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MEMORANDUM FOR PRS (In-House Publication)

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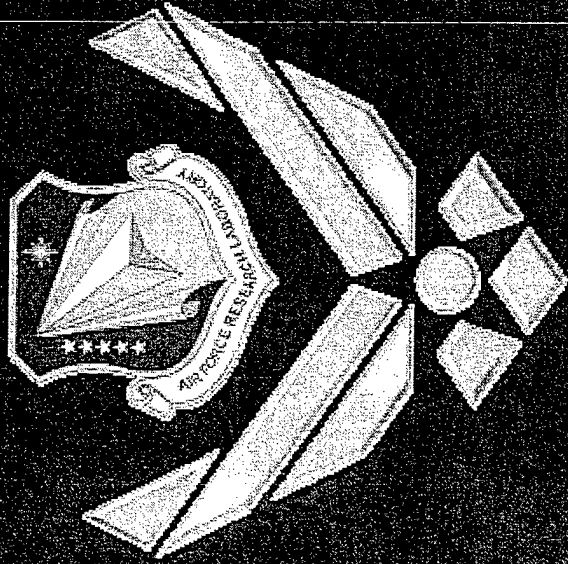
22 February 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-037**
Rusty Blanski, "Molecularly Reinforced Polymers"

Minnesota Technology Forum
(Minnesota, 15 February 2002) (Deadline: PAST DUE)

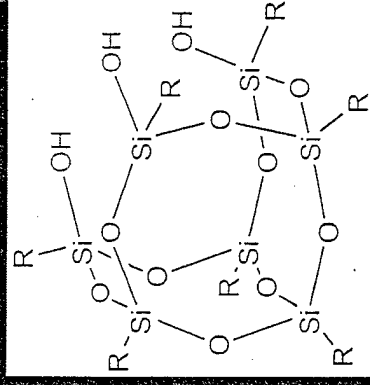
(Statement A)

Molecularly Reinforced Polymers



Dr. Rusty L. Blanski
Polymer Working Group
Air Force Research Lab, Edwards

DISTRIBUTION STATEMENT A:
Approved for Public Release -
Distribution Unlimited



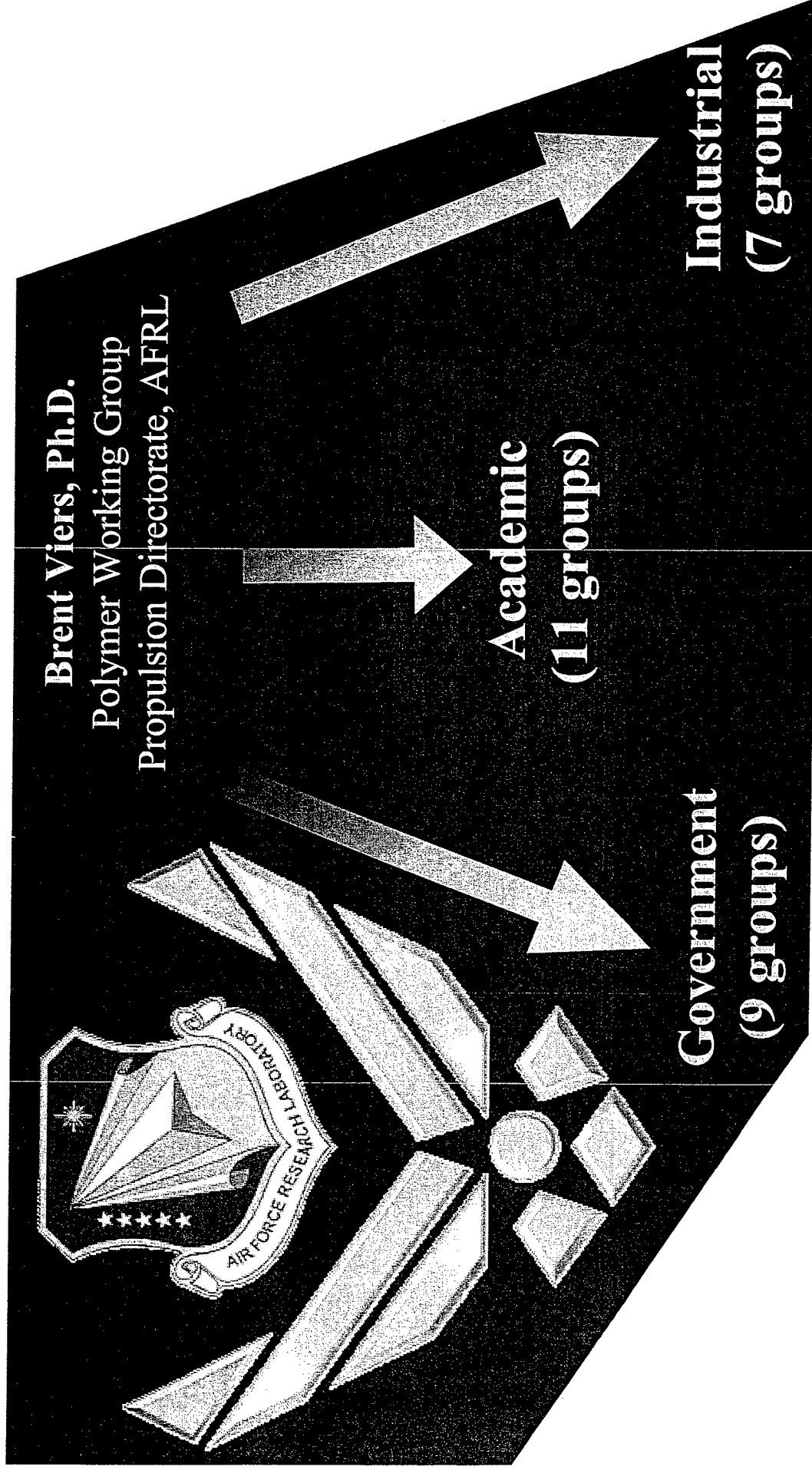
**Timothy S. Haddad, Frank J. Feher, Brent D. Viers,
Rene I. Gonzalez, Maj Steven A. Svejda,
Joe Lichtenhan, Joe Schwab**

Overview

- Introduction
- POSS Monomer Synthesis
- POSS Blends
- POSS Applications

POSS-Polymer Research is a Large Collaboration

Government-Academia-Industry



Acknowledgements

Polymer Working Group

Dr. Tim Haddad
Dr. Rusty Blanski
Dr. Brent Viers
Capt Rene Gonzalez
Brian Moore
Major Steve Svejda, Ph.D.
Justin Leland
Pat Ruth
New Post-Doc: Polymer Synthesis

Edwards

Dr. Kevin Chaffee
Mr. Paul Jones

External

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Dr. Joe Schwab - HP
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Dr. Jeff Gilman - NIST
Prof. Ben Hsiao - SUNY SB
Prof. Bryan Coughlin - UMass
Prof. Gar Hoflund - UF
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Dr. Seng Tan - WMR
Prof. Mark Gordon - Iowa St. U
Dr. Howard Katzman - Aerospace
Mr. Don Geidt/Mike Blair - CSD/Thiokol

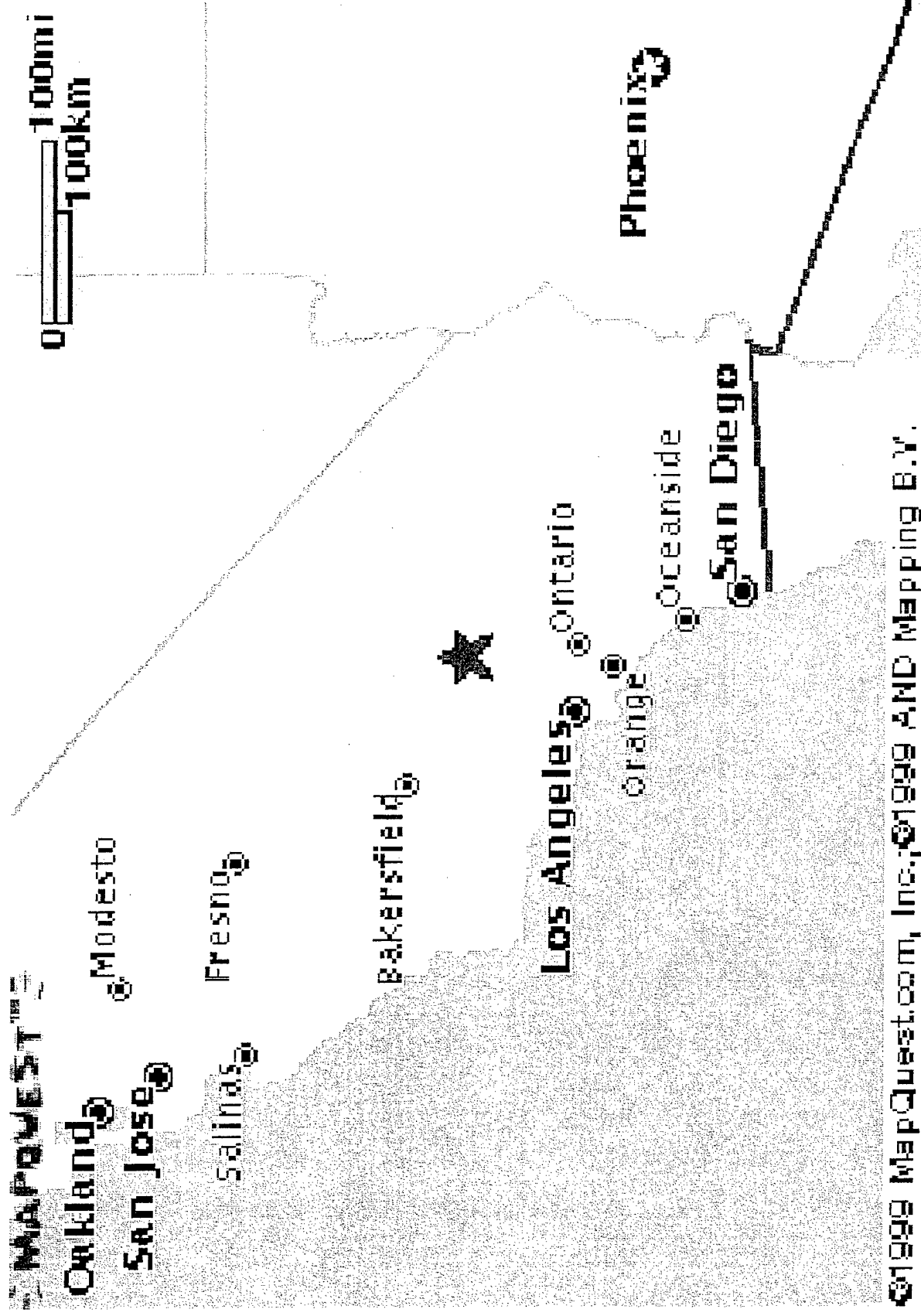
Funding: AFOSR (Dr. Charles Lee), AFRL, Hybrid Plastics

Basic R&D

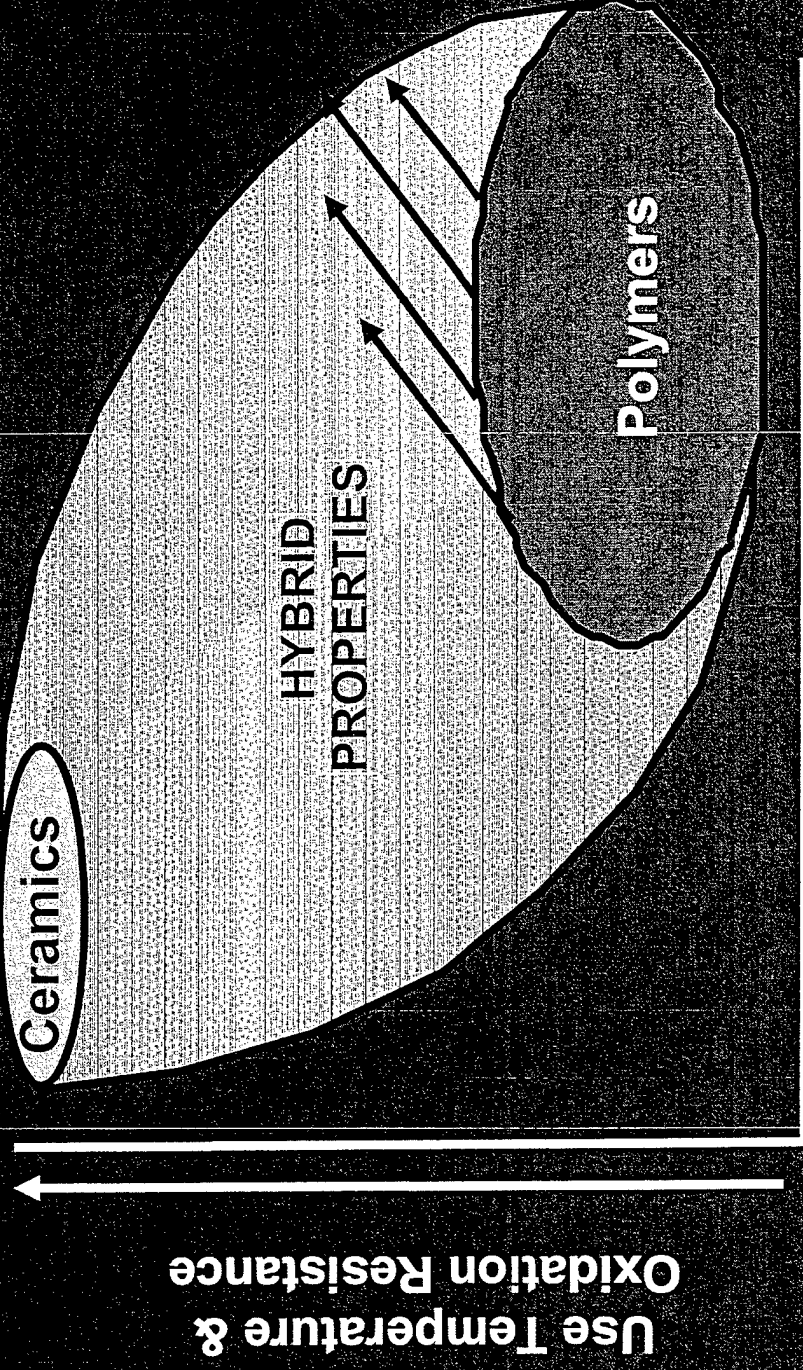
Applications R&D

Air Force Research Laboratory

Located ~ 100 miles from LA

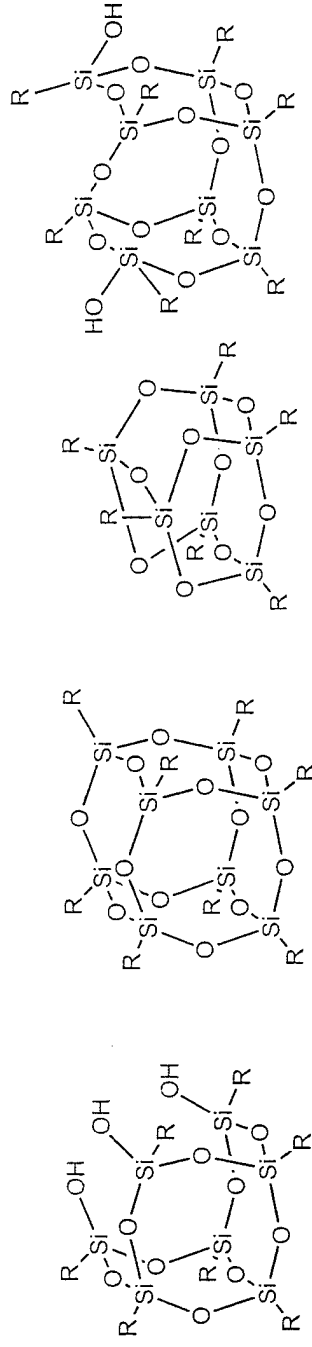


Multiple Applications/Multi-Function



- Improve High Performance Polymers/ Transform Commodity Polymers into High performance Polymers
- Develop Multi-Functional Materials/ Replace Metal Parts with Polymers

POSS = Polyhedral Oligomeric Silsesquioxane: General Synthesis



R = Cyclohexyl
Cyclopentyl
Cycloheptyl
Vinyl
Methyl

R = Cyclohexyl
Cyclopentyl
Cycloheptyl

R = Cyclohexyl
Cyclopentyl
Vinyl
Methyl

R = Cyclohexyl

R = Cyclohexyl

R = Cyclohexyl: Brown and Vogt 1965

Feher, Newman, Walzer 1989

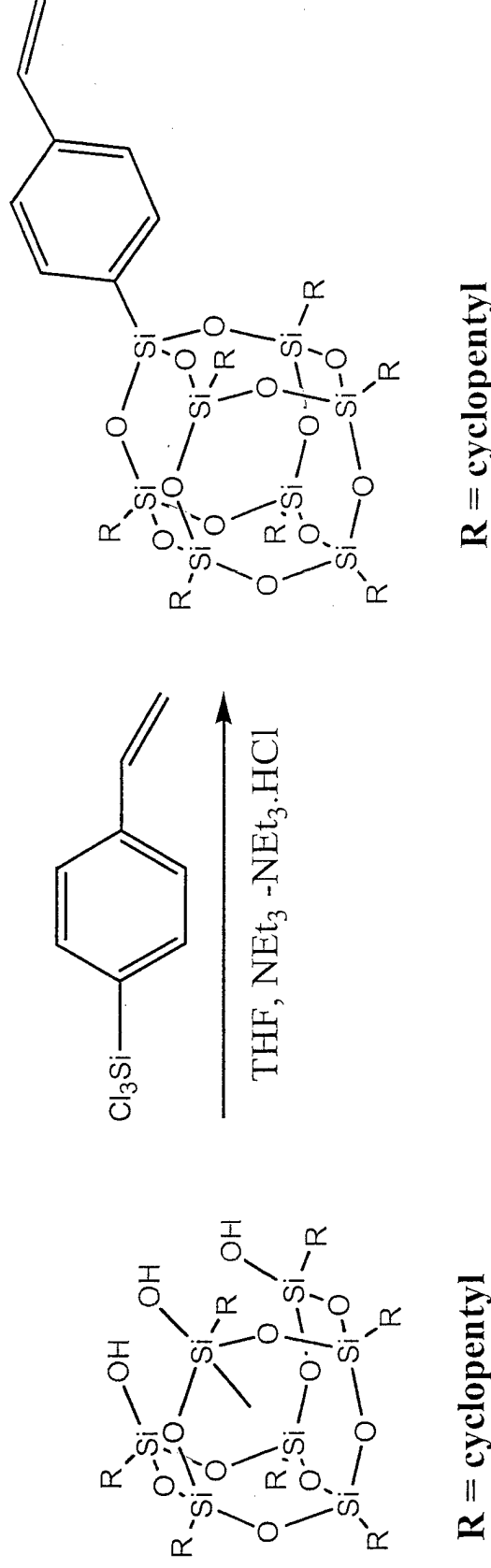
* Lichtenhan (AFRL, mid '90's) Optimized Purification

Cyclopentyl: Feher, Budzichowski, Weller, Blanski, Ziller 1990

* Lichtenhan (AFRL, 1993) Optimization

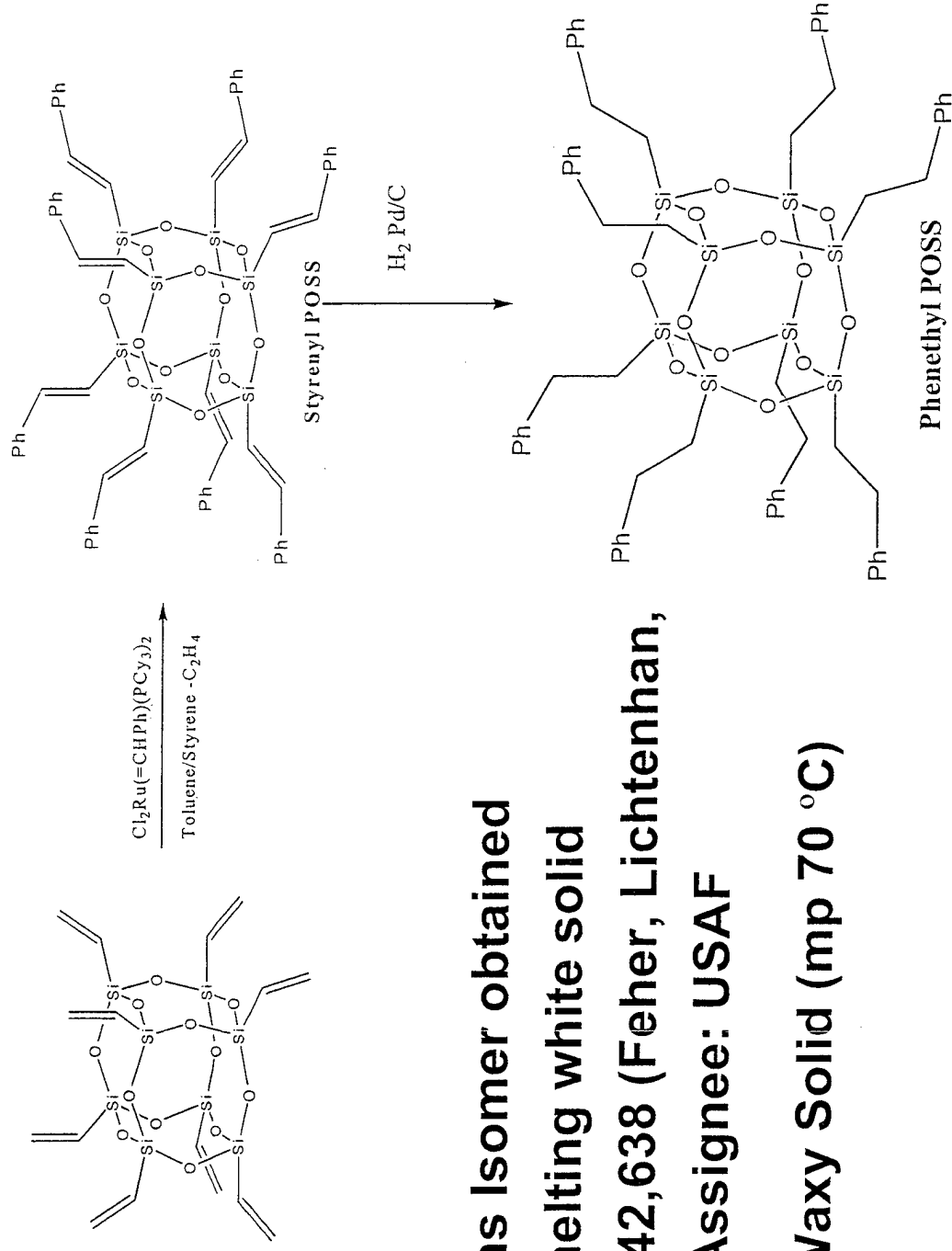
All of these materials are colorless solids at ambient temp

POSS = Polyhedral Oligomeric Silsesquioxane: General Synthesis



- Functionalized POSS Monomers for Polymerization in traditional systems (styryl, norbornyl, methacrylpropyl, etc.)

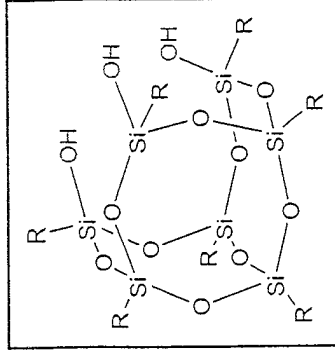
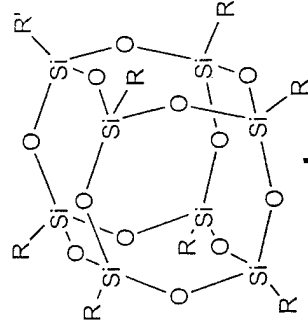
POSS = Polyhedral Oligomeric Sil₃sesquioxane General Synthesis



- All trans Isomer obtained
- High melting white solid
- US 5,942,638 (Feher, Lichtenhan, et al) Assignee: USAF

White Waxy Solid (mp 70 °C)

POSS Monomer/Polymer Trees



halides

alcohols

esters

acids

bisphenols

acid chlorides

aryldiacids

nitriles

amines

isocyanates

arylbisamines

aryldiisocyanates

silanes

silanols

siloxanes

olefins

styryls

acrylics

norbornyls

cyclopropyls

epoxies

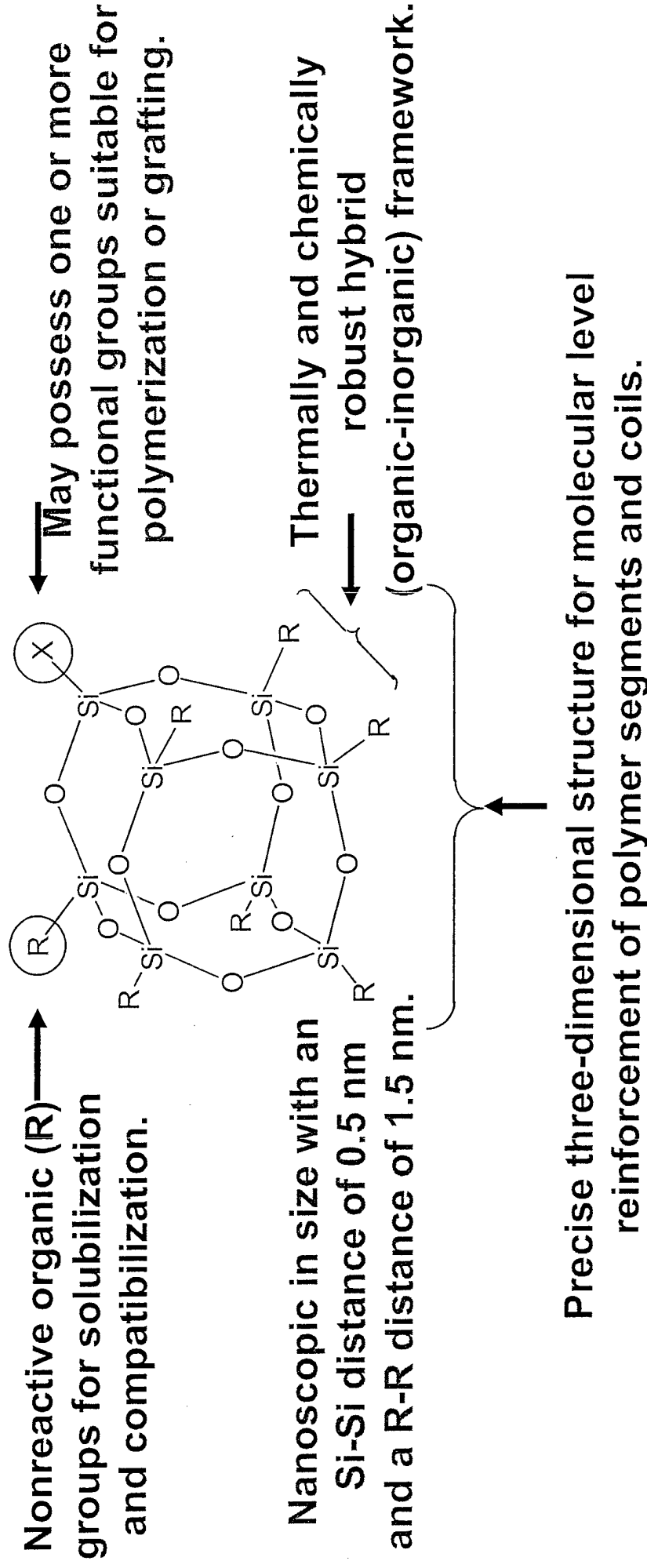
>100 polymer systems

- POSS-rubber*
- POSS-urethane*
- POSS-epoxy*
- POSS-phenolic*
- POSS-imide*

monomers and polymers.

***“POSS-technology is sustainable
via dual-use markets”***

Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS) Molecule



The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)

Key Roadblocks for POSS Materials, Sept. 1998

- Time for Production of POSS feedstocks
- Cost of POSS feedstocks/monomers/polymers
- Volume of POSS feedstocks/monomers
- Structure/Property Relationships
- Blends & Processing

POSSTM Commercialization and Cost Reduction Campaigns

In October 1998 Hybrid Plastics and the Air Force Research Laboratory entered into a Cooperative Research and Development Agreement (CRADA) for the commercialization of POSSTM Nanotechnology.

Technical Objective:

- Commercialization of POSSTM Technology.

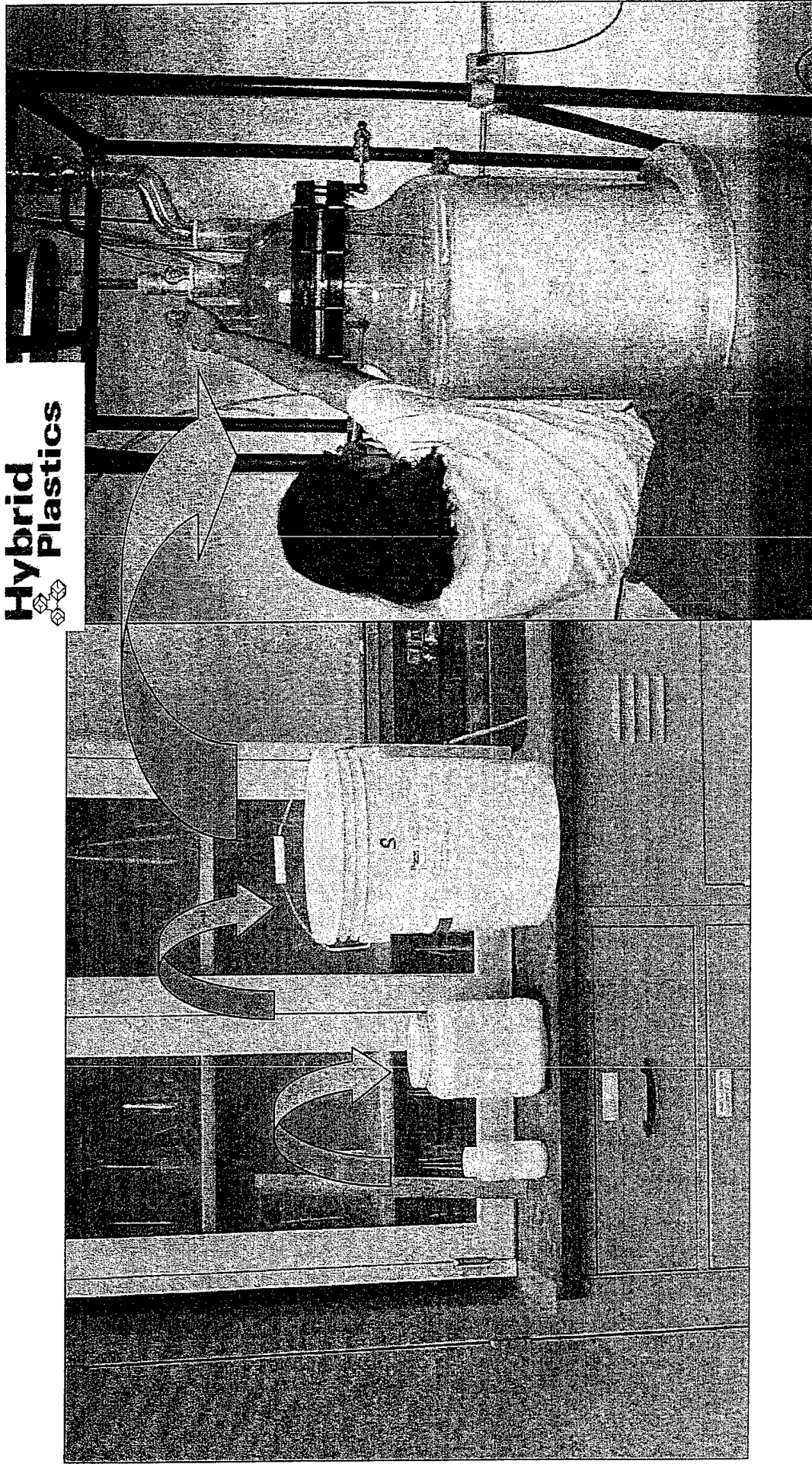
Also in October 1998 Hybrid Plastics was awarded a 3-year, \$2 million grant by NIST's Advanced Technology Program (ATP) to reduce the cost of POSS NanostructuredTM Chemical Technology by a factor of 100.

Technical Objective:

- Reduce costs of POSSTM Technology from \$1000-\$5000/lb to \$10-50/lb.

Technology Transfer = Scalability = Price Reduction, Sustainability

**Hybrid
Plastics**

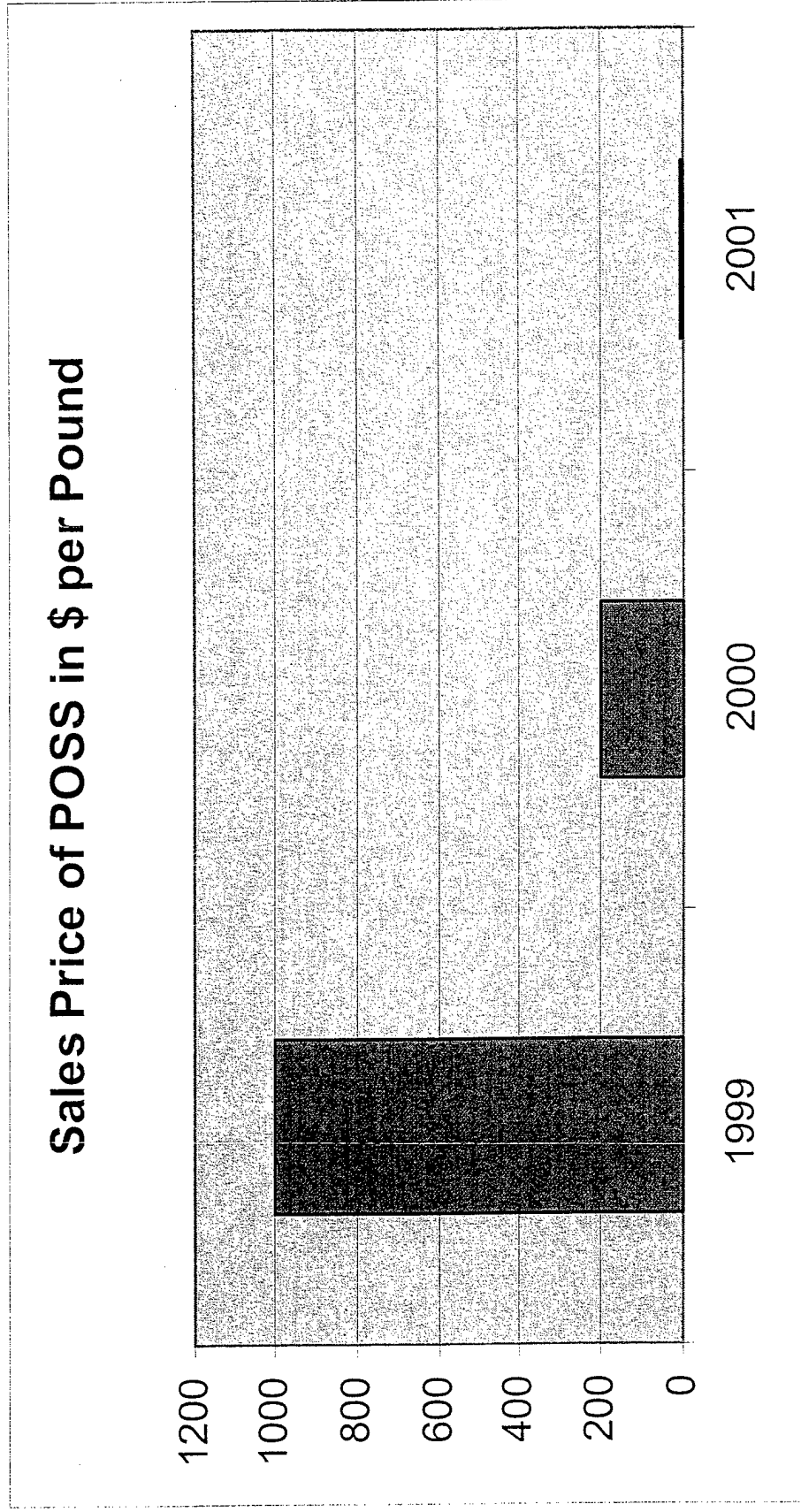


Time	1991	1994	1998	2000
Quantity	< 50g	2-5 lb	20-40 lb	> 400 lb
Price	???	\$1000-5000/lb	\$1000-5000/lb	\$20-250/lb

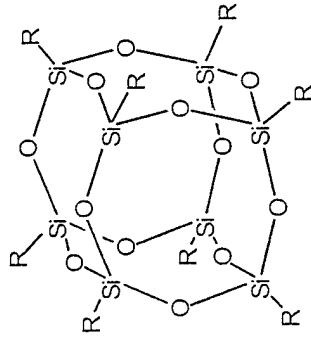
Plant



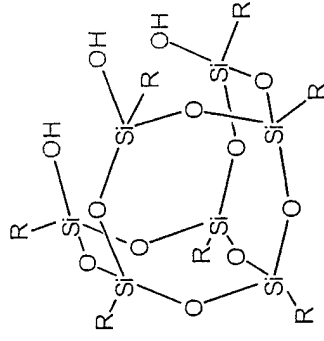
Retail Prices of POSS



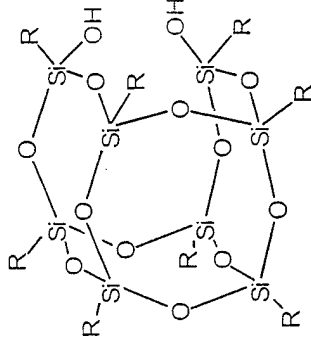
POSS Diversity



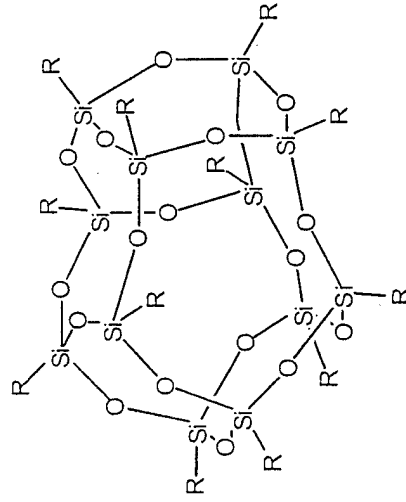
R = Methyl Isooctyl
 Isobutyl Phenyl
 Cyclopentyl Phenethyl
 Cyclohexyl Octadecene



R = Isobutyl
 Cyclopentyl
 Cyclohexyl
 Isooctyl
 Ethyl

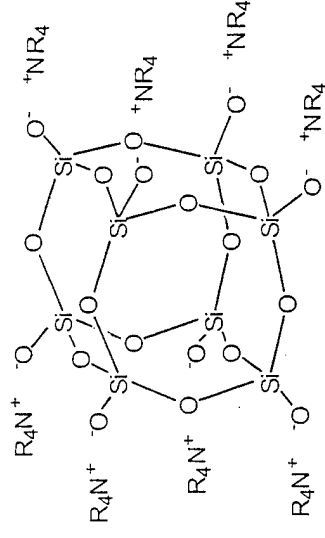


R = Isobutyl
 Cyclopentyl
 Cyclohexyl
 Isooctyl



R = Phenyl
 Trifluoromethylpropyl

Polydisperse Cages
 (T_8 , T_{10} , T_{12})

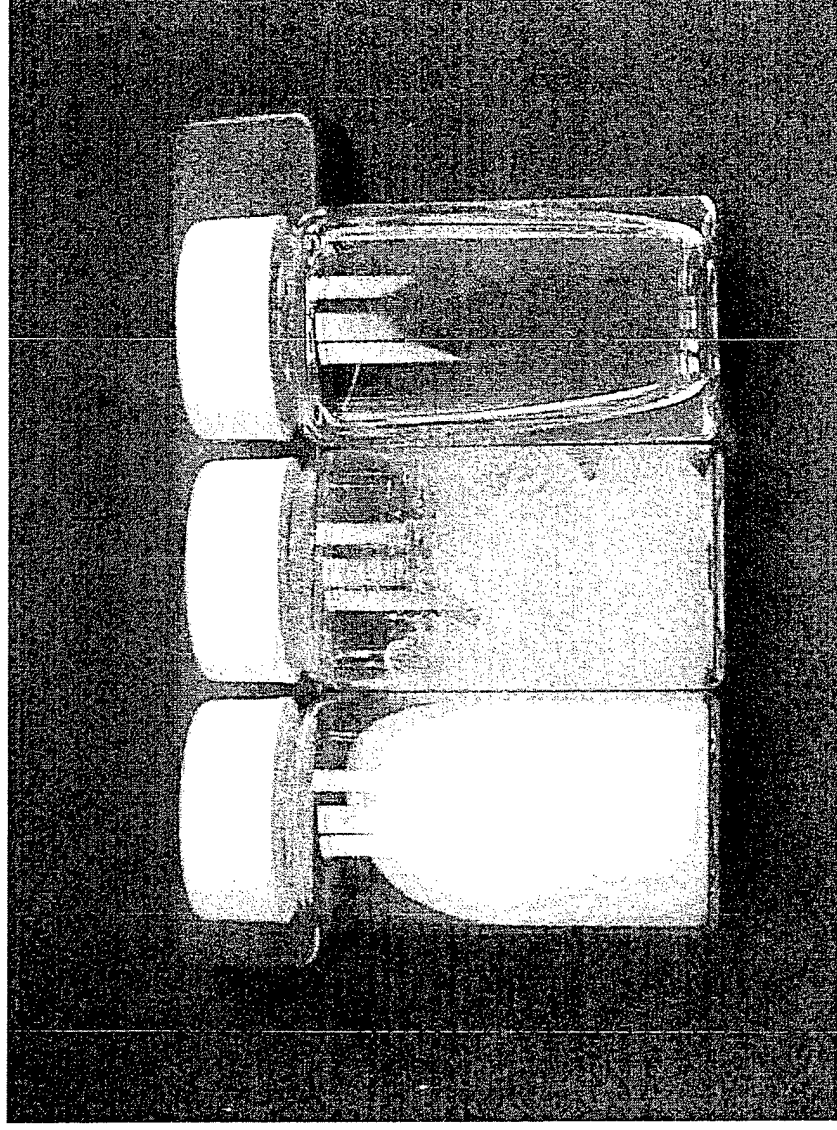


R = Vinyl
 Phenethyl

R = Methyl

Nanostructured™ POSS Chemicals

Physical Form of Products



Crystalline Solids

Wide melting range 24°C to 400°C+

Waxes

Liquids & Oils

Wide viscosity range 40cSt. to 400cSt

Global Sales of Nanostructured™ Chemicals

R&D chemical catalog sales (1997 to present)

Aldrich Chemical Company

Gelest Inc.

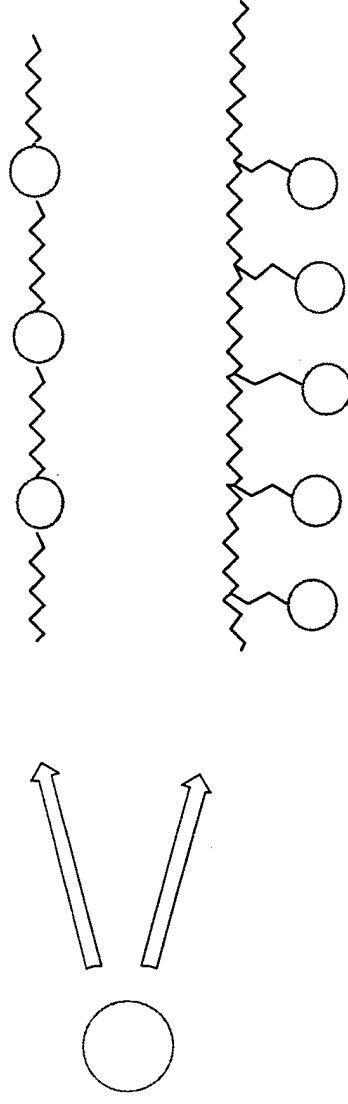
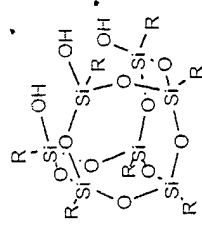
Trends in Hybrid Plastics' R&D/bulk chemical sales

65% Asia and Europe

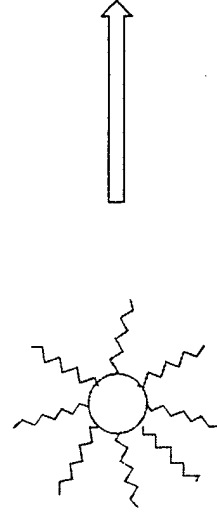
30% US Domestic

5% Government Sales

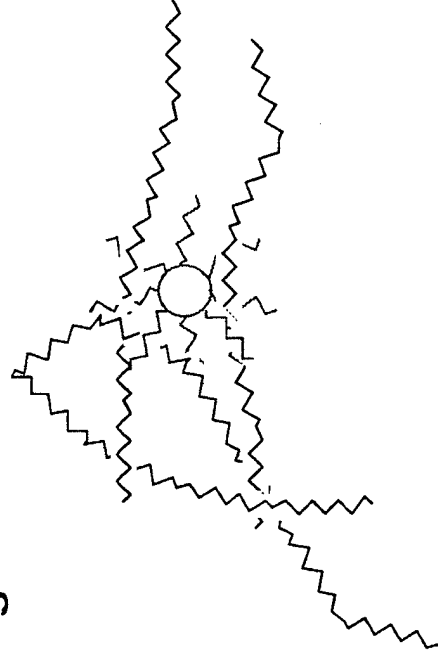
POSS Polymer Incorporation



POSS Copolymerization/Grafting



POSS Blending



- improved mechanicals
- increased T_g , T_m , T_{dec}
- decreased creep
- improved processing
- optically transparent

Size & Shape

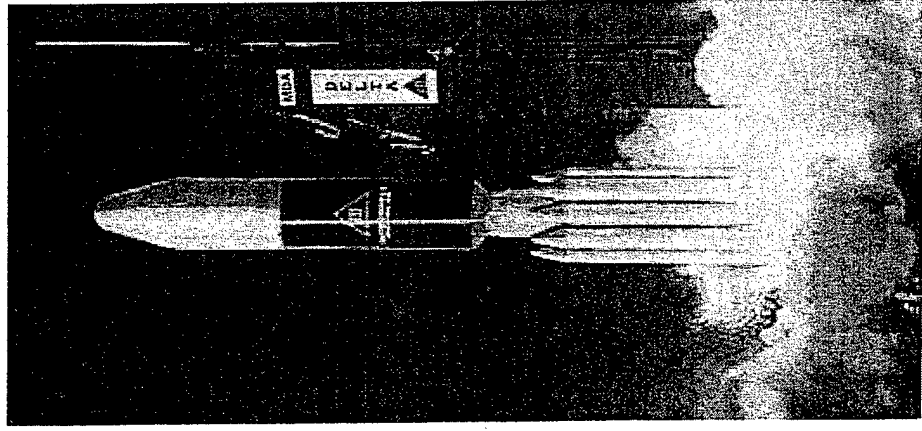
POSS-Polymer Blends for Air Force

Applications

- **GOAL:** To increase the performance characteristics of polymers by blending in POSS

Potential Applications of POSS-Polymer Blends

- **High Temperature Insulation for Solid Rockets Motors**
- **Capacitors**
- **Space-survivable Materials and Coatings**
- **Low/High Temp. Hybrid Lubricants**
- **Plastic Tubing and Ducting for Liquid Rockets Engines**
- **High Temperature/High Translation Strength Composites**
- **Improved Radome Materials**



POSS-Polymer Blends

Why Use Blendables?

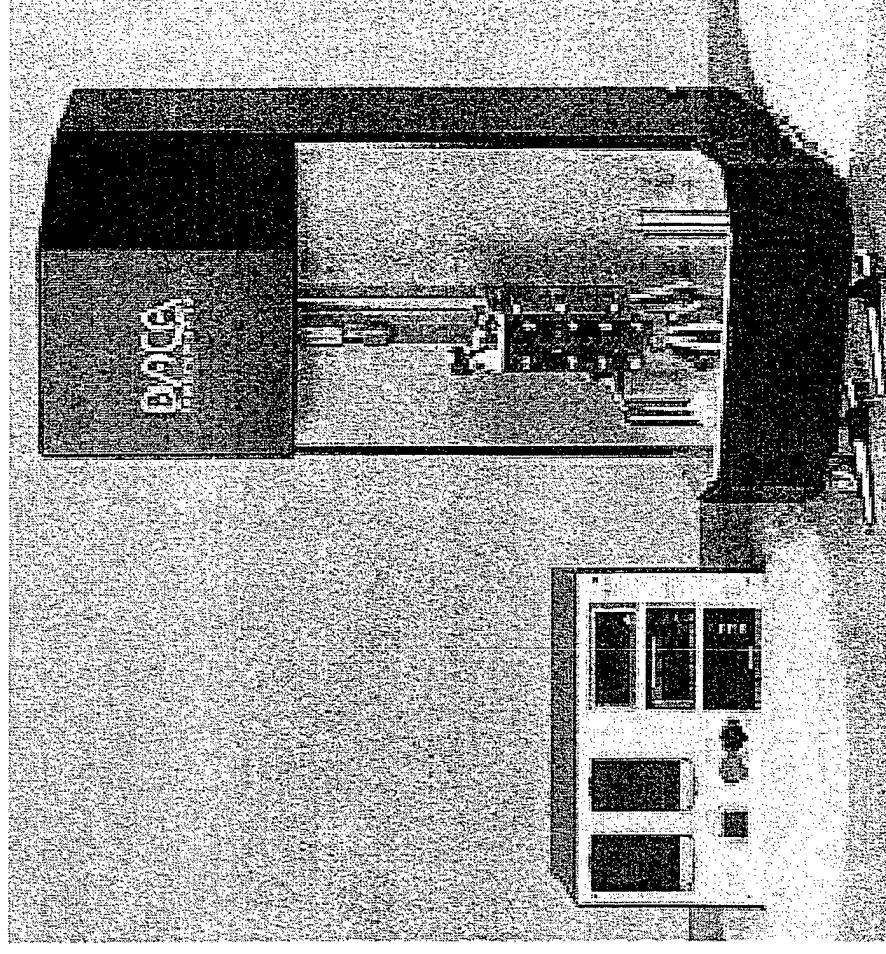
- Easier to tailor the organic side groups of the POSS molecule to give a polymer-compatible species
- Simple blending techniques can be used instead of copolymerization with reactive POSS monomers: decreased development time
- Potential Drop-in molecular modifier without requiring expensive replacement of processing equipment

Preparation of Polymer- POSS Blends

Twin Screw

Processing

- Place Polystyrene in Extruder
- Add POSS
- Blend 2-5 Minutes
- Use a DACA for small scale (4 g)
- Very High Shear

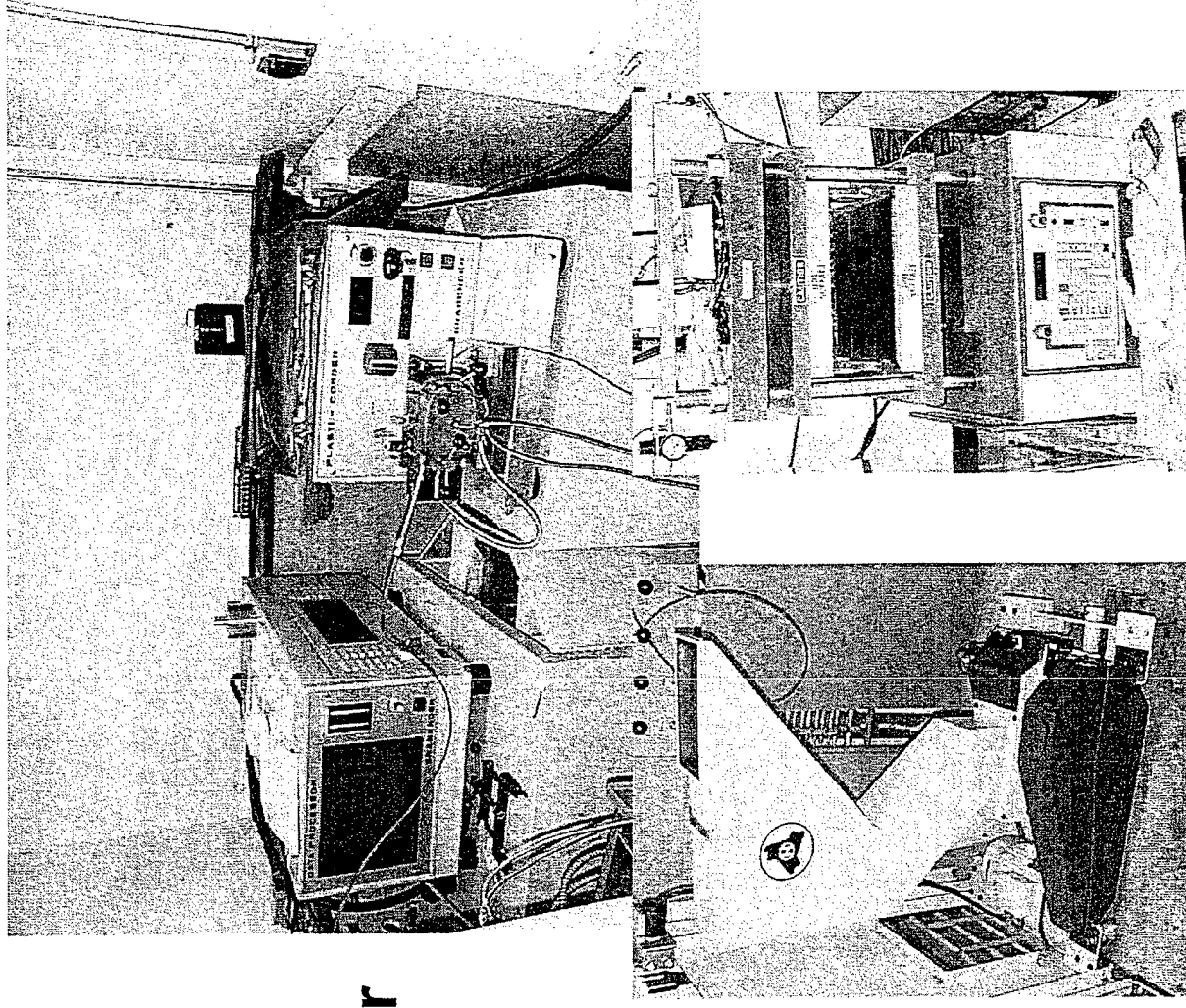


Preparation of Polymer-POSS Blends

Traditional Processing:

Brabender Mixer

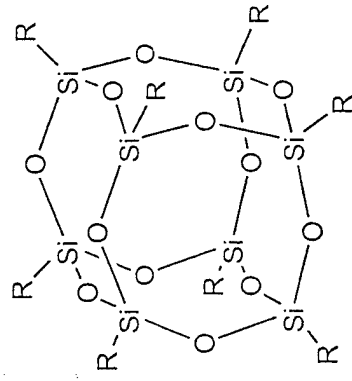
- Place Polystyrene in Mixer at temperature
- Add POSS
- Blend 5-10 Minutes
- Grind
- Press into disks/extrude/
injection mold
- 60 gram scale



POSS Blends

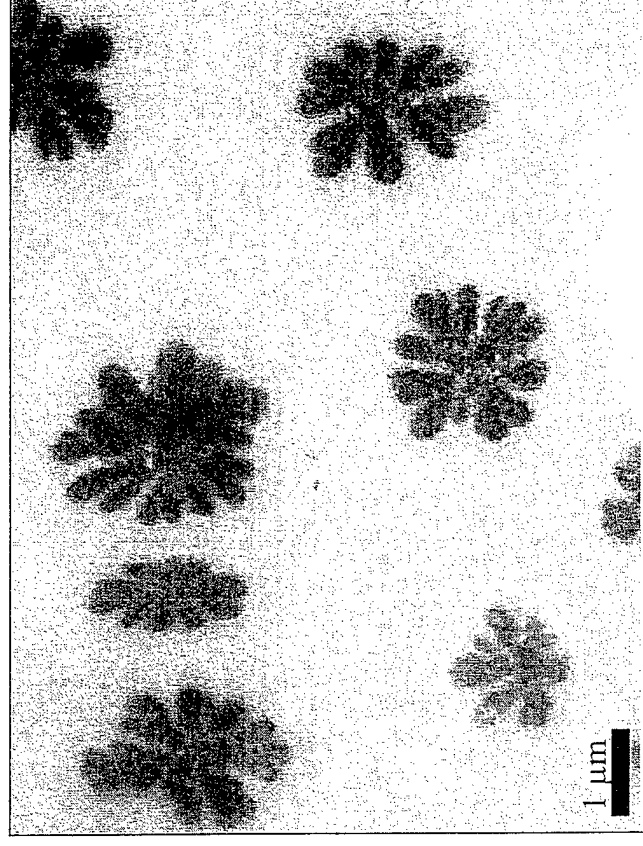
Importance of Organic Side Groups

50 wt % Cp_8T_8 in 2 million mol. wt. Polystyrene



R = cyclopentyl

Cp_8T_8

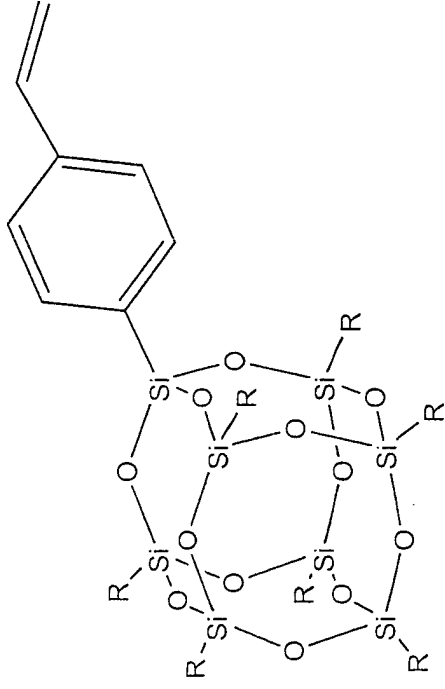


- TEM image clearly shows formation of immiscible POSS crystallites (20-50k molecules)
- Film is Cloudy

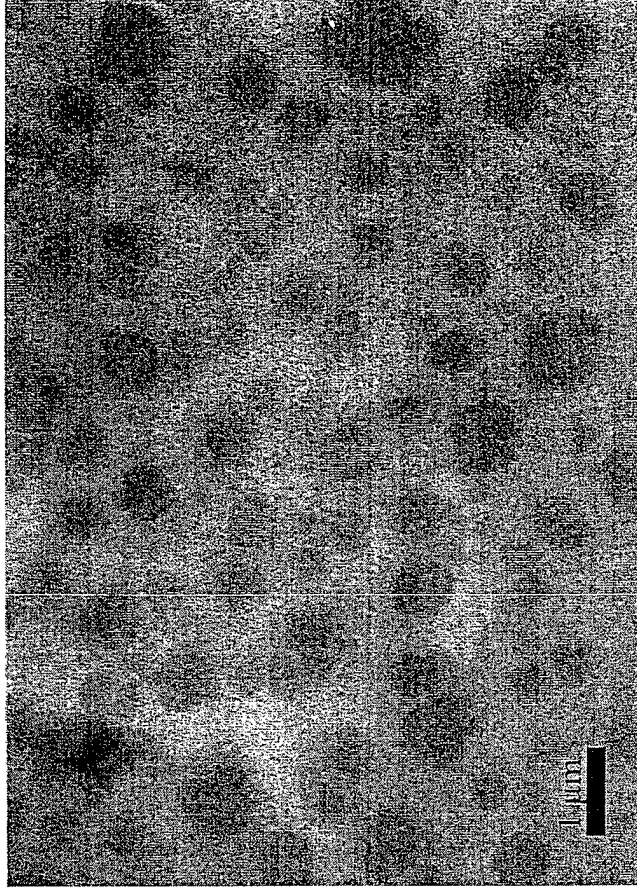
POSS Blends

Importance of Organic Side Groups

50 wt % Cp₇T₈Styryl in 2 million mol. wt. Polystyrene



R = cyclopentyl

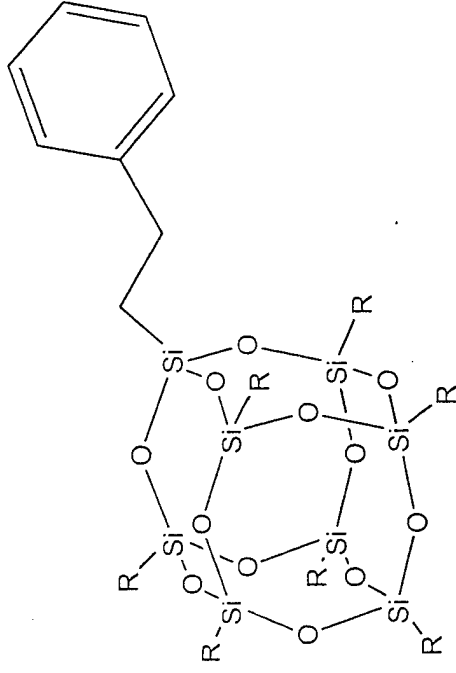


- TEM image shows significant decrease in size of crystallites
- Film is Cloudy

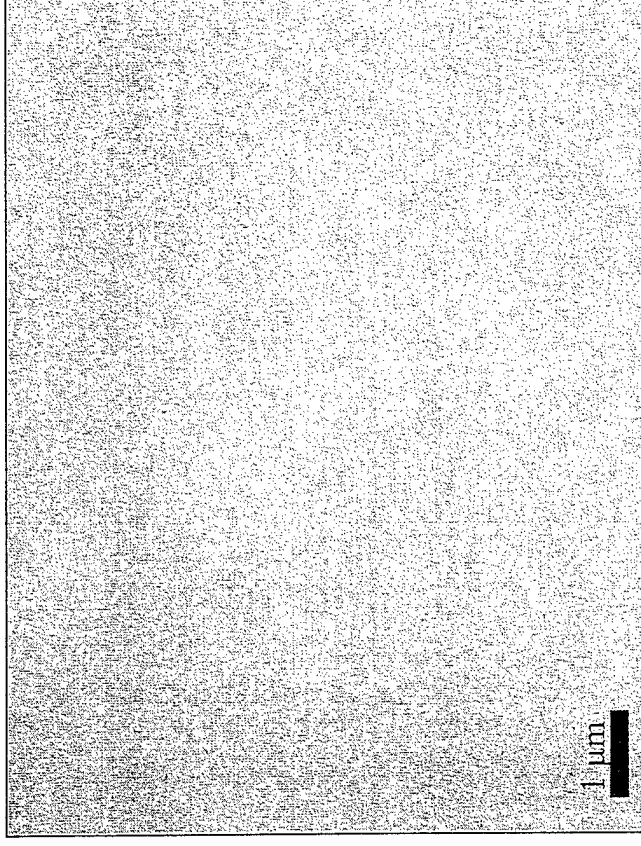
POSS Blends

Importance of Organic Side Groups

50 wt % Phenethyl₈T₈ in 2 million mol. wt. Polystyrene



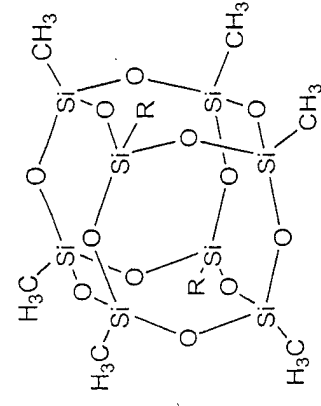
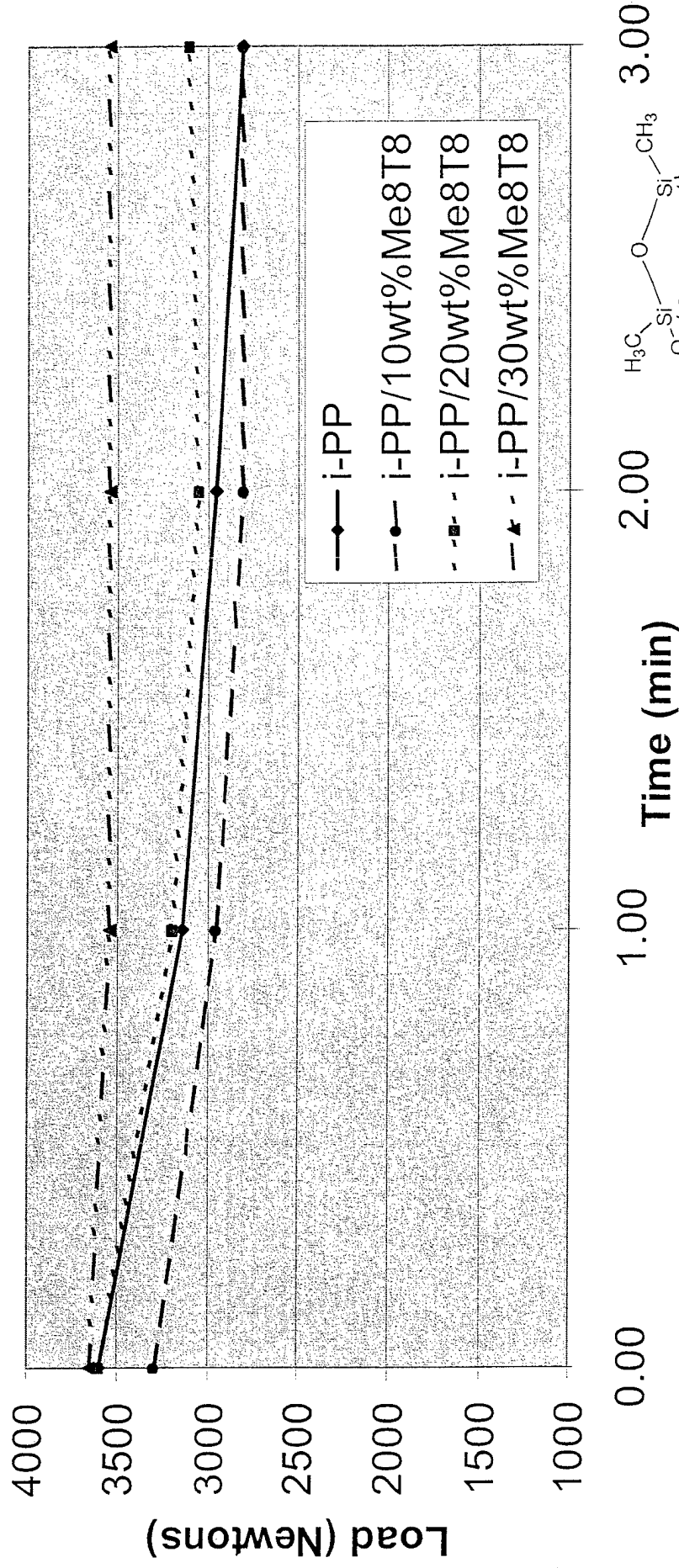
R = Phenethyl



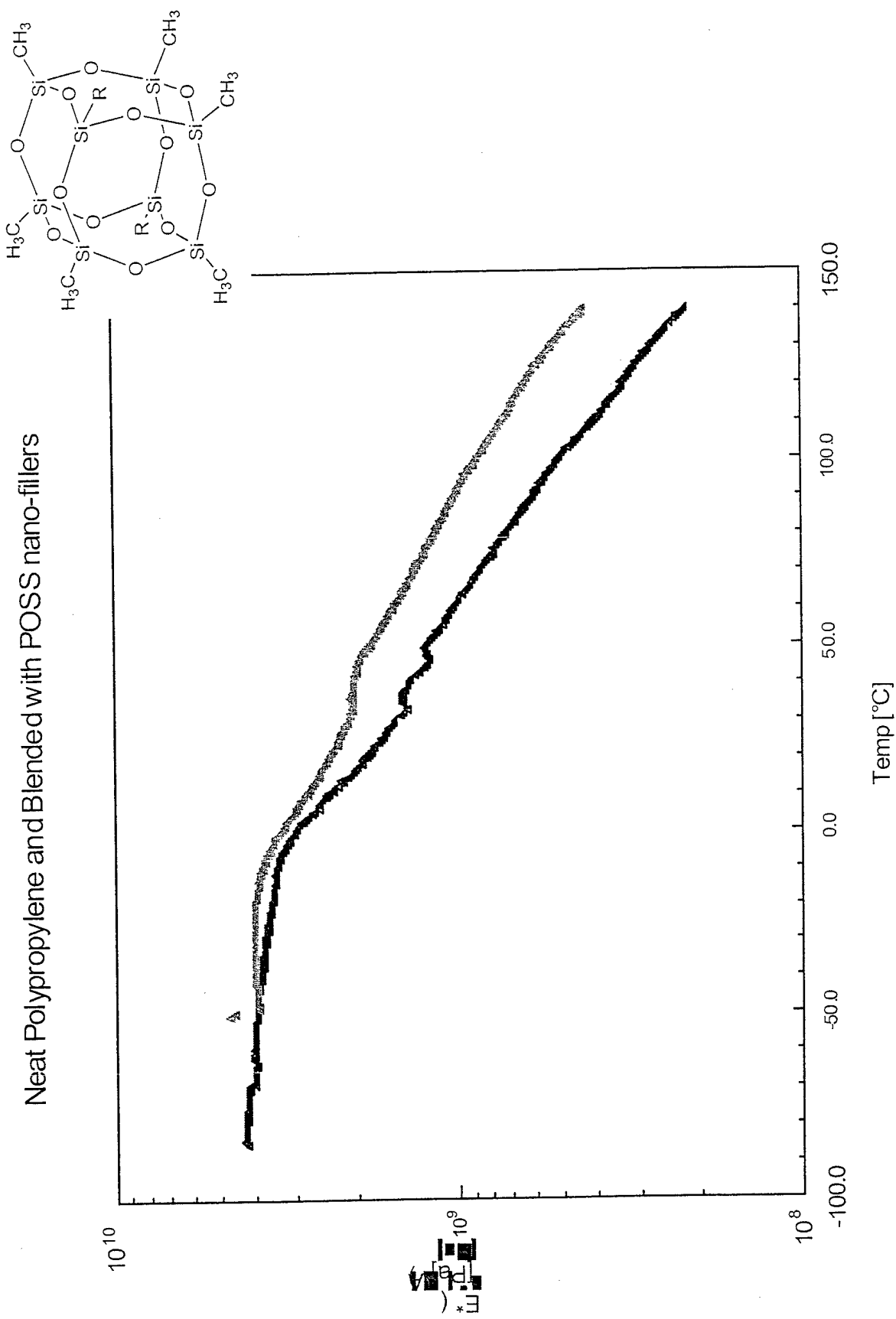
- Demonstrated Complete Compatibility!
- Grey domains represent miscible POSS/polystyrene
- Black dots are POSS crystallites (<100 POSS molecules)
- Film is Clear

i-PP/Me₈T₈ Processing Studies

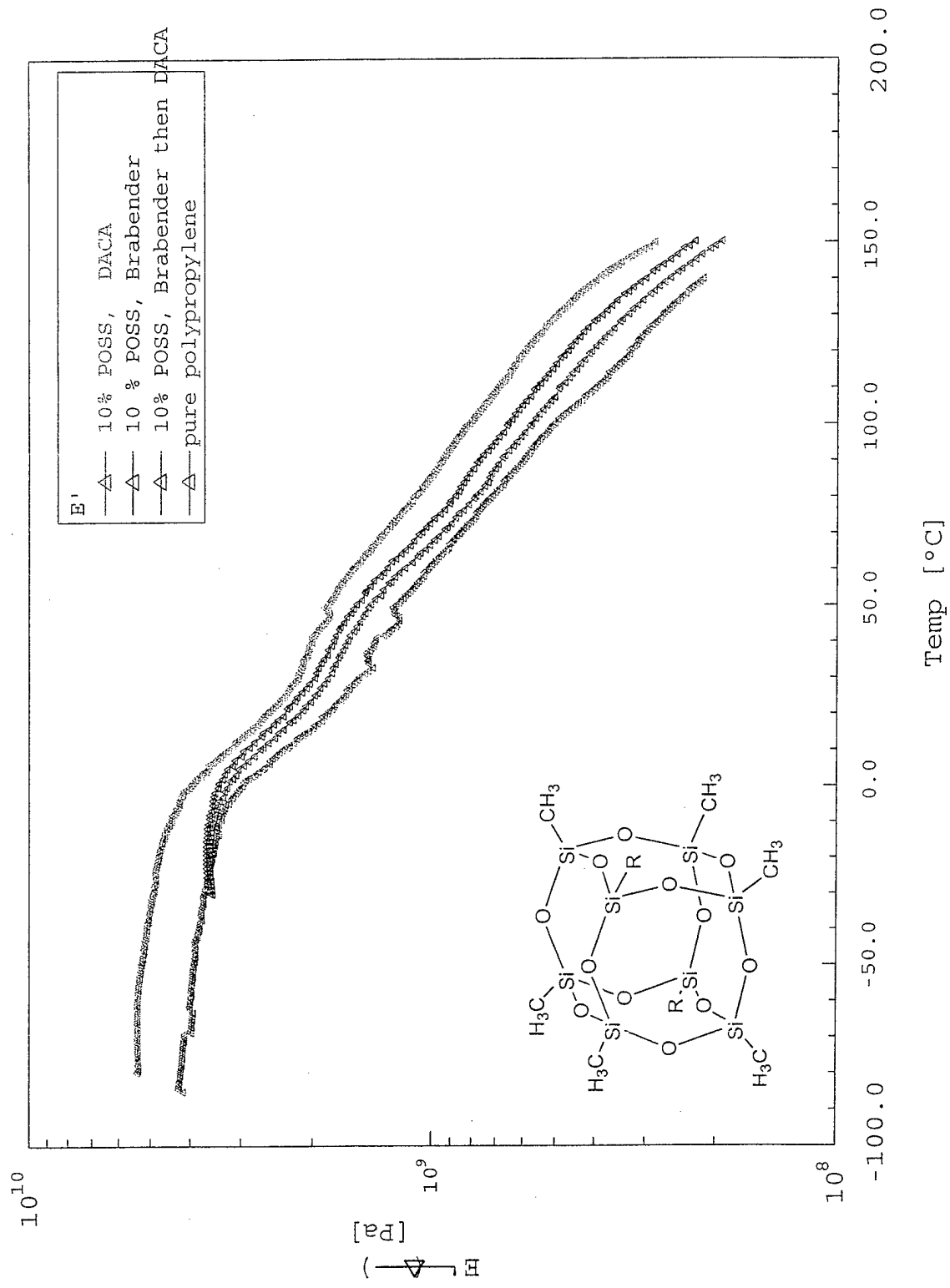
iso-Polypropylene w/ Me8T8



i-PP/Me₈T₈ Processing Studies

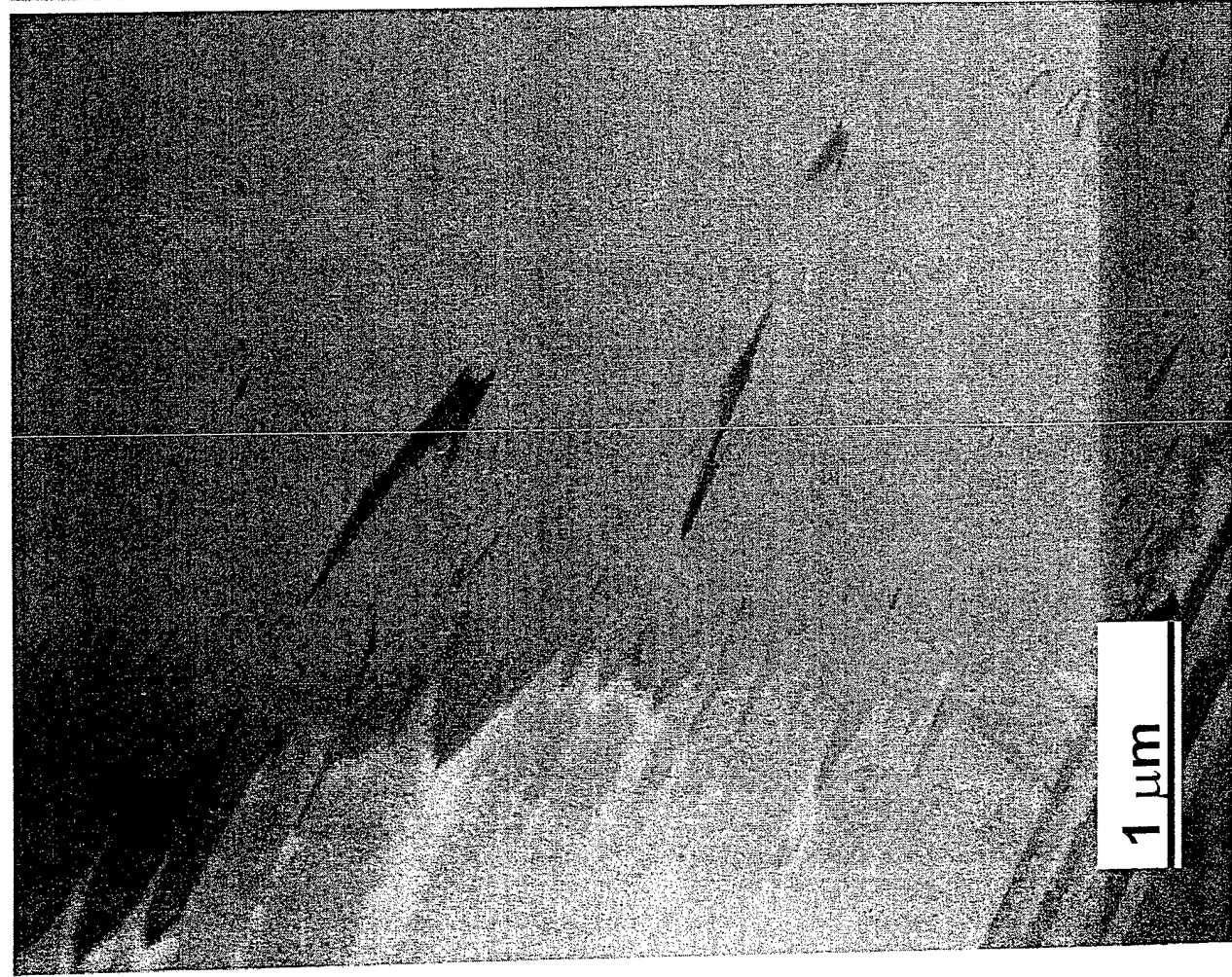


i-PP/Me₈T₈ Processing Studies

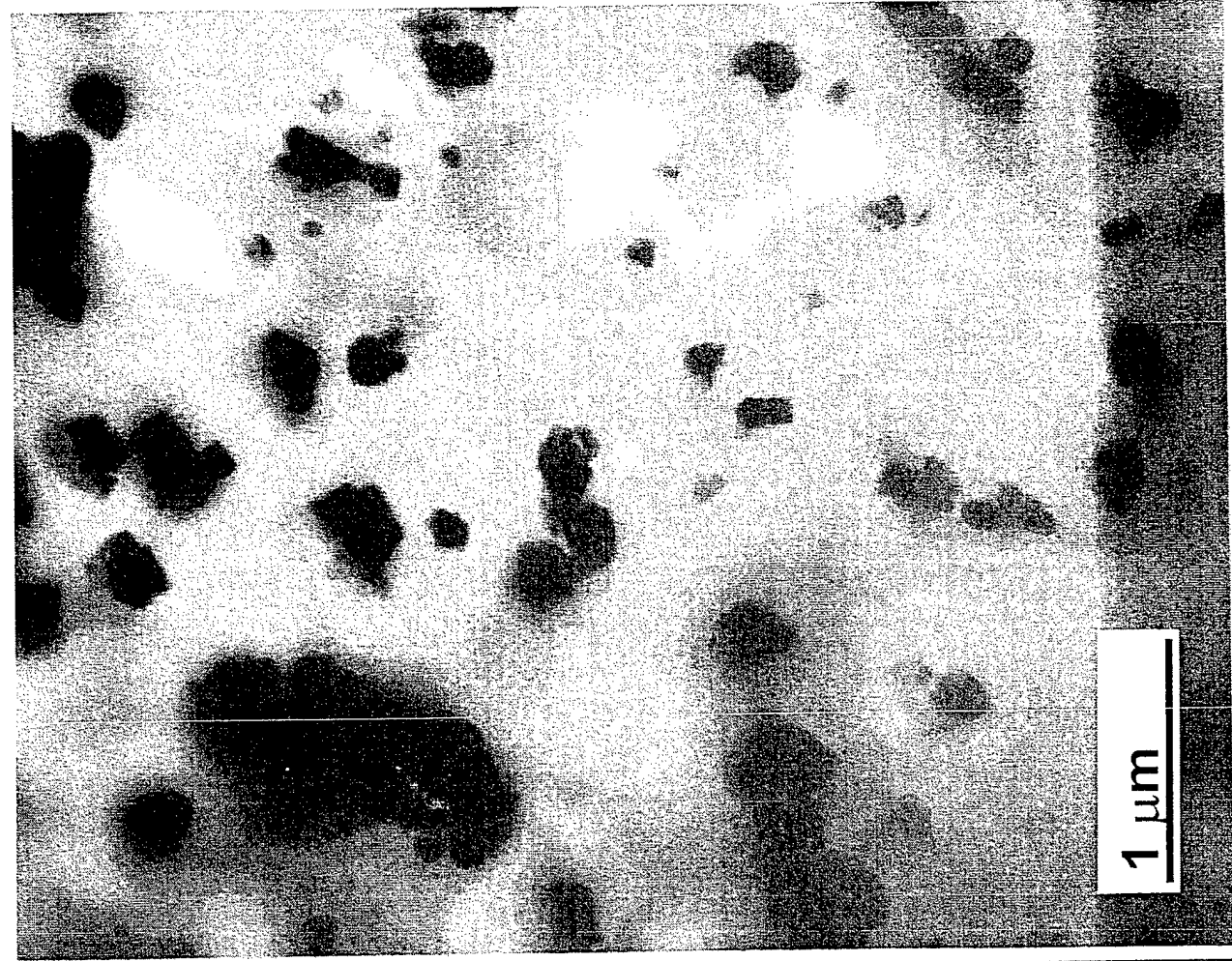


i-PP/Me₈T₈ Blends – Processing Issues

Brabender

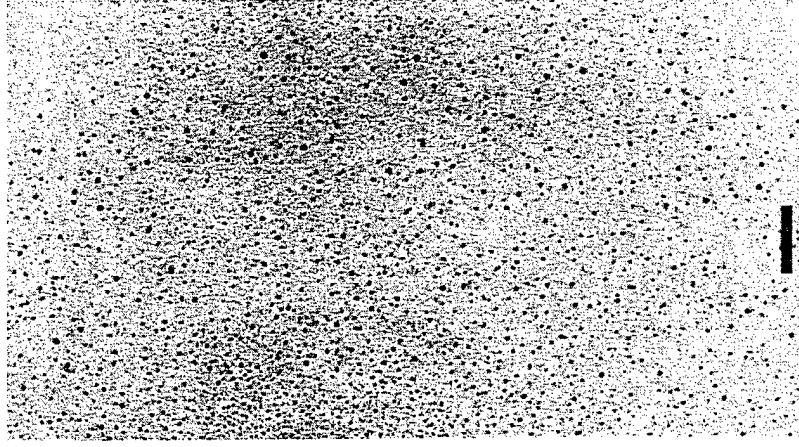


Twin-Screw Extruder



Nanoreinforced™ iso-PP via Molecular Silicas™

Imaging studies on Nanoreinforced™-PP fibers
Molecular Silica™ dispersion confirmed at molecular level.
* Each “black dot” represents a 1.5nm POSS cage.



*scale of bar = 50nm

Mechanical Data on Me₈T₈/i-PP

Prof. Andre Lee - Michigan State University

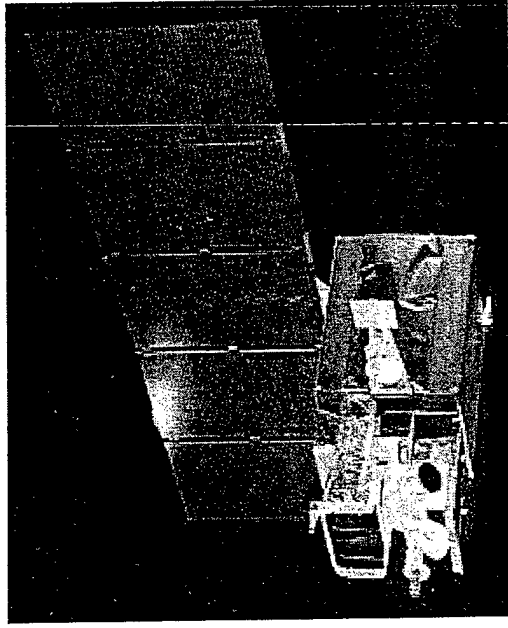
	Dow data	Neat <i>i</i> -PP (processed)	<i>i</i> -PP blended 2 wt% Methyl ₈ T ₈	<i>i</i> -PP blended 5 wt% Methyl ₈ T ₈	<i>i</i> -PP blended 10 wt% Methyl ₈ T ₈
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min, 1% secant); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

- The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.

Summary: POSS-Polymer Blends

- The organic side groups on the POSS molecule are extremely important in determining the compatibility of the POSS in polymers
- In the case of Me_8T_8 (10%) in isotactic polypropylene, an increase in the Heat Distortion Temperature of 25 °C is observed
- Processing issues can be critical

POSS Application: Develop Multi-Functional, Space-Survivable Materials



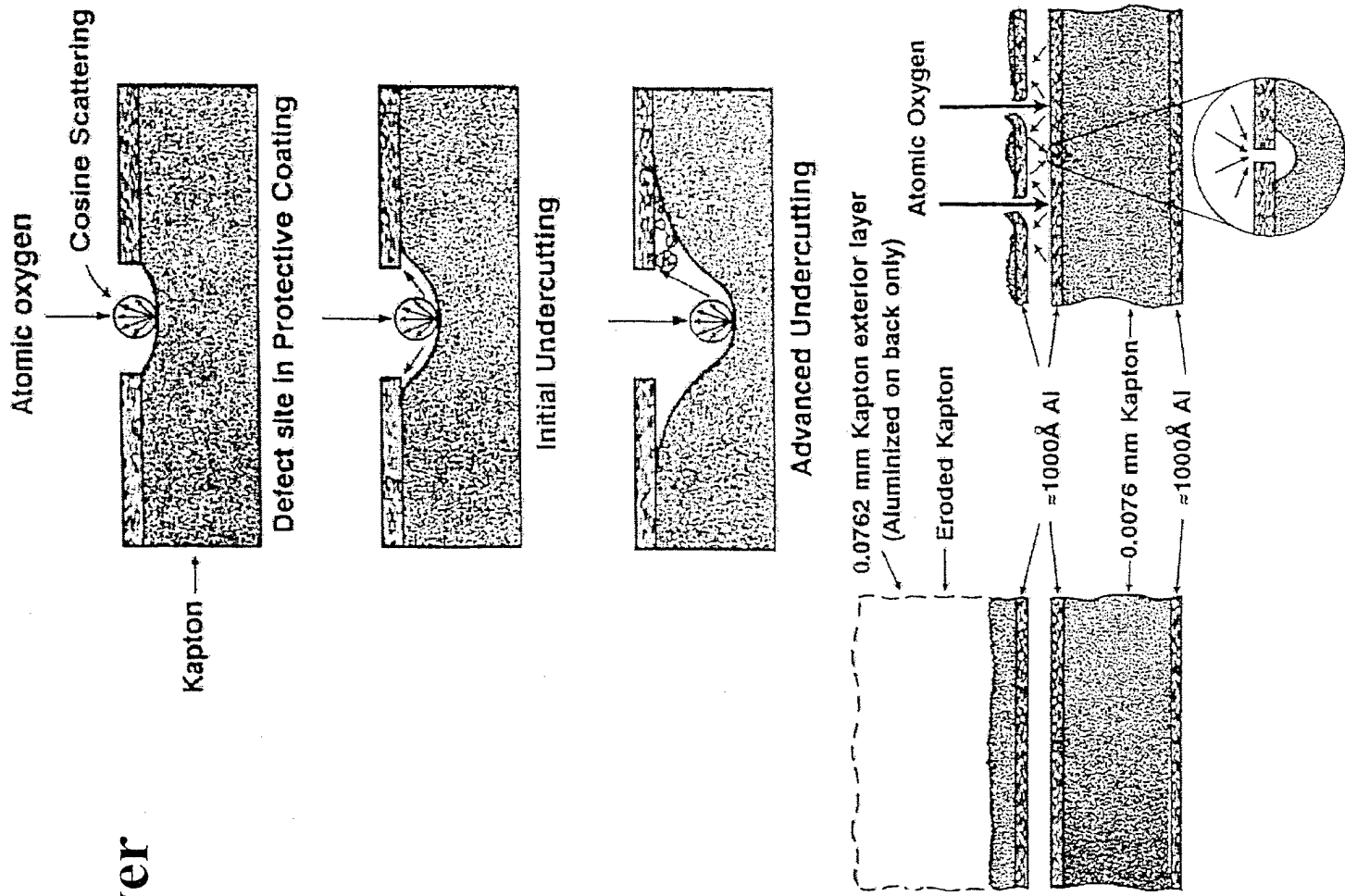
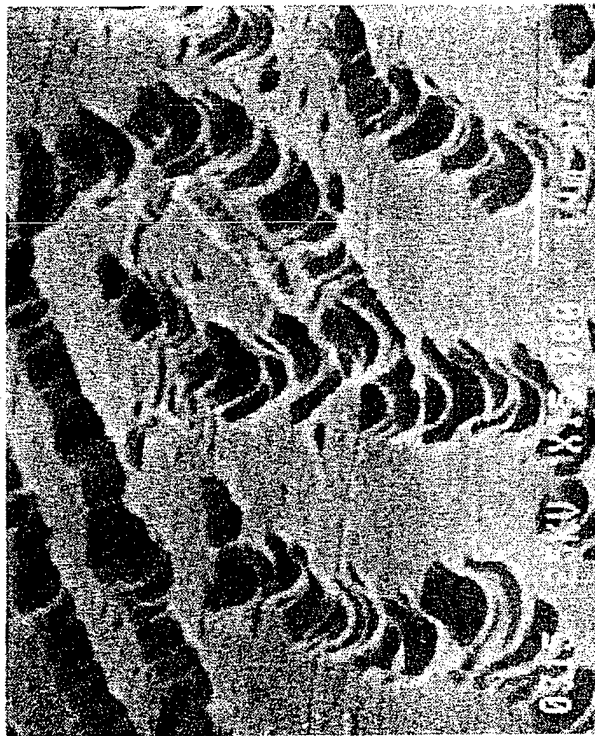
Satellites & Space Systems

Bond	Dissociation Energy (eV)	λ (nm)	Material
-C ₆ H ₄ -C(=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

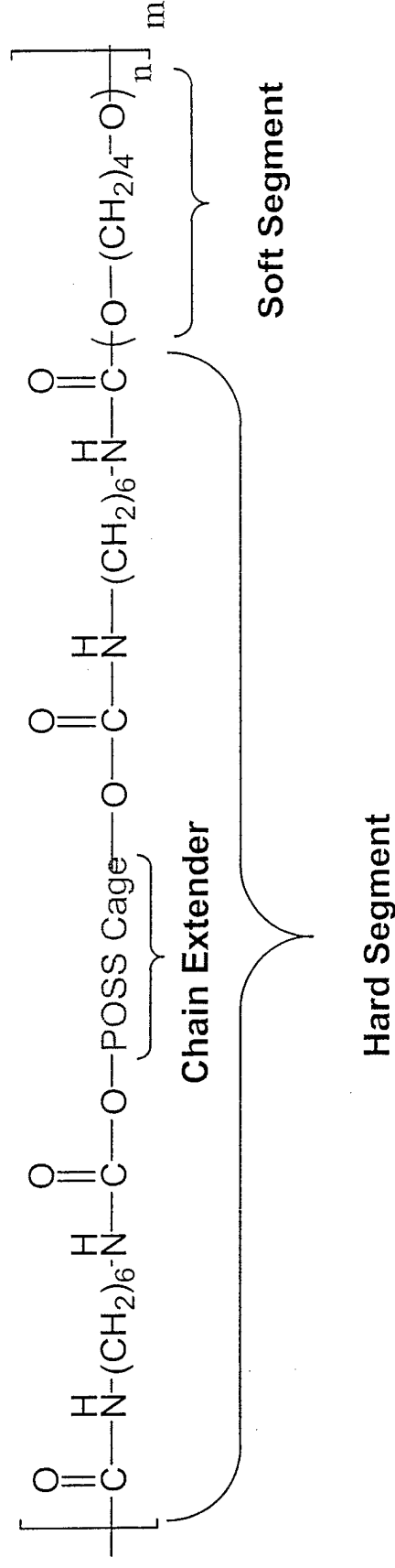
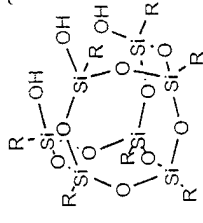
Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation



POSS-polyurethane Properties



POSS-polymer improvements

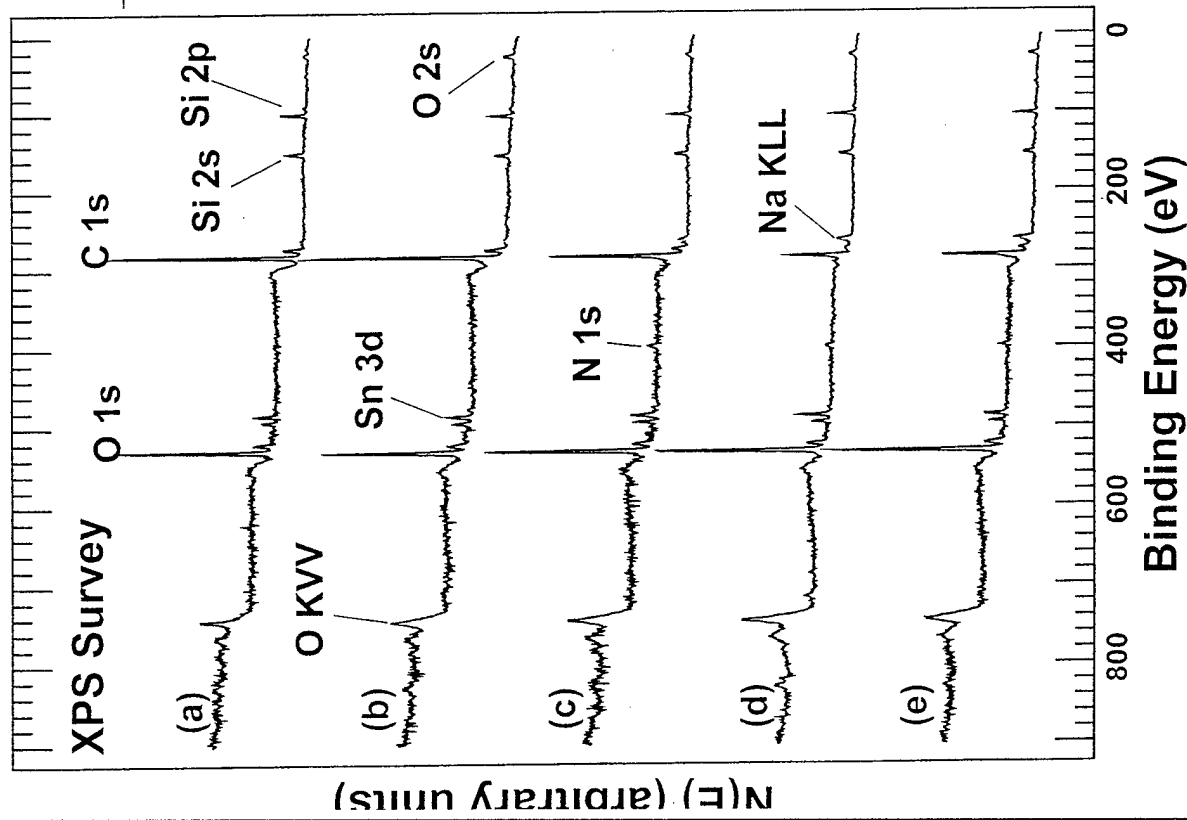
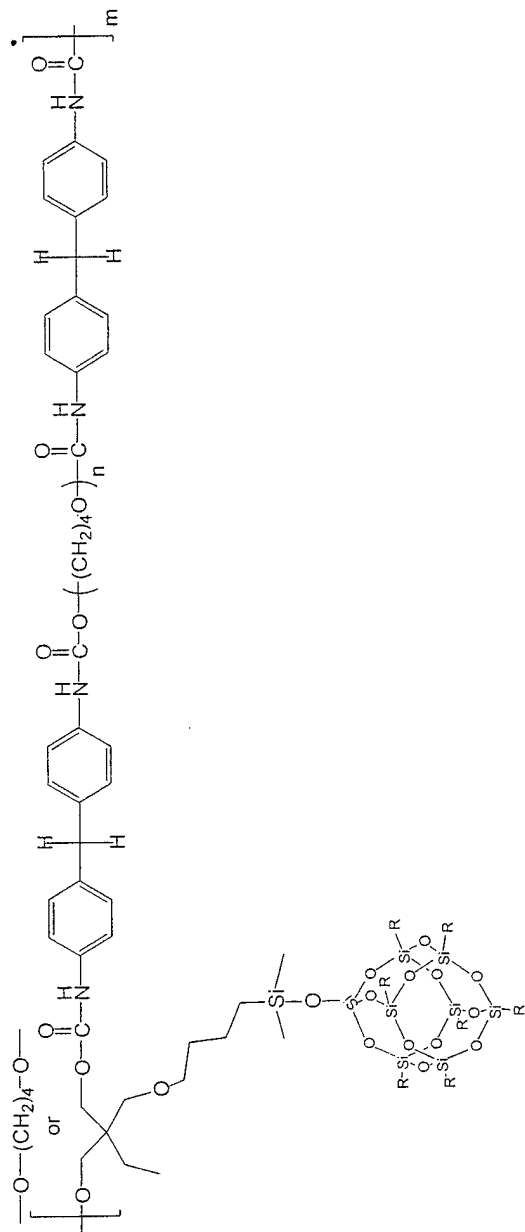
Up to 300 °C increase in the melt transition temperature (rheological studies show the transition from an oil to a true thermoplastic elastomer)

Up to a 100 °C increase in T_{dec} (29 wt% POSS, still TPE)

Up to 10X increase in moduli (>400% elongation with no destruction of hard segments))

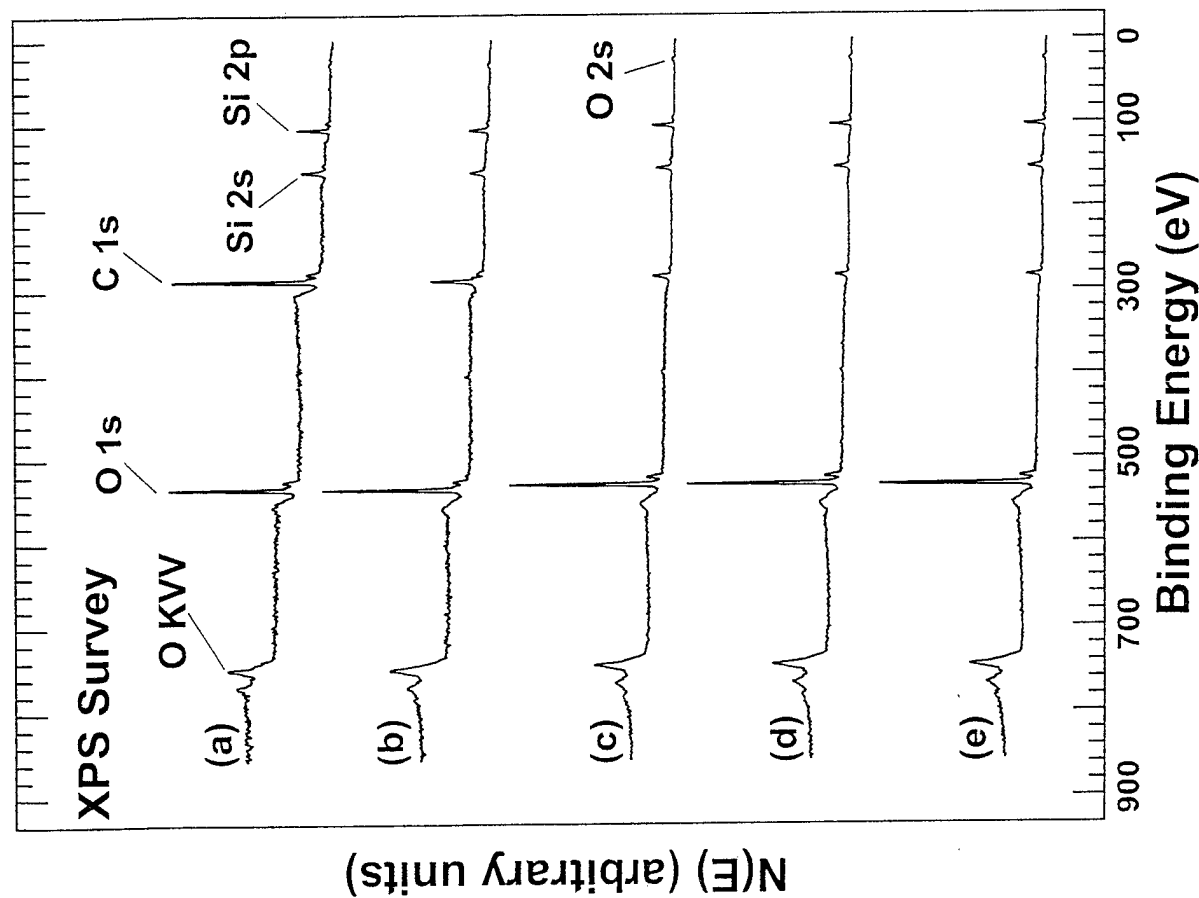
17% POSS incorporation ----> 3X increase in Hardness (Shore A)

POSS Polyurethane

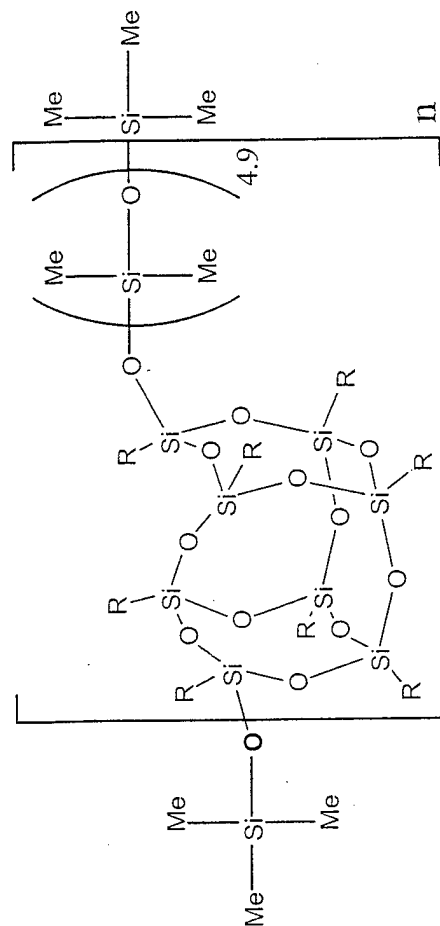


Sample Treatment	O	C	Si	Sn	Na	N
As entered	18.2	70.1	11.3	0.4	-	-
2.0-hr	17.5	70.2	11.2	0.7	0.4	-
24.0-hr	23.7	58.2	13.2	0.9	1.4	2.6
63.0-hr	35.3	37.3	20.4	1.3	3.0	2.7
3.3-h air	31.6	48.5	14.6	1.0	2.7	1.6

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.

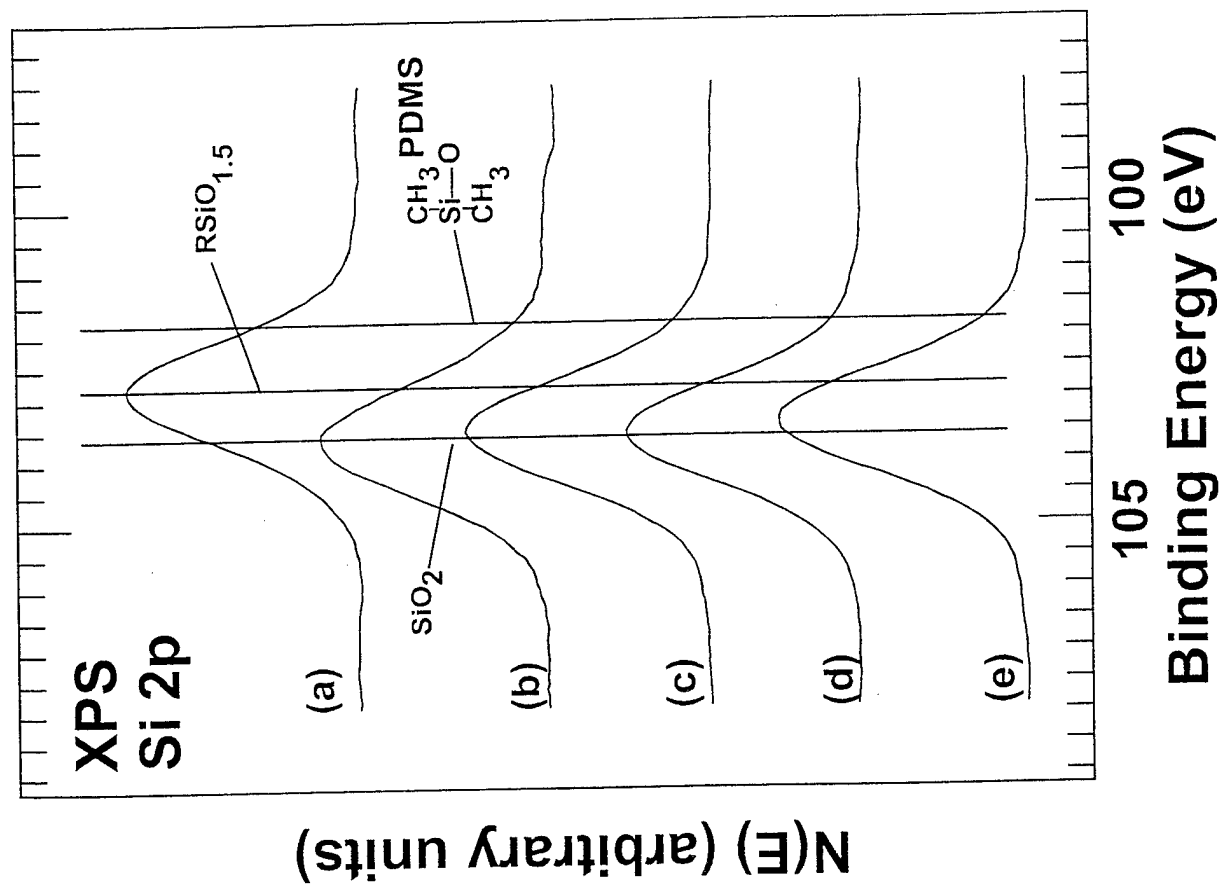


POSS Siloxane



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

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.

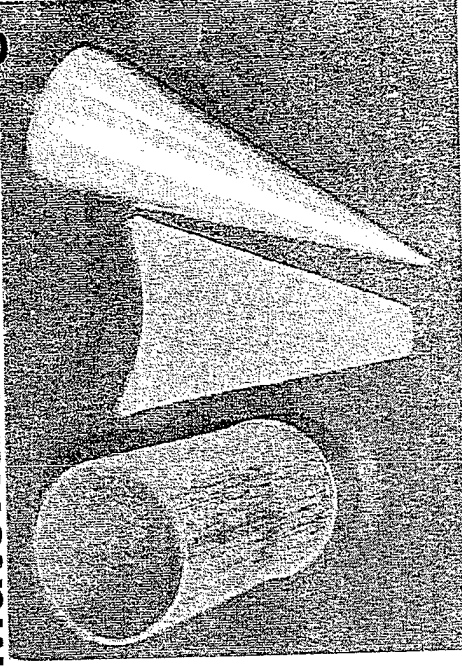
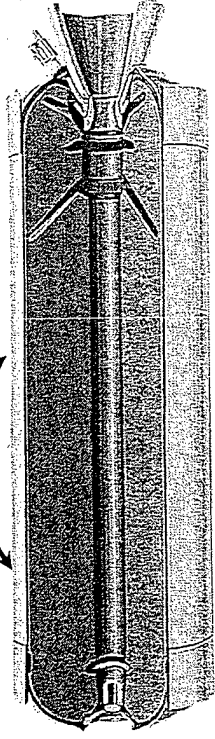


High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

In-House SRM Insulation Testing

Low Cost/Low Volume Materials Screening

Case Insulation



POSS-Insulation Sample

Goal: 50% Lower Erosion of Insulation (44 % weight reduction, 7.4% booster payload increase) – Phase III IHPRPT

Objective: Development of Ceramic Forming Polymer

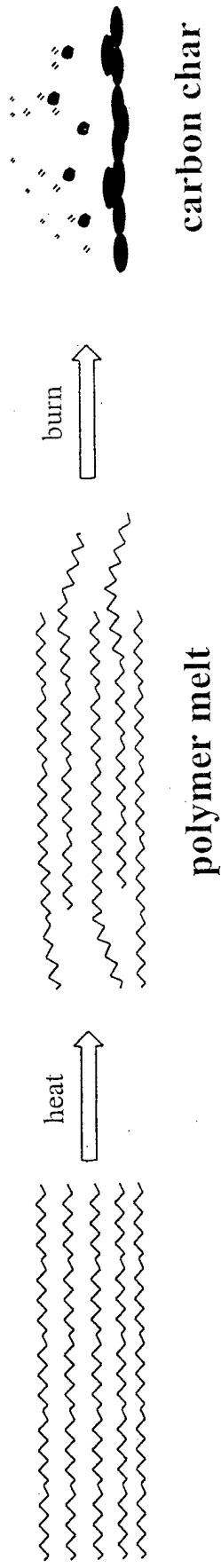
POSS-Polymer Insulation - Advantages:

- High loadings of POSS can be incorporated without embrittlement
- Si to O ratio is 1:1.5, proven to oxidize up to 1:2 (SiO₂)
- Tailorability of POSS monomers improve physical/mechanical properties
- Capabilities for Large and Small scale testing (Hybrid Plastics)

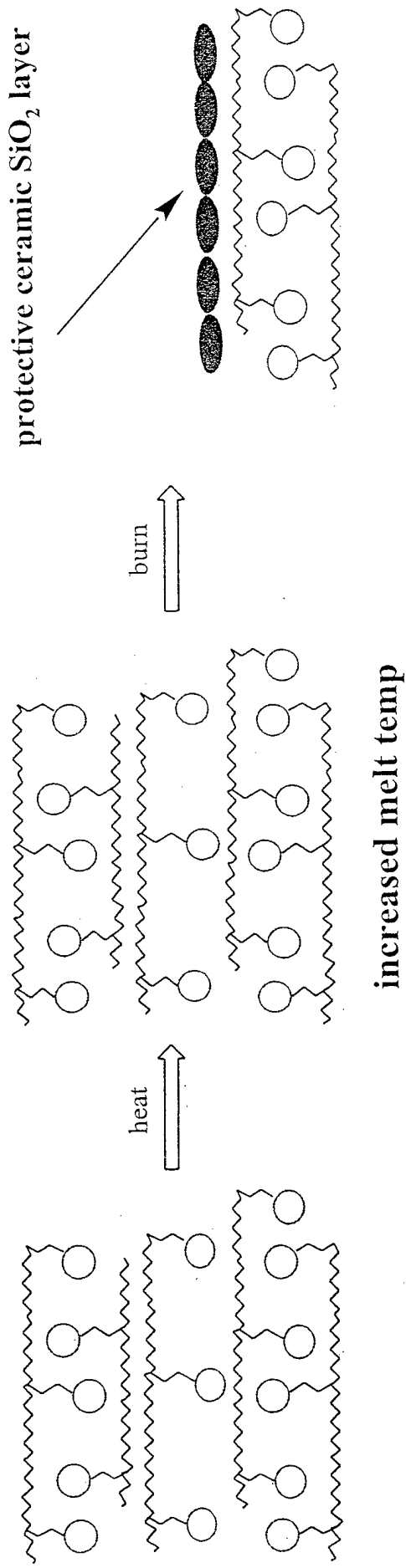
In-House SRM Insulation Testing

Formation of Silica Char Layer May lower ablation

Traditional Polymer



POSS Polymer

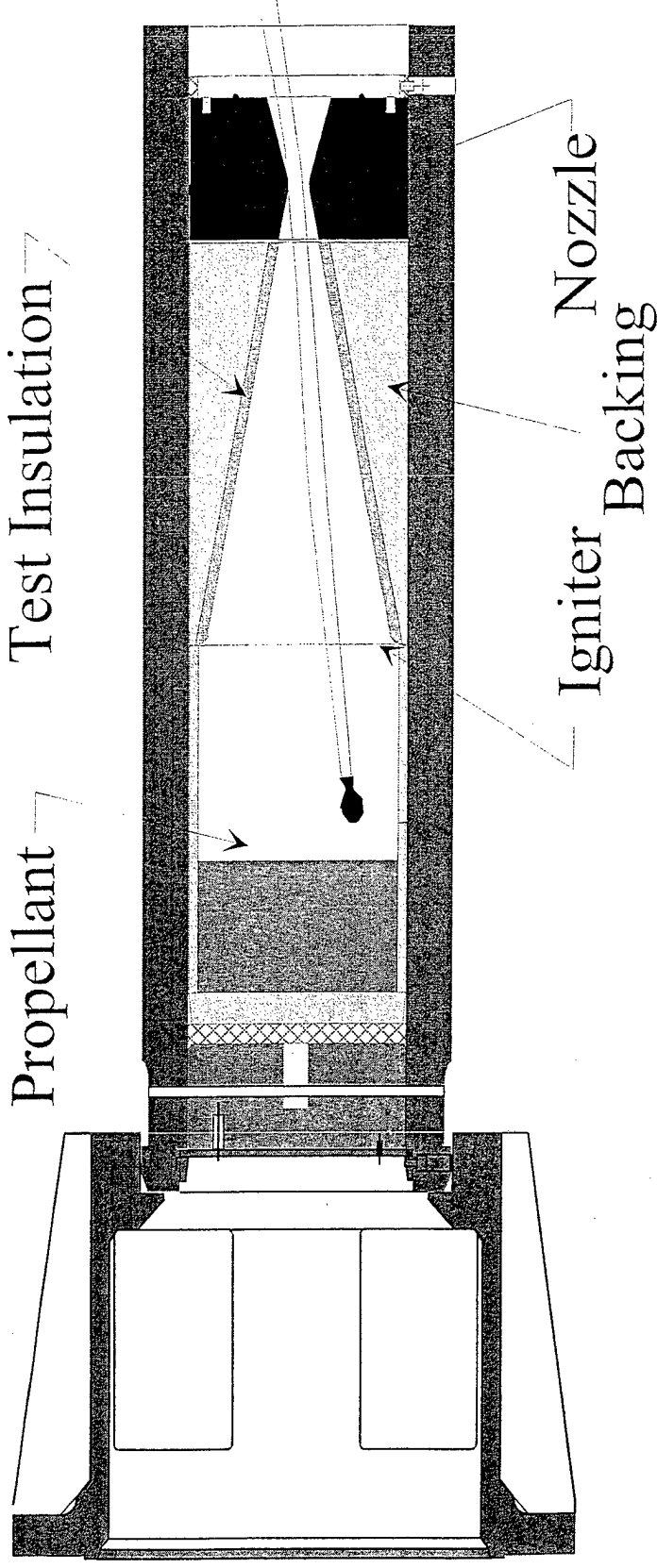


In-House SRM Insulation Testing

Low Cost/Low Volume Materials Screening

Capabilities:

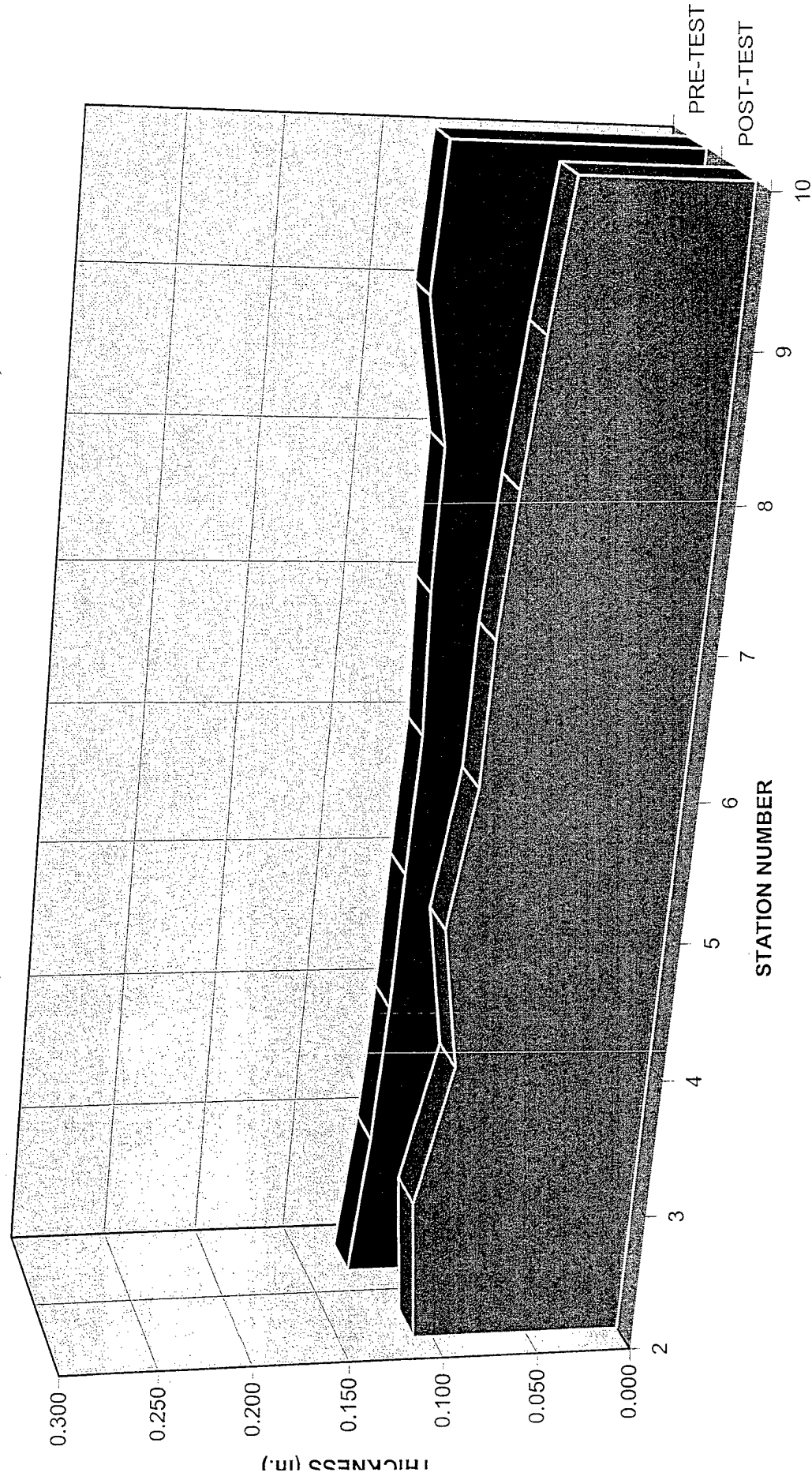
- Edwards AFRL (4" Pi-K Motor): volume reduction (5 Kg to 75 g)
- Total Cost (synthesis, part fabrication, ablation test, analysis) ~ \$1K
- Rapid testing of 5-6 samples per day



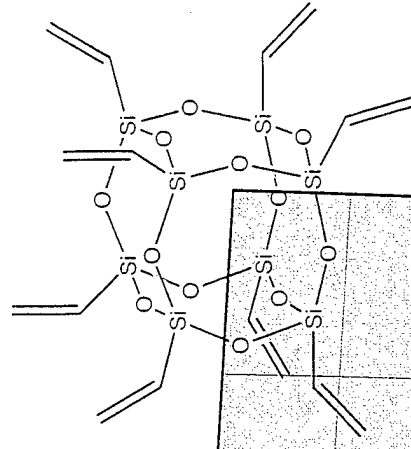
In-House SRM Insulation Testing

Low Cost Screening of New Materials

CHAR-063 ABLATION (S10 - EPDM / Kevlar STANDARD)



CHAR-063 ABLATION (T10 - EPDM/V₈T₈)

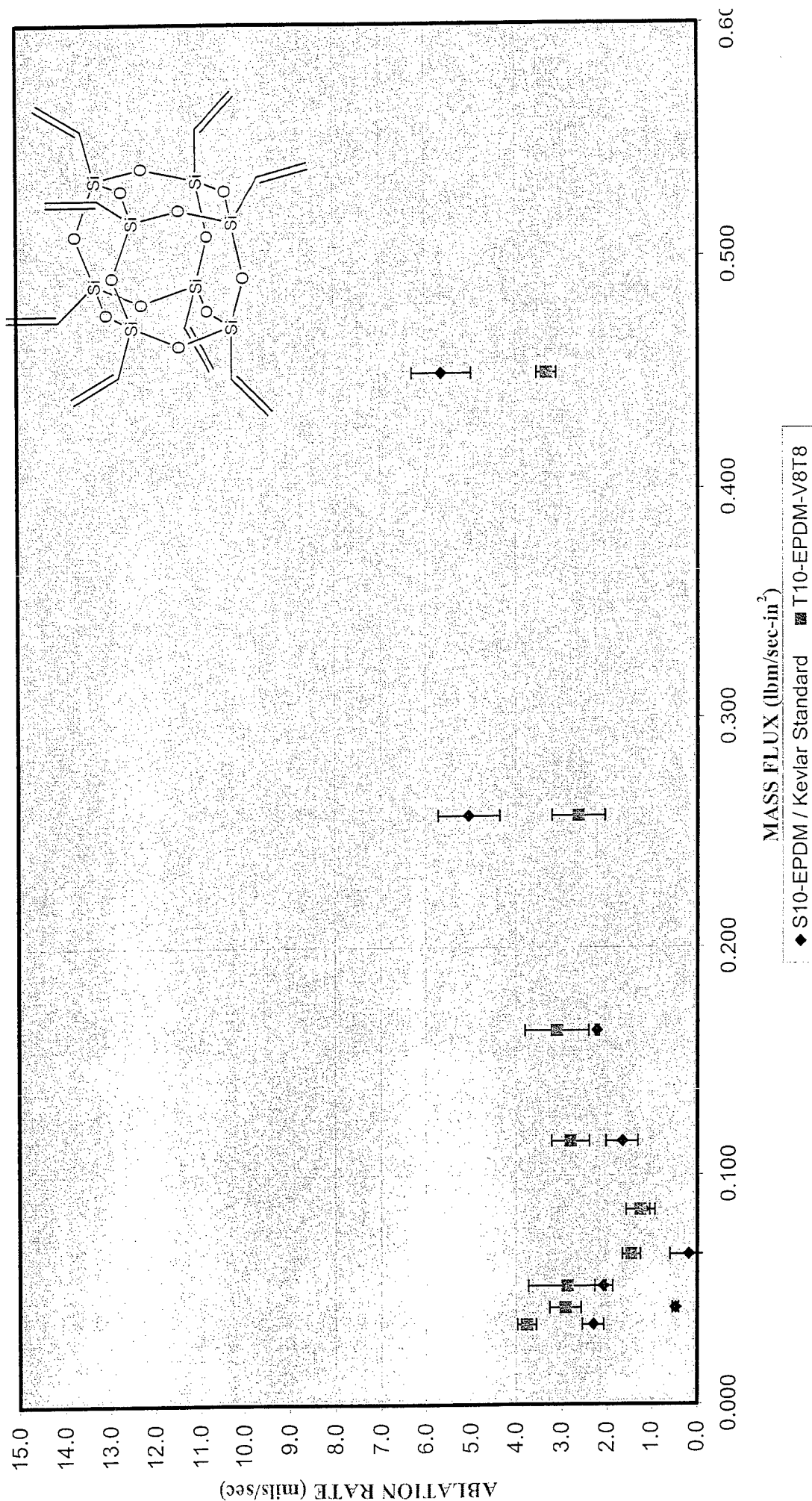


In-House SRM Insulation Testing

Ablation Rate Decreased when Using POSS

CHAR-063 ABLATION RATE

EPDM-Kevlar STANDARD (S10) / EPDM-V₈T₈ (T10)

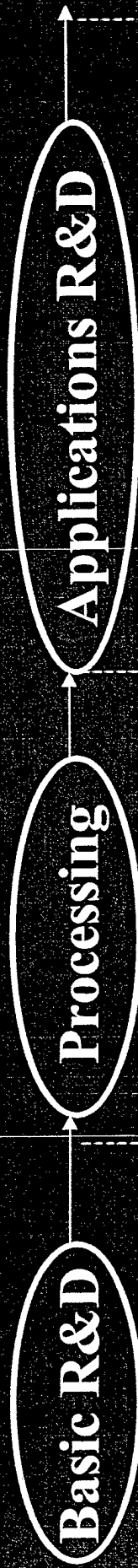


Summary - Applications

- Demonstrated that POSS forms protective Silica layer when exposed to atomic oxygen in space-like conditions
- Initial evidence in SRM insulation tests suggests that POSS can act as an ablative in SRM insulation. Additional studies to confirm this are underway.

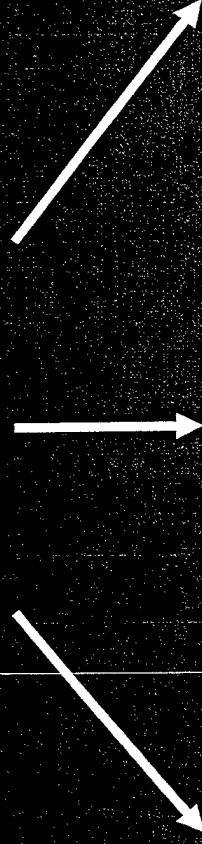
Programmatics: Dual Use & Leveraging

Polymer Working Group



Programmatics: Dual Use & Leveraging

Polymer Working Group



Solid Rocket Motor Insulation
Liquid Rocket Engine Ducting
High Temp Lubricants

Basic R&D

Processing

Applications R&D

Plastic Jet Canopies
Missile Radomes
Space-Survivable Materials



CONCLUSIONS

Academic/Government Lab Collaborations are essential

Polymer Working Group

Basic R&D goal for controlling/understanding POSS affects on polymer properties is already ahead of schedule (including processing).

Cost, Volume and Production time goals have all been met thanks to Hybrid Plastics & Prof. Frank Feher.

Understanding processing is a key area that is being heavily worked.

POSS applications within government are on critical paths, while industrial interest has increased exponentially with technology transfer in 1998.