

# REPORT DOCUMENTATION PAGE

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08 May 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-101**  
Tim Haddad (ERC) and Brent Viers (PRSM), "Organic Polymers Modified with Inorganic Polyhedra"

**Canadian Society for Chemistry**

(Statement A)

**(2-5 June 2002, Vancouver, Canada) (Deadline: 31 May 2002)**

## ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA.

Timothy S. Haddad and Brent D. Viers  
ERC Inc., Air Force Research Lab,  
10 E Saturn Boulevard  
Edwards Air Force Base, CA 93524

Nanostructured composites of thermoplastics and inorganic clusters have been developed by incorporating polyhedral oligomeric silsesquioxane (POSS) macromers into organic polymers. These hybrid inorganic/organic thermoplastics based on styrenes, acrylics, imides, norbornenes or siloxanes, are reinforced by covalently linking monodisperse inorganic POSS clusters to the polymer backbone. A typical POSS-macromer,  $R_7P(Si_8O_{12})$ , is a well-defined octomeric polyhedron containing a single "P" functionality for polymerization and seven "R" groups to solubilize and compatibilize the inorganic filler with the organic matrix. A nanoreinforcement effect from the POSS groups is strongly influenced by the seven "R" groups (cyclopentyl, cyclohexyl, isobutyl or phenyl). Covalently attached POSS groups result in significant change to the observed characteristic relaxation time of the polymer; rheological measurements on molten polymer indicate that interactions between the POSS groups generate a reversible network material with rubbery properties. TEM images show that the inorganic POSS moieties associate to form a nanoscale network within the polymer matrix.

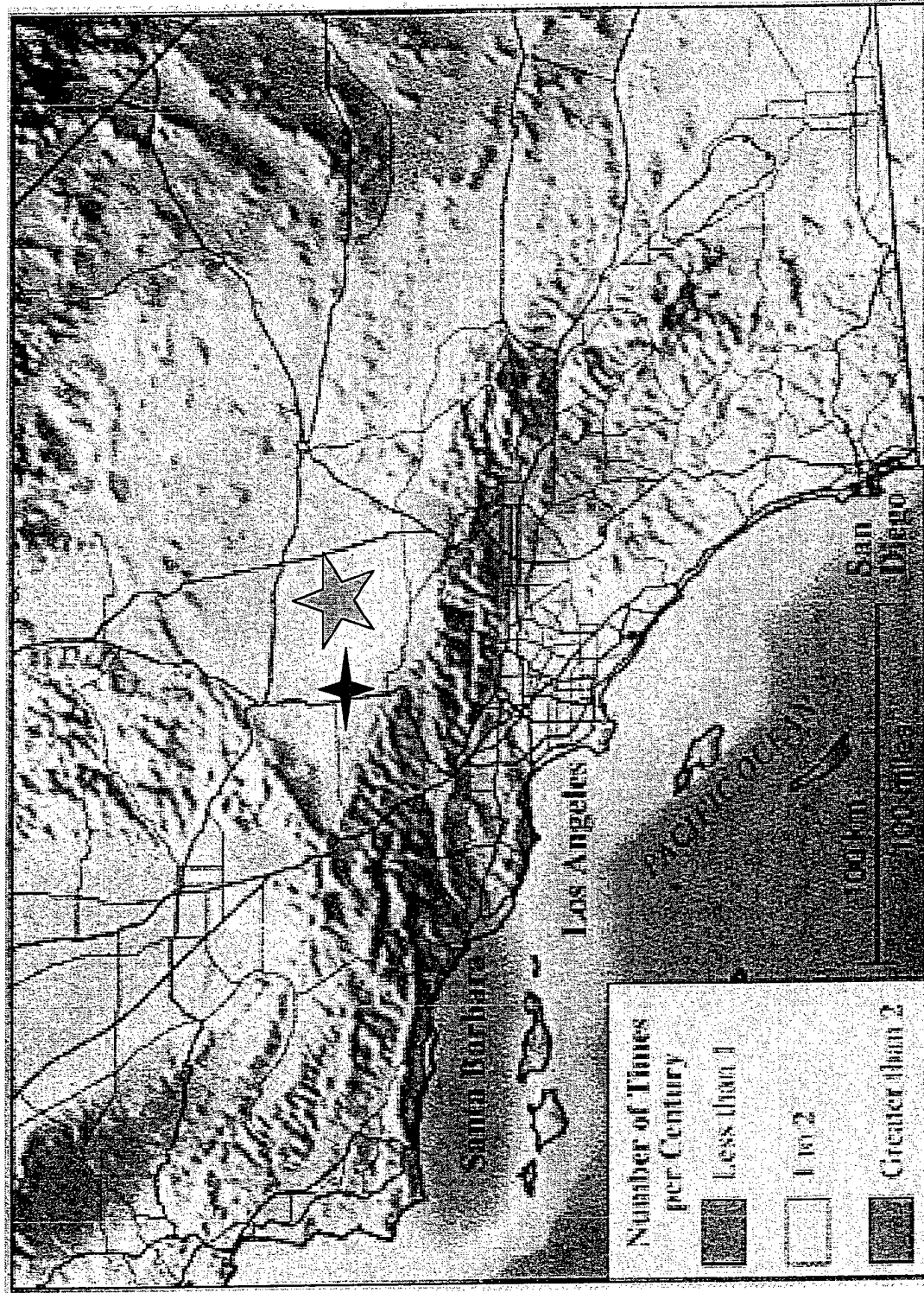
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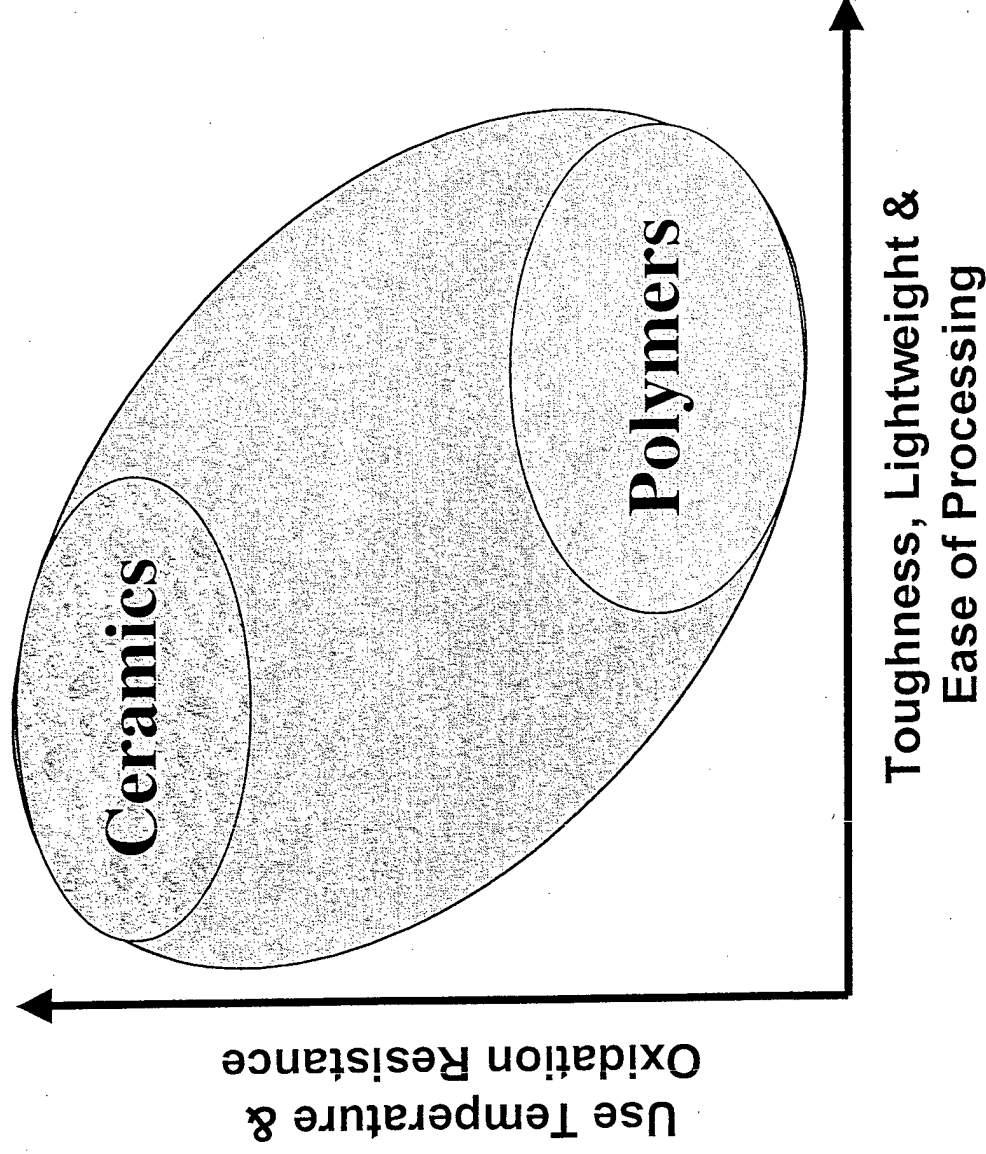
# **ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA**

**Tim Haddad and Brent Viers  
ERC Inc., Air Force Research Lab**

# Edwards Air Force Base, CA



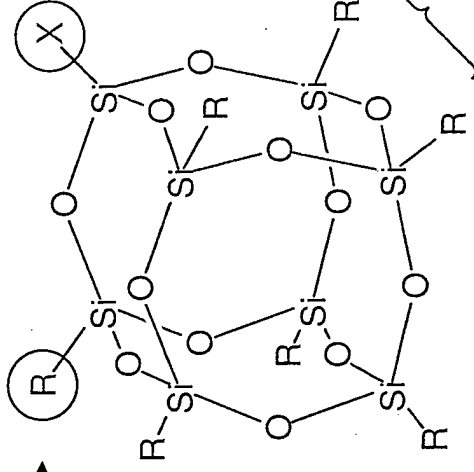
## Hybrid Inorganic/Organic Polymers



Hybrid plastics can bridge the differences between ceramics and polymers

# Anatomy of a POSS Macromer

Nonreactive organic (R) groups for solubilization and compatibilization.

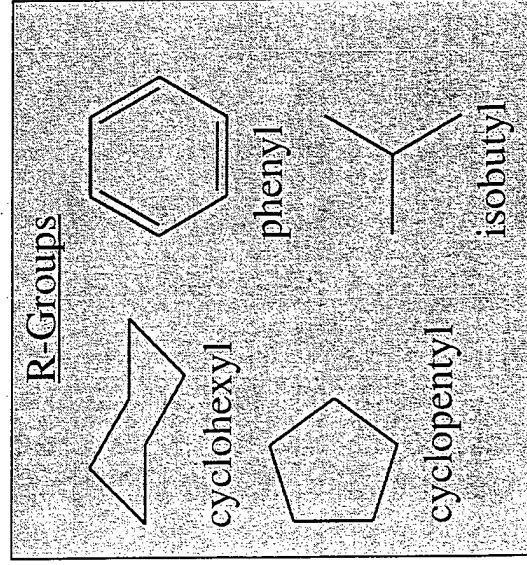


May possess one or more functional groups suitable for polymerization or grafting.



Nanosopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

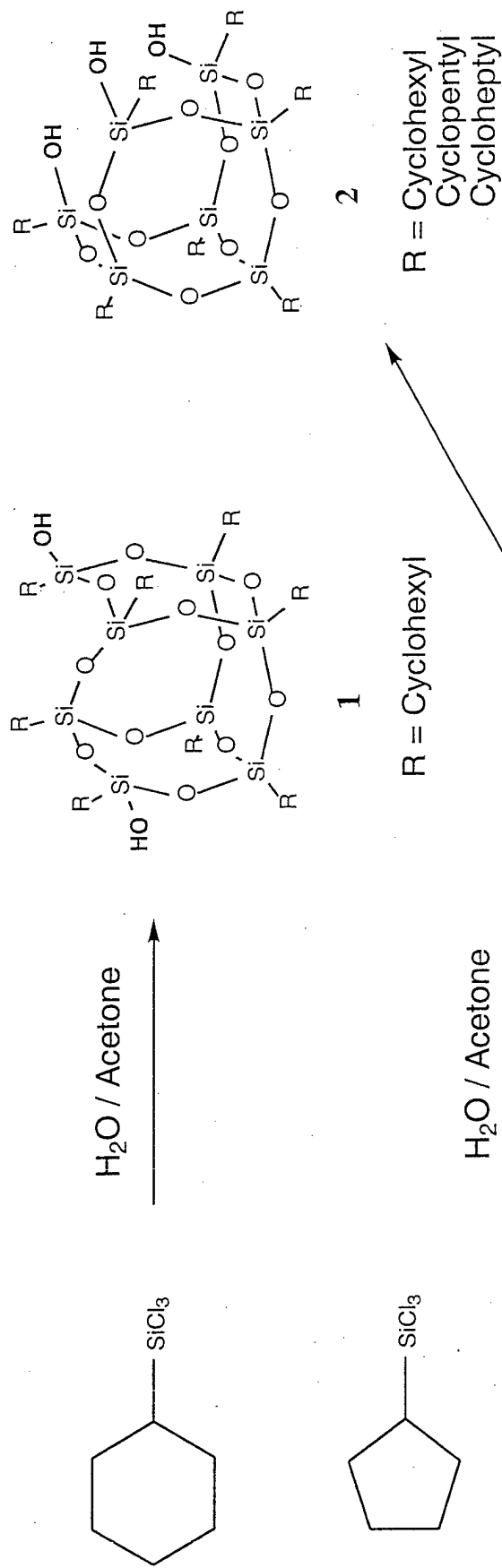
Thermally and chemically robust hybrid (organic-inorganic) framework.



Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

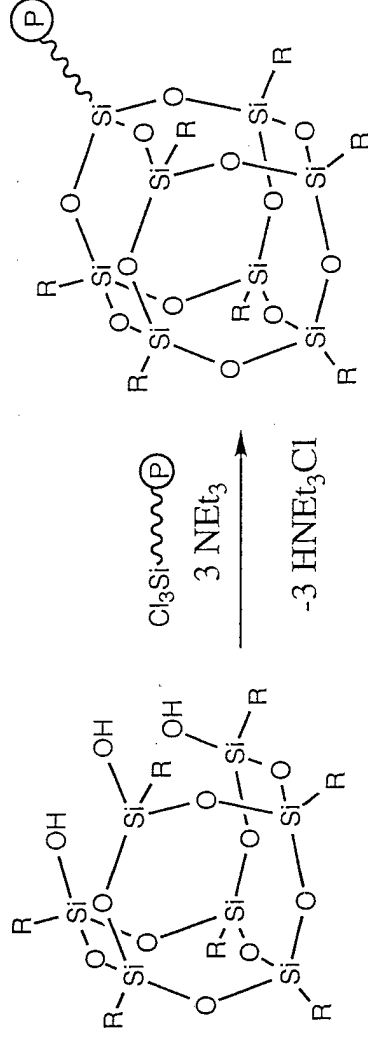
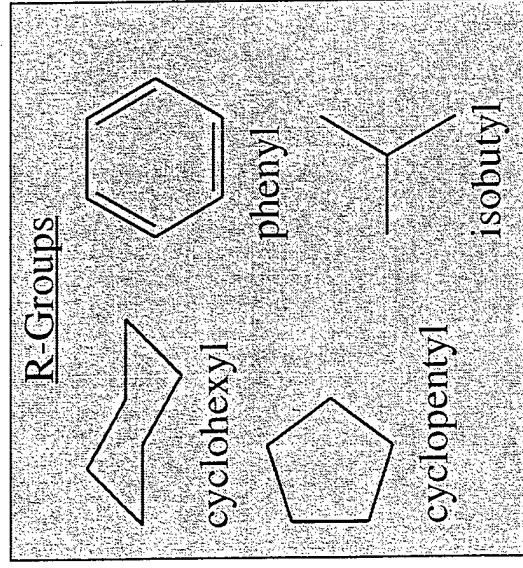


# POSS Silanol Synthesis



Brown & Vogt: JACS, 1965, p. 4313  
 Feher et al: JACS, 1989, p 1741;  
 Organometallics, 1991, p 2526

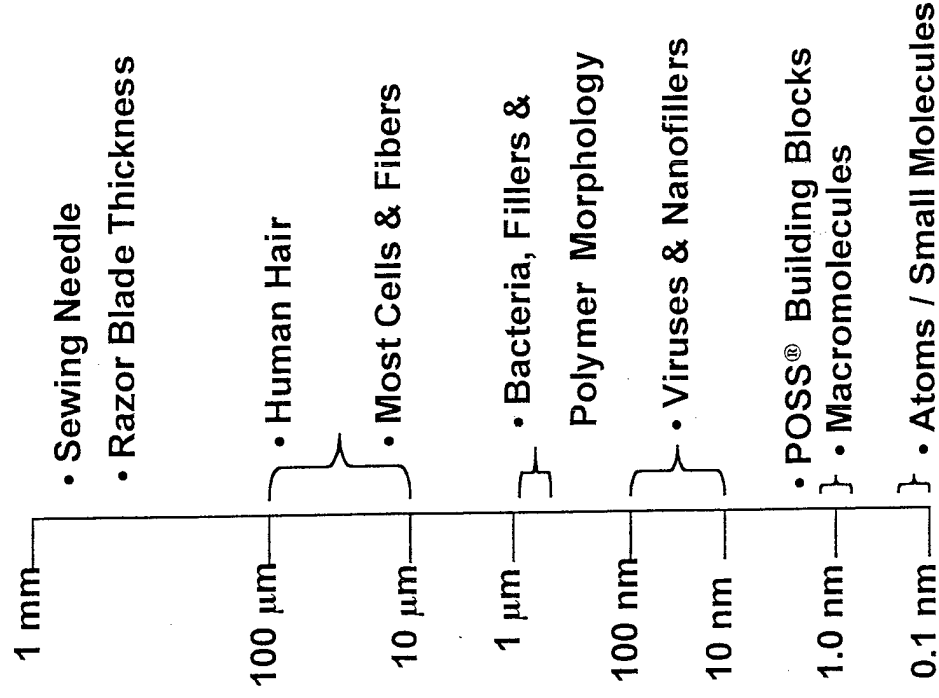
# POSS Macromers For Nanocomposites



|            |             |                |                   |
|------------|-------------|----------------|-------------------|
| Halides    | Nitriles    | Silanes        | Styryls           |
| Alcohols   | Amines      | Silanols       | $\alpha$ -olefins |
| Esters     | Isocyanates | Silylchlorides | Acrylics          |
| Bisphenols | Epoxides    |                | Norbornenyls      |

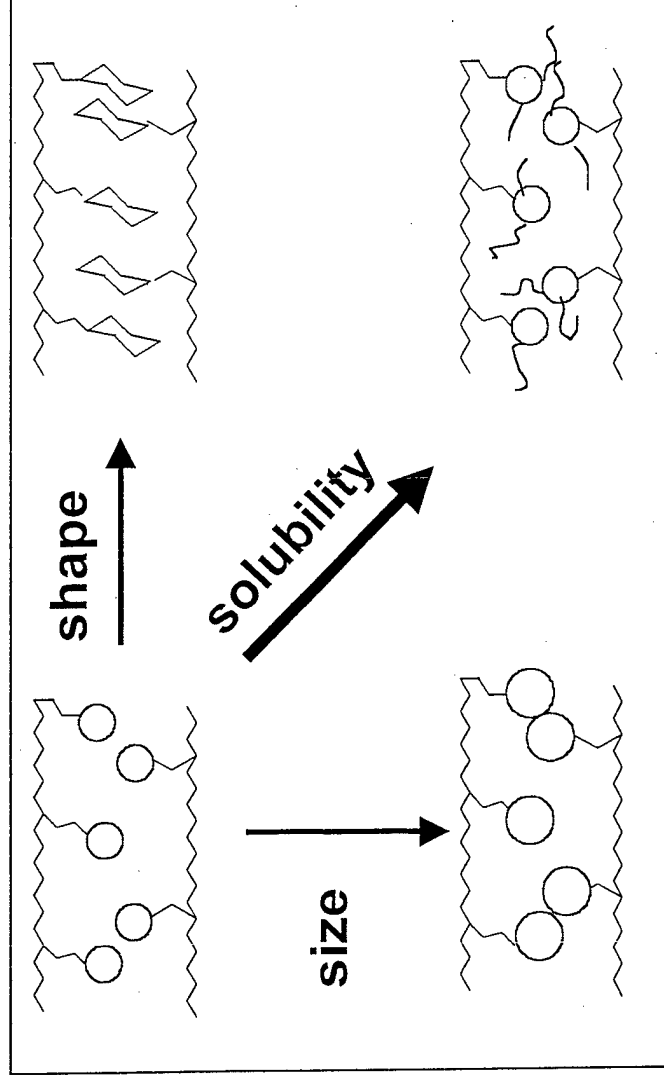
POSS-based macromers are now available through either **Geleste** or **Aldrich**  
 POSS technology is commercialized by **Hybrid Plastics** in Fountain Valley CA

# Why POSS and Why Nano?



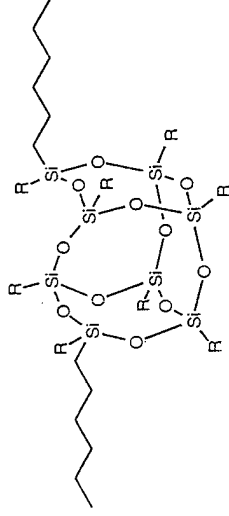
| Field       | Property                | Critical Length |
|-------------|-------------------------|-----------------|
| Electronics | Tunneling               | 1-100 nm        |
| Optical     | Quantum Well            | 1-100 nm        |
|             | Wave Decay              | 10-1000 nm      |
| Polymers    | Primary Structure       | 0.1-10 nm       |
|             | Secondary Structure     | 10-1000 nm      |
| Mechanics   | Dislocation Interaction | 1-1000 nm       |
|             | Crack Tip Radius        | 1-100 nm        |
|             | Entanglement Rad.       | 10-50 nm        |
| Therm-Mech. | Chain Motion            | 0.5-50 nm       |
| Nucleation  | Defect                  | 0.1-10 nm       |
|             | Critical Nucleus Size   | 1-10 nm         |
|             | Surface Corrugation     | 1-10 nm         |
| Catalysis   | Surface Topology        | 1-10 nm         |
| Biology     | Cell Walls              | 1-100 nm        |
| Membranes   | Porosity Control        | 0.1-5 nm        |

## Structure-Property Relationships

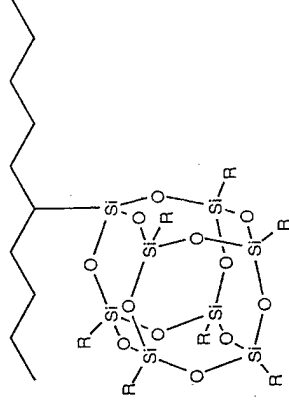


- Maximizing property enhancements through changes at the nano level
- Polymer miscibility vs. POSS/POSS interactions

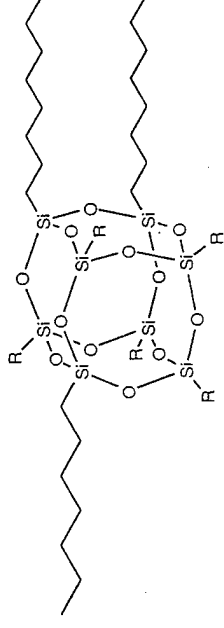
# POSS Polymer Incorporation



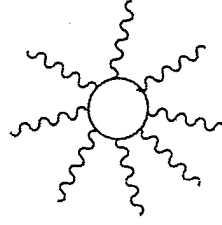
POSS Bead



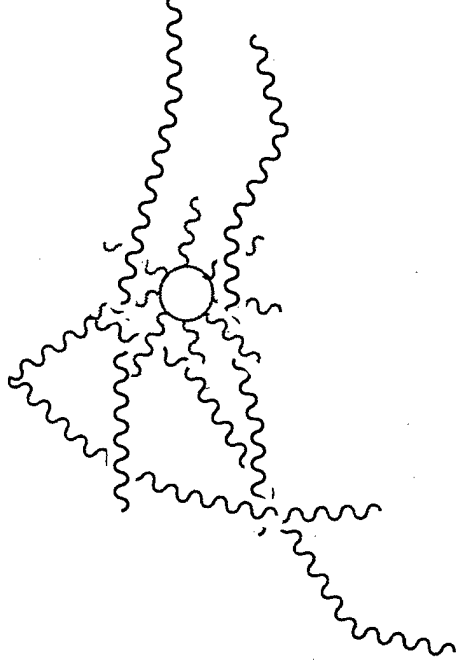
POSS Pendant



POSS Crosslinking

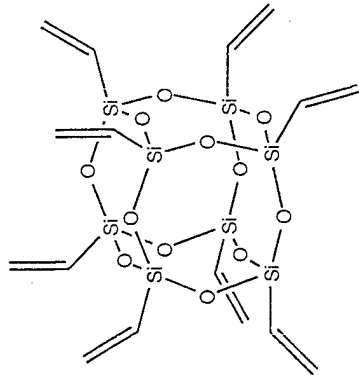


POSS Blending

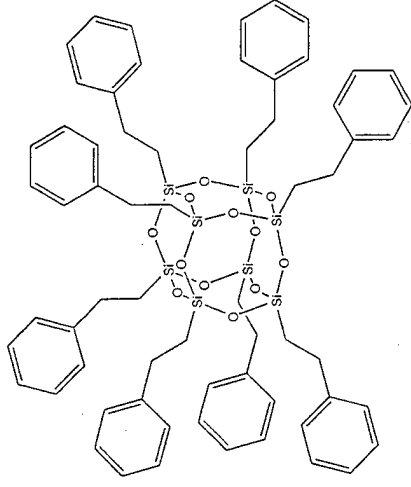


Size & Shape

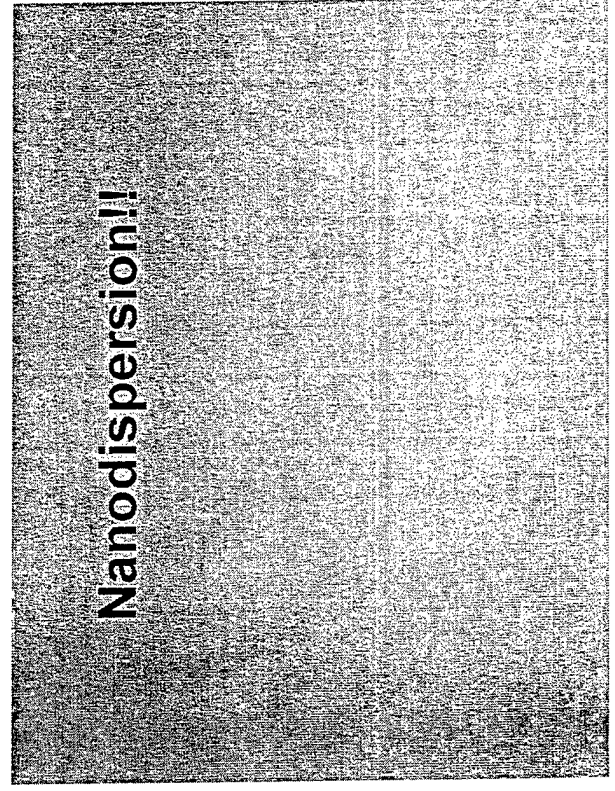
# 50 Wt % POSS Blends in 2 Million MW Polystyrene



Vi<sub>8</sub>T<sub>8</sub>

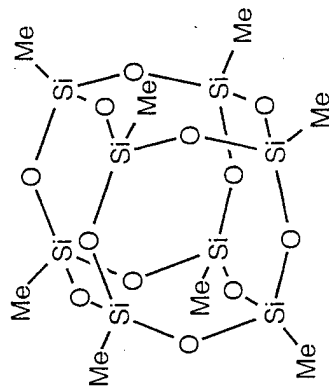
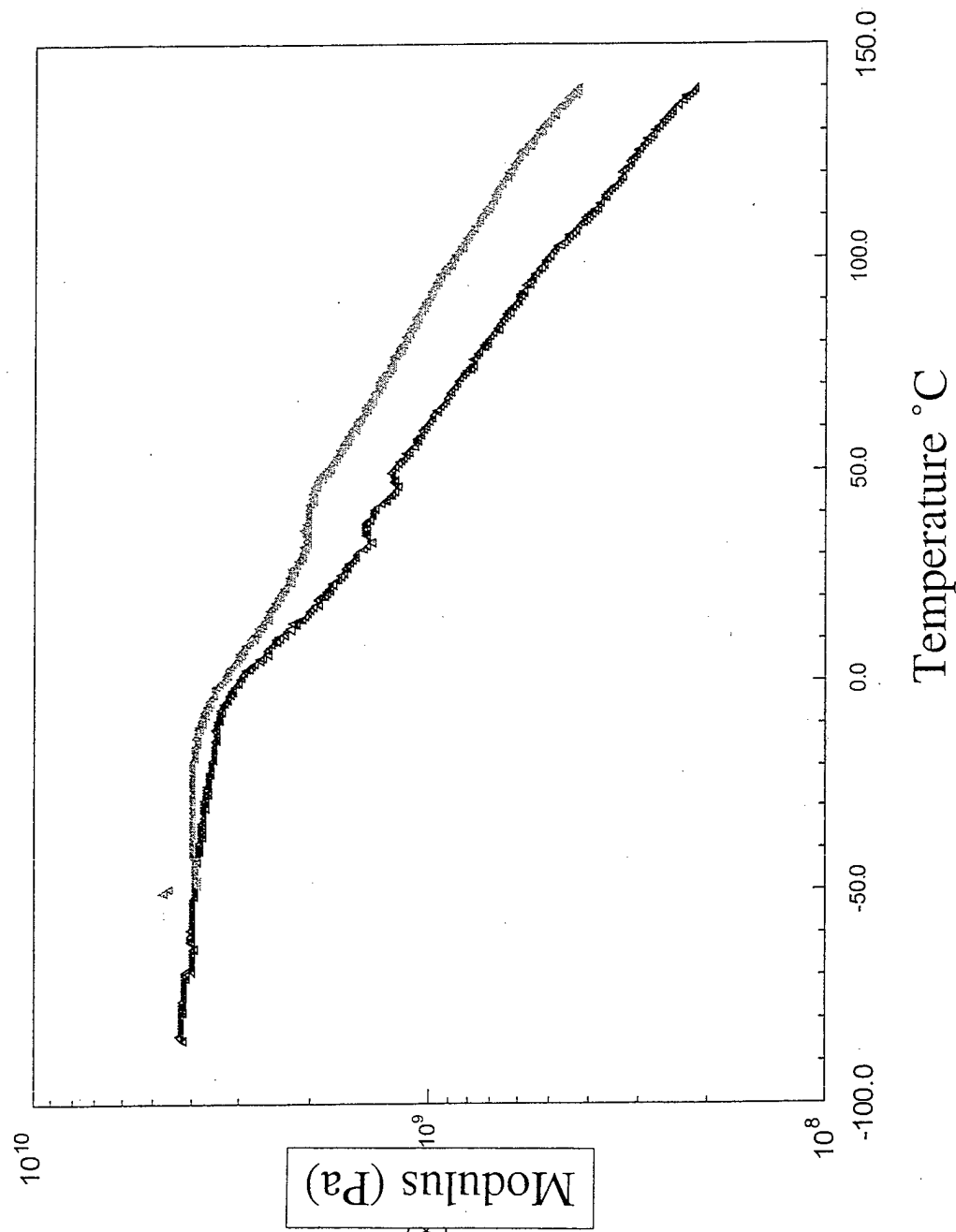


Phenethyl<sub>8</sub>T<sub>8</sub>



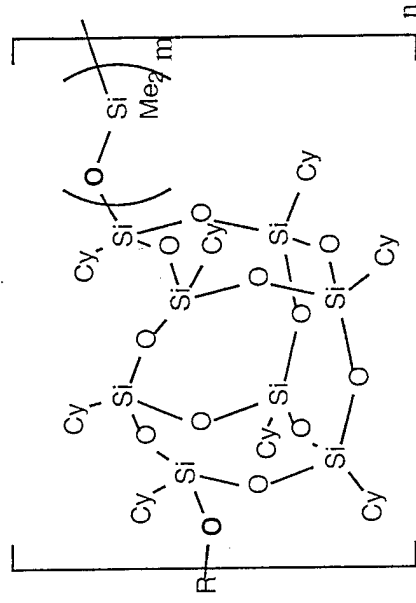
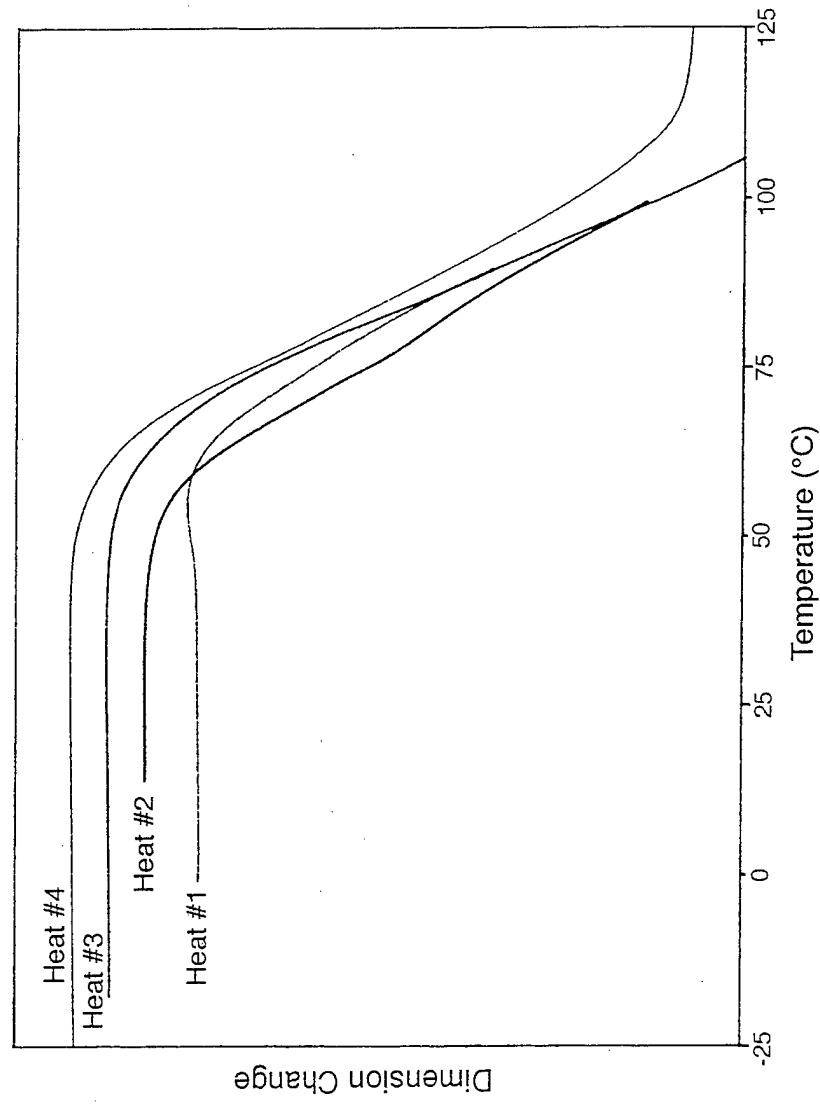
1  $\mu$ m

# DMA of 10 Wt % POSS in isotactic Polypropylene

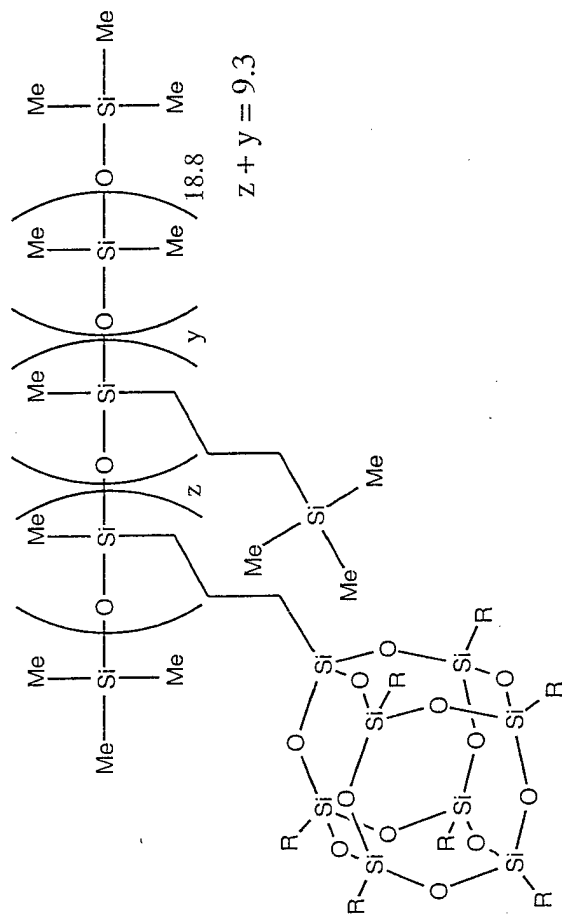
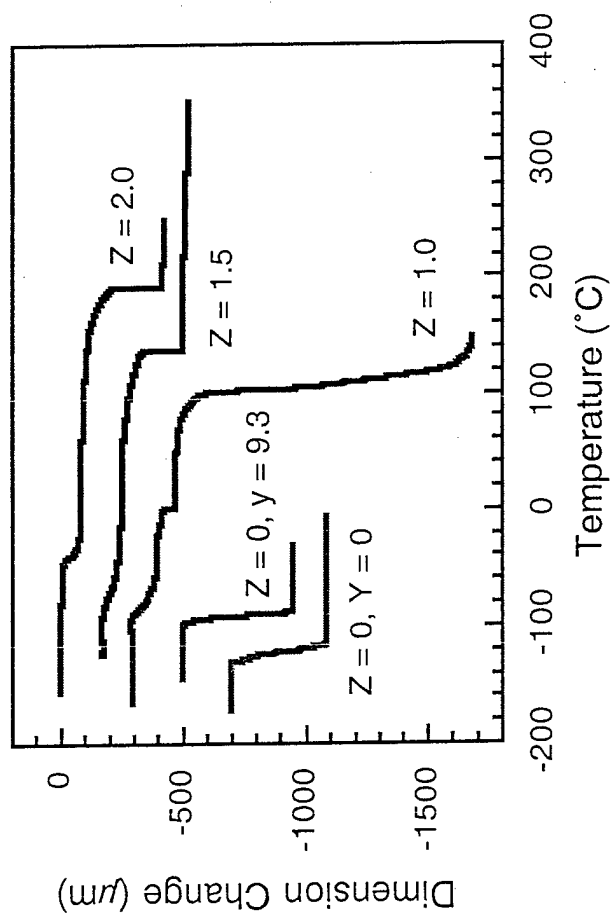


# PDMS-POSS TMA Characterization

The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.



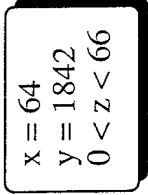
# TMA of Pendent POSS-Siloxanes



$$z + y = 9.3$$

18.8

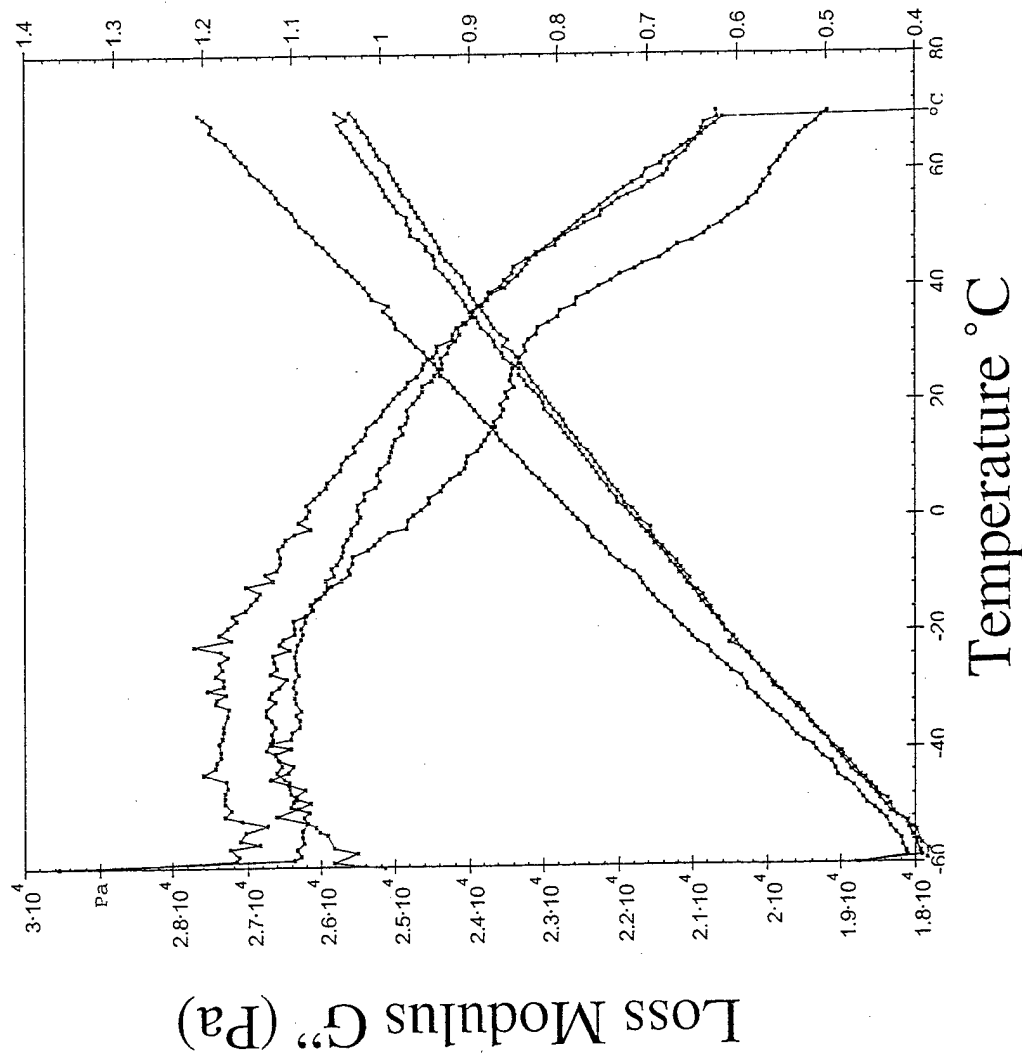
# Hydrosilation to High MW PDMS



There are about 7 POSS-macromers per PDMS chain

There are about 7 POSS-

# Comparison of Three T8-POSS Macromers

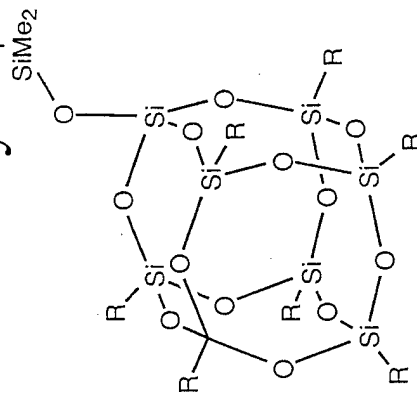


PDMS + 5 wt % POSS

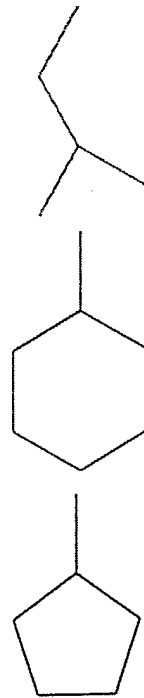
Blue = cyclopentyl

Red = cyclohexyl

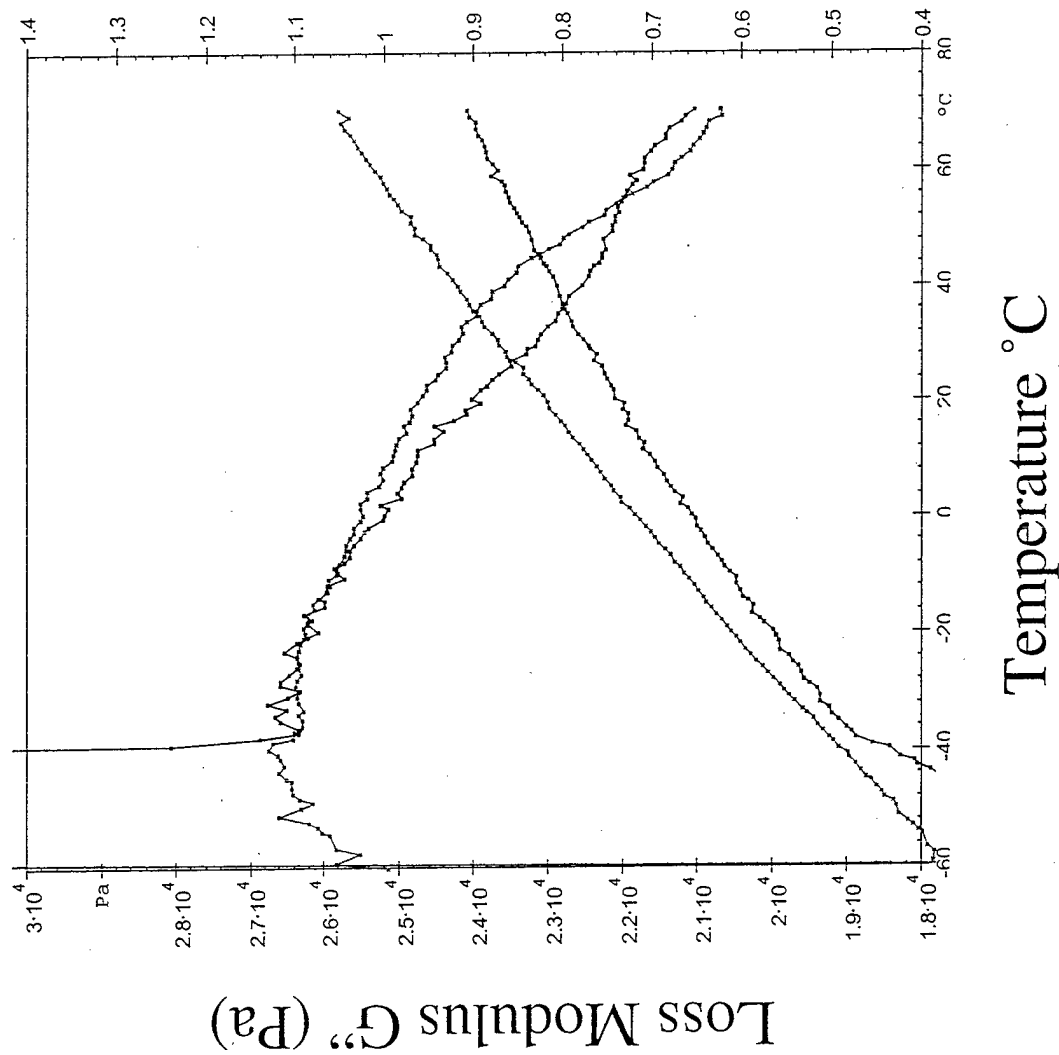
Purple = isobutyl



$\tan(\delta)$

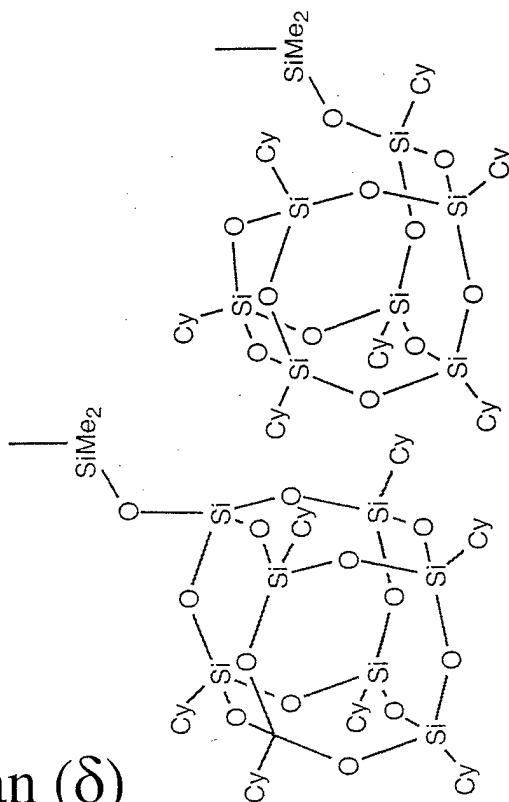


# Comparison of Two POSS Polyhedra

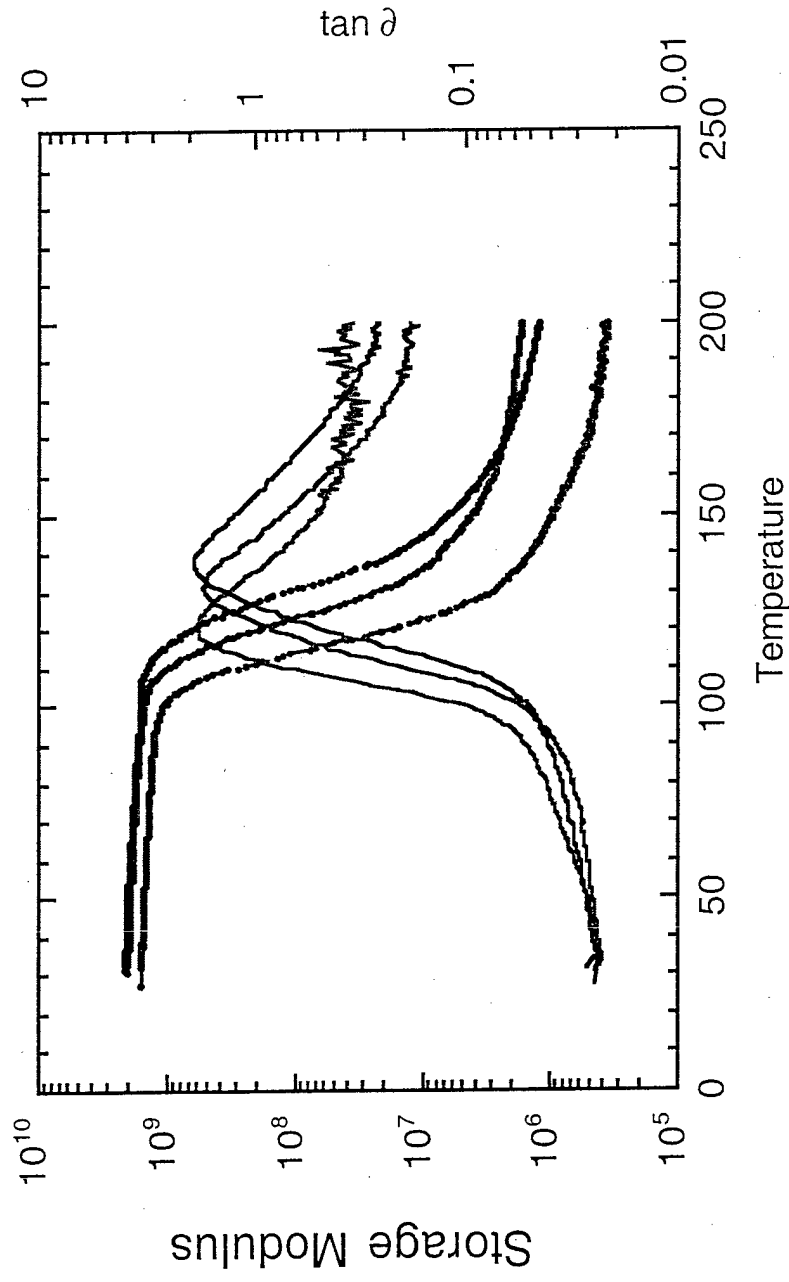


PDMS + 5 wt %  
CyclohexylPOSS  
Red = T8-POSS  
Blue = T7-POSS

$\tan(\delta)$

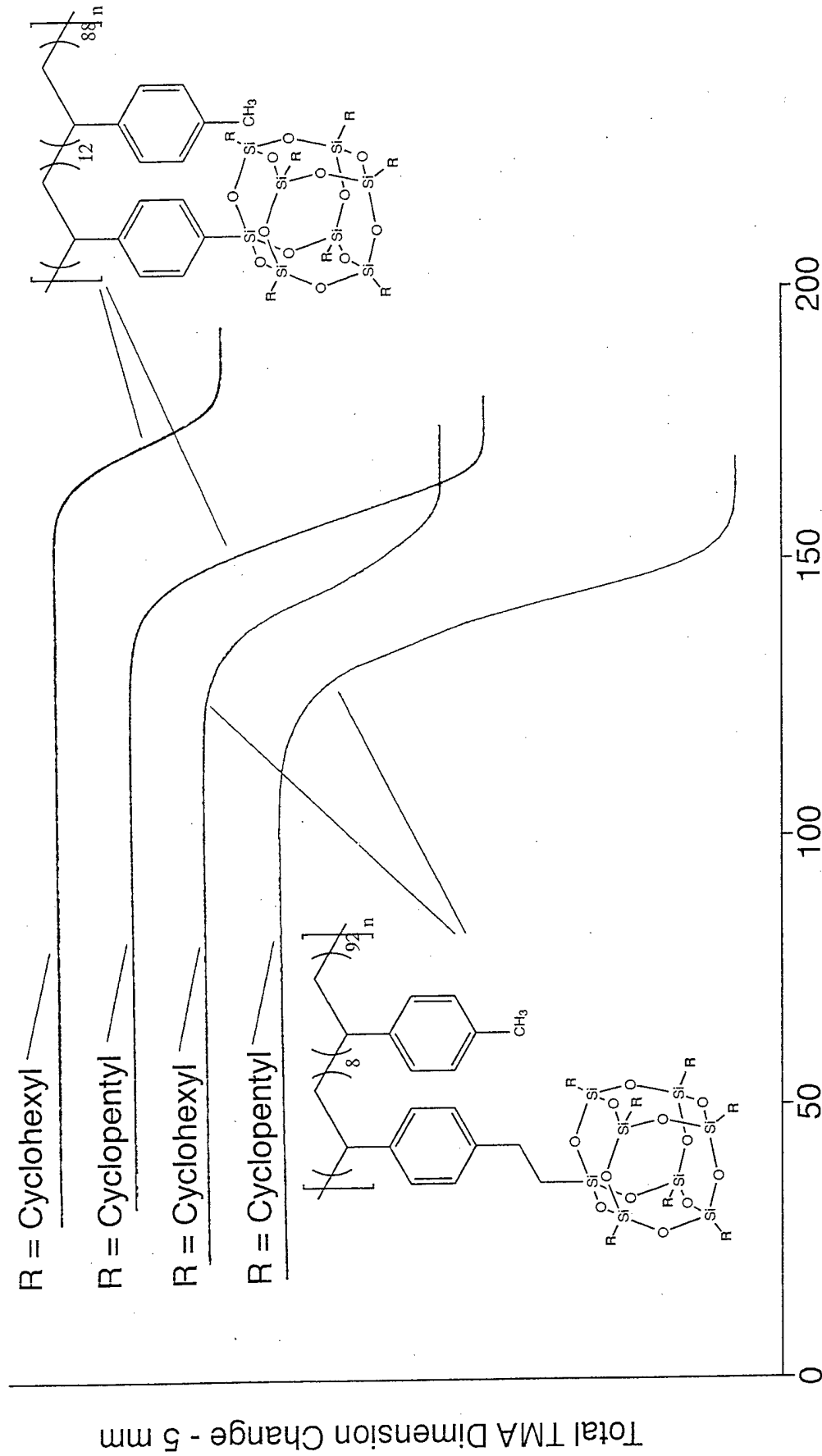


## DMA of 30 wt % POSS Polystyrenes

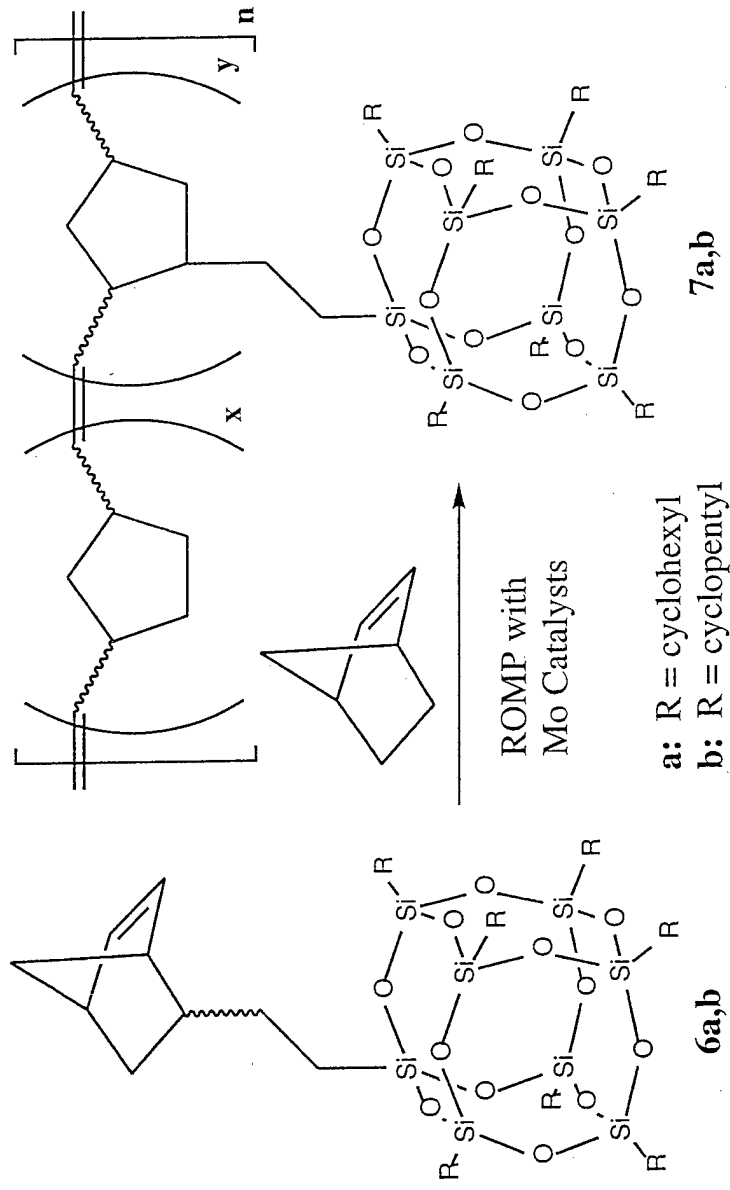


- Comparison of isobutyl, cyclopentyl & cyclohexyl
- Bulk polymerized samples

# TMA Plot Comparison For POSS-Styryl and POSS-EthylStyryl Polymers (R = Cyclohexyl and Cyclopentyl)



# Polymerization of POSS Norbornenes



Both block and random copolymers were synthesized.

The wt. % POSS was varied from 0 to 50 wt. % POSS.

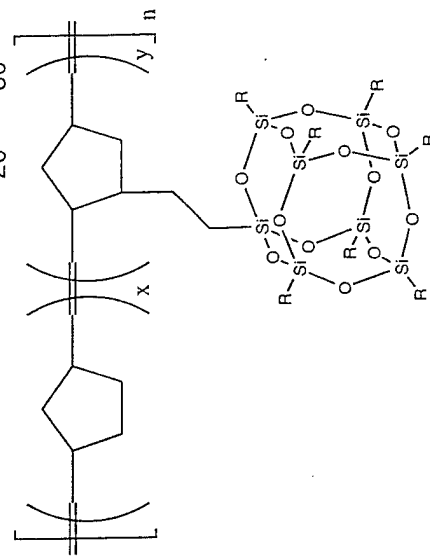
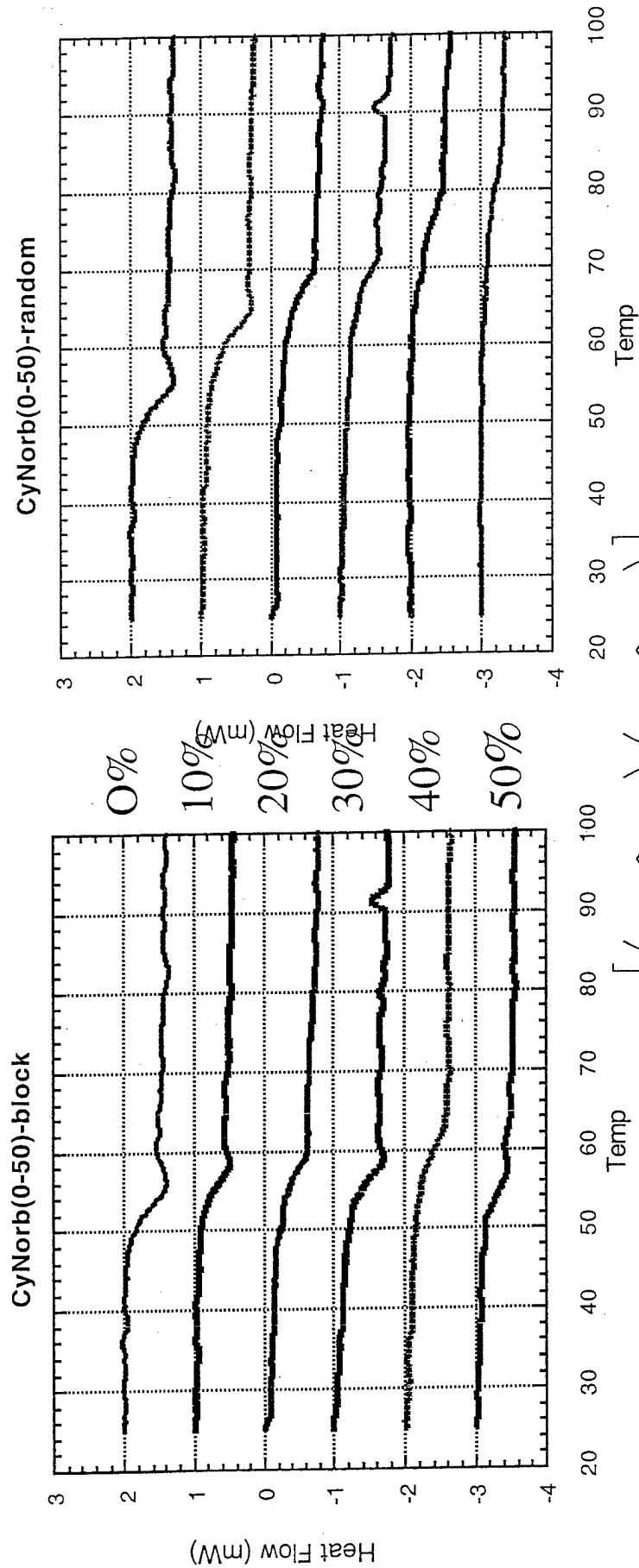
An ideal polymerization would yield polymers with 500 monomer units.

0 wt % POSS, 0 mole % POSS: x = 500, y = 0

10 wt % POSS, 1 mole % POSS: x = 495, y = 5

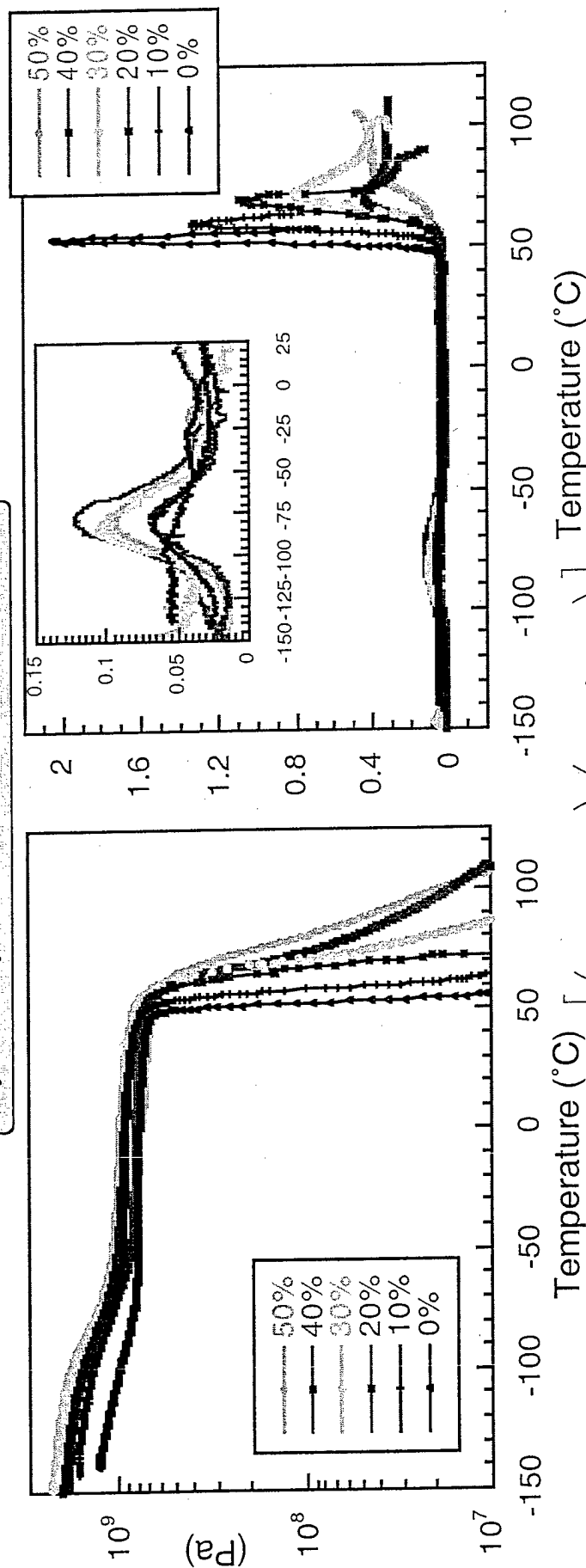
50 wt % POSS, 8 mole % POSS: x = 460, y = 40

# DSC Data for POSS-Norbornenes

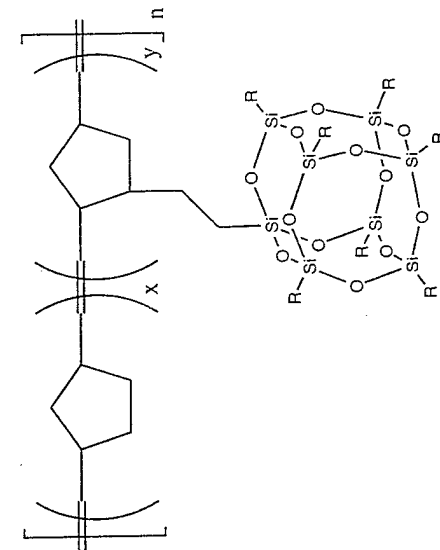


# Storage Modulus and Loss Tangent

Cyclohexyl Relaxation: 14.7 kcal/mol



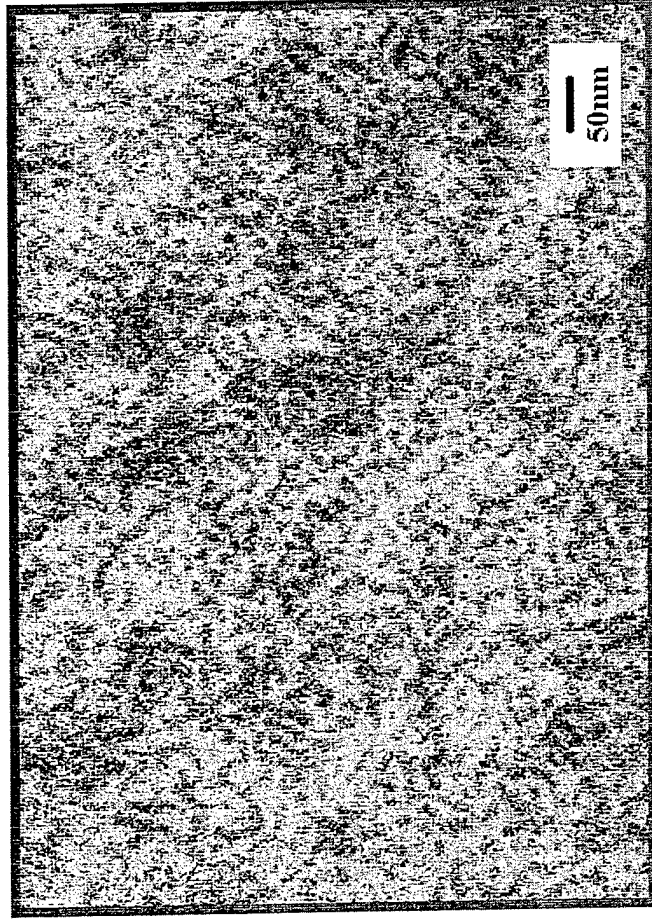
No Maximum for  
50% CyPOSS



Various Wt % Cyclohexyl  
POSS Polynorbornene  
Random Copolymers

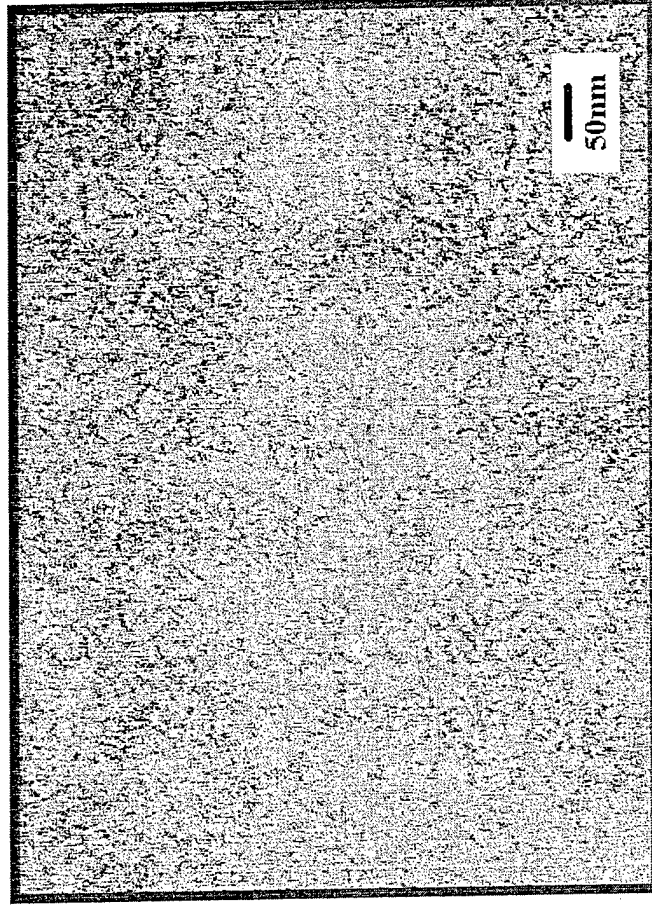
# TEM of Random POSS Norbornenes

50CyPOSS/PN



“Coarse” Cylinder Nanostructure  
(Diameter ~ 12nm)

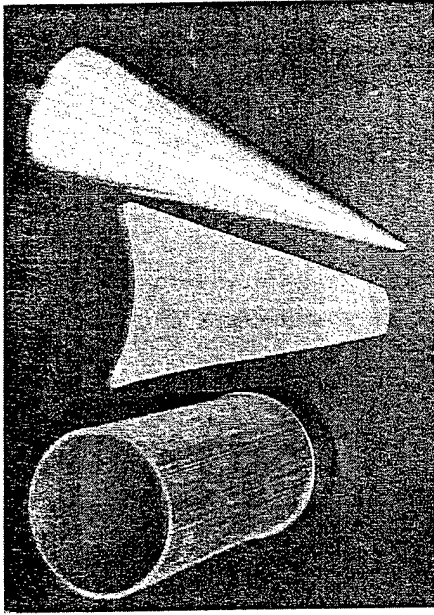
50CpPOSS/PN



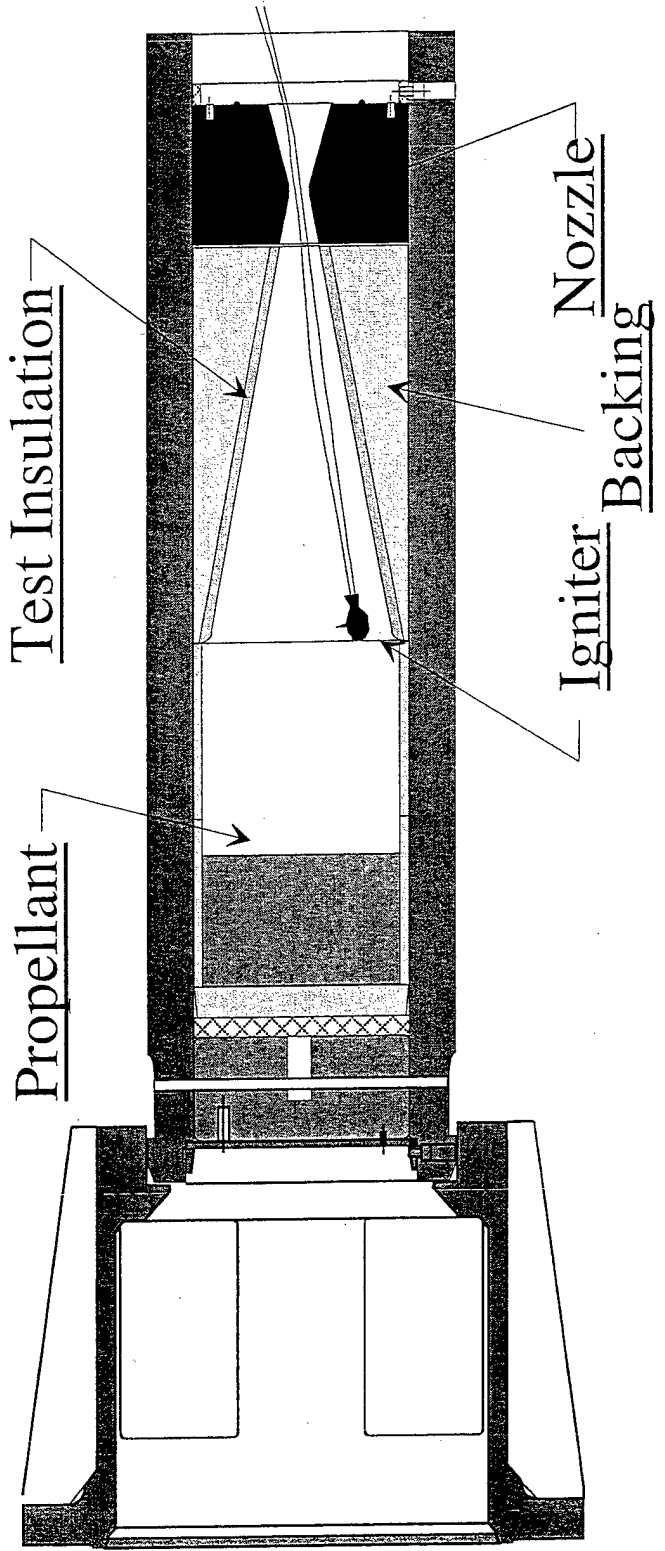
“Fine” Cylinder Nanostructure  
(Diameter ~ 6nm)

CyclohexylPOSS-rich domains may entrain more unoriented polynorbornene chains than CyclopentylPOSS-rich domains.

# Solid Rocket Motor Insulation



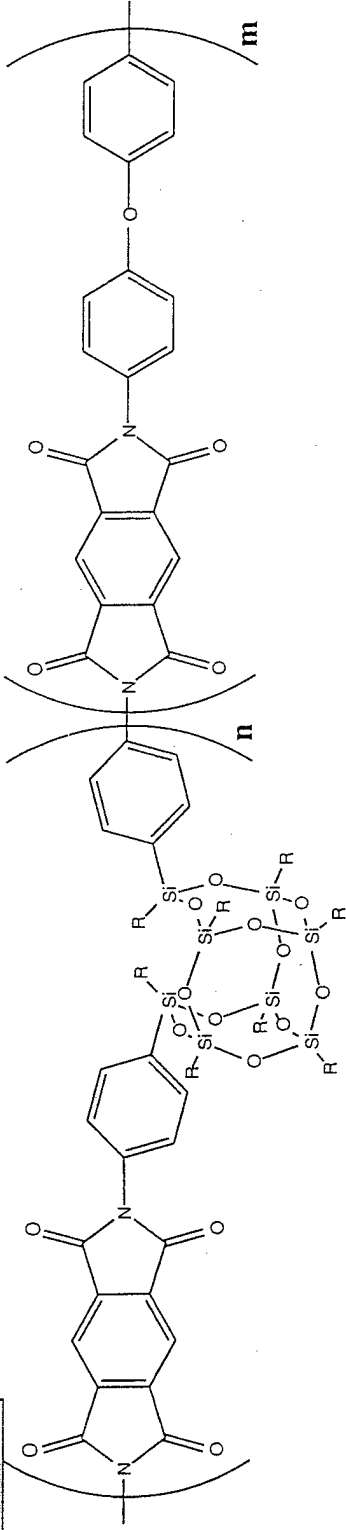
*POSS-Insulation Sample*





# O-Atom Etching Experiment

$8.47 \times 10^{20}$  atoms  $\text{cm}^{-2}$



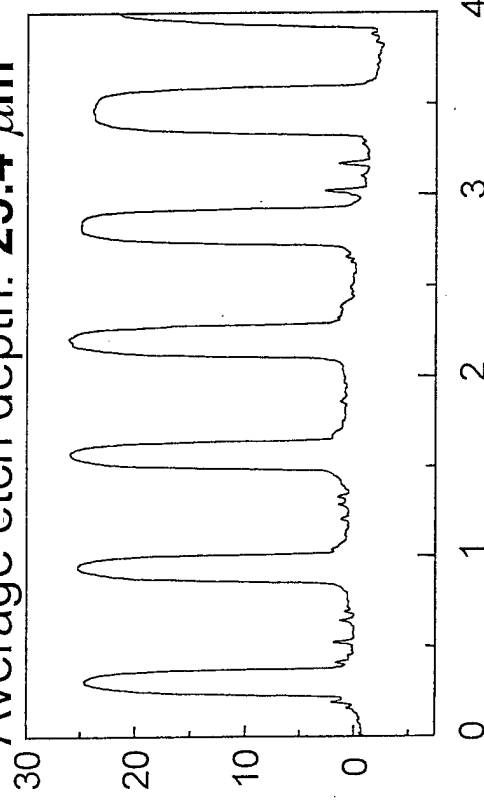
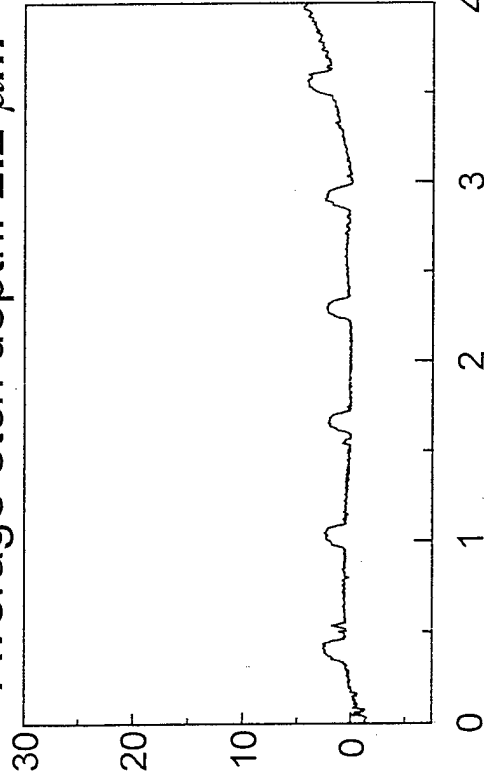
**Kapton 10 wt% POSS**

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

**Kapton H Standard**

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

Etch Depth (microns)



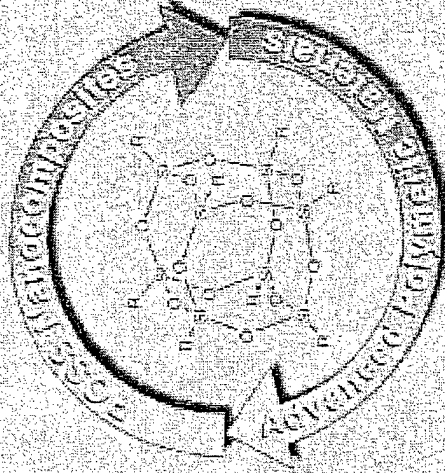
Scanning Length (mm)

## Summary

- The successful incorporation of nano-sized inorganic clusters (POSS) into a wide variety of polymers has been demonstrated.
- These POSS clusters have a remarkable effect on the thermal transitions and mechanical properties of the polymers they are copolymerized into.
- The POSS effect on the properties of analogous polymers shows a dependency on the type of alkyl group on the POSS cluster.
- TEM images of randomly copolymerized polymers illustrate this dependency, as the size of the POSS domains are alkyl-group dependent.
- Rheology of high molecular weight PDMS grafted with small amounts of POSS illustrates a dependence on both the POSS-alkyl-group and POSS shape.

# Acknowledgements

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Prof. Gar Hoflund UF  
Prof. Tim Mitten MSU

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