

# High performance polymeric materials: Some examples of science-based performance assessments and new material developments

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**JAIST NANOTECH 2007, 1<sup>st</sup> Int. Symposium on Ultimate Stability of Nano-structured Polymers and Composites, October 12-13, 2007, JAIST, Ishikawa, JAPAN**

**Our challenge: Better materials through knowledge of basic performance features and innovation**

# South-Western United States

Las Vegas      Albuquerque  
Grand Canyon



- Dry semi-desert, but lots of science
- Nuclear, electronics, nano-technology



# The National Institute for Nano Engineering

## Creating the Next Generation of Innovators & Innovations

***Government  $\leftrightarrow$  University  $\leftrightarrow$  Industry***

**Regan Stinnett**

**The National Institute for Nano-Engineering**

**Sandia National Laboratories**

**(rwstinn@sandia.gov)**

**Albuquerque, NM USA**

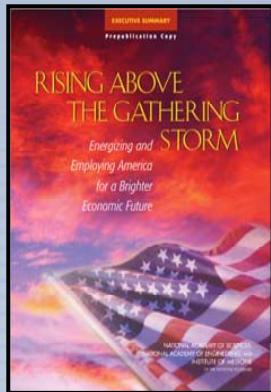


Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.



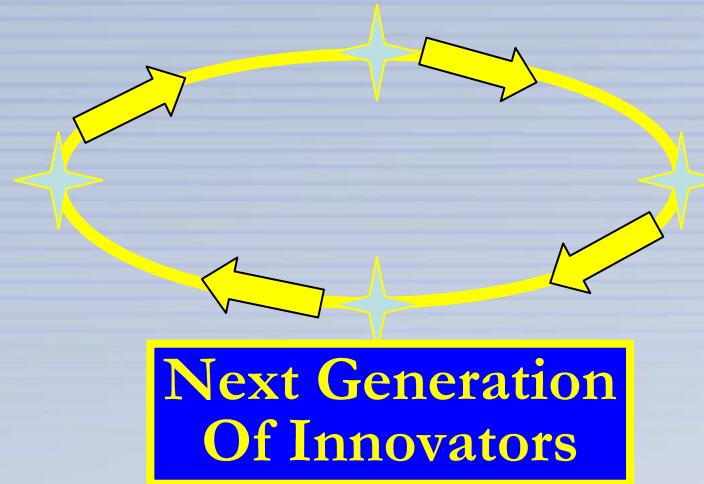


# The U.S. is developing an aggressive plan



Rising Above the Gathering Storm  
December 2005

## America COMPETES Act President Signs 8/9/07



Discovery Science  
and Engineering  
Innovation  
Institutes

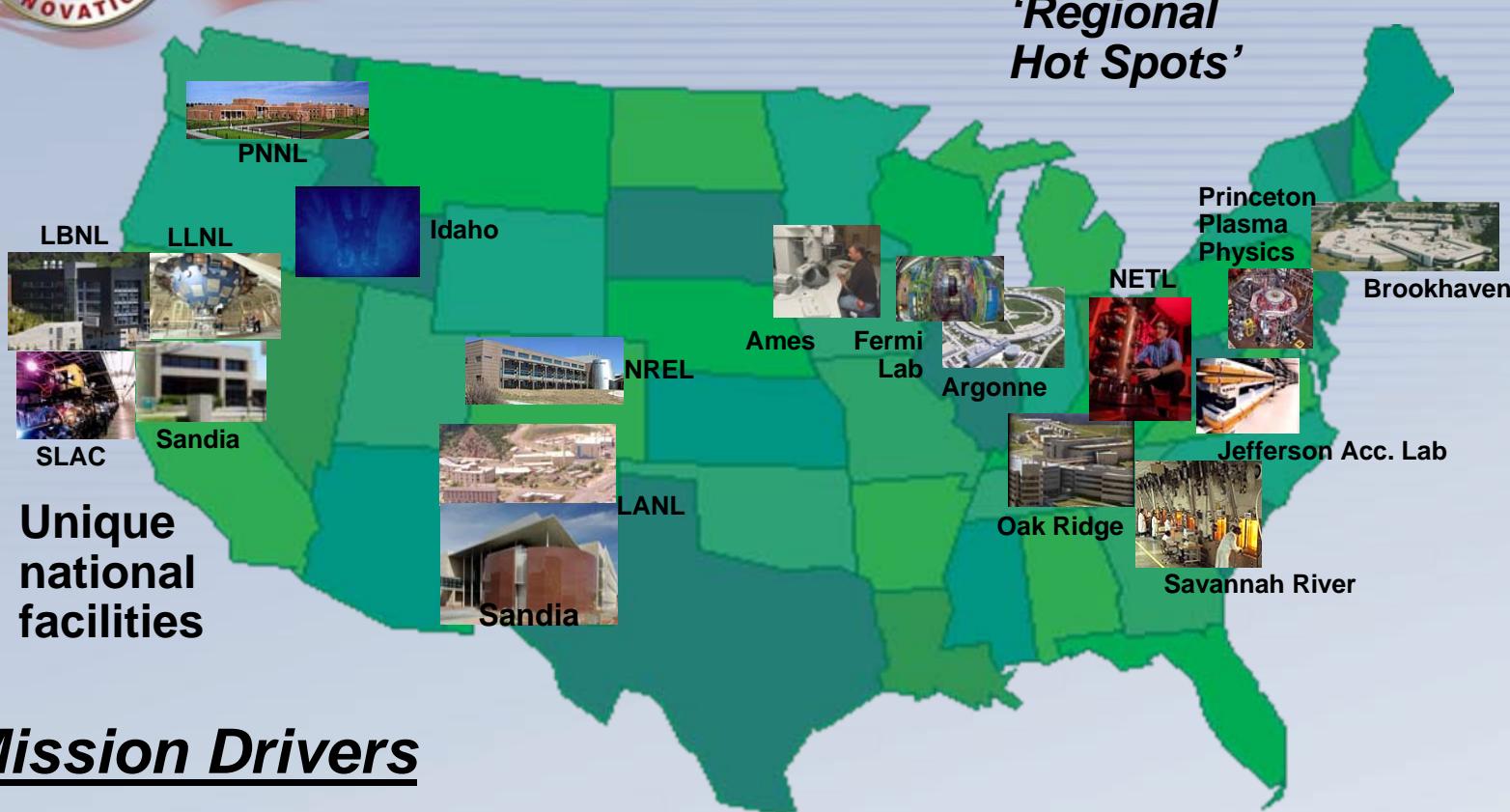
Bringing  
together ...



*'Innovation is the only competitive advantage in the global economy'*



# The DOE is in a position to 'change the game'



## Mission Drivers

- Meeting national security needs
- New solutions for energy needs
- Sustaining the environment
- Economic security

**Department of Energy**  
25,000 scientists  
and engineers



# Sandia National Labs began to respond to these challenges more than a year ago

## Accelerating Engineering Innovation Summit, Sandia National Labs

Albuquerque, May 31<sup>st</sup> - June 2nd, 2006



### Participants

Corning	Harvard	Harvey-Mudd
Exxon-Mobil	U Florida	RPI
Goodyear	U Michigan	MIT
Hewlett Packard	U Wisconsin	Notre Dame
IBM	U Illinois	Yale
Intel	UC Davis	U New Mexico
Lockheed Martin	UC Santa Barba	U Texas Austin
Microsoft	Rose-Hulman	Oak Ridge NL
Monsanto	Los Alamos NL	DOE

### A few key issues were identified

- 1) **Partnerships** will be the key to future breakthroughs.
  - Engineers need to know how to partner effectively.
  - Partnering among universities, labs and companies must be simpler.
- 2) Engineers and scientists need **broader experience**.
  - Multi-disciplinary education is important, but the challenges are great.
- 3) A concerted effort is needed to **attract, inspire & retain top students**.
  - Bright minds want important problems and capabilities to solve them.



# Discovery Science & Engineering Innovation Institutes: A New Idea



University

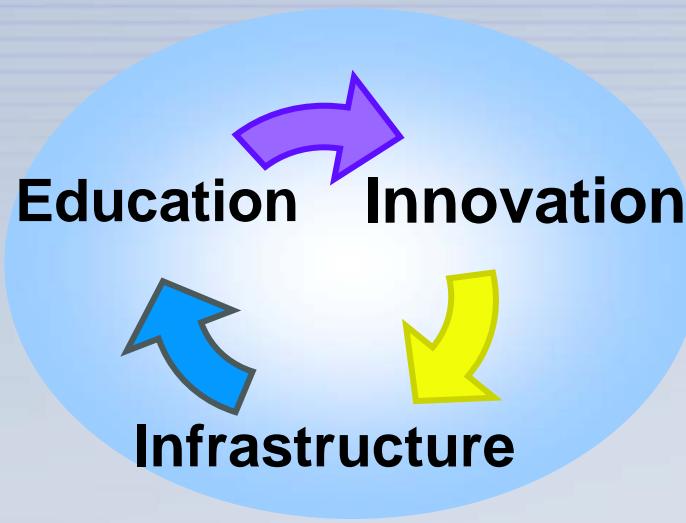
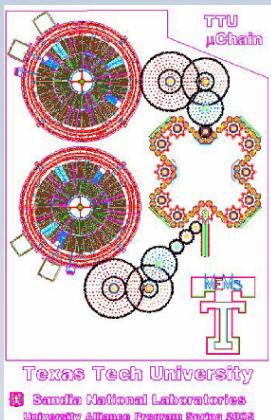


Government



Industry

*Innovation  
Institutes –  
National Centers  
of Excellence*



Future Innovators &  
Next-Generation Innovations

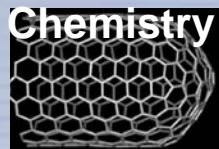
Agreement to work  
together, share info, IP



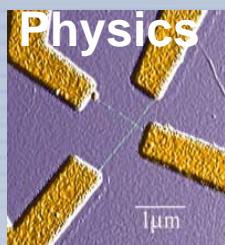
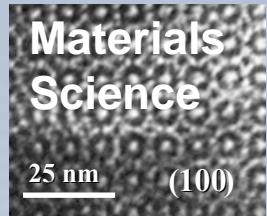


# Prototyping the Innovation Institute Concept: *The National Institute for Nano-Engineering*

**Nano-engineering will be a critical competitive hinge for the U.S.**

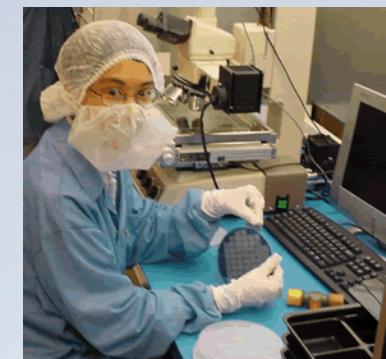


Theory &  
Modeling



- New electronics – beyond Si
- Sensors
- Catalysts
- Optics
- High-performance materials
- Energy applications
- ...

**NINE Mission:** Help develop the next generation of engineering leaders needed to drive future innovations in micro- and nano-technology



Nano-Engineering is a critical U.S. topic for education/ workforce preparation, innovation and technology transfer \*

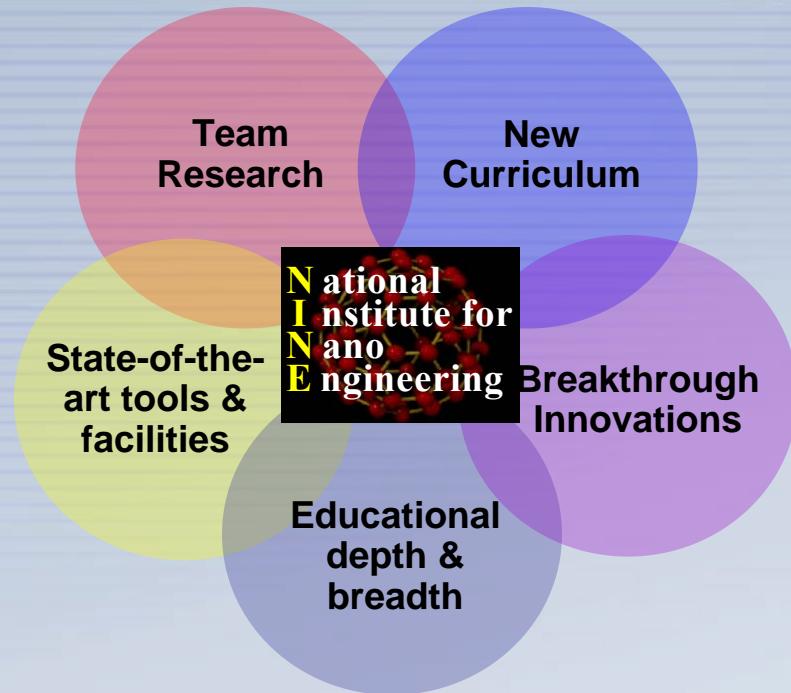
\* PCAST report on Nanotechnology R&D, May 2005



# We are developing NINE now!

## NINE Goals

- **Transform** engineering education in this new, interdisciplinary field
- **Inspire** a new generation of nano-engineers skilled in working across multiple disciplines and institutions using the latest engineering tools and facilities
  - ✓ Graduate focus, undergraduate involvement, outreach to teachers
- **Pilot** government-academic-industry education & innovation hubs
  - ✓ Build off previous experience and successful models (e.g., SRC, Sematech)
- **Capitalize** on DOE investments to address problems of national importance



NINE began initial operation this summer

# High performance polymer materials



**Utilities, Energy**



**Defense**



**MATERIALS  
PERFORMANCE  
OPTIMIZATION  
Dept. 1821/SNL**



**Space, Satellites**



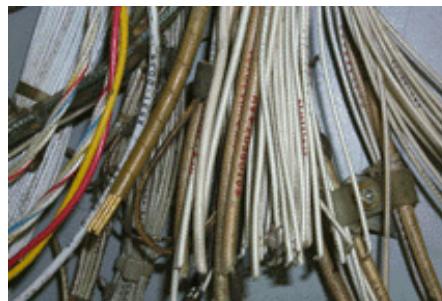
**Industry**



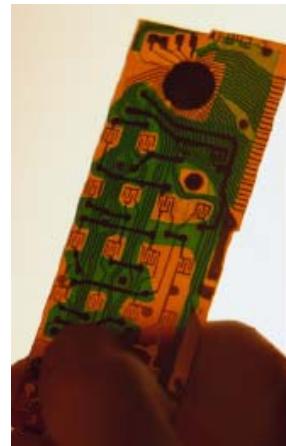
# Polymer materials



## Elastomers



We deal with all types of polymers  
in demanding applications  
(Dept. 1821, "Polymers Are Us")



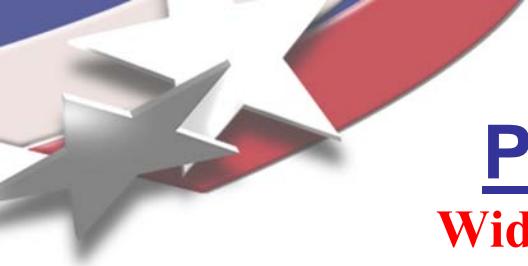
## Thermoplastics



## Thermosets, thermal cure

## Engineering materials

## Foams



# Polymers and components

**Wide range of polymers/materials/components**

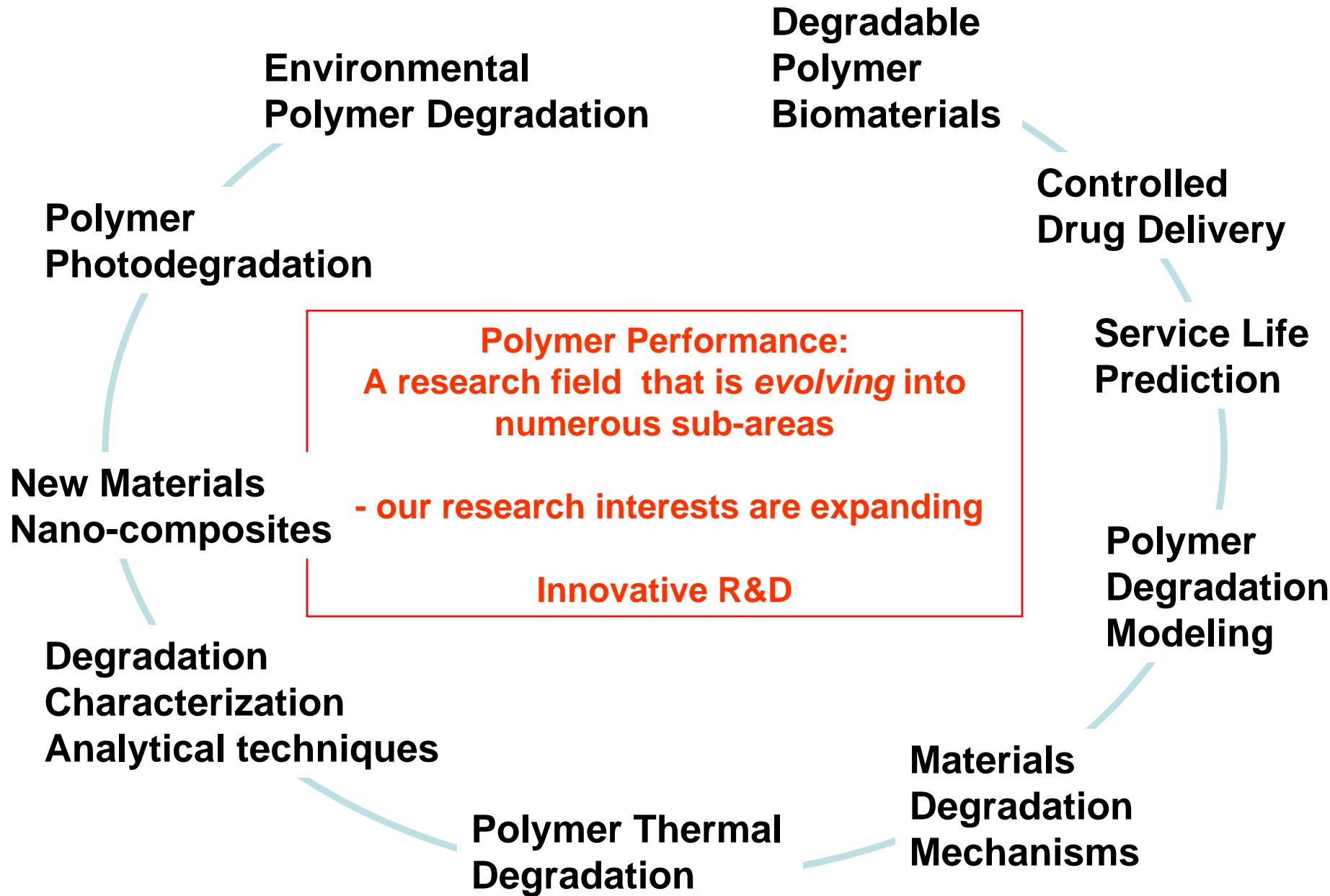
- **Polymeric materials**

- Elastomers, butyl, nitrile, neoprene, EPDM, EPR's, natural rubbers
- Fluoro-polymers, PVDF and copolymers in adaptive film applications
- Polyurethanes, polyolefins, nylon and kevlar
- Epoxies, PEEK, PI, PO (radiation/thermal/chemical performance)

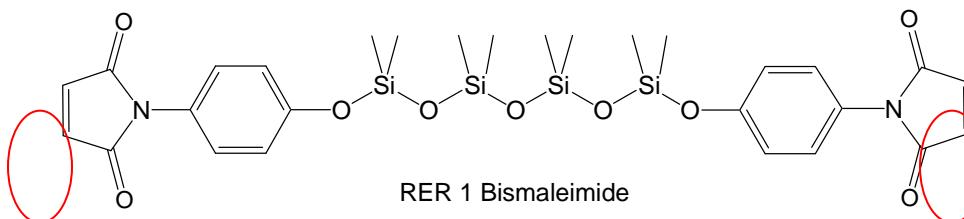
- **Components**

- Cable insulation, jackets, seals, O-rings
- Wire insulation, fluoro-polymers, polyimides, nylon, PVC
- Energetic material binders, butadiene and polyether/ester based PU's
- Foams, PU and silicone materials
- Submarine shock absorbers and seals
- Encapsulants and dielectrics
- Engineering polymers, surface modification, radiation effects
- Temp. sensors, gauges, motors, gear trains, in radiation environments
- Parachute materials

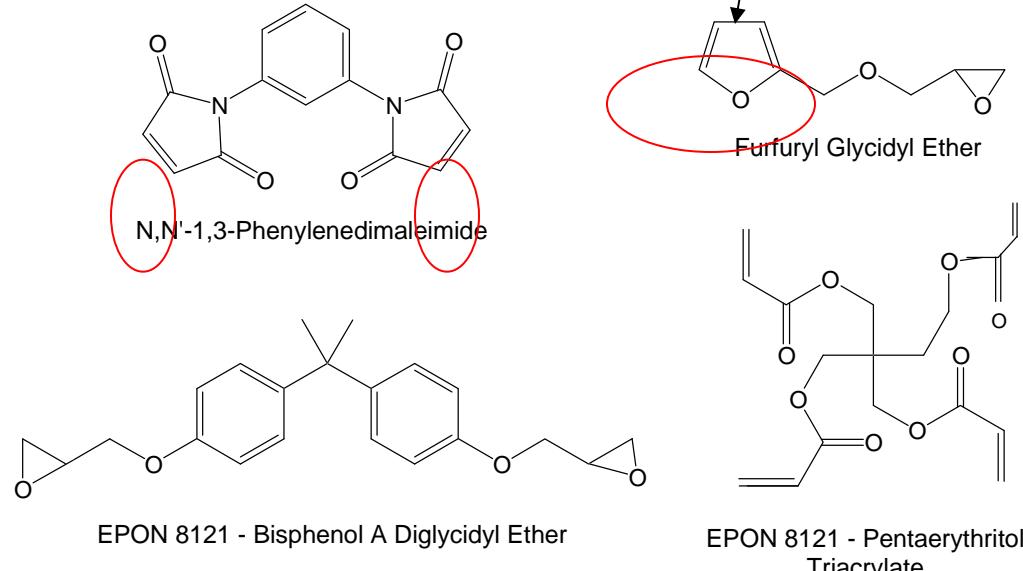
# Polymer Performance, Degradation and Materials Optimization



# Example: Reversible epoxy foam



Thermally reversible D/A chemistry  
Combined Michael addition and epoxy curing

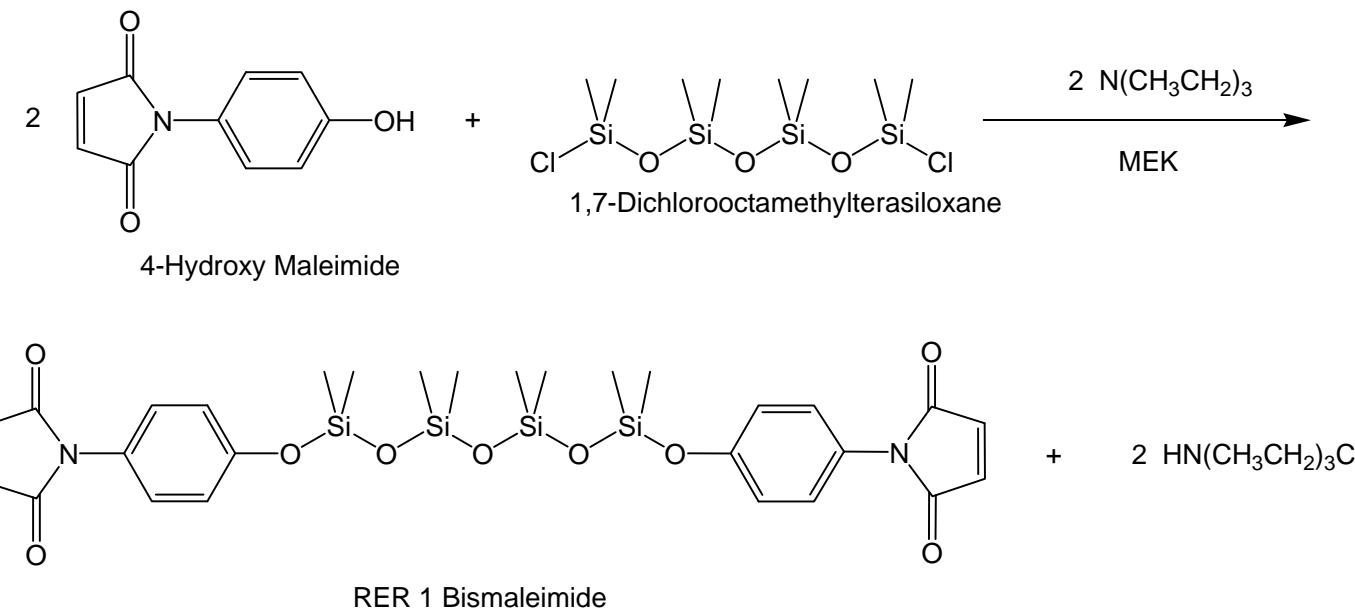


**Constituents have double bonds and epoxy groups to react**

McElhanon JR, Russick EM, Wheeler DR, Loy DA, Aubert JH. **Removable foams based on an epoxy resin incorporating reversible Diels-Alder adducts.** *J Appl Polym Sci* 2002;85:1496  
McElhanon JR, Wheeler DR. **Thermally Responsive Dendrons and Dendrimers Based on Reversible Furan-Maleimide Diels-Alder Adducts.** *Organic Letters* 2001;3:2681

# Flexible bis-maleimides

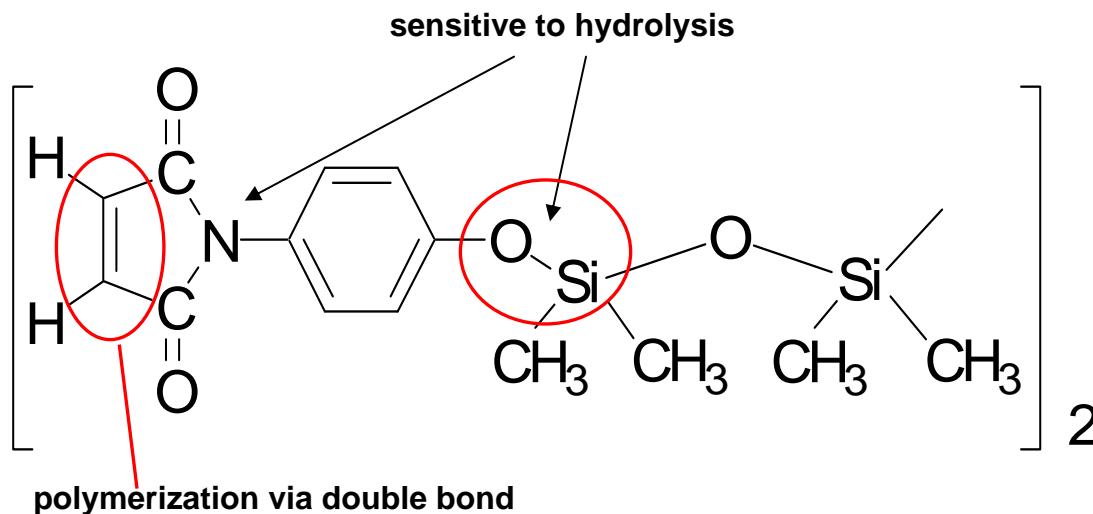
## hydroxyl- chloro-siloxane condensation



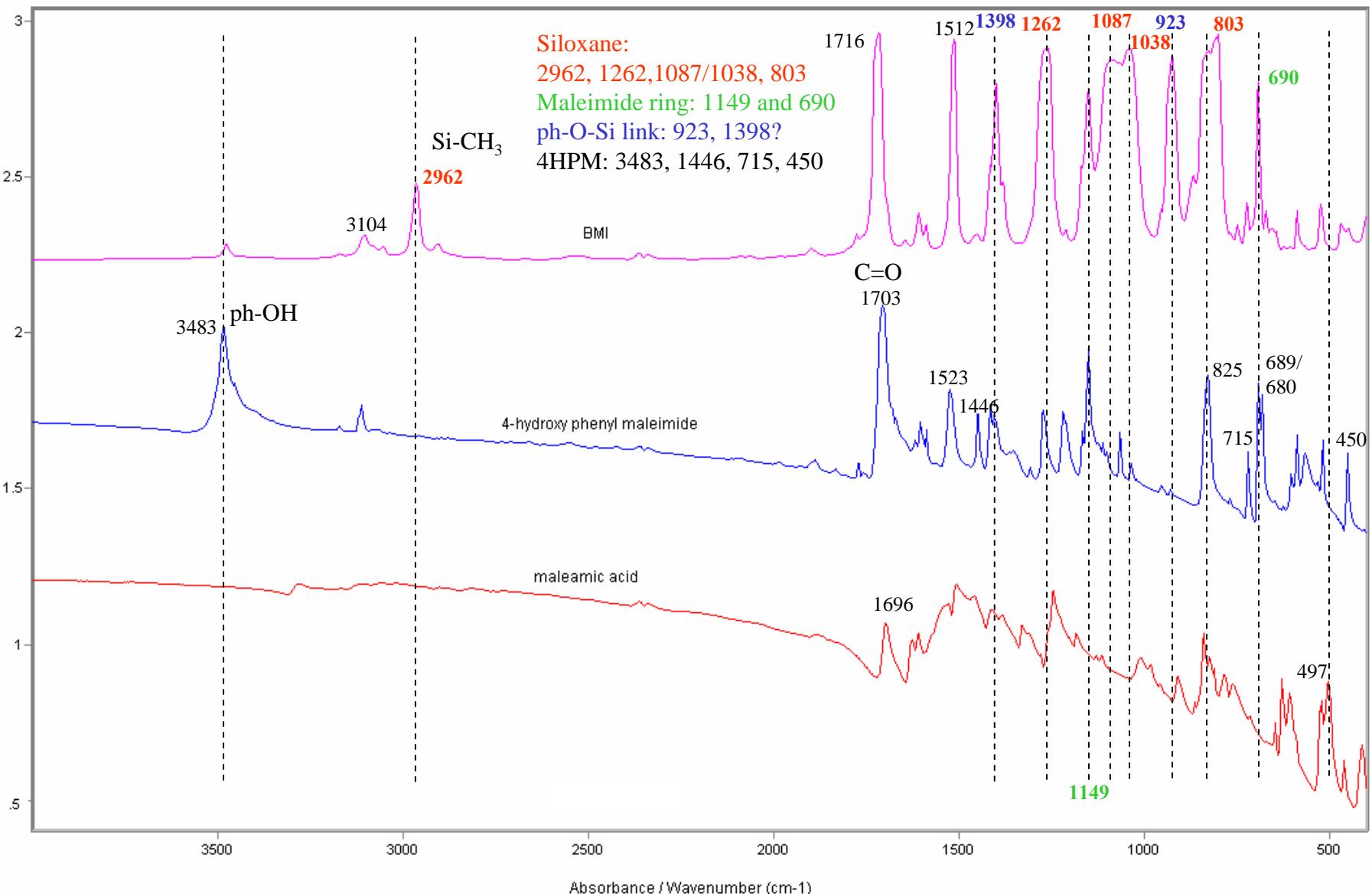
Materials are in solvents (MEK, THF, EAc) and experience elevated T

# Bismaleimide with a siloxane bridge (BMI)

- A reactive intermediate with a flexible linkage, low Tg
- A dienophile for Diels-Alder adducts, i.e. furfuryl glycidylether
- Unfortunately, also a molecule that shows sensitivity to self-polymerization and hydrolysis

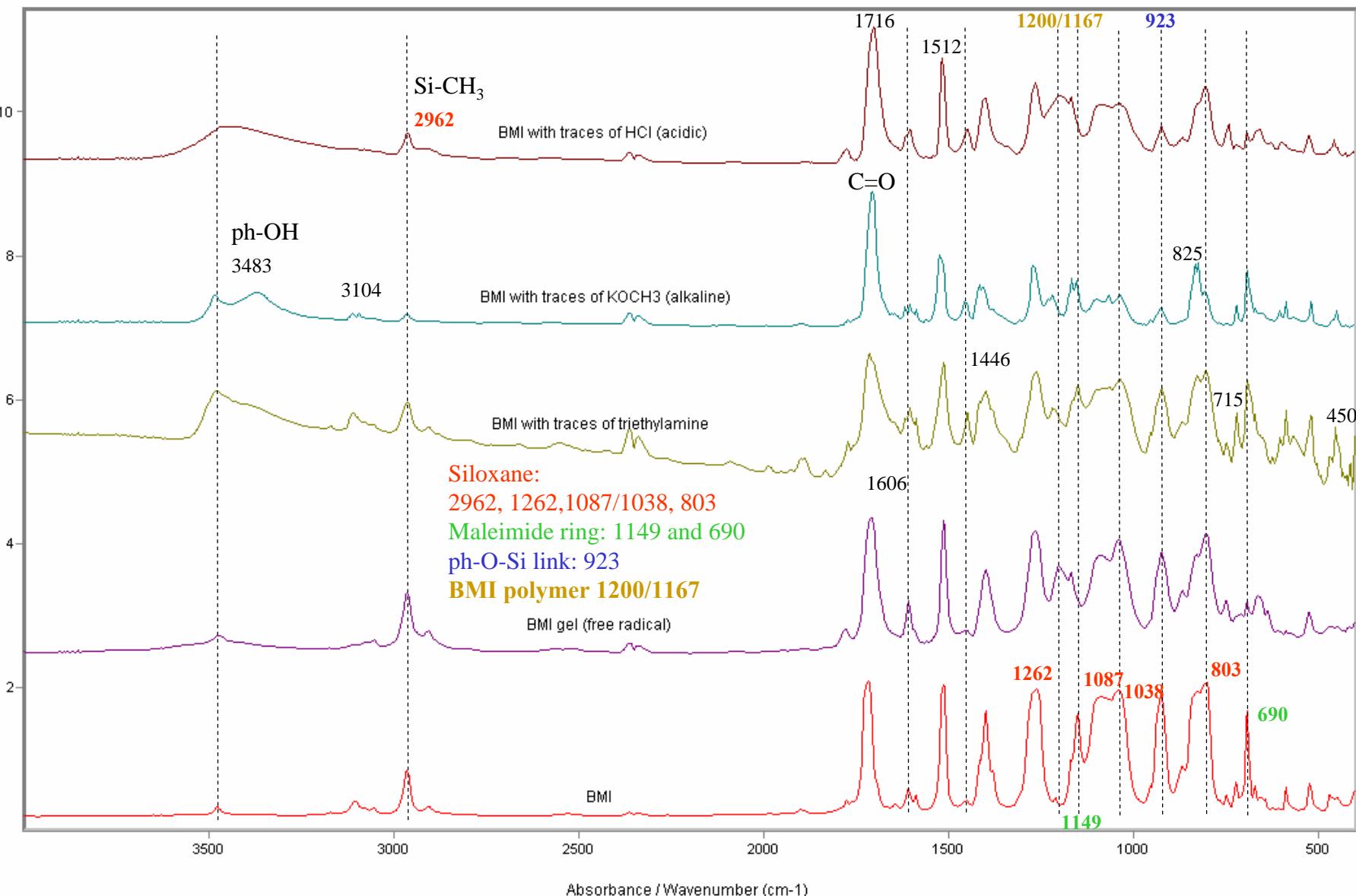


# Constituents of BMI, IR analysis



Nearly every band can be assigned

# BMI stability under different chemical conditions



Acidic is worse than alkaline, hydrolytic and free radical reactions

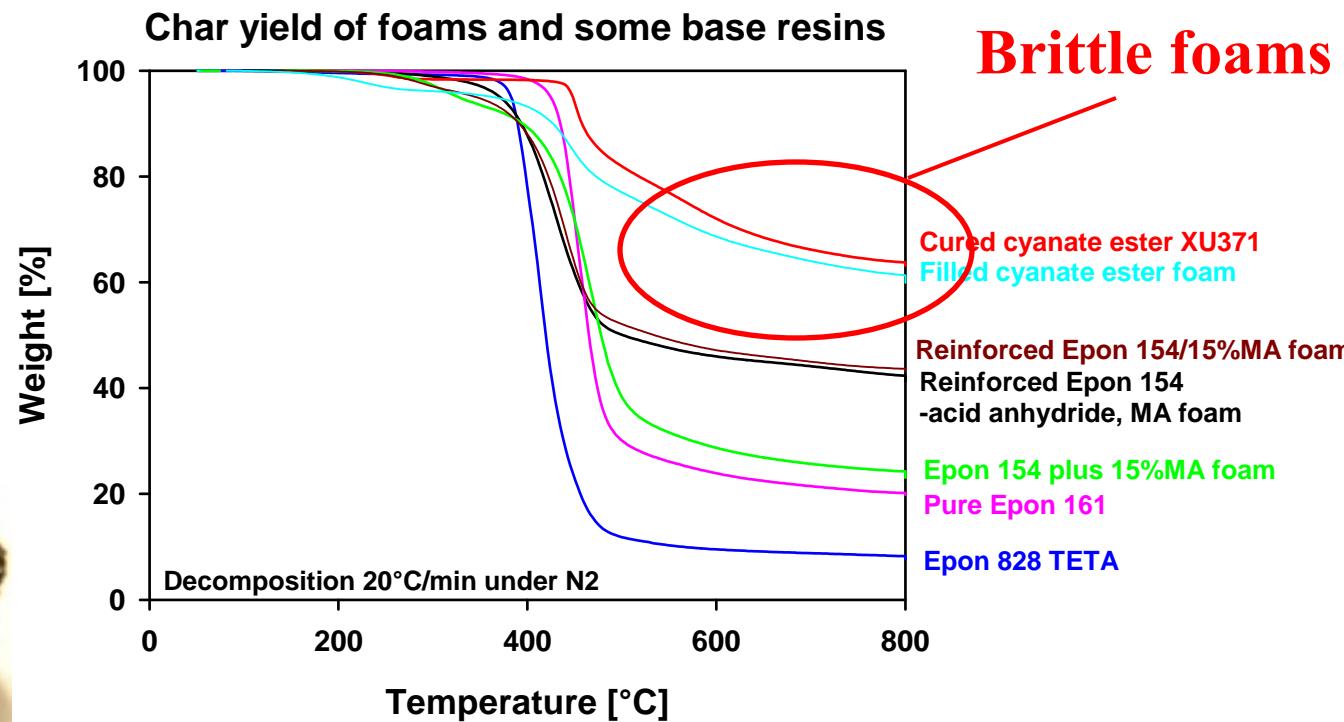
# Development of high temperature foam materials

**Challenge:** Synthesize foam materials with high char yield, low volatiles

**Safety relevant application:** Low gas yield, maintaining insulation properties



Pyrolysis will lead to a carbon foam at 800°C exposure



Issues: Resin selection, cure kinetics, thermal decomposition, improved toughness foam processing

**Issue:** When encapsulant foam materials decompose under abnormal thermal conditions, gaseous volatiles are produced resulting in deleterious pressure increases.

### Encapsulant Synthesis Process

$X + Y + Z$  resins + catalysis

+ surfactants:

- X,Y & Z: High char Epoxy, Urethane and Cyanate-ester reagents
- Hybrid chemistry/complex catalyzed cure
- Low defoaming action surfactants

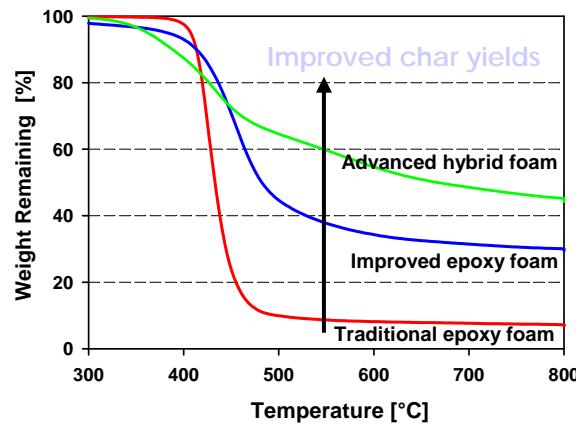
Process

Structure

Properties

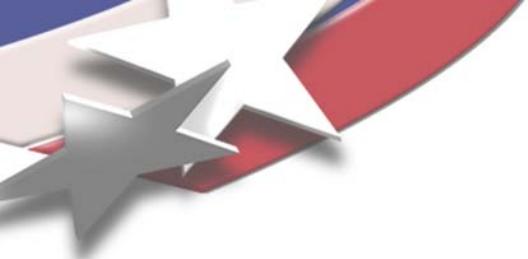
Process produces high-char foam encapsulants with structural strength and good adhesion.

Future work will focus on reducing shrinkage, delamination and controlled degradation at high T

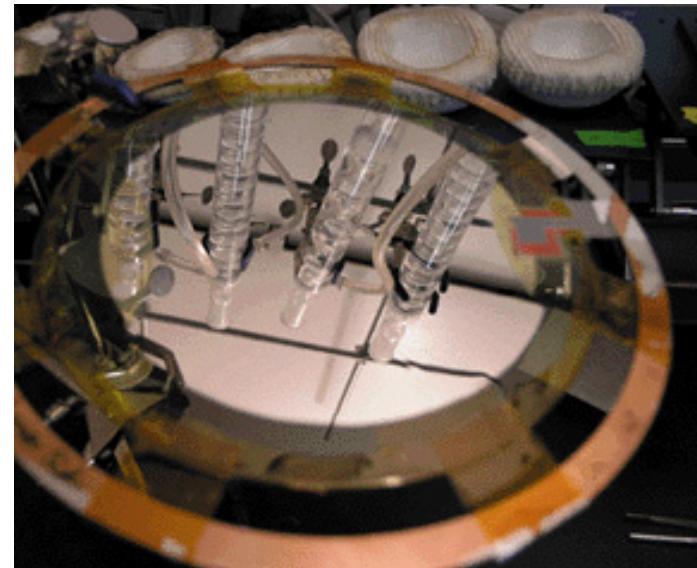


**New Hybrid Foam Encapsulant**  
(Prepared using curable system with CO<sub>2</sub> foaming agent)

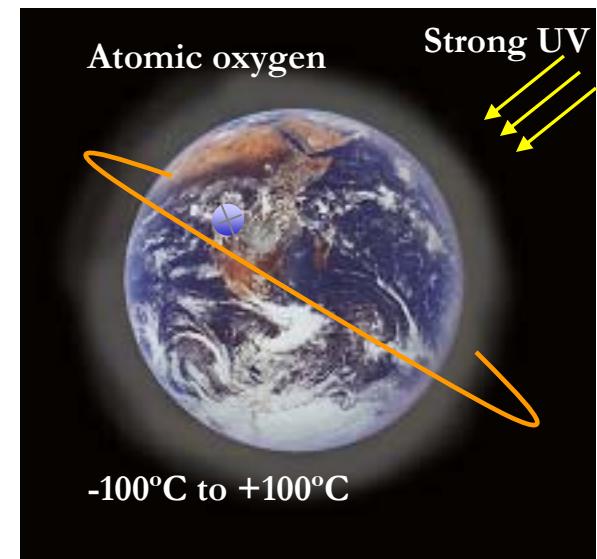
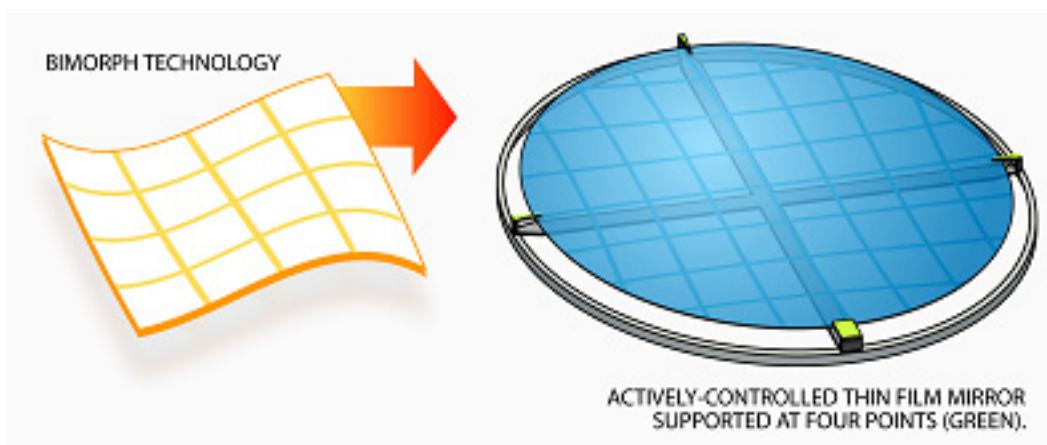
**Impact:** Through the selection of special resins, synergistic cure catalysis and non-traditional chemistry, we have developed a **hybrid foam material that is CO<sub>2</sub> foamed** and has considerably higher char than commercial foams.\*



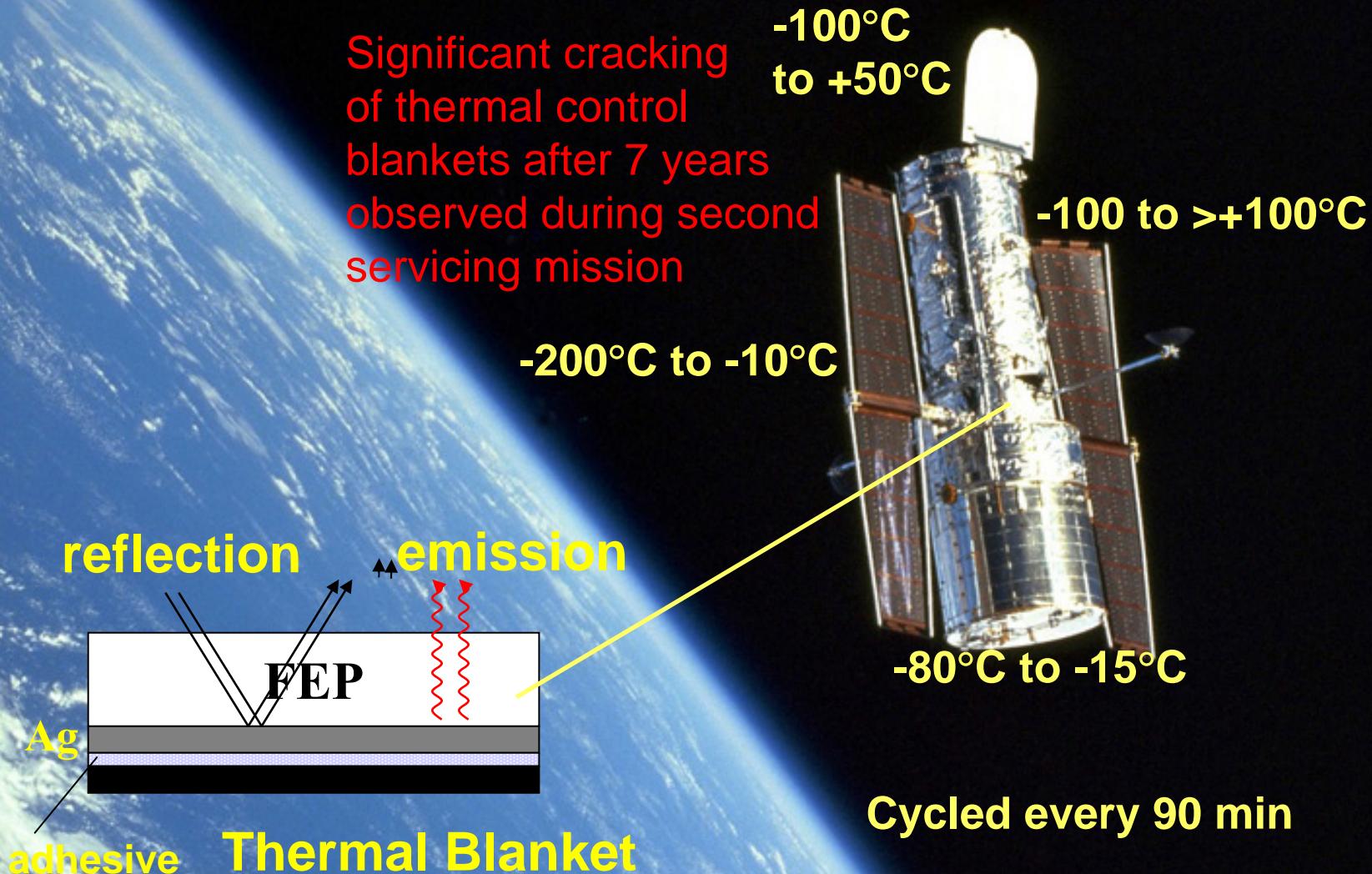
# Materials development for new applications in space

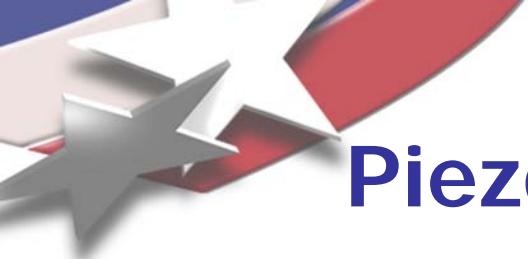


**Schematic of thin bimorph as an **active mirror**.**  
**Aim: achieve large apertures with low mass**



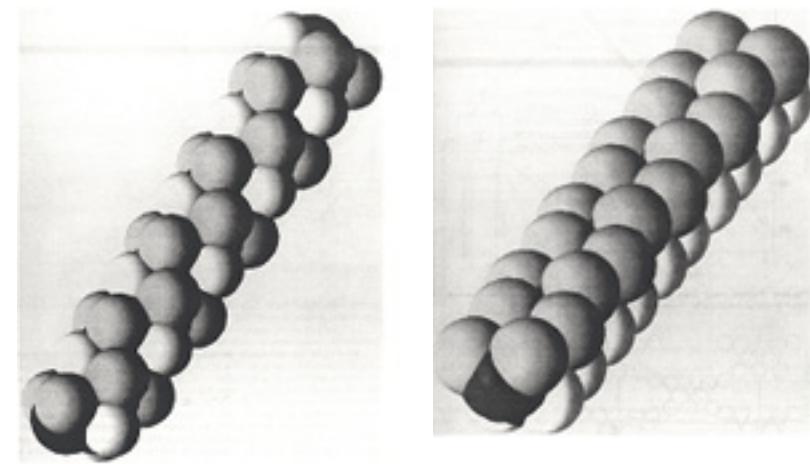
# Temperatures of FEP on HST





# Piezoelectric effect in polymers

- Piezoelectric effect in PVDF  $(\text{CH}_2\text{-CF}_2)_n$  discovered 1969 by Kawai
- Attributed to dipoles in certain crystalline phases



*trans-gauche*  
non-polar  $\alpha$ -phase

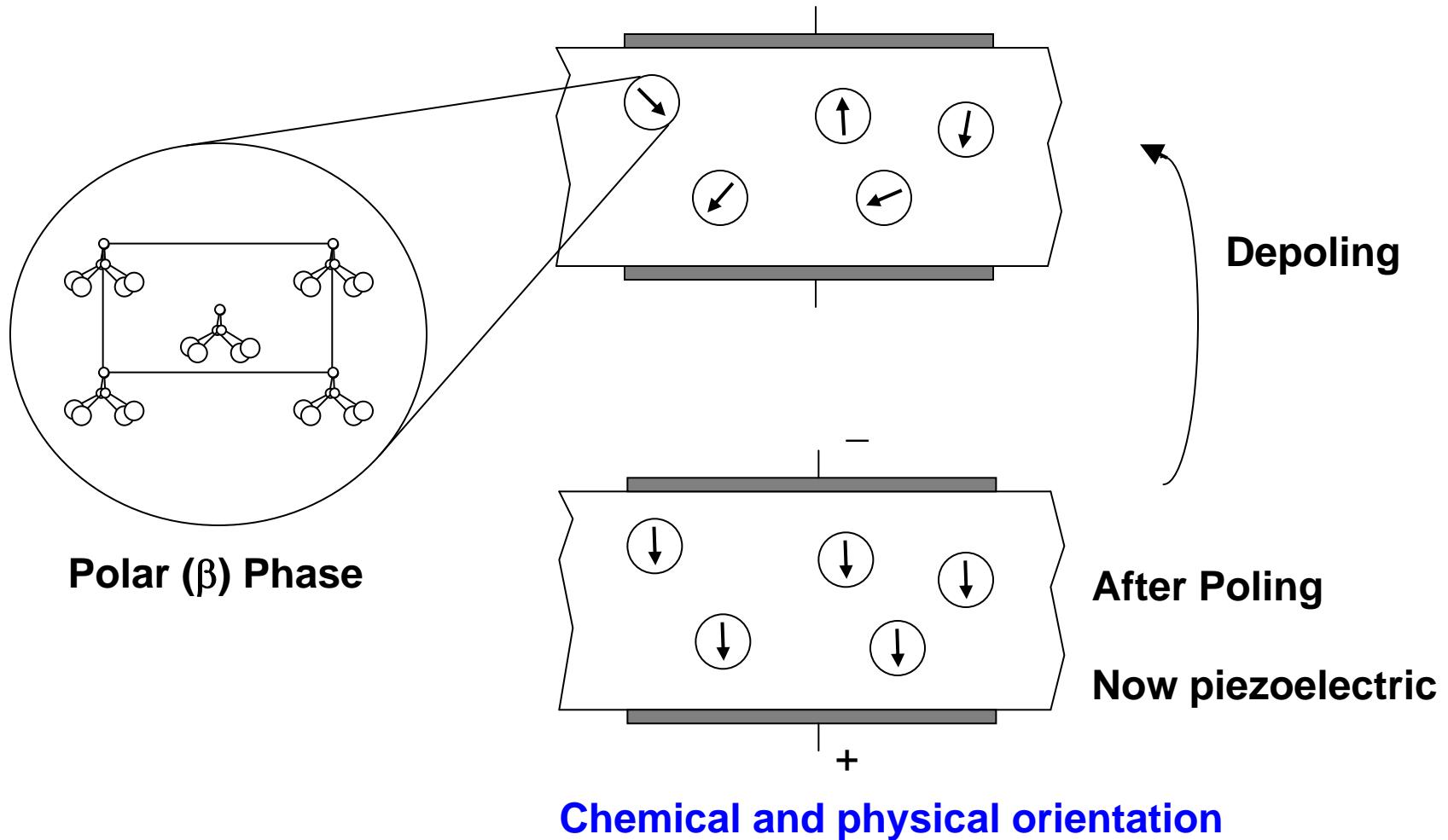
*all-trans*  
polar  $\beta$ -phase



Stretching or chemical means

Source: Kepler, R.G. Ferroelectric, Pyroelectric, and Piezoelectric Properties of Poly(vinylidene Fluoride), In Ferroelectric Polymers 1995

# Poling - permanent orientation of dipoles



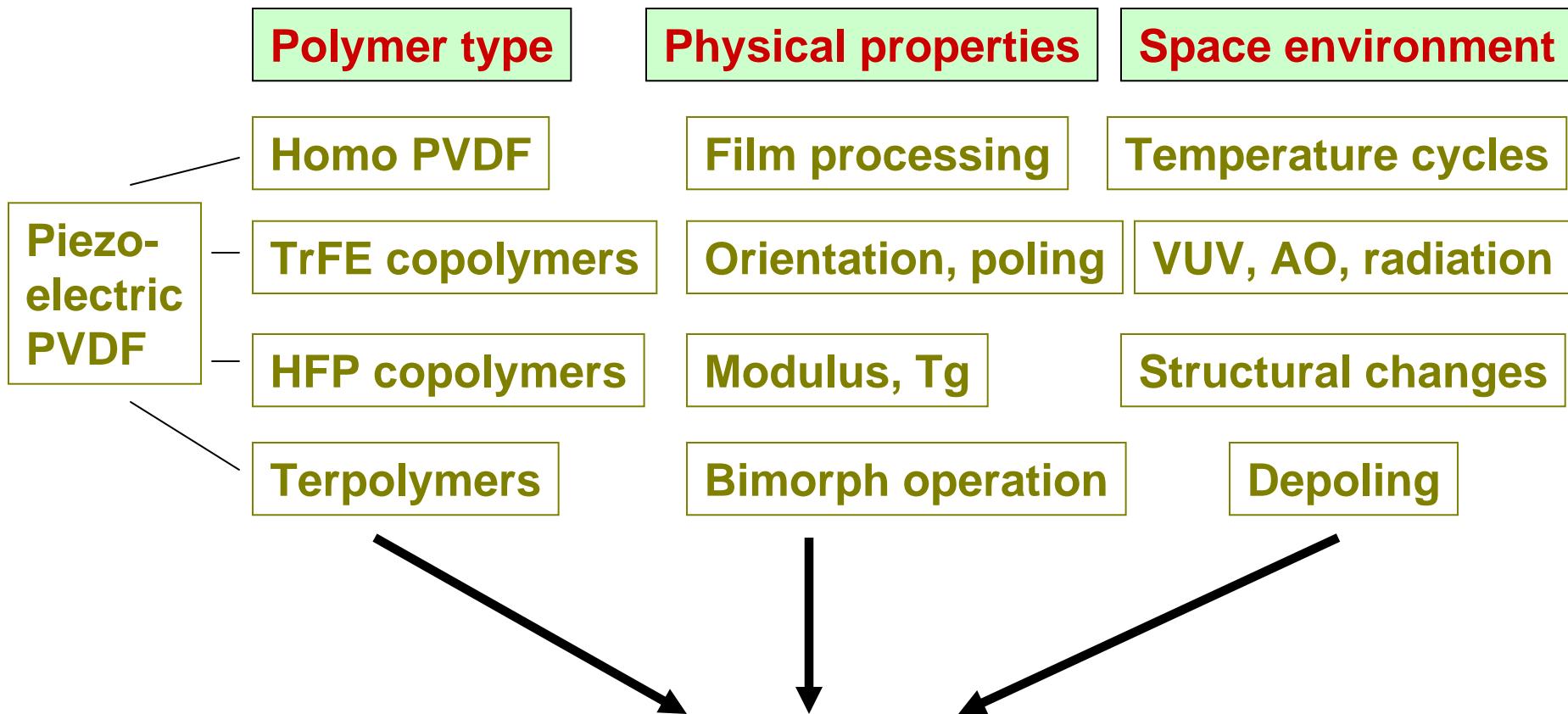


# What are the issues for piezoelectric PVDF film performance in space ?

- Many PVDF based polymers to chose from
- Different film manufacturers and processing conditions
- Different approaches for poling to make them piezoelectric
- Molecular structure, chemistry, physics, processing issues
- How do they vary? Which material is a suitable candidate?
- What is their performance in space?
- What are the environmental conditions?
- How do we monitor any degradation?
- What are the leading causes for failure?
- Are there better materials than using type XYZ off the shelf?
- **Aim: Select compromise material with optimized desirable properties and understand long-term performance in space**

# High performance PVDF selection

- Many variables needed to be evaluated
- Composition, poling features and degradation



Material selection and performance optimization

# Polymer evaluation in space - LDEF + MISSE

**LDEF: Long Duration Exposure Facility (1980's)**

**MISSE: Materials International Space Station Experiment**

- ❖ Passive samples, active components and data feed
- ❖ Exposure with 6-8 months missions in LEO



<http://misseone.larc.nasa.gov>

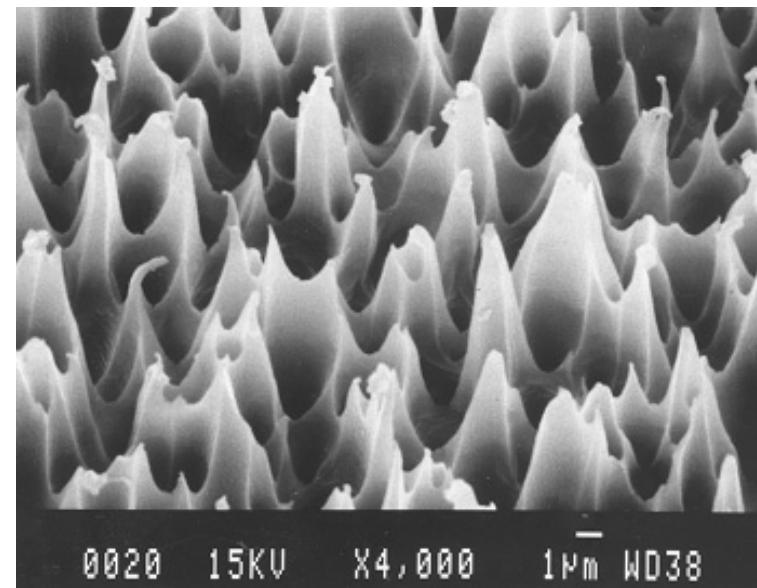
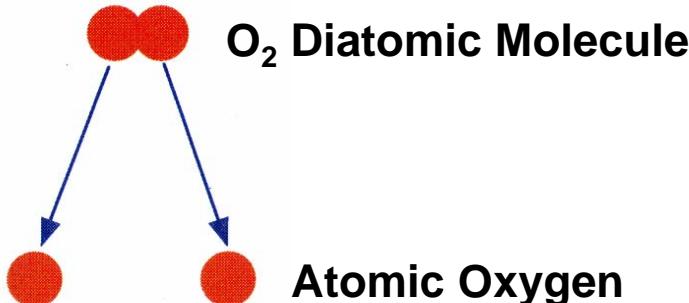
# Atomic Oxygen in Low Earth Orbit

Photodissociation of  $O_2$

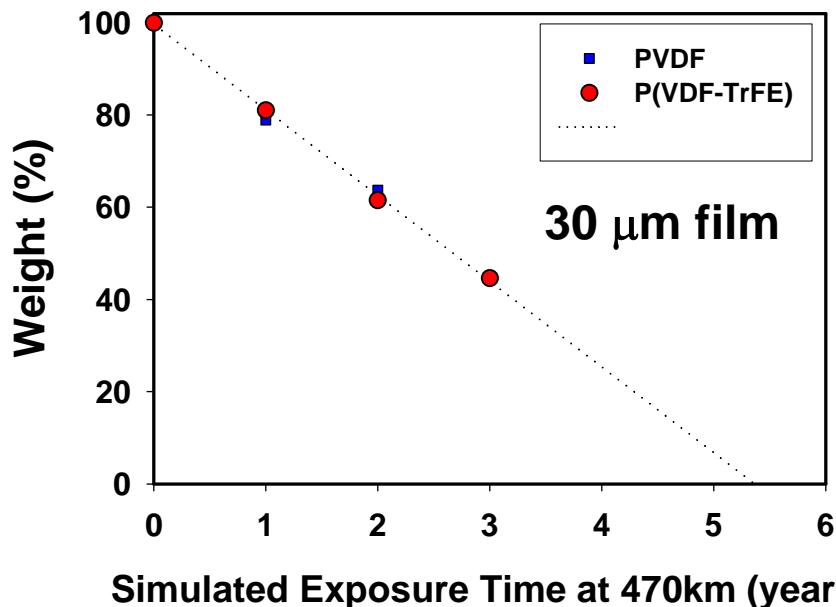


- AO is the predominant species from 200-650km
- The average ram  $\sim 4.5\text{eV}$

UV  
 $E = h\nu > 5.12 \text{ eV} (< 243 \text{ nm})$



# Erosive damage - Weight loss



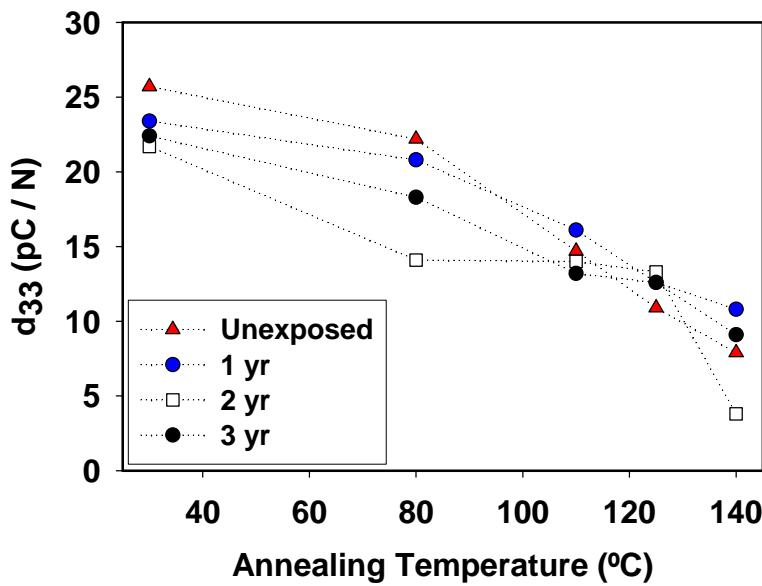
**Erosion Rates:**  
 $2.5-2.8 \times 10^{-24} \text{ cm}^3/\text{atom AO}$



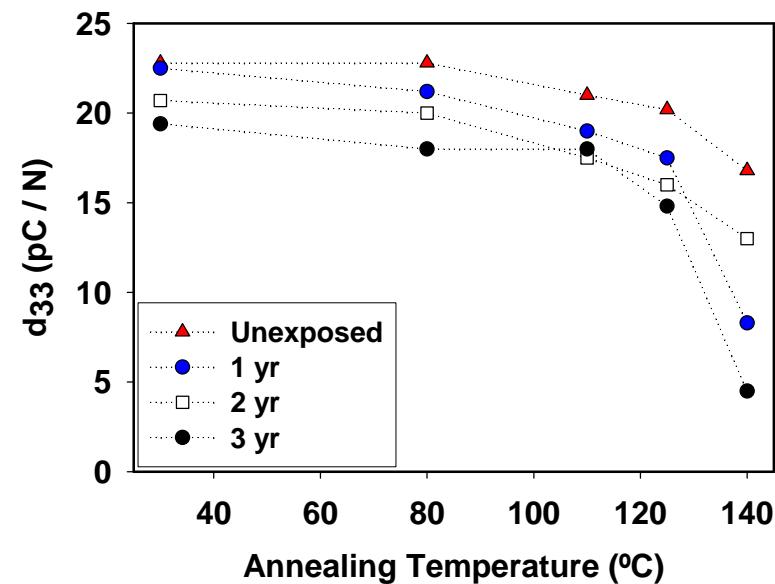
**30μm film completely lost within 5 years**  
**Lifetime for operation 3 years ?**

# Effect of AO/VUV on high-temperature stability of piezoelectric properties

PVDF homopolymer



TrFE Copolymer



Limited loss of  $d_{33}$  in bulk material (mostly due to T)

Also: Only limited morphology changes as studied by DSC

# From lab to applications

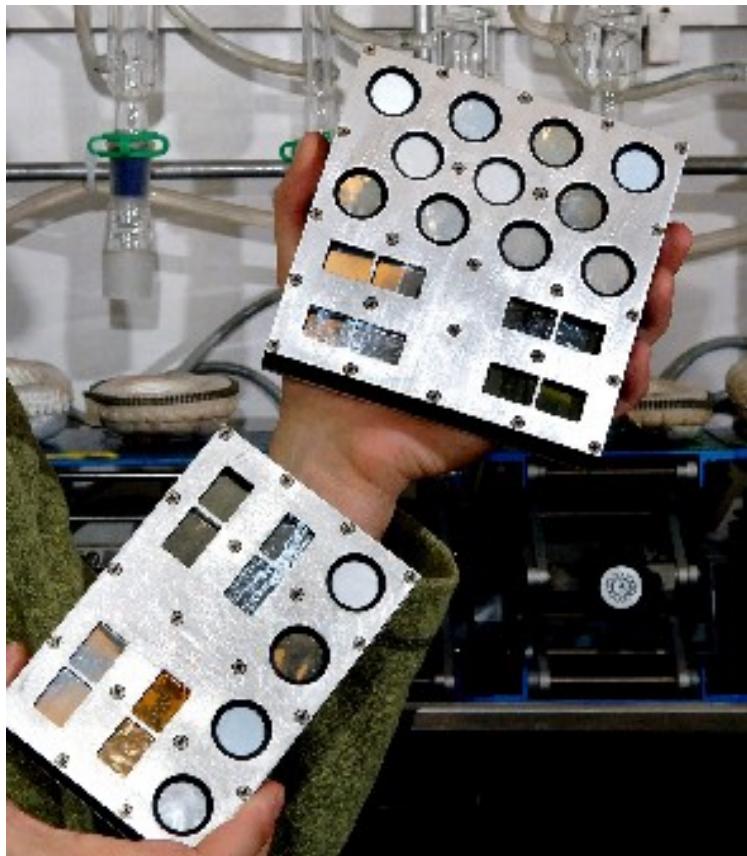
- **Ground testing: Required for pre-selection**
- **Enabled understanding of degradation pathways**
- **Absolutely critical to assess material suitability**
- Thermal stability (depoling): TrFE > PVDF
- Materials relatively insensitive to VUV
- Change in  $d_{33} \propto$  to electromechanical performance
- AO erosion rates significant, but only minor bulk changes, piezoelectric features unaffected
- Modulus is important and depends on temperature

## Next:

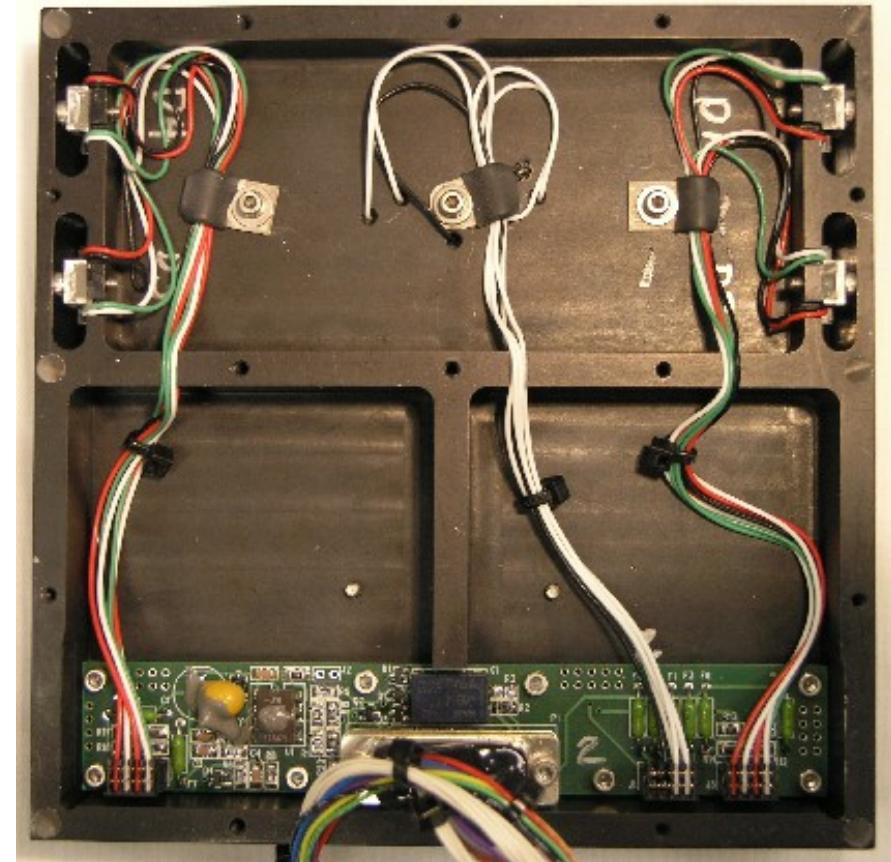
- **MISSE-6: compare ground testing with space exposure, in-situ materials evaluation, explore synergistic effects**
- **Provide performance feedback for systems engineering**

# Novel experiment in space

- Different polymer types, bimorphs and coatings
- Passive film samples and active film deformation
- Monitor degradation and performance in LEO



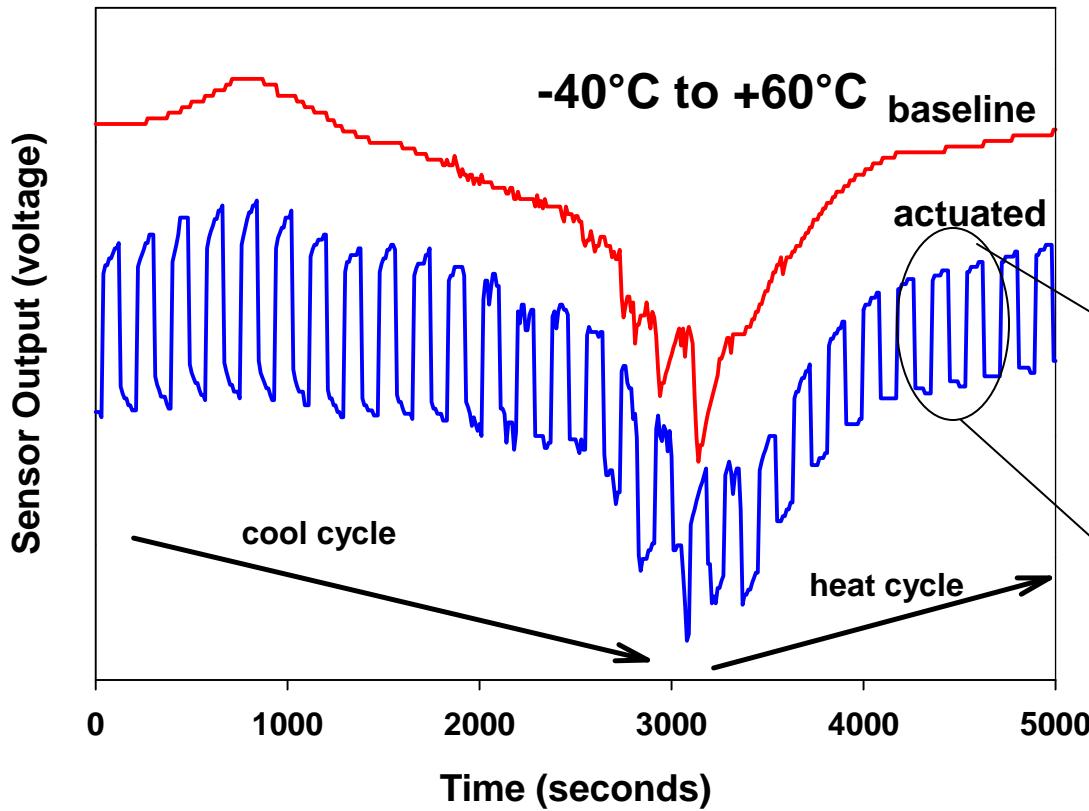
2 units, VUV and AO exposure



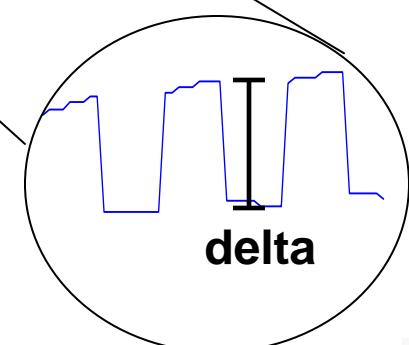
Timed HV excitation and data acquisition

# Photo-microsensor detection of bimorph position

- Monitor performance with cumulative LEO exposure



- Remote monitoring
- Change in delta with time in LEO will provide performance feedback.

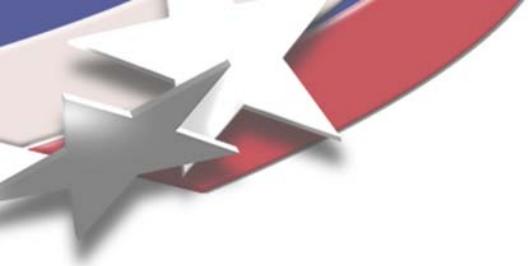


# Deployment of 3 SNL experimental units aboard the ISS

- **Significance:** First active experiments in space evaluating long-term performance of piezoelectric PVDF polymer films



SNL experiments will be deployed in Dec. 2007



# Acknowledgements

**Thanks for collaboration and a creative team environment are due to:**

**Ken Gillen, Roger Assink, Roger Clough, Jim Aubert,  
Tim Dargaville, Leanna Minier, Julie Skutnik**

**Many years of DOE/DoD funding:**

**Sandia is a multiprogram laboratory operated by Sandia Corporation,  
a Lockheed Martin Company, for the United States Department of Energy's  
National Nuclear Security Administration under Contract DE-AC04-94AL85000**



# Did you recognize this picture ?

Yes! The famous picture from the Al Gore movie!

**“An inconvenient truth!”**

**Space is an unfriendly environment**

