Luna Innovations seminar
August 18 2008

SAND2008-5312P

Robert Klein
Graduate and postdoctoral work

PENNSTATE 1855

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COLLEGE OF EARTH AND MINERAL SCIENCES

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NSLS
NATIONAL SYNCHROTRON LIGHT SOURCE

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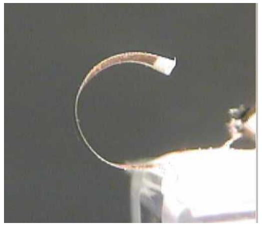
CHEMICAL ENGINEERING

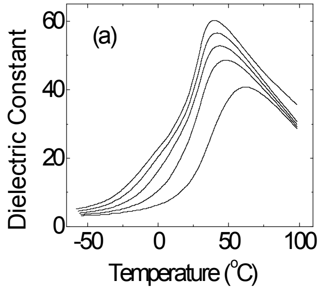
(undergraduate)

***Advisors**

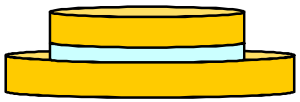
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Highlights of my past and present research in organic materials



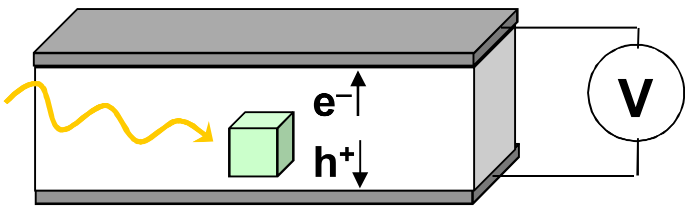


PVDF-based terpolymers for electroactive transducers and high ε capacitors

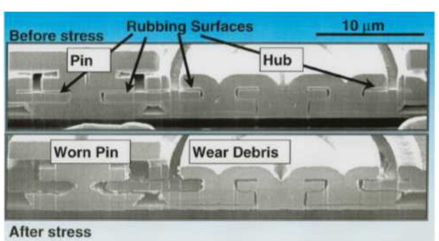


$\varepsilon^*(f, T)$

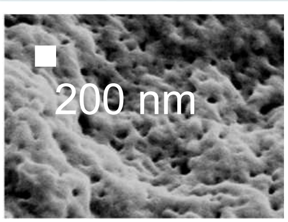
Polymer and ion dynamics in ionomers and polymer electrolytes

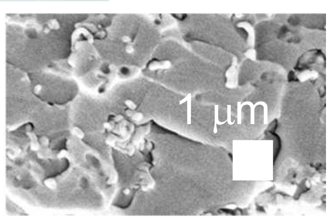


Radiation tolerance in polymer dielectrics*



Self-assembled monolayers for anti-stiction in MEMS

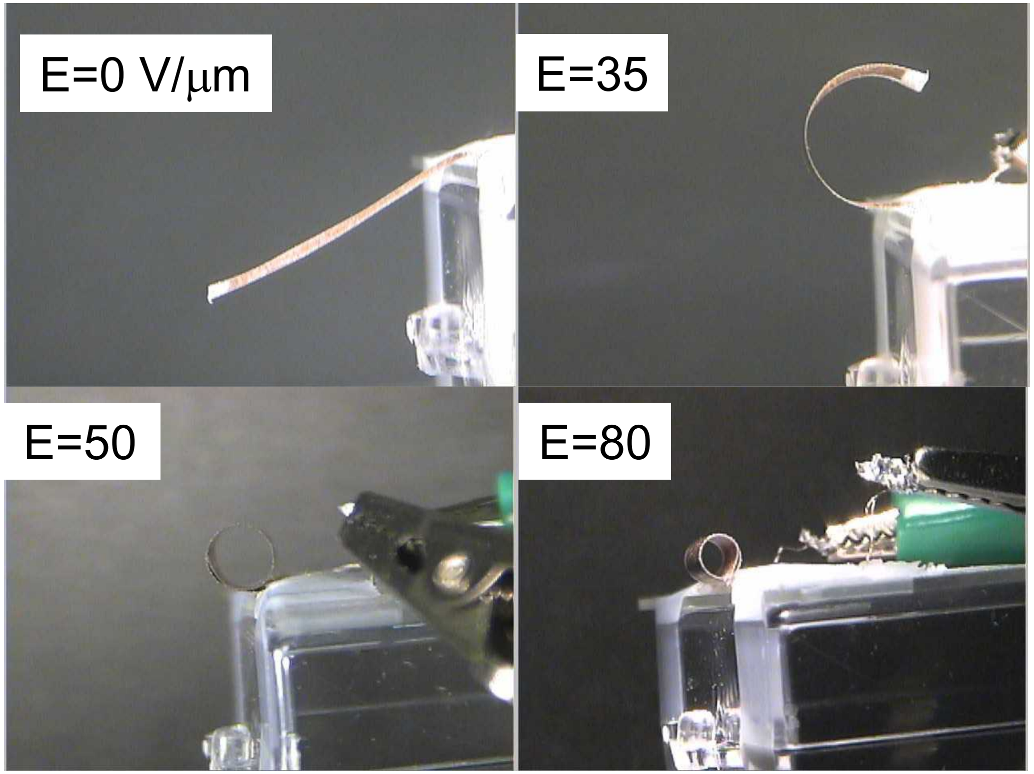




Polymer composites: porous and alumina filled epoxies

Modified PVDF-TrFE offers a high dielectric constant and very high electroactive strain

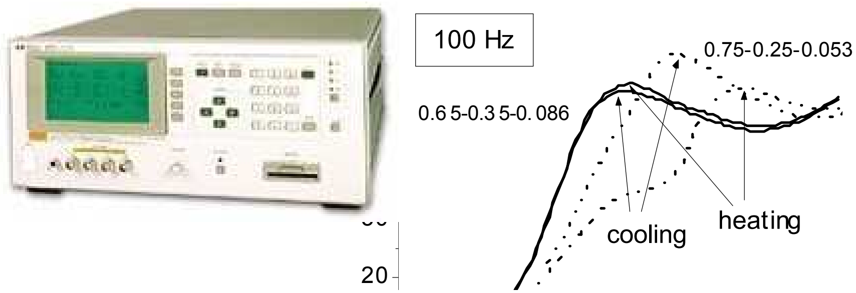
Unimorph: thickness 21 μm, length 22 mm



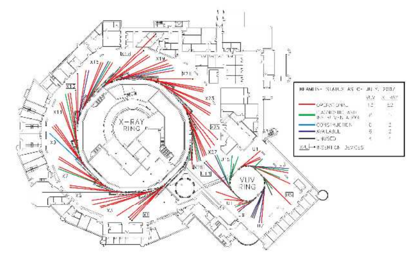
P(VDF-TrFE-CFE) 62/38/4 Terpolymer

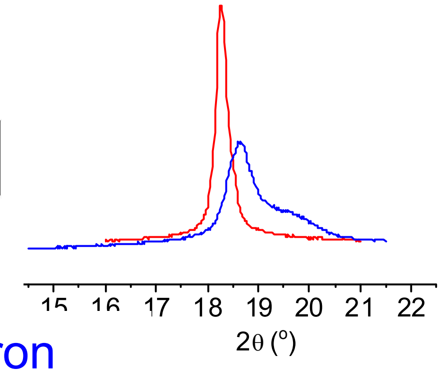
Source: Qiming Zhang, PSU

PVDF-based EAPs and dielectric materials: Characterization techniques

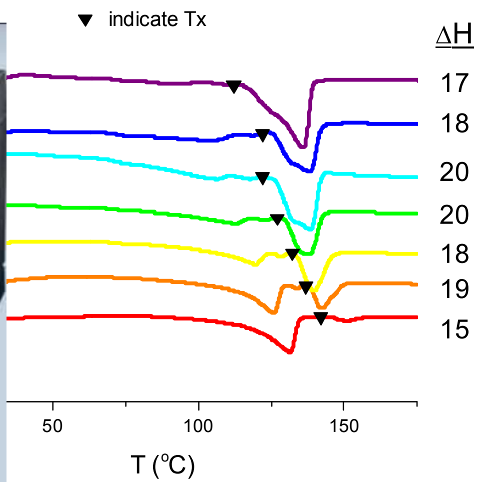


HP 4284A dielectric analyzer with temperature chamber



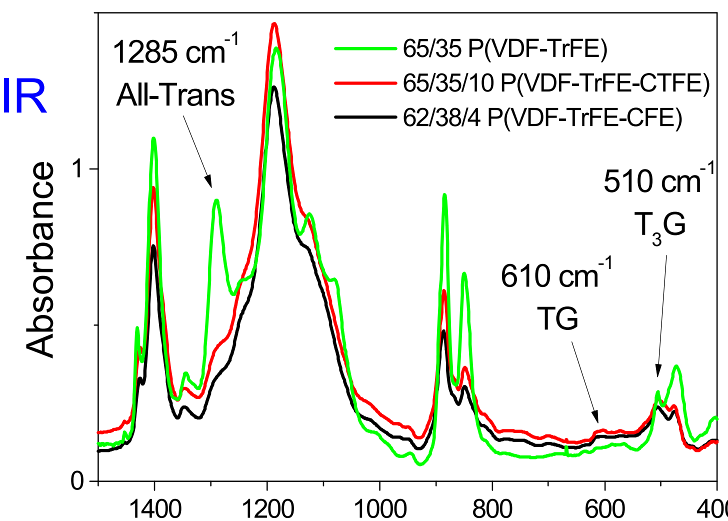


WAXD by synchrotron (Brookhaven) and Cu-Kα



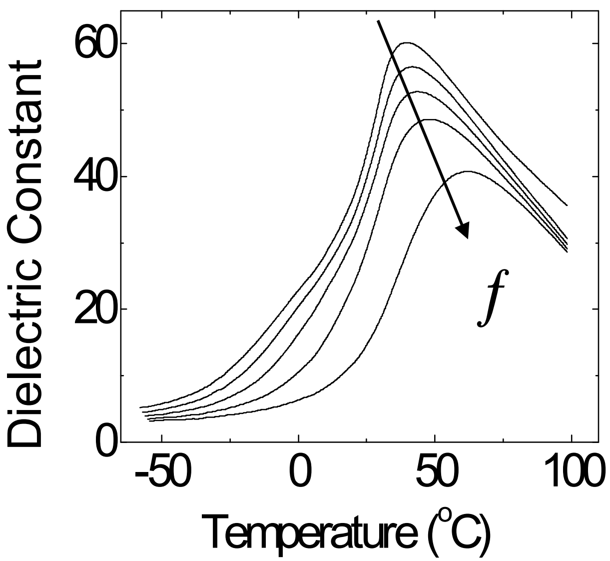
DSC

FT-IR

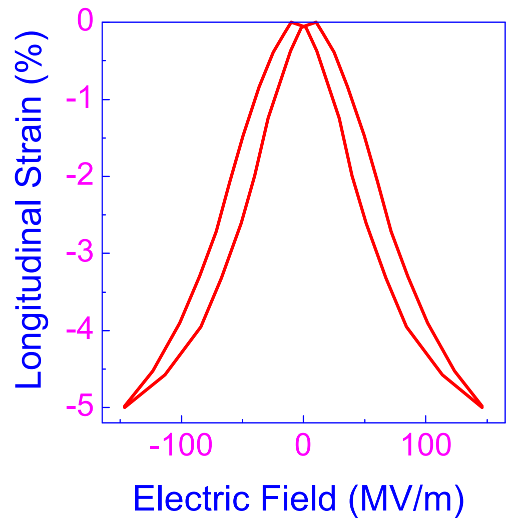


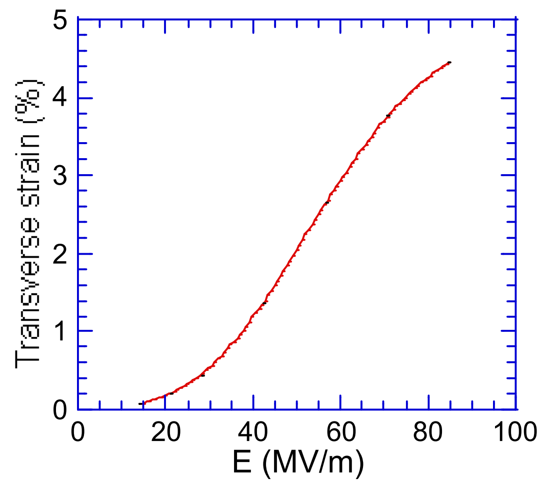
Strain measurement device (high voltage electrodes, laser interferometer, lock-in amplifier)

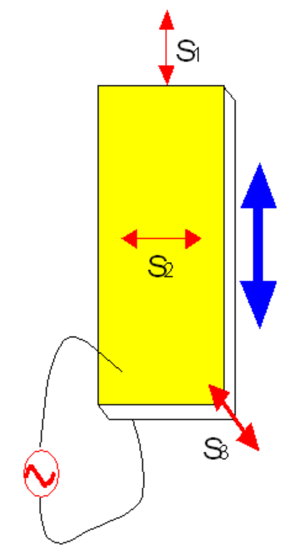
Modified PVDF-TrFE offers a high dielectric constant and very high electroactive strain



High ε increases EAP efficiency and makes a good capacitor







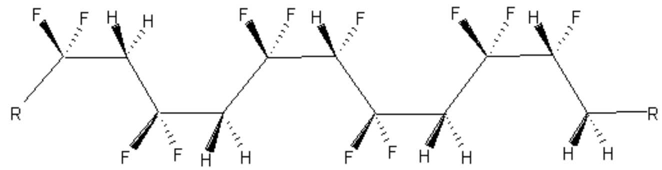
P(VDF-TrFE-CFE) 62/38/4 Terpolymer

PVDF-based EAPs and dielectrics

Controlled defects in the polymer chain enhance the morphological transitions

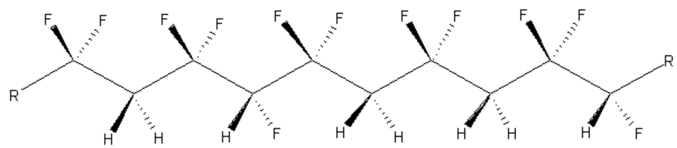
at 25 ^{o}C

PVDF: α phase



(can be poled to β phase, but permanent transition = ferroelectric)

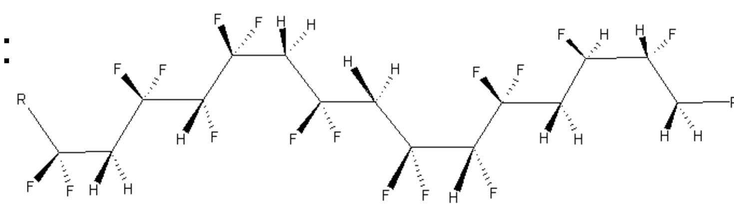
PVDF-TrFE: β phase, with large domains



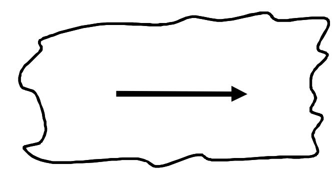
(transitions to α phase upon heating = ferroelectric and paraelectric)

Add irradiation or chemical defects

Defected PVDF-TrFE: β+γ phases, with small domains



(transitions to β phase upon electric field = relaxor ferroelectric)



Macroscopic strain

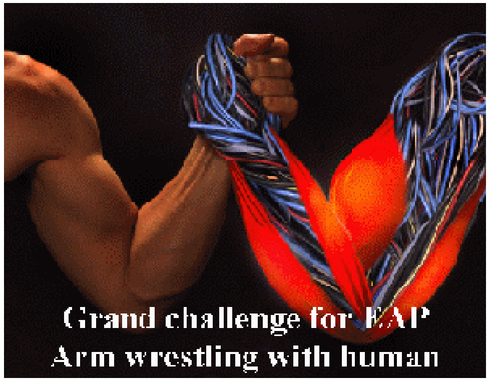
PVDF-based EAPs and dielectric materials: Future directions

Variations on the PVDF-terpolymer are being commercialized now for capacitor applications (Strategic Polymer Sciences, Inc.)

Still room for improvement on the PVDF-based chemistry:

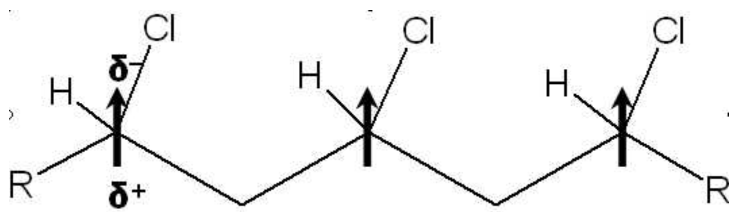
- EAPs of this material are excellent in terms of response time and max strain

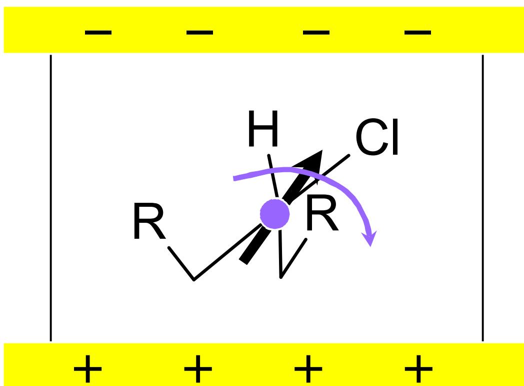
  (Better than wet EAPs, silicones, conductive doped polymers, piezoelectric ceramics)
- But the voltage requirements are too high (kV/device) and the electrical properties have large T dependence

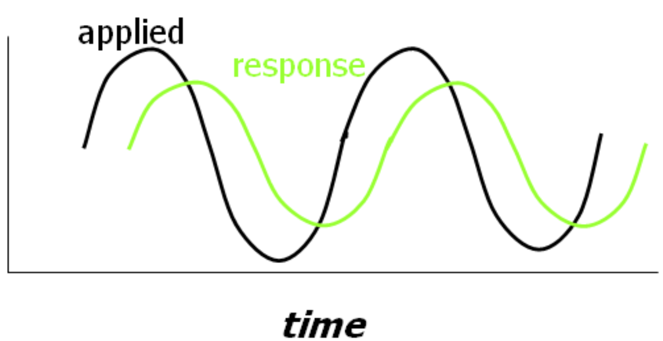


eap.jpl.nasa.gov,
Yoseph Bar-Cohen

Polymer dynamics have important impact on mechanical properties and conductivity







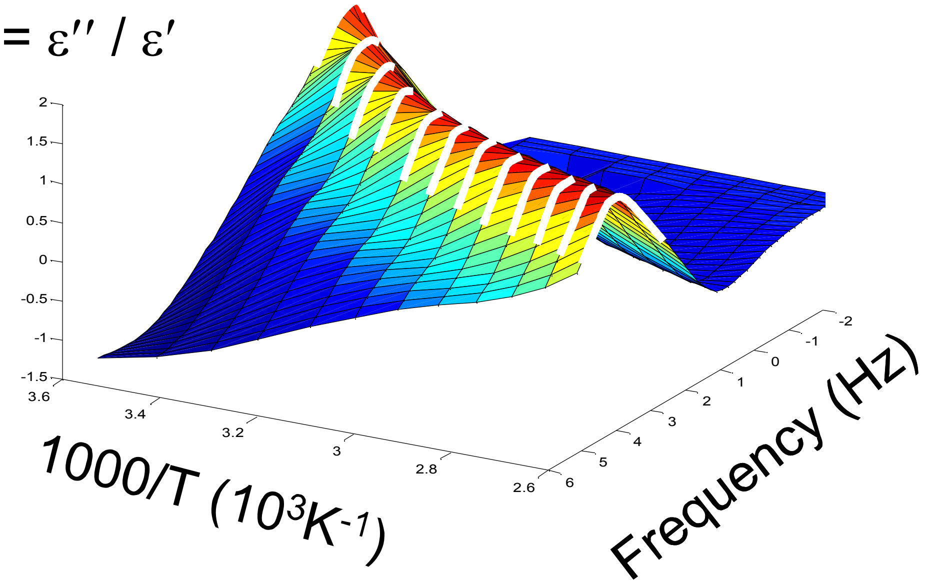
Ability to rotate or translate with field is related to:

- Polymer T_g
- Local (β) relaxations (e.g., in PMMA)
- Ion transport
- Liquid crystal transitions (e.g., smectic to nematic to disordered)

Dynamics in ion-containing polymers: Characterization techniques

Novocontrol broadband dielectric analyzer with temperature controller

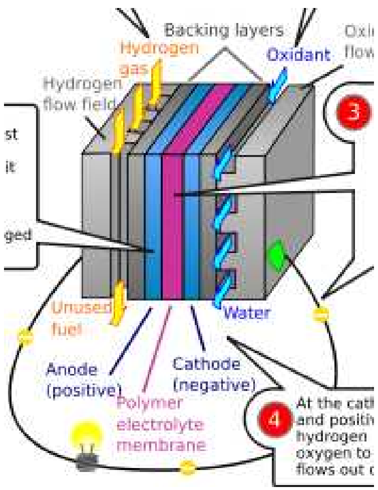
$\tan \delta = \varepsilon'' / \varepsilon'$



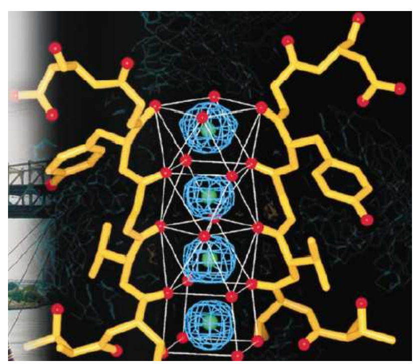
DSC, FTIR, DMA (T_g behavior, coordinated state of oxygen species)

Ion transport is dependent on ion-polymer interactions and polymer dynamics

Battery electrolytes
(secondary Li batteries)



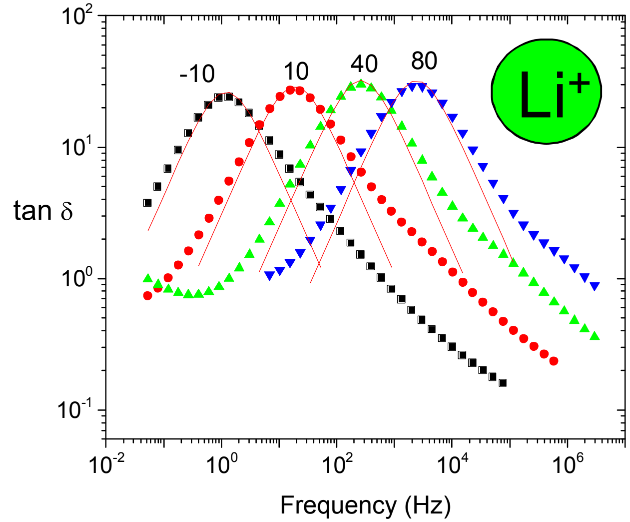
Fuel cell
membranes

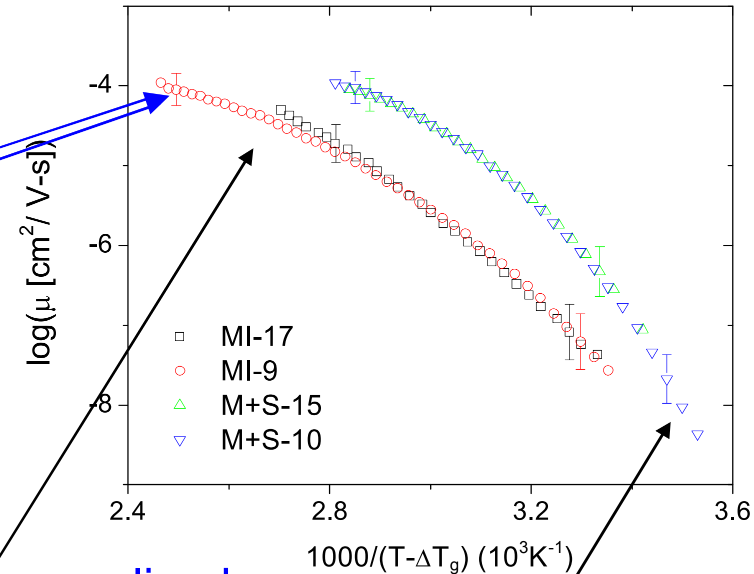


Biological ion
channels

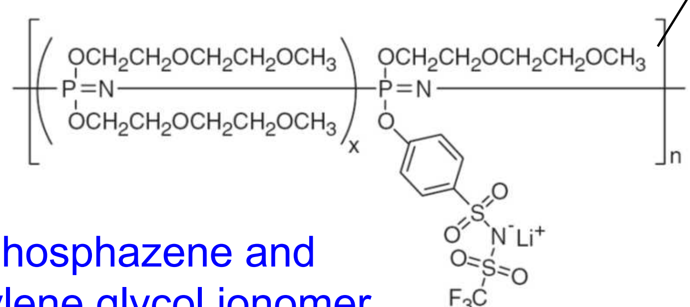
Sources: Wikipedia, Nature v418 p268

Ion and polymer dynamics are typically coupled

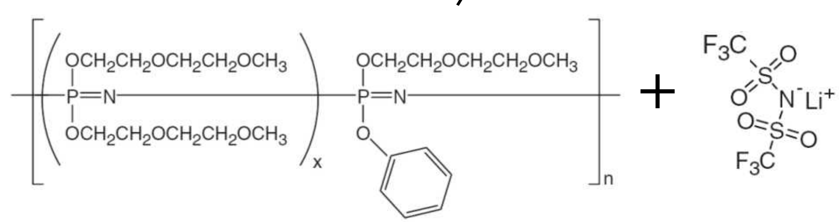




Mobility of ions normalized by T_g collapse by chemistry



phosphazene and ethylene glycol ionomer



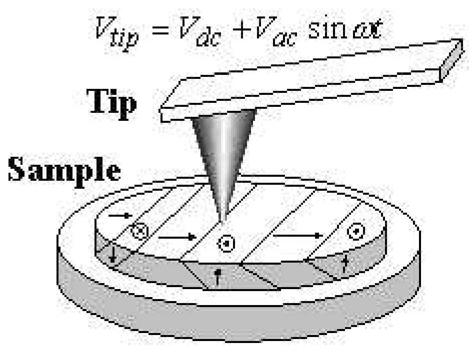
phosphazene and ethylene glycol polymer with added salt

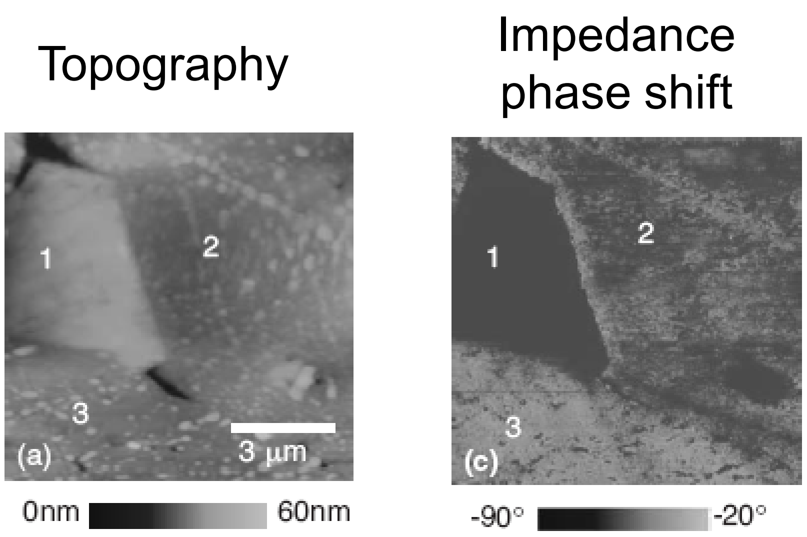
Dynamics in ion-containing polymers

Dielectric spectroscopy of polymers: Future directions

Dielectric spectroscopy will continue to be an important technique for polymers, especially in the membrane and ionic transport fields

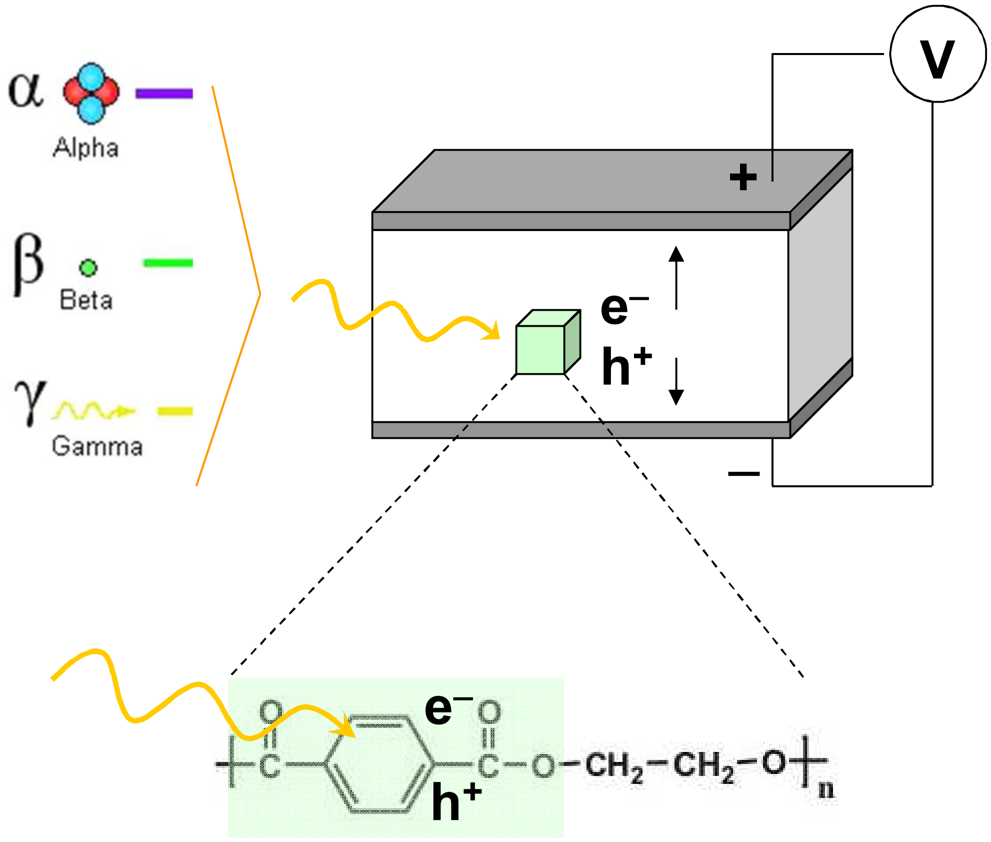
In particular, combination of smaller probes (AFM or micro-contacts) with dielectric analyzers will provide key interfacial and surface information





nanotransport.ornl.gov/Research/nanopfm.html, Shao et al 2004 JJAP

Ionizing radiation degrades dielectric capability by forming electrons and holes

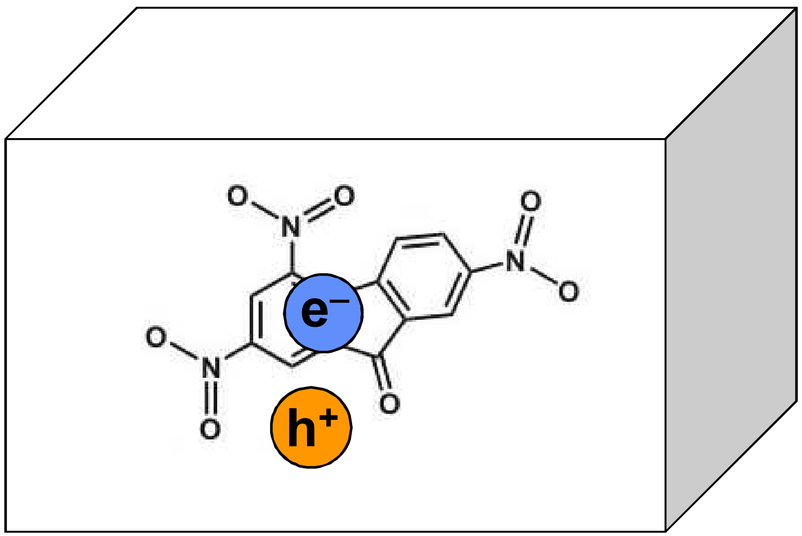


Electric field leads to charge separation, degrading charge storage

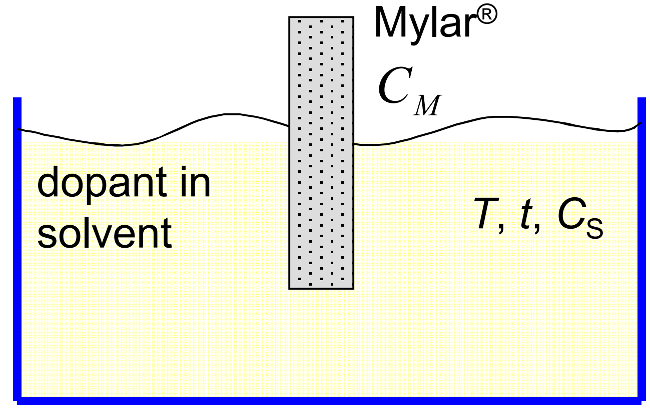
Probable interaction site in poly(ethylene terephthalate)

By adding an electron trap to the polymer, we reduce RIC to a working level

A deep electron trap reduces RIC by pinning the electron until it recombines with a hole

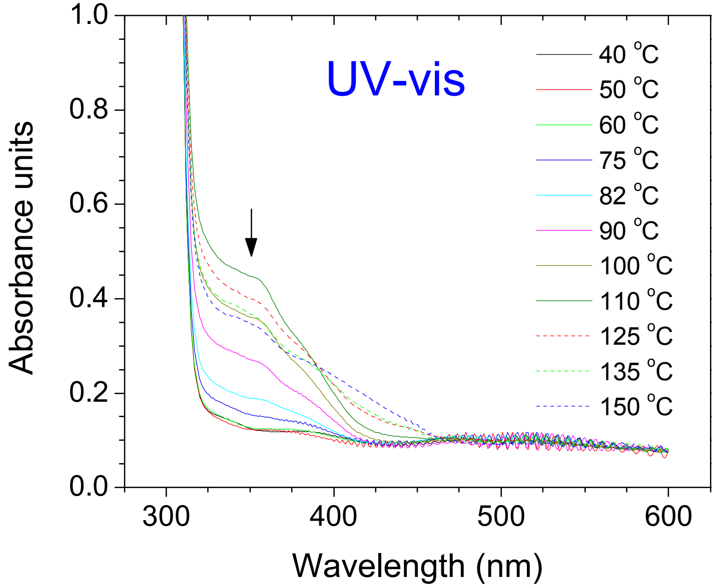


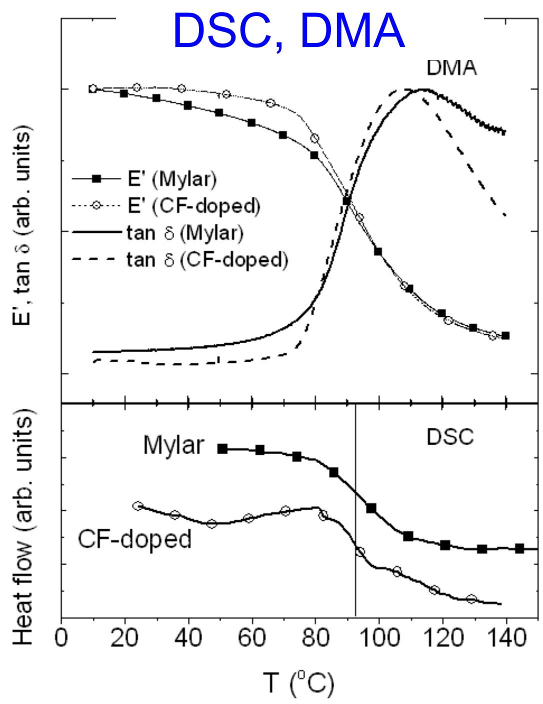
in Mylar film (PET)

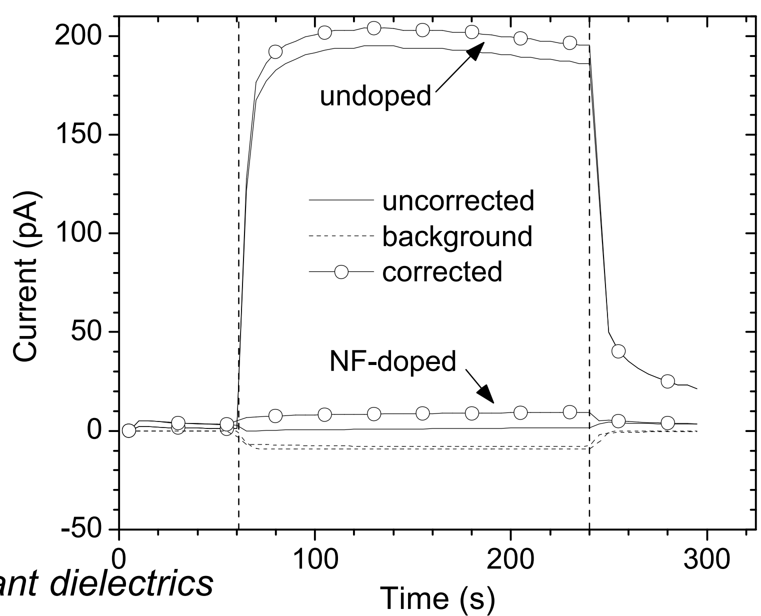


We add electron traps by by dissolving dopant in solvent and immersing film above T_g

Radiation tolerant dielectrics: Characterization techniques





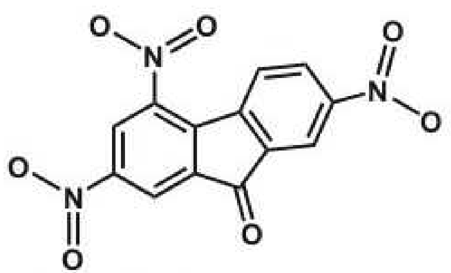


High flux radiation sources with electrical analyzers

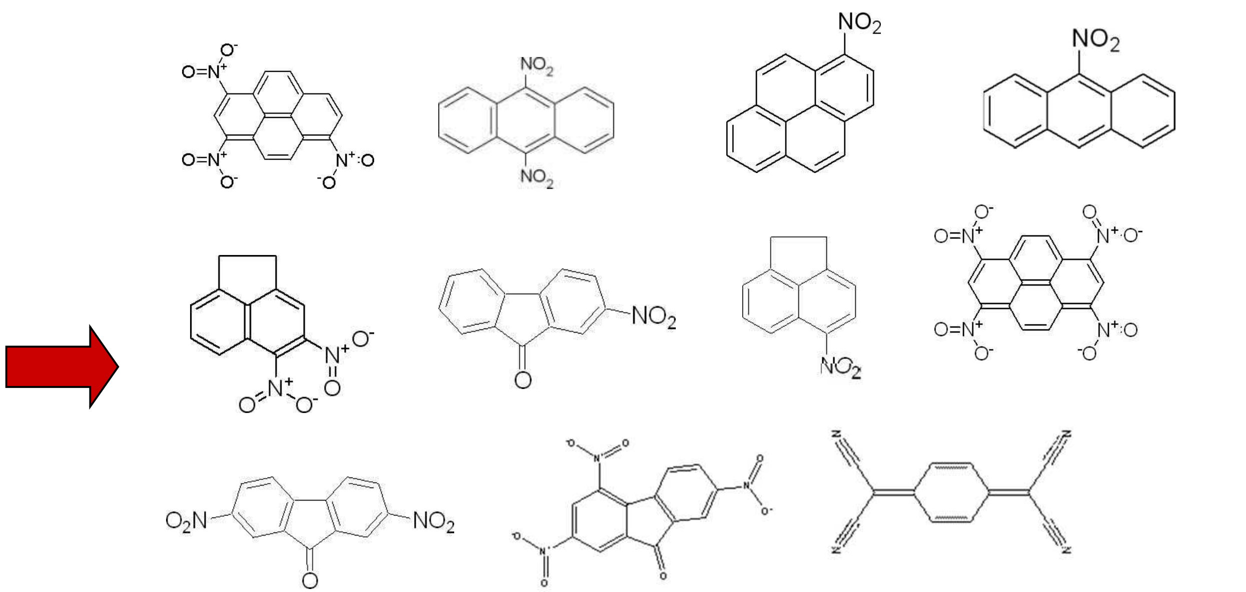
Radiation tolerant dielectrics

Recent work in radiation tolerant dielectrics

1) Expanded viable dopant list from 1 to >10
2) Constructed pilot plant for processing large batches
3) Established dopant chemistry link to radiation tolerance
4) Modeled kinetics and thermodynamics of doping process on theoretical basis



TNF

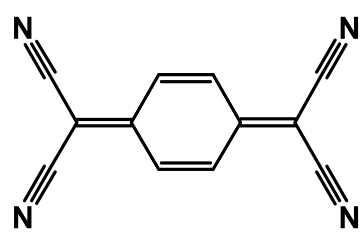


1) TNF classified as an explosive in late 1990's and external vendors will no longer use
2) Process not optimized and expensive
3) Ethylene glycol selected as solvent without clear understanding

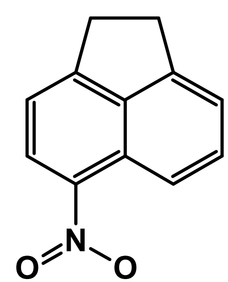
Several small molecules have capability to reduce RIC significantly

Lenhart *JAP* 2008: 30 rad/s

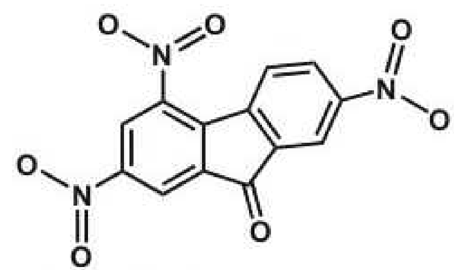
Dopant	Conc. dopant (mol/m^3)	RIC (pA)	RIC reduction (%)
none	0	204	0
TCQM	1.1	29	86
NAN	14	14	93
TNF	50	3.0	98



Tetracyanoquinodimethane (TCQM)



Nitroacenapthene (NAN)



Trinitrofluorenone (TNF)

Recent work in radiation tolerant dielectrics

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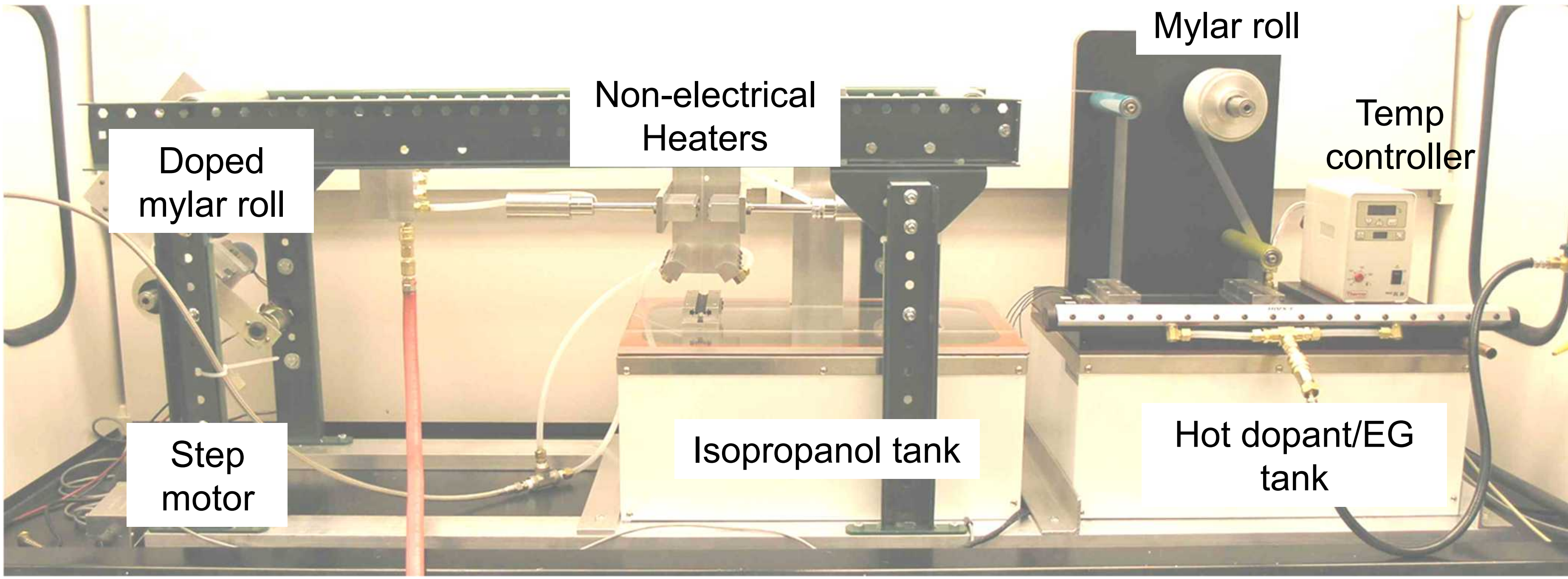

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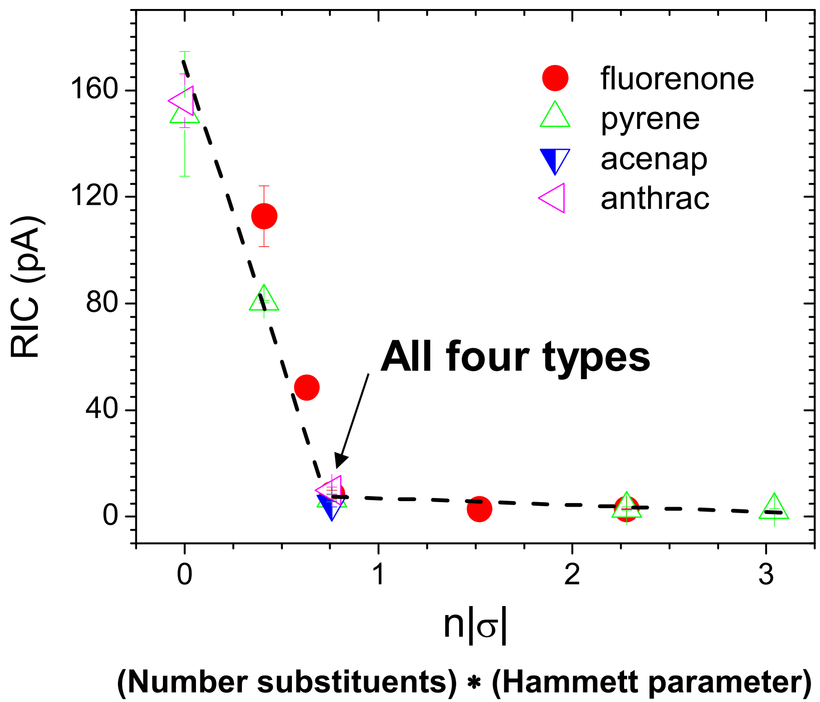
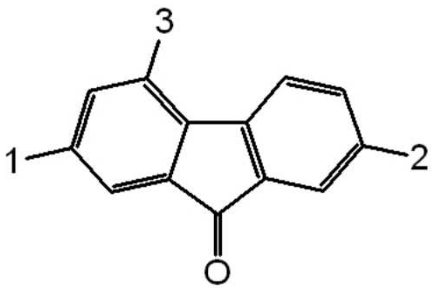
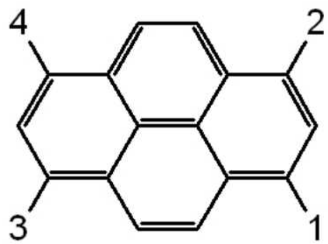


Predictive model for impact of substituent

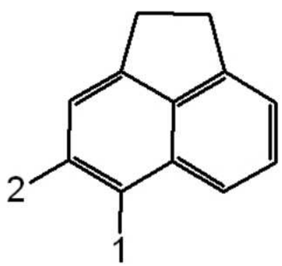
We selected dopants with conjugated cores and electron-withdrawing groups



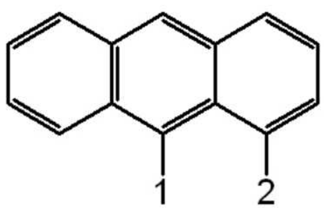
Fluorenone (F)



Pyrene (P)

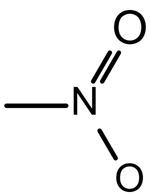


Acenaphthene (Ac)



Anthracene (Ant)

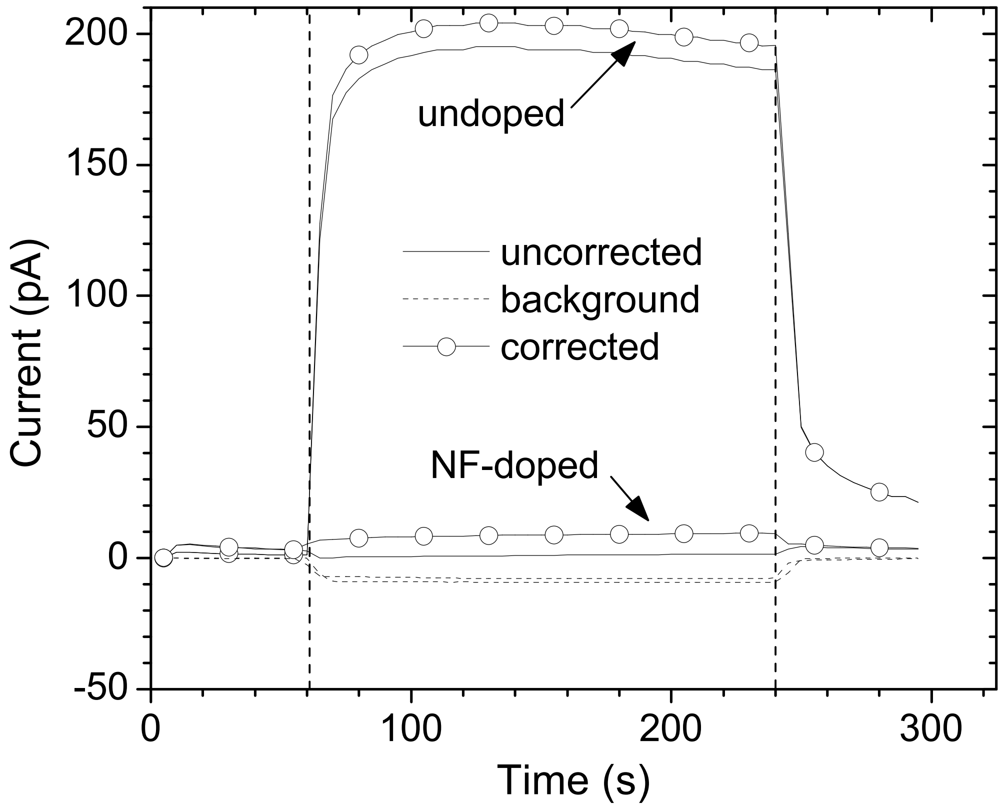
Numbered positions may represent:



Nitro

Cyano Amino

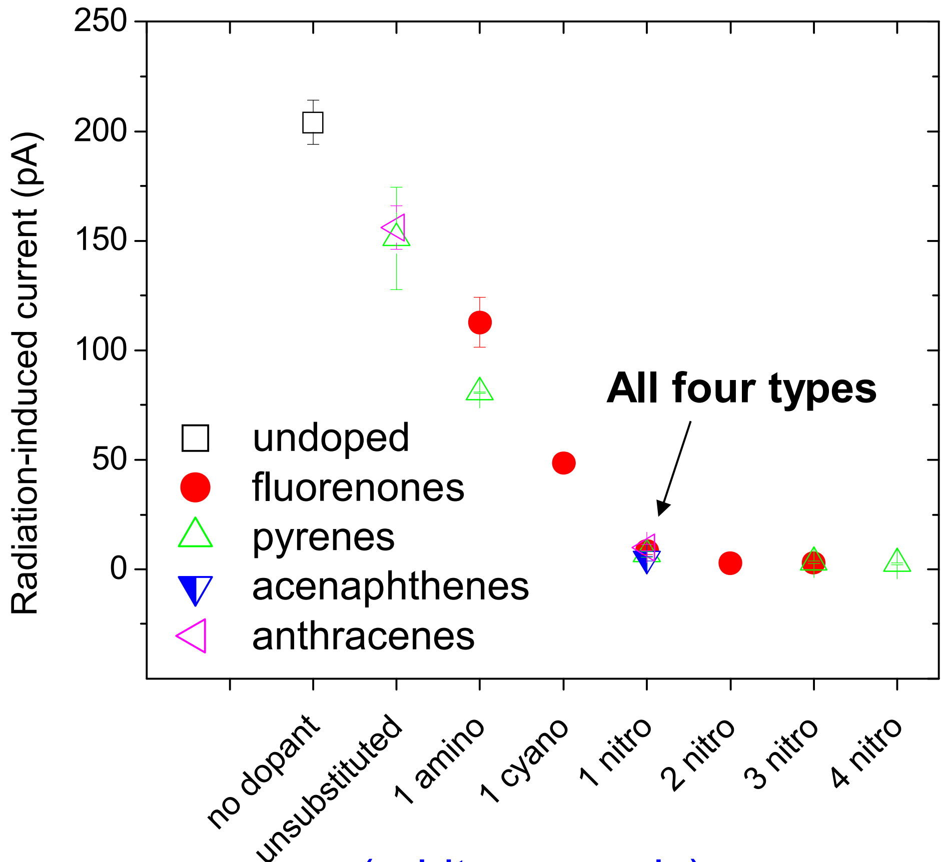
RIC is evaluated as the plateau in I(t)



Uncorrected = 29 V/μm

Background = 0 V (slightly negative due to radiation interacting with wires and epoxy)

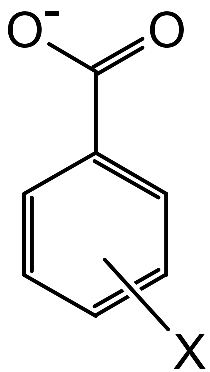
Trend in RIC emerges as a function of substituted group



(arbitrary x-axis)

Electron-withdrawing ability of substituent roughly correlates with lowered RIC, *for all conjugated cores*

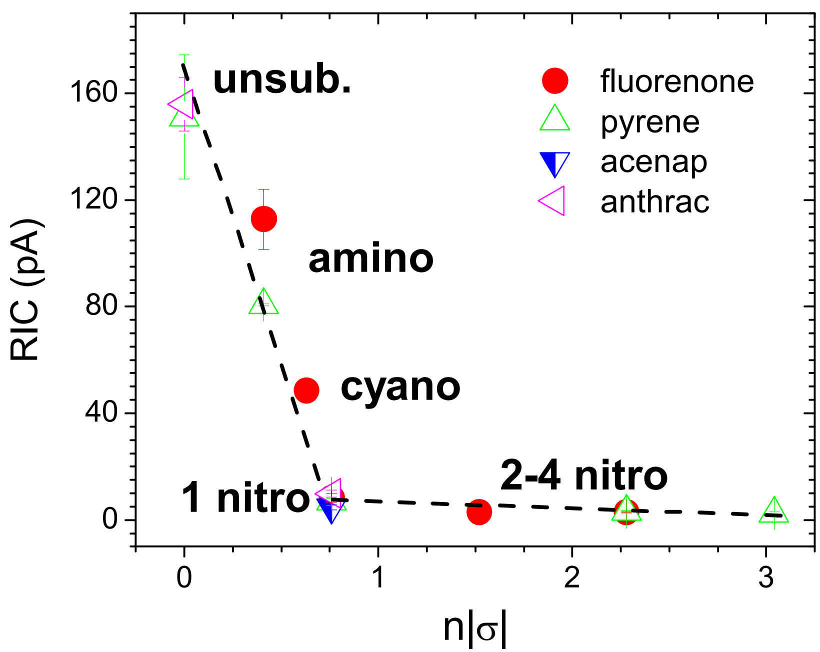
RIC behavior can be (semi)-quantified by Hammett parameter



Evaluated by Hammett for variously substituted benzoic acid: e⁻ withdrawing substitutent stabilizes acidity*

$$\sigma_X = \log \frac{K_X}{K_H}$$

Substituent	σ_{para}	σ_{meta}
$-NO_2$	0.77	0.74
$-C{\equiv}N$	0.65	0.61
$-NH_2$	-0.63	-0.21
-H	0	0



Establishes *predictive* model for impact of substituent

* A. Pross, *Theoretical and Physical Principles of Organic Reactivity*, 1995

Radiation tolerant dielectrics

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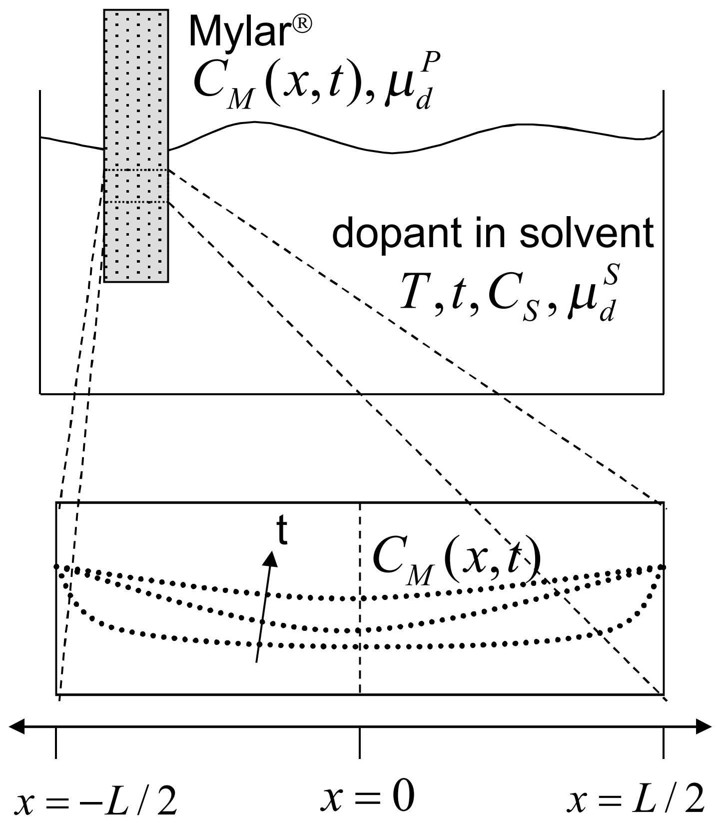
4) Modeled kinetics and thermodynamics of doping process on theoretical basis

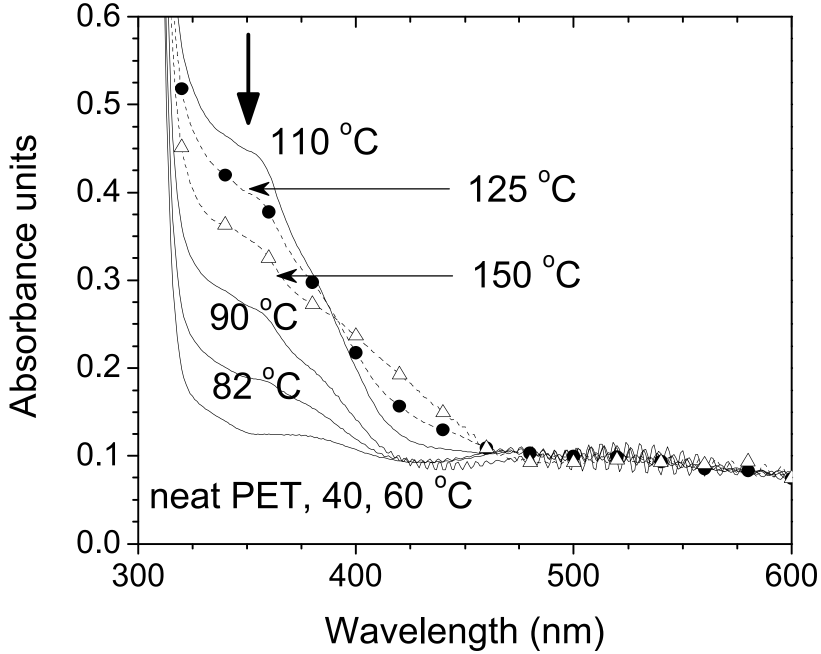
Dopant concentration evaluated by UV-vis

And fit with model to obtain physical parameters

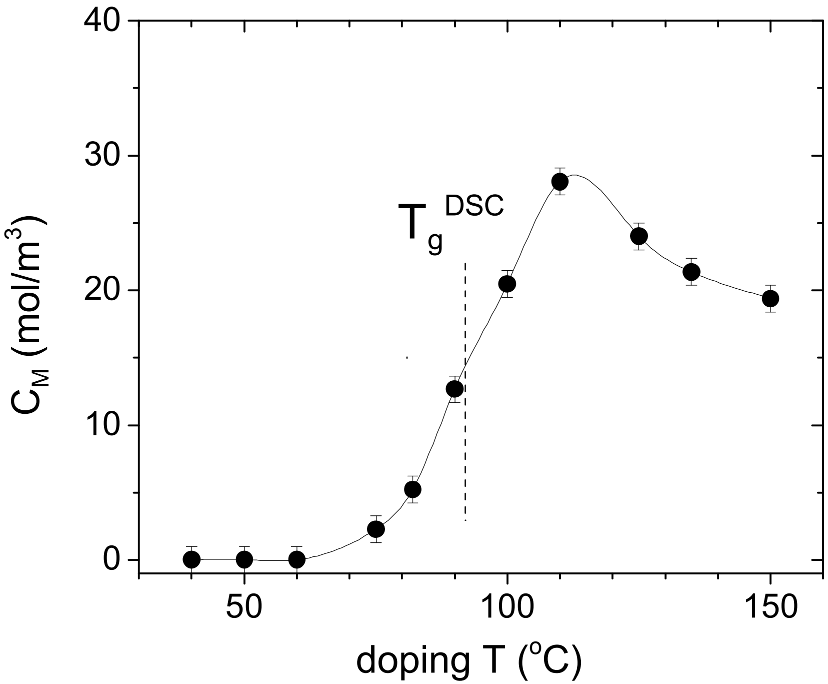


Diffusion efficient only above polymer T_g

Baselined UV-vis spectra of TNF-doped PET



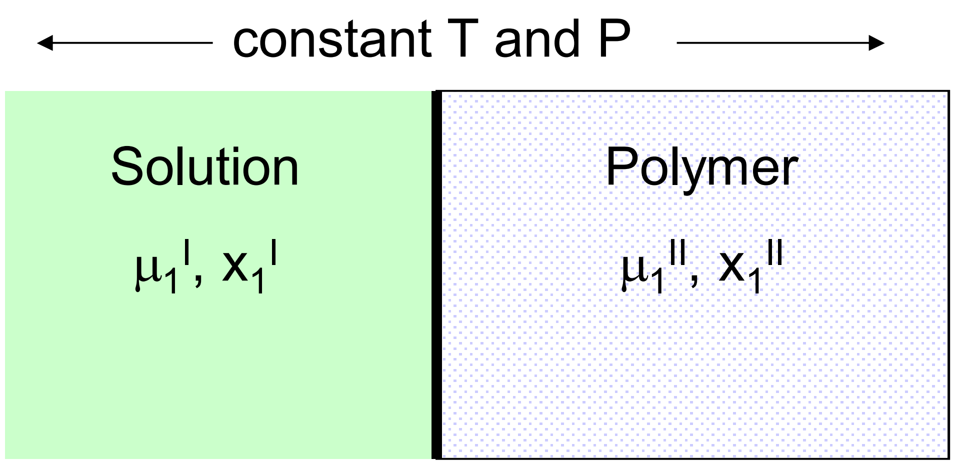
Corresponding C_M *(after 20 h)* as a function of *T*



Partition coefficient (thermodynamics) can be predicted from chemical potential theory

Fugacities of component partitioned between two phases provides K based on activity coefficients

In order to predict K we need estimates for the activity coefficients!



Ultimately, we found a combination of theories worked to predict behavior:

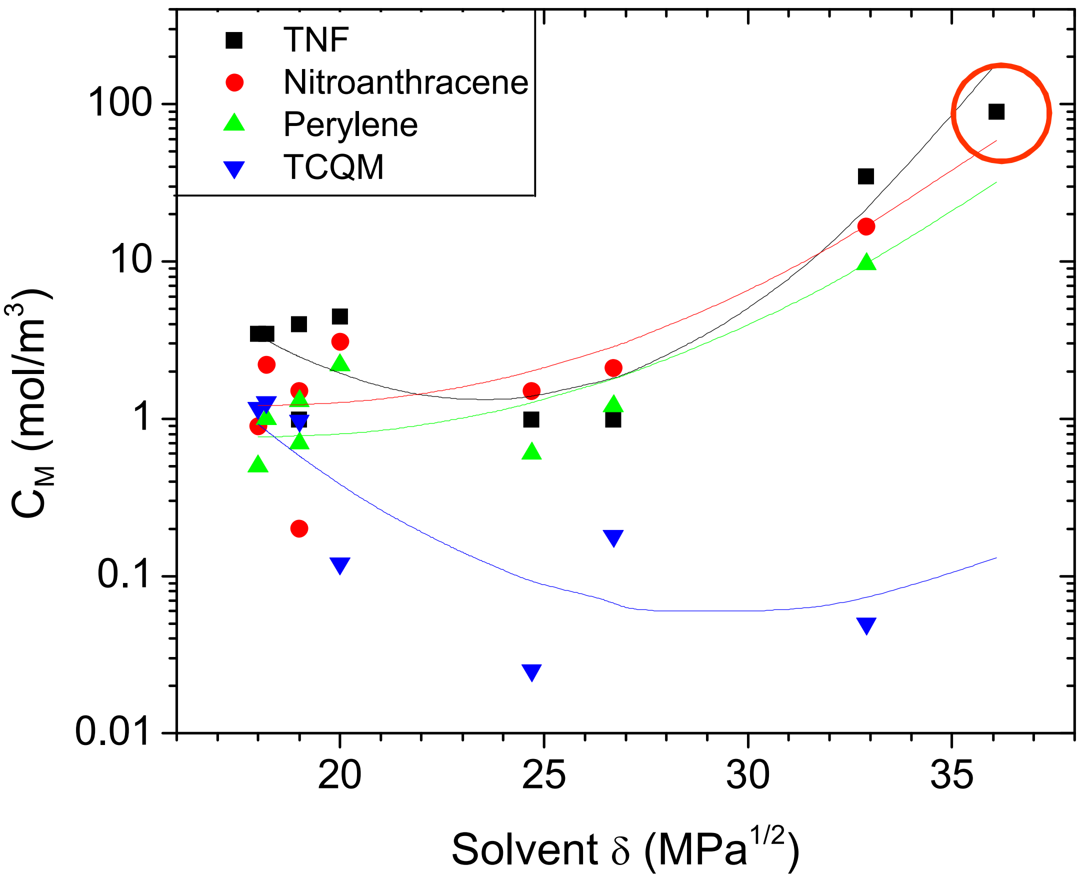
1) Flory-Huggins
2) χ parameters predicted from solubility parameters
3) Solubility parameters from experiment or group contribution theory
4) Additional term to account for H-bonding in solution

Experimental data for wide variety of dopants and solvents linked to theory

$$C_M = a_1 \exp\left\{b_1\left[v_m^{d.S}\left(\delta_S - \delta_d\right)^2 - v_m^{d.P}\left(\delta_P - \delta_d\right)^2\right]\right\}$$

Very strong correlations between solvent solubility parameter and final C_M

Glycerol predicted to be better than EG for TNF, and this is confirmed by experiment



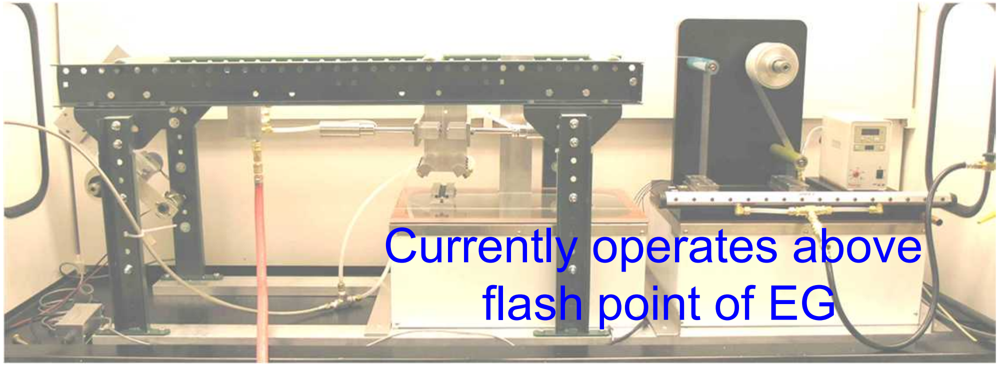
Radiation tolerant dielectrics: Future directions

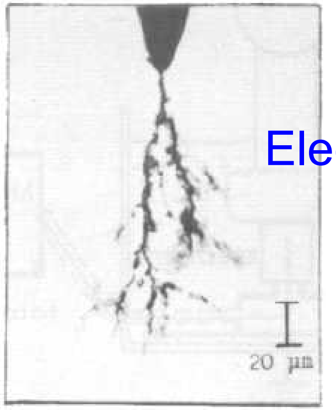
Improvements to process already underway

(lower cost materials, safer and more dependable process)

Electron traps at high conc lower the breakdown voltage by acting as defect sites. Based on breakdown theory in insulators, holes should have the opposite effect

So we are pursuing doping with hole traps to increase breakdown voltage in Mylar as well as in filled systems





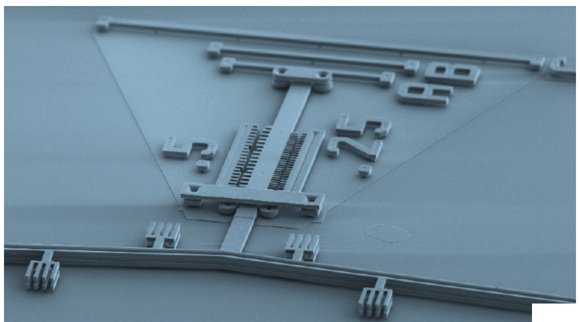
Electrochemical treeing

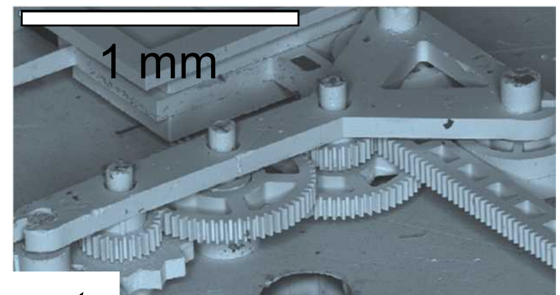
Pulfrey 1972 J Phys D

SAMs for anti-stiction of MEMS

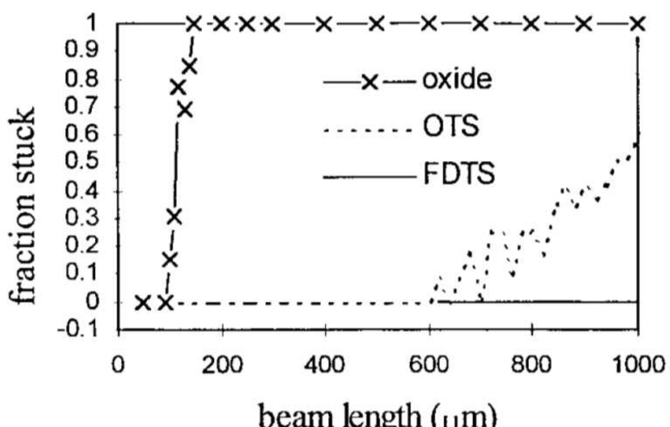
Motivation: Class III and IV MEMS devices (impacting/rubbing surfaces)

- Untreated MEMS last for 10^2 to 10^3 cycles
- MEMS with single-layer SAMs last for 10^4 to 10^5 cycles
- Reliable devices require 10^6 to 10^8 cycles

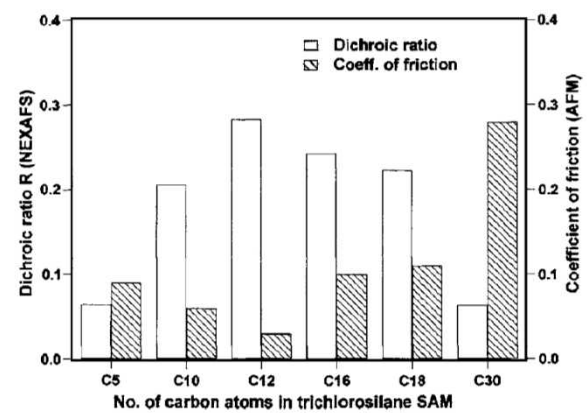




Oliver 2002 *Sand Report*



Srinivasan 1998 *J MEMS*

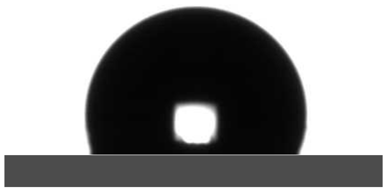


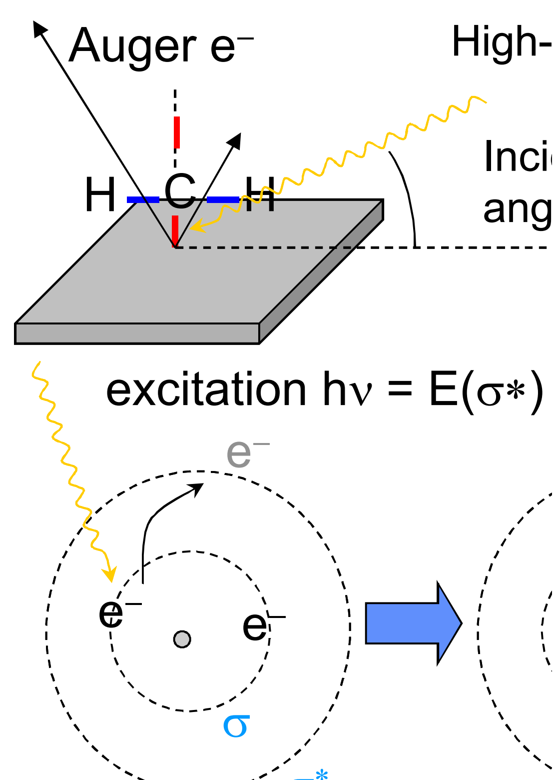
Sambasivan 2006 J Vac Sci Tech A

SAMs for anti-stiction in MEMS

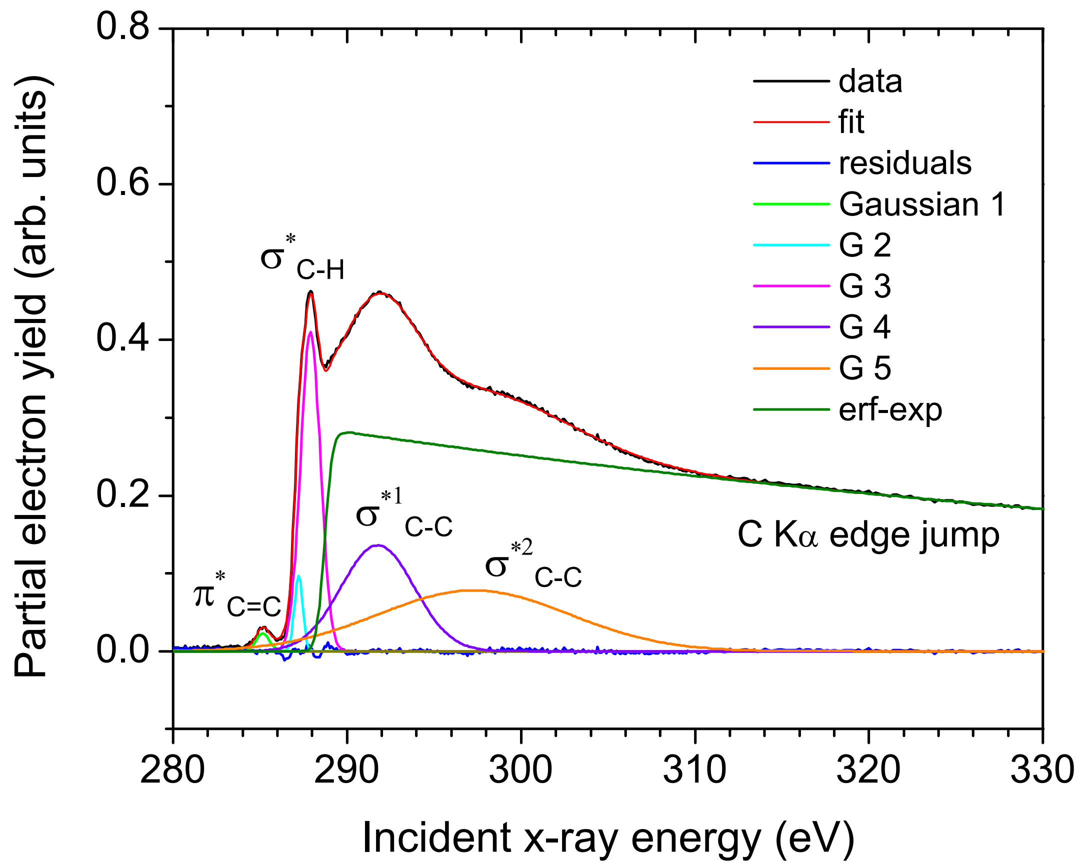
SAMs for anti-stiction in MEMS: Characterization techniques

Sessile/advancing/receding goniometry





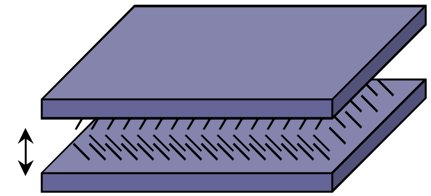
Near edge x-ray absorption fine structure (NEXAFS)



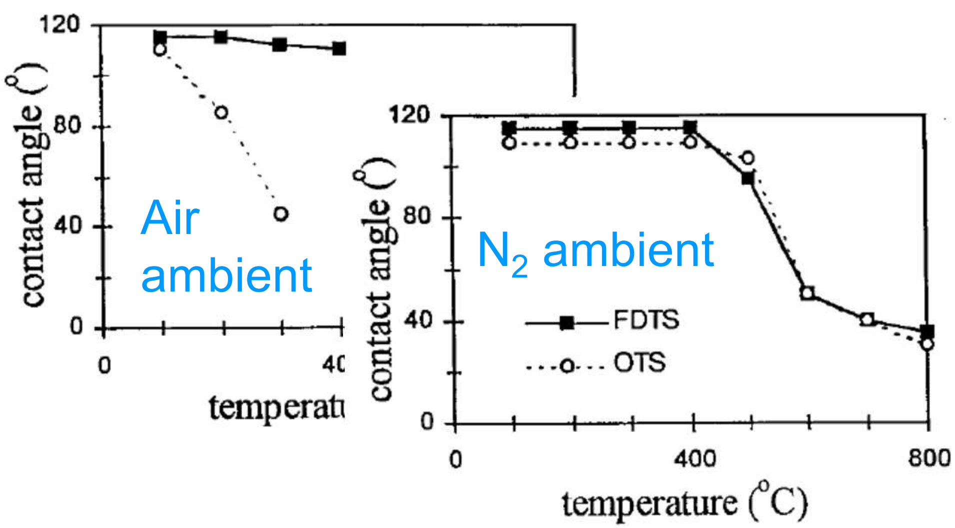
SAM wear leads to device failure

3 routes envisioned to SAM failure

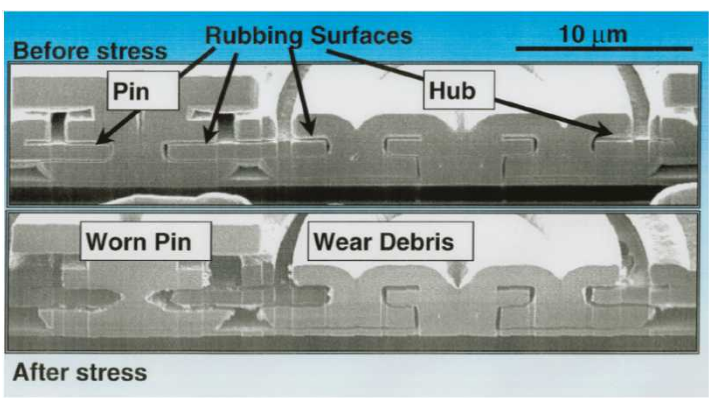
- Wear leads to local heating, cleaving C-C bonds
- Wear scratches silicon surface and 'uproots' SAMs
- Mechanical heating and humidity hydrolyzes Si-O-Si bonds



~2 nm separation between surfaces



Srinivasan 1998 *J MEMS*

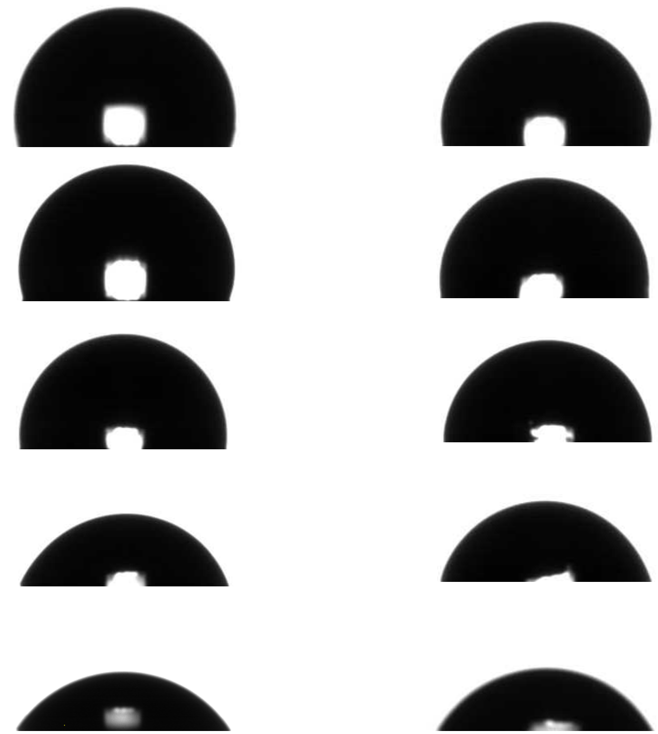


Jenkins 2004 *Sand Report*

Comparison of degradation mechanisms

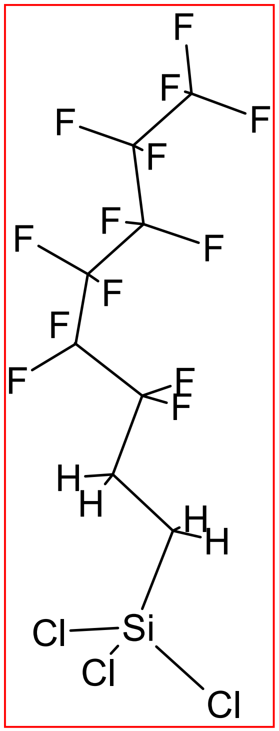
clean Si wafer

Heat treated | Worn



(1 h heating under air atmosphere)

(1-d rubbing, 2 FOTS surfaces, 1 Hz, 1 kg force)



Contact angle measurements show basic trend;
NEXAFS provided fundamental chemical changes

SAMs for anti-stiction in MEMS

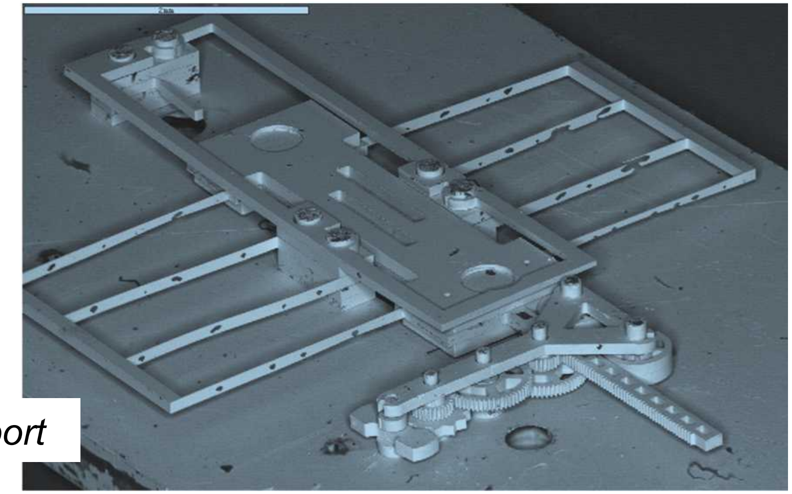
SAMs for anti-stiction in MEMS: Future directions

Fluorinated trichlorosilanes, although ideal for fundamental study, are not sufficient for use in MEMS with rubbing surfaces

However, we have evidence that certain chemistries form a regenerating, non-covalent, protective layer*

If a source is hermetically sealed into a MEMS device, lifetime is extended to tens of millions of cycles. NEXAFS will be used to characterize the wear mechanisms

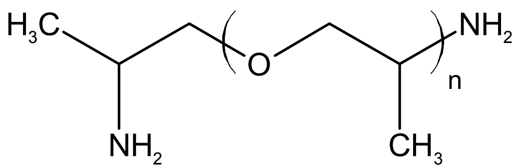
*Collaboration with Mike Dugger at Sandia



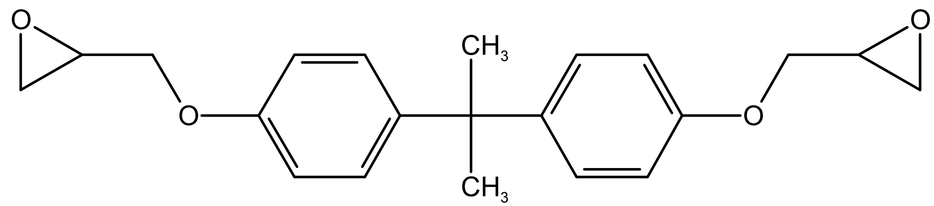
Oliver 2002 *Sand Report*

A sacrificial filler with a catalyst for the epoxide chemistry produces controlled pore sizes

Matrix: epoxide and amine

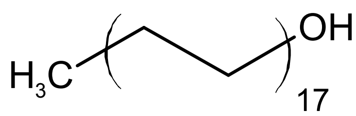


D230



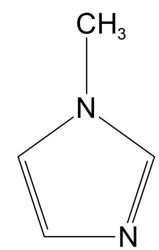
BADGE

Filler



1-octadecanol

Catalyst

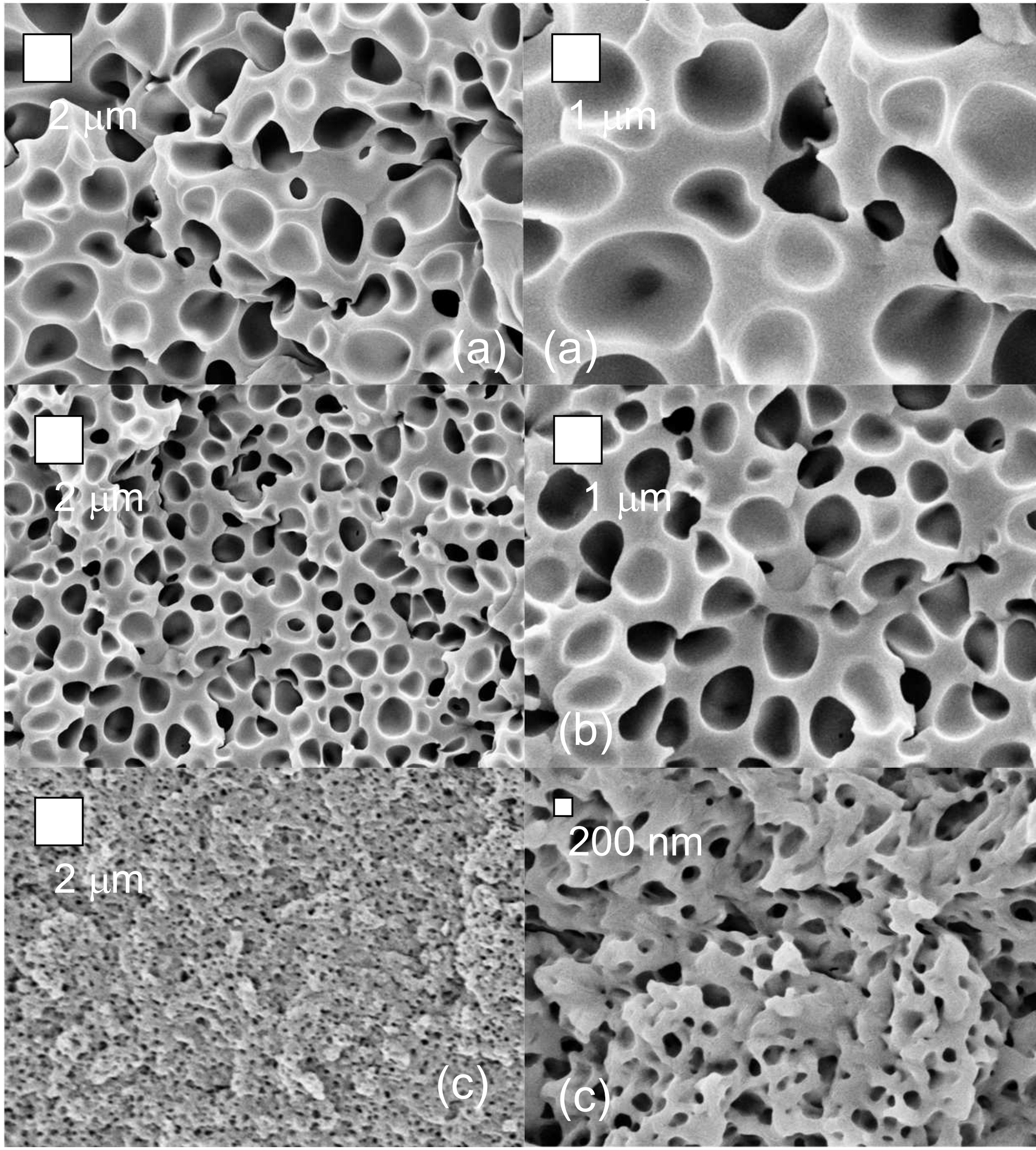


1-methylimidazole

Characterization techniques:

SEM, 3-point fracture test (ASTM)

A sacrificial filler with a catalyst for the epoxide chemistry produces controlled pore sizes



90 ^{o}C cure, 40 wt% octadecanol

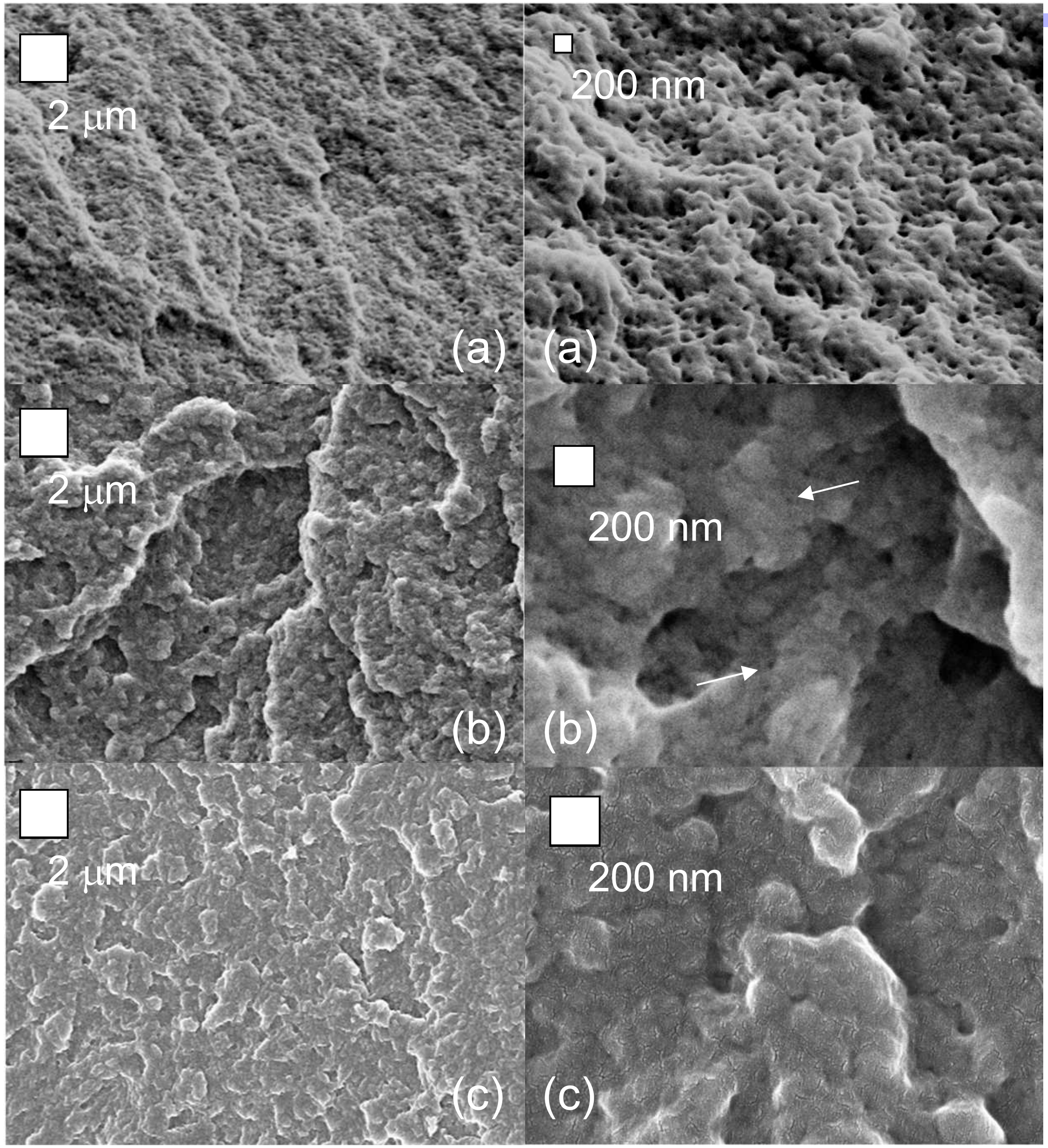
0.3 wt% imidazole

0.4 wt% imidazole

0.5 wt% imidazole

Porous and filled epoxies

A sacrificial filler with a catalyst for the epoxide chemistry produces controlled pore sizes



90 °C cure, 40 wt% octadecanol

0.6 wt% imidazole

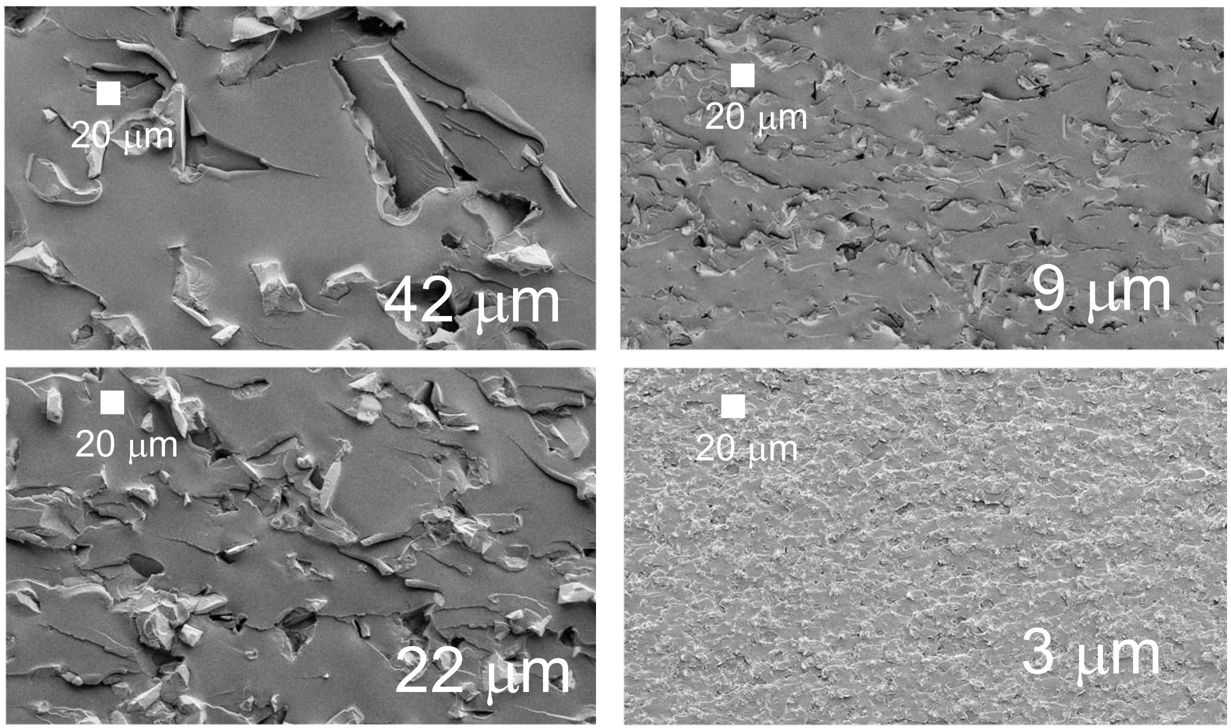
0.8 wt% imidazole

0.9 wt% imidazole

Porous and filled epoxies

Alumina filler increases ε, E_Y, and K_{IC}, and decreases CTE; any benefit to smaller particles or coupling agents?

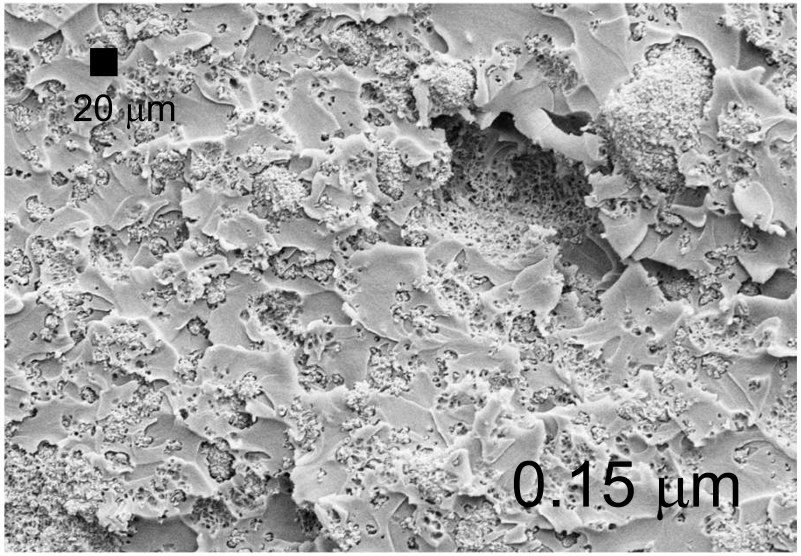
Fracture direction



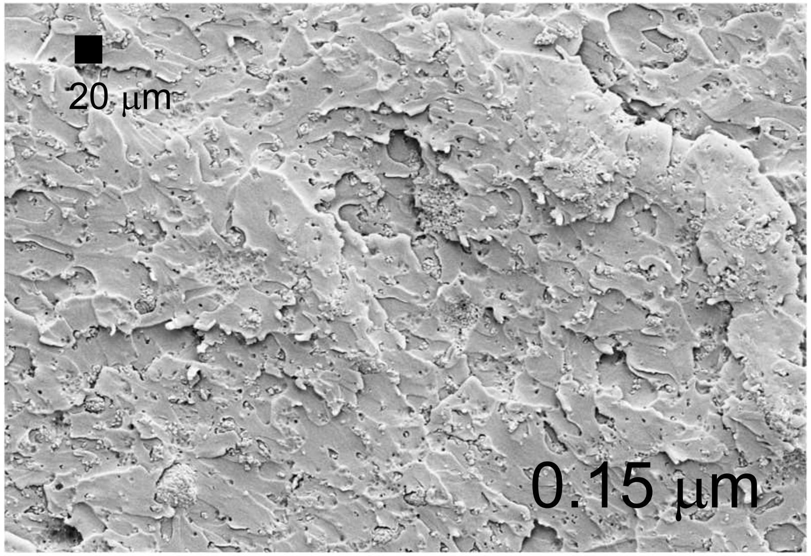
Well-dispersed particles

Fracture surface gets rougher with smaller particles

Alumina filler increases ε, E_Y, and K_{IC}, and decreases CTE; any benefit to smaller particles or coupling agents?



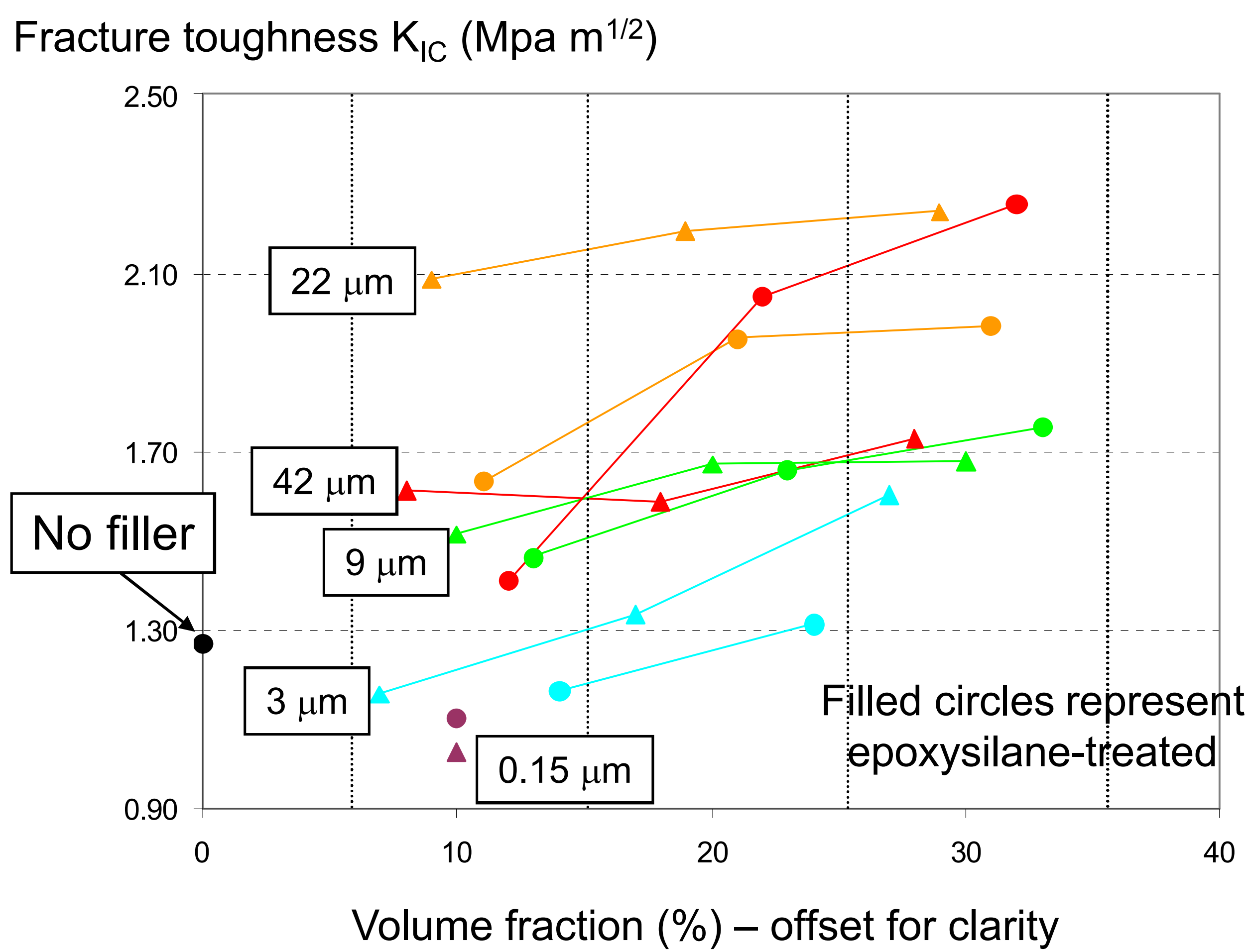
Untreated, dispersed with sonic horn and mechanical mixer



Treated with epoxyhexyltrichlorosilane, dispersed with sonic horn and mechanical mixer

Surface treated particles lead to better dispersion

Alumina filler increases ε, E_Y, and K_{IC}, and decreases CTE; any benefit to smaller particles or coupling agents?



K_{IC} is not improved by nanofillers or silane coupling agent

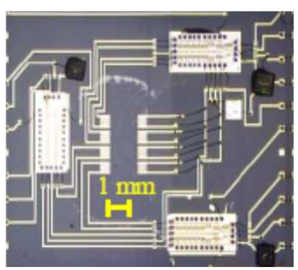
Porous and filled epoxies: Future directions

Filled epoxies: provide a baseline for the impact of particle size on processing (viscosity) and mechanical properties (fracture toughness)

A better understanding of rheological percolation and crack deflection as a function of size will lead to better design parameters

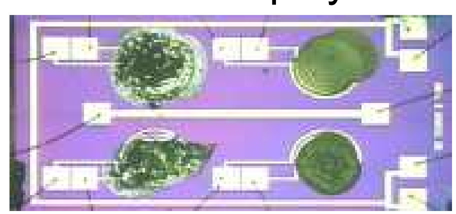
We can also try to design coupling agents to decrease viscosity while increasing particle-polymer interactions in the solid state

Porous epoxies: besides traditional applications at Sandia, also very important for chemical sensors

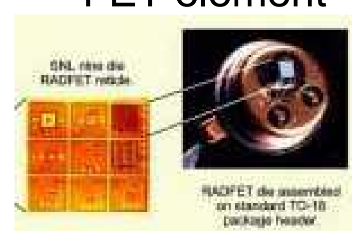


SAWs with gel

Conductive polymer

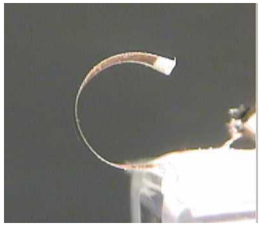


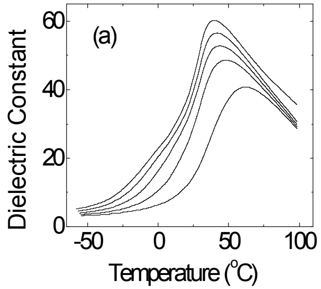
FET element



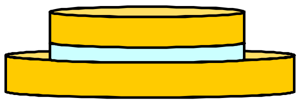
Various sensors from Sandia – Ho 2004 Sand Report

Highlights of my past and present research in organic materials



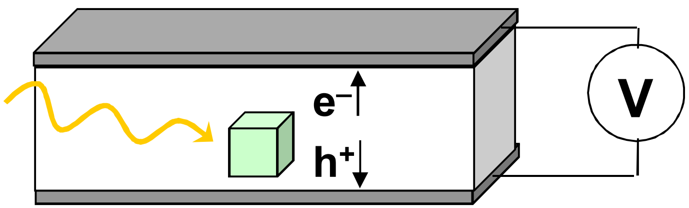


PVDF-based terpolymers for electroactive transducers and high ε capacitors

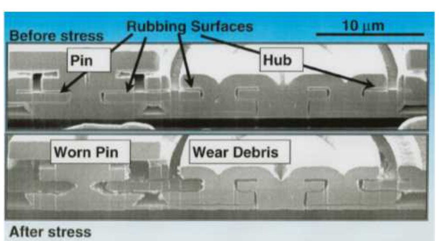


$\varepsilon^*(f, T)$

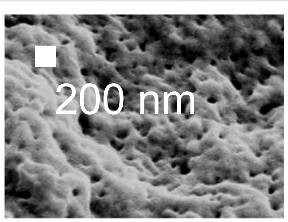
Polymer and ion dynamics in ionomers and polymer electrolytes

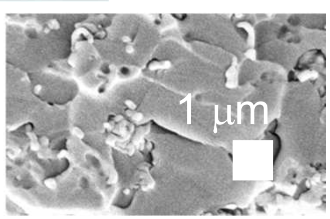


Radiation tolerance in polymer dielectrics*



Self-assembled monolayers for anti-stiction in MEMS





Polymer composites: porous and alumina filled epoxies

Luna Innovations seminar
August 18 2008

Robert Klein
Graduate and postdoctoral work

PENNSTATE

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
COLLEGE OF EARTH AND MINERAL SCIENCES

Qiming Zhang*
Mike Lanagan, Feng Xia, Cheng Huang, Kailiang Ren, Francois Bauer

Jim Runt*
Ralph Colby, Harry Allcock, Paul Painter, Ron Hedden, Pornpen Atorngitjawat, Shihai Zhang, Shichen Dou, Dan Welna

Sandia National Laboratories

Joe Lenhart*
Phil Cole, Mat Celina, Jim Aubert, Lothar Bieg, Bob Anderson, Doug Adolf, Randy Mrozek, John Schroeder, Shana Cole, Mike Belcher, Mark Stavig

NSLS
NATIONAL SYNCHROTRON LIGHT SOURCE

Dan Fischer
Cherno Jaye, Zugen Fu

University of California, Santa Barbara
CHEMICAL ENGINEERING

(undergraduate)

***Advisors**

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

First author papers (1)

1) Systematic wear and heat treatment of self-assembled monolayers for anti-stiction, characterized by near edge x-ray absorption fine structure and contact angle
RJ Klein, DA Fischer, JL Lenhart, *in preparation*

2) Porous epoxies by phase separation of removable alcohols: control of spherical pore size by mass fraction, cure temperature, and reaction rate
RJ Klein, MC Celina, and JL Lenhart, *submitted to Chemistry of Materials*

3) Radiation tolerance in polymeric dielectrics by small-molecule doping I: Dopant uptake as a function of temperature, time, and chemistry
RJ Klein, SM Cole, ME Belcher, JL Schroeder, PJ Cole, JL Lenhart, *submitted to Polymer*

4) Radiation tolerance in polymeric dielectrics by small-molecule doping II: Thermodynamic and kinetic parameters
RJ Klein, SM Cole, ME Belcher, JL Schroeder, PJ Cole, JL Lenhart, *submitted to Polymer*

5) Systematic oxidation of polystyrene by ultraviolet-ozone, characterized by near edge x-ray absorption fine structure and contact angle
RJ Klein, Daniel A. Fischer, JL Lenhart, *Langmuir* **2008** 24 8187

6) Reduction of radiation-induced conductivity in poly(ethylene terephthalate): Effect of dopant structure
RJ Klein, JL Schroeder, SM Cole, ME Belcher, PJ Cole, JL Lenhart, *Polymer* **2008** 49 2632

First author papers (2)

7) Plasticized Single-Ion Polymer Conductors: Conductivity, Local and Segmental Dynamics, and Interaction Parameters
RJ Klein, J Runt, *Journal of Physical Chemistry B* **2007** 111 13188

8) Counterion effects on ion mobility and mobile ion concentration of doped polyphosphazene and polyphosphazene ionomers
RJ Klein, DT Welna, AL Weikel, HR Allcock, J Runt, *Macromolecules* **2007** 40 3990

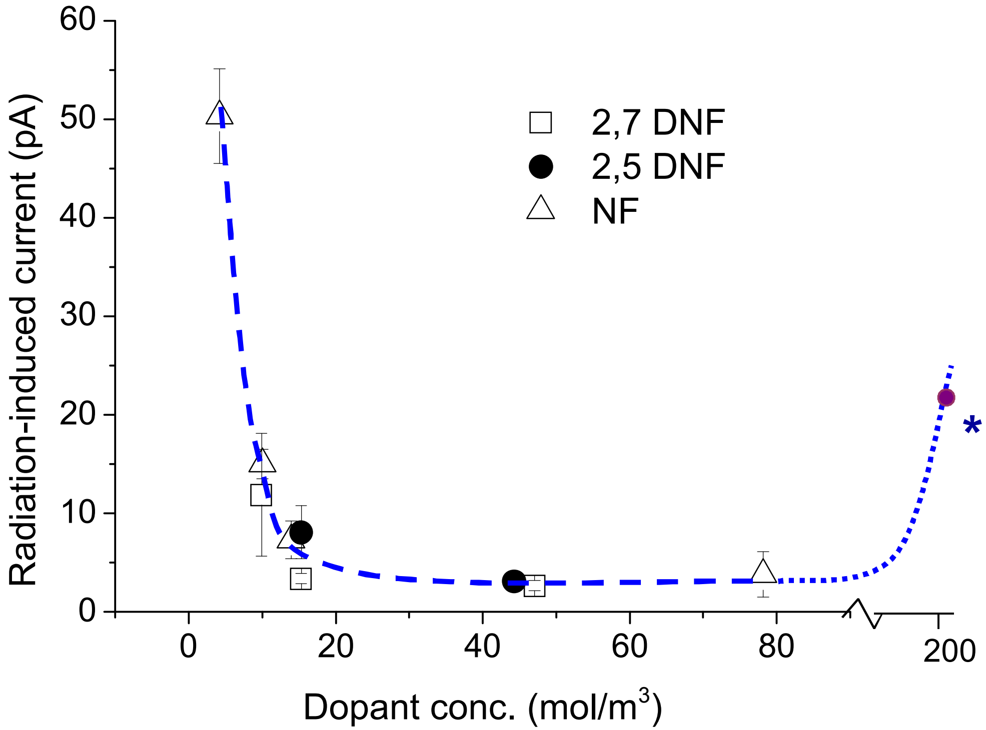
9) Modeling electrode polarization in dielectric spectroscopy: ion mobility and mobile ion concentration of single-ion polymer electrolytes
RJ Klein, SH Zhang, SC Dou, BH Jones, RH Colby, J Runt, *Journal of Chemical Physics* **2006** 124 144903-1

10) Influence of composition on relaxor ferroelectric and electromechanical properties of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)
RJ Klein, F Xia, QM Zhang, F Bauer, *Journal of Applied Physics* **2005** 97 094105

11) Influence of crystallization conditions on the microstructure and electromechanical properties of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymers
RJ Klein, J Runt, QM Zhang, *Macromolecules* **2003** 36 7220

12) Producing super-hydrophobic surfaces with nano-silica spheres,
RJ Klein, RM Biesheuvel, BC Yu, CD Meinhart, FF Lange, *Zeitschrift fur Metallkunde* **2003** 94 377

Within a wide range, dopant concentration has little effect on RIC



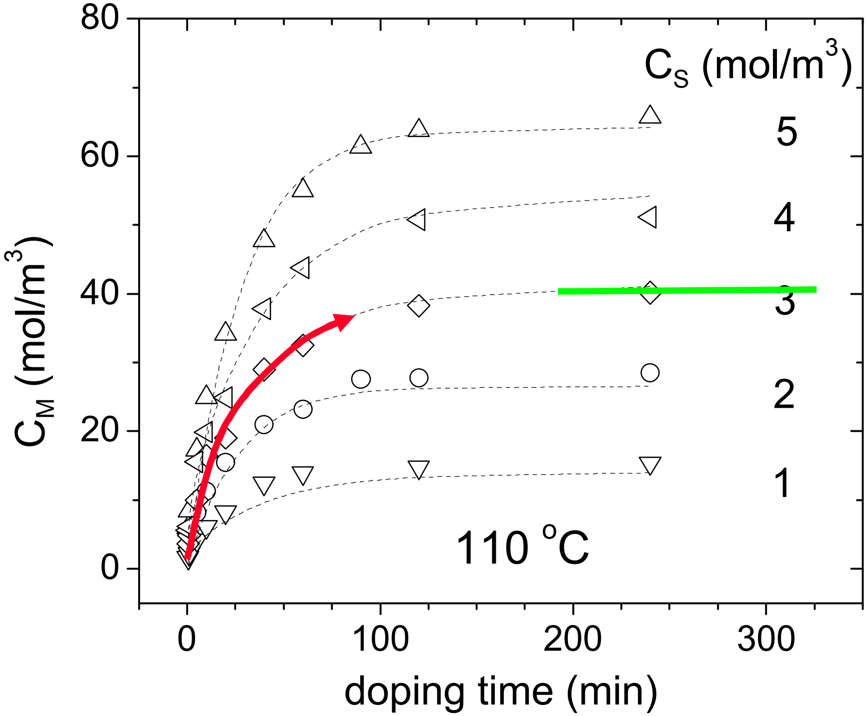
This plateau is typical of all dopants

Stable from 10 mol/m^3 (6 x 10^{18} cm^{-3}) to <200 mol/m^3 (1 x 10^{20} cm^{-3})

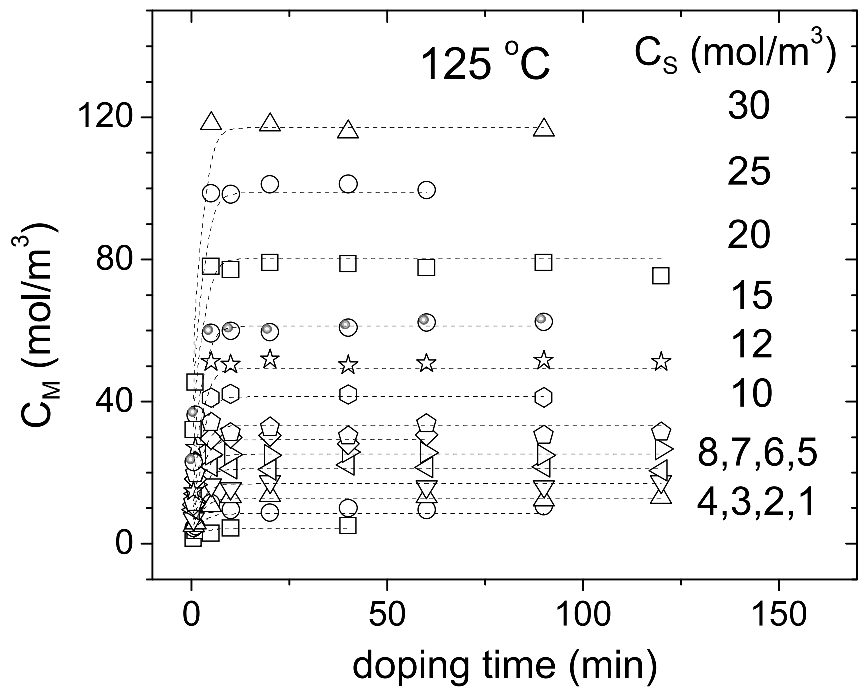
* TNF, from Kurtz *IEEE Trans Nucl Sci* 1983

Model fits rise and plateau in $C_m(t)$ very well

TNF at 110 °C



NF at 125 °C



Radiation tolerant dielectrics

Kinetics follow simple Fickian diffusion through an amorphous solid

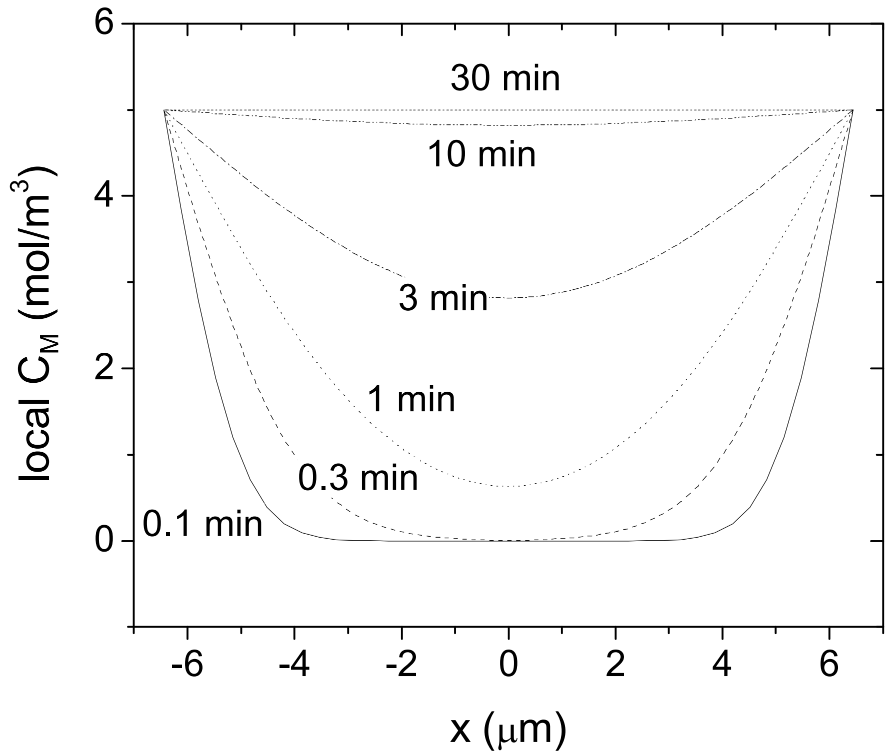
$$D\frac{\partial^2 C_M}{\partial x^2} = \frac{\partial C_M}{\partial t}$$

$$C_M(x,t) = C_M^{eq}\left\{1 - 2\sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1/2)\pi}\exp\left[-(n+1/2)^2\pi^2\frac{Dt}{(L/2)^2}\right]\cos\left[(n+1/2)\pi\frac{x}{L/2}\right]\right\}$$

$C_M(t)$ data modeled with single parameter D (diffusivity)

*Due to crystallinity actual diffusivity is higher than observed by

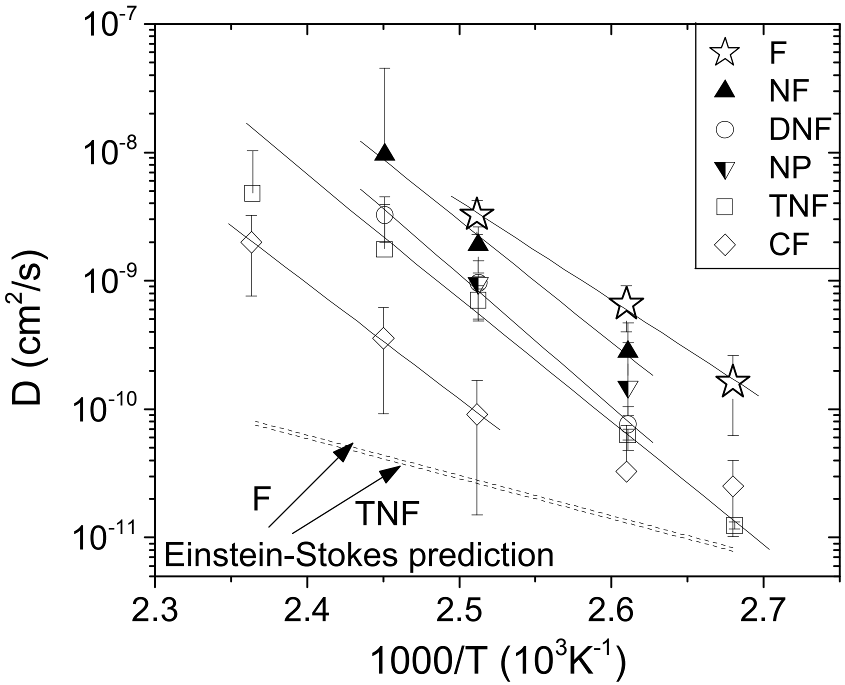
$$D = \frac{D_A\phi}{\tau}$$



Diffusion of small molecules slowed by the addition of functional groups

Molecular size (volume), which often plays the major role in diffusion[1,2], is insignificant

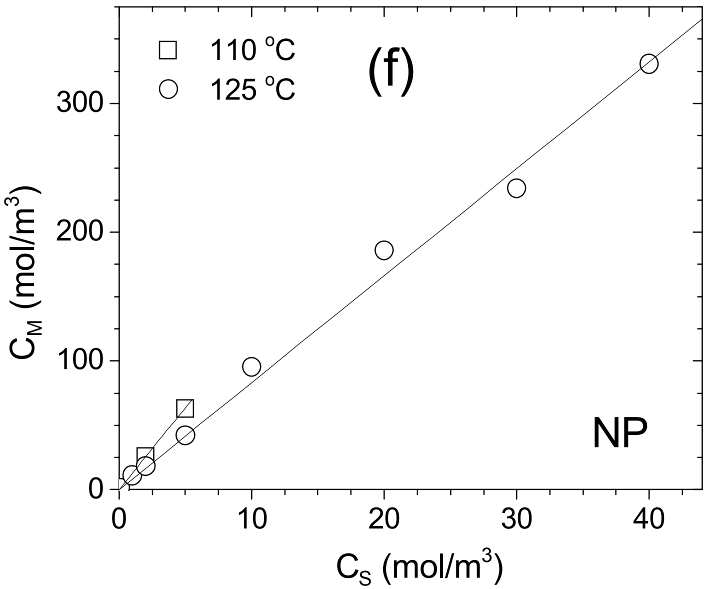
Ordering of dopants is instead based on retarding influence of functional groups



Thermodynamics of partitioning are more complex

First-glance model proceeds by Henry's law approach

$$C_M^{eq} = K_C C_S$$



Initial Mylar® doping process developed in 70's and 80's at SNL, and commercial batches produced

- Edwards[1] surveyed PVDF, Mylar® (PET), and polysulfone
- Kurtz, Arnold, and Hughes[2] continued work and selected PET for dielectric properties and low water uptake; found RIC reduced 99% with doping TNF from benzyl alcohol[3]
- Courtalds Performance Films (Virginia) produced TNF-doped Mylar® in 50,000 sq. ft. batches[4] (late 1980's to 1993)

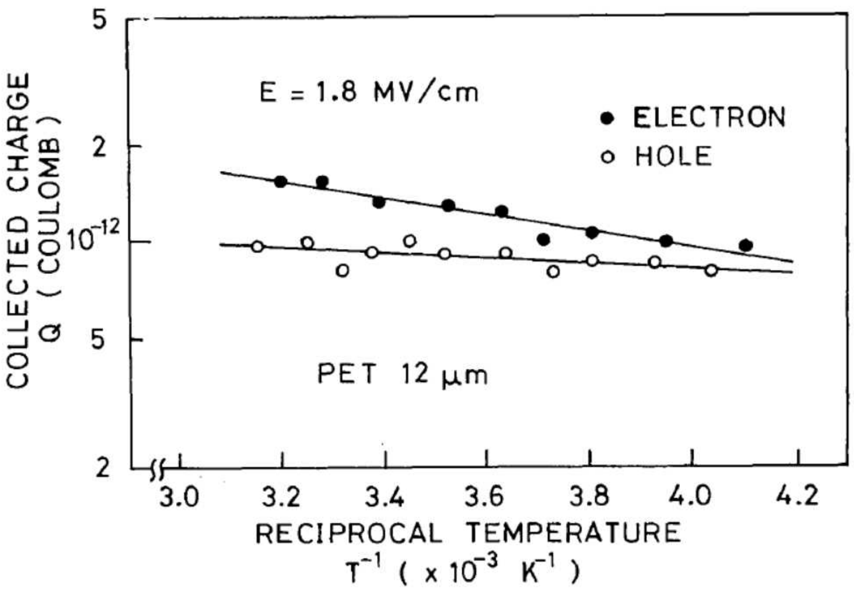
Problems at the time:

1) TNF classified as an explosive in late 1990's and external vendors will no longer use
2) Process not optimized and expensive
3) Ethylene glycol selected as solvent without clear understanding

[1] L.R. Edwards, *Sandia Report* 1981 SAND-81-0667C
[2] S.R. Kurtz, R.C. Hughes, *JAP* 1983 54 p229-237
[3] S.R. Kurtz, C. Arnold, R.C. Hughes, *IEEE Trans Nucl Sci* 1983 30 4077-4080
[4] G.C. Bischoff, L.R. Edwards, Sandia Report 1990 SAND-90-2362C

Reduction by amino group may arise from hole trapping

Hayashi *JJAP* 1975

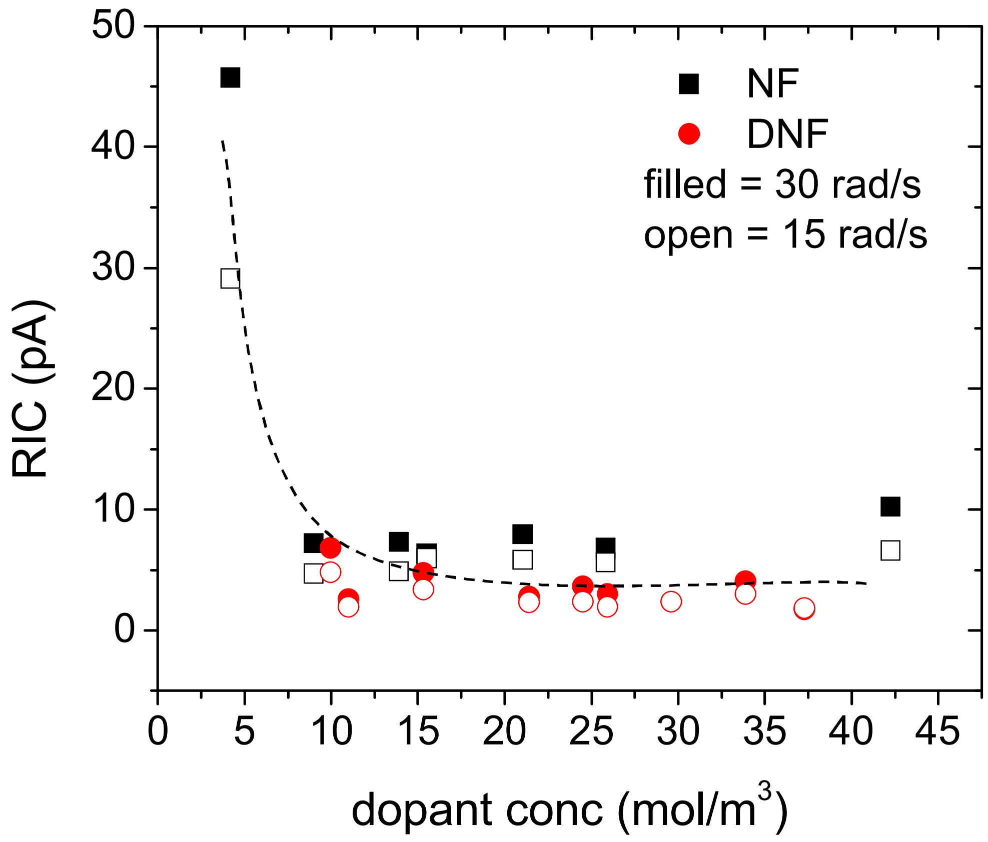


Electron transport dominates* in PET (lifetimes are much longer), but trapping of holes also important

* Hayashi *JJAP* 1975 (pulsed electron beam bombardment, measured as charge collected over time of flight)

* Kurtz *JAP* 1985, Khatipov *High Energy Chem* 2001, Tyutnev *High Energy Chem* 2006

RIC as function of dopant concentration



- 10 to 40 mol/m^3 provides 95 to 98 % reduction in RIC

Best method we found was Flory-Huggins model with additional term for H-bond interactions

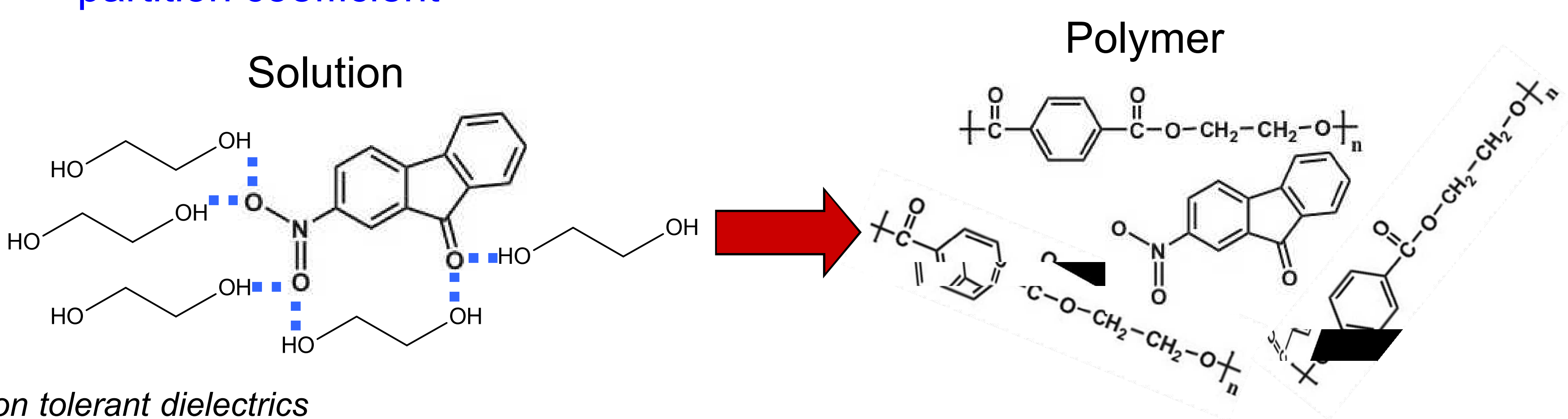
$$K_x = m_{d.S} m_{P.d} \exp\left(m_{d.S} + 1/m_{P.d} - 2\right) \exp\left(\chi_d^S - \chi_d^P\right)$$

$$\chi_{AB} = \frac{v_m \left(\delta_A - \delta_B\right)^2}{RT} \qquad \delta = \left(\frac{\sum_i E_i}{\sum_i V_i}\right)^{1/2}$$

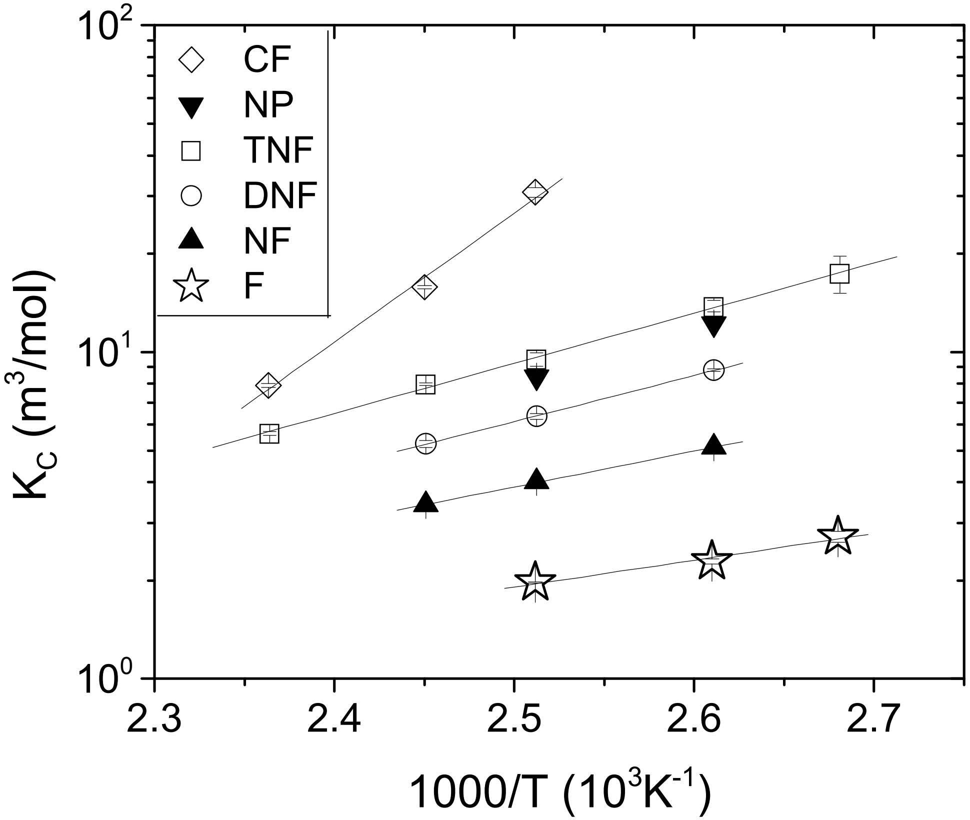
$$\gamma_d^{S(H)} \approx \exp\left(-2a\right)$$

Only one unknown in this set of equations: $a \equiv$ number of H-bonds per molecule

H-bonding in solution (ethylene glycol to dopant) has effect of decreasing partition coefficient



From slopes and magnitudes of K we can estimate the number of H-bonds

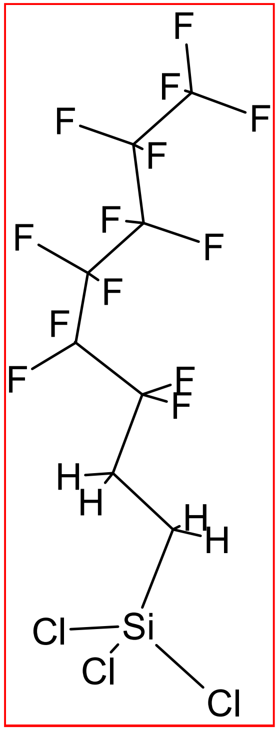


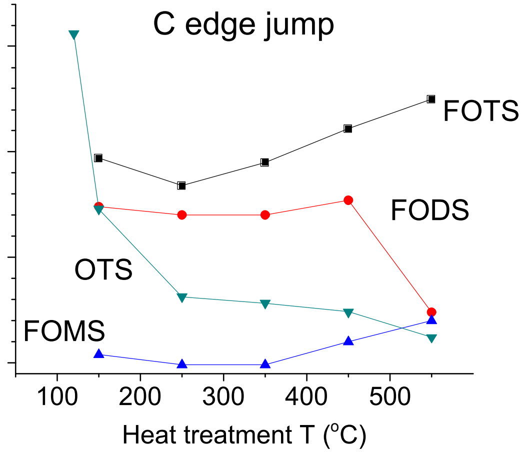
Dopant	a
F	4
NF	7
DNF	10
TNF	13
CF	-

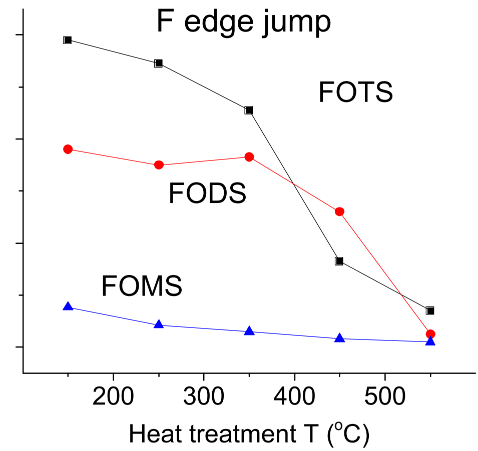
FOTS, FODS, and FOMS

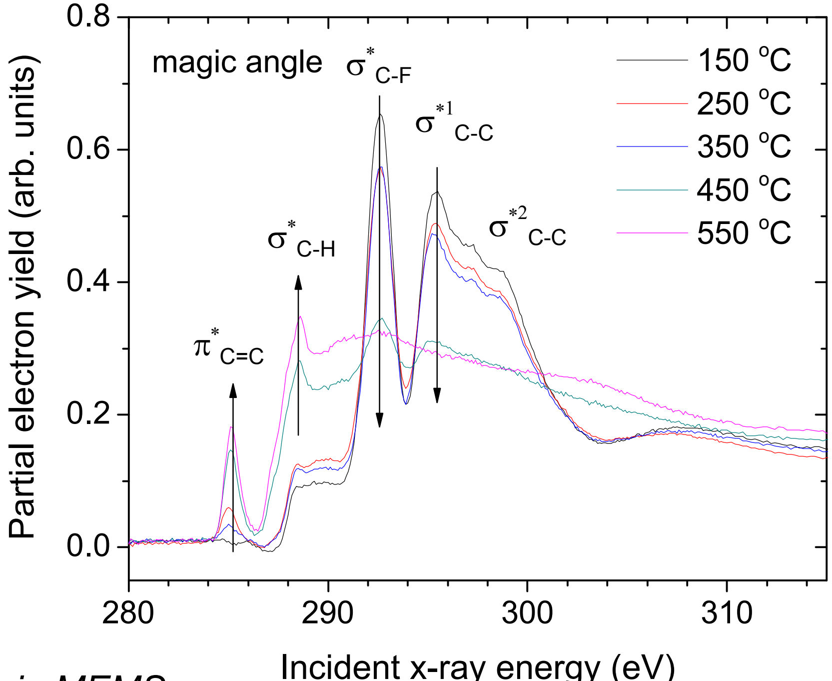
Fluorinated octyl <u>tri</u>chlorosilane

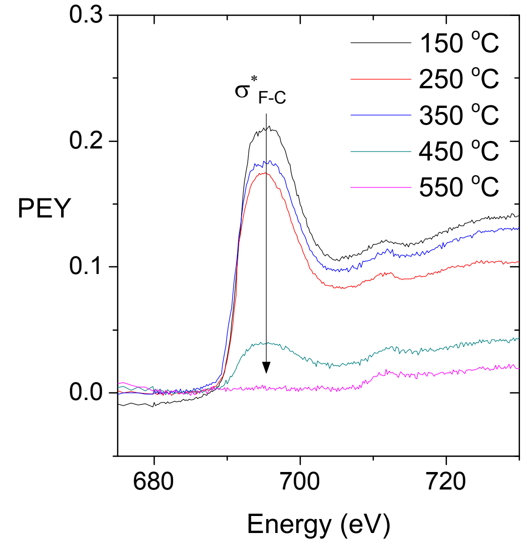
FOTS











SAMs for anti-stiction in MEMS