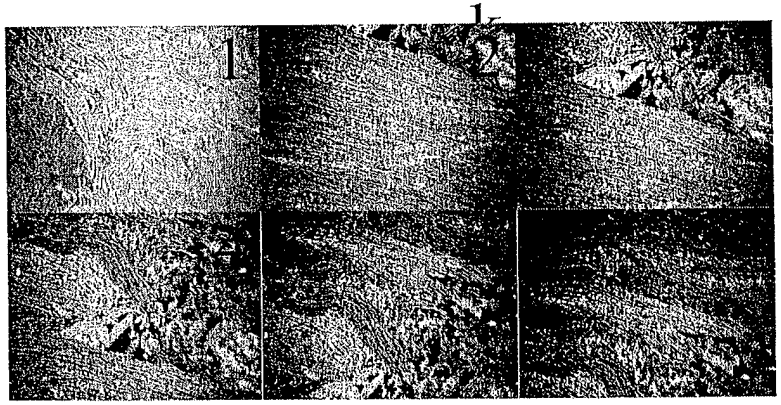


1-6 show the solid state film during 2nd compression

Cyclohexyltrisilanol-POSS @ 22.5°C

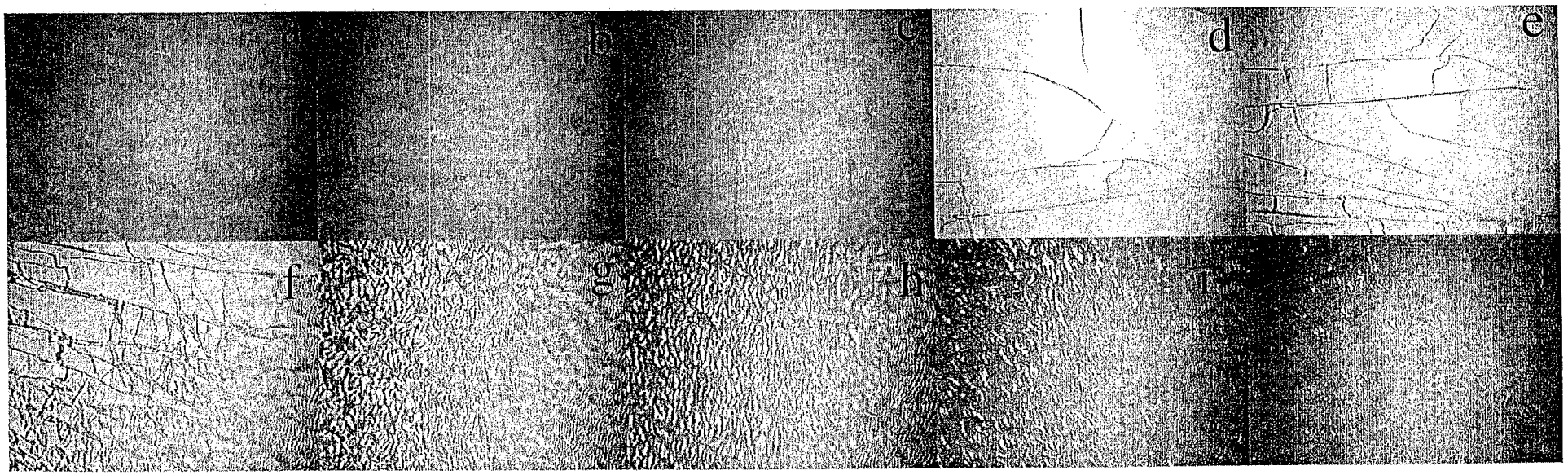


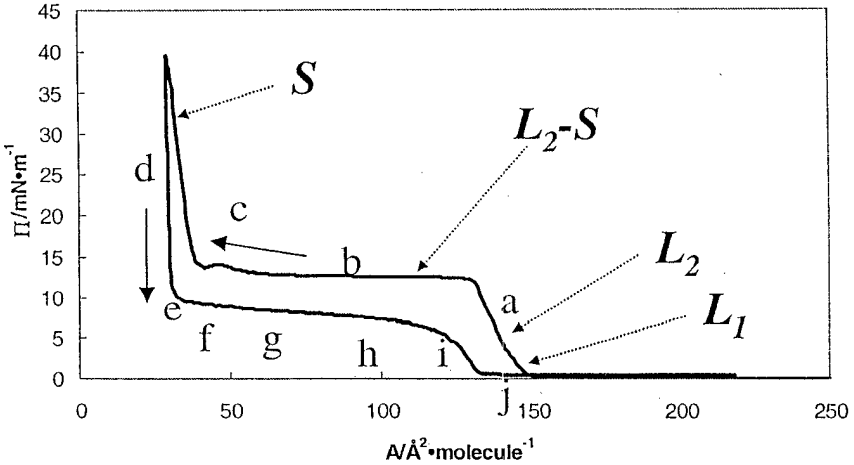


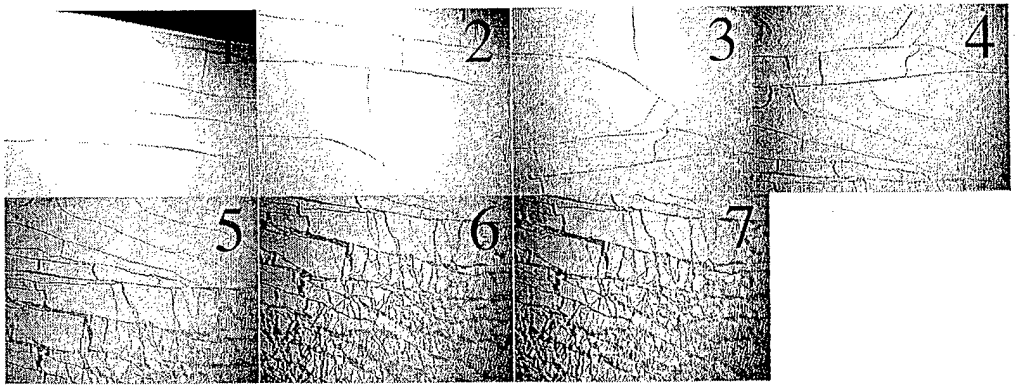


1-6 show the solid state film during 2nd compression

Phenyltrisilanol-POSS @ 22.5°C



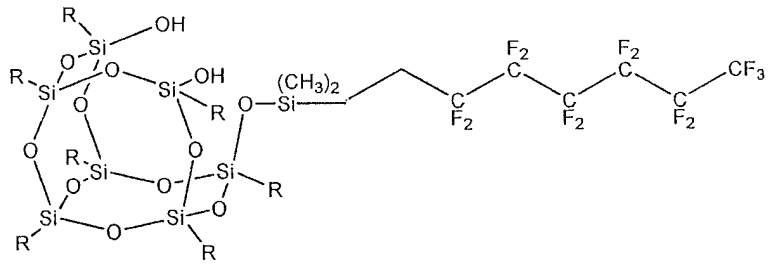




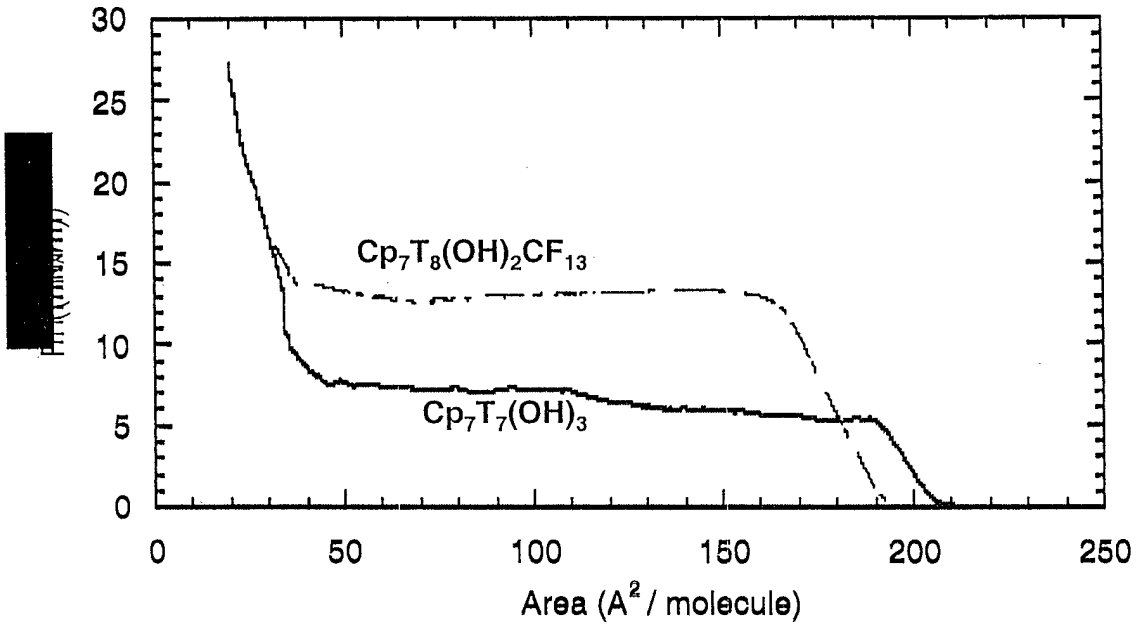
1-7 show the early details of solid state film break-up upon expansion

POSS in a "traditional" surfactant

Quantitative substitution of first silanol



R = cyclopentyl



Pressure-Area behavior is very similar to POSS precursor

Conclusions

- POSS with hydrophilic silanol groups can spread to form monolayers on a water surface
- Different POSS geometries (functionality) can change the compression behavior in a Langmuir Blodgett apparatus
- POSS surfactants can have complicated collapse behavior which likely affects the filler behavior (vis a vis aggregation effects)
- Transfer experiments are underway

Acknowledgments

- POSS group at AFRL-Edwards (Shawn Phillips, Rusty Blanski, Tim Haddad, Brian Moore, Justin Leland, Pat Ruth, Capt. Rene Gonzalez, Maj. Steve Svejda)
- Hybrid plastics (Joe Lichtenhan, Joe Schwab, Bill Reinerth)
- AFOSR (Dr. Charles Lee), Edwards AFRL-propulsion directorate