FROM HEAT SHRINK TO SHAPE MEMORY TO FLEXIBLE BIOELECTRONICS:
WHY RADIATION DOESN'T DESERVE A BAD WRAP

Walter Voit

1. McDermott Faculty
   Materials Science and Engineering
   Mechanical Engineering
   UT Dallas
2. Chief Technical Officer
   Syzygy Memory Plastics
3. Treasurer
   CIRMS

CIRMS 20th anniversary meeting - NIST

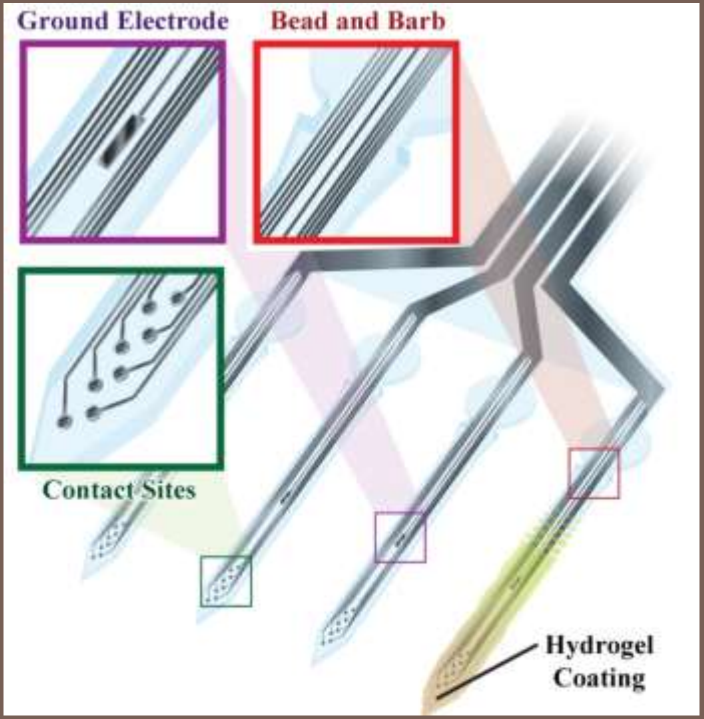
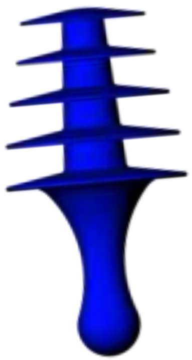


Image by Brock Wester

Introduction

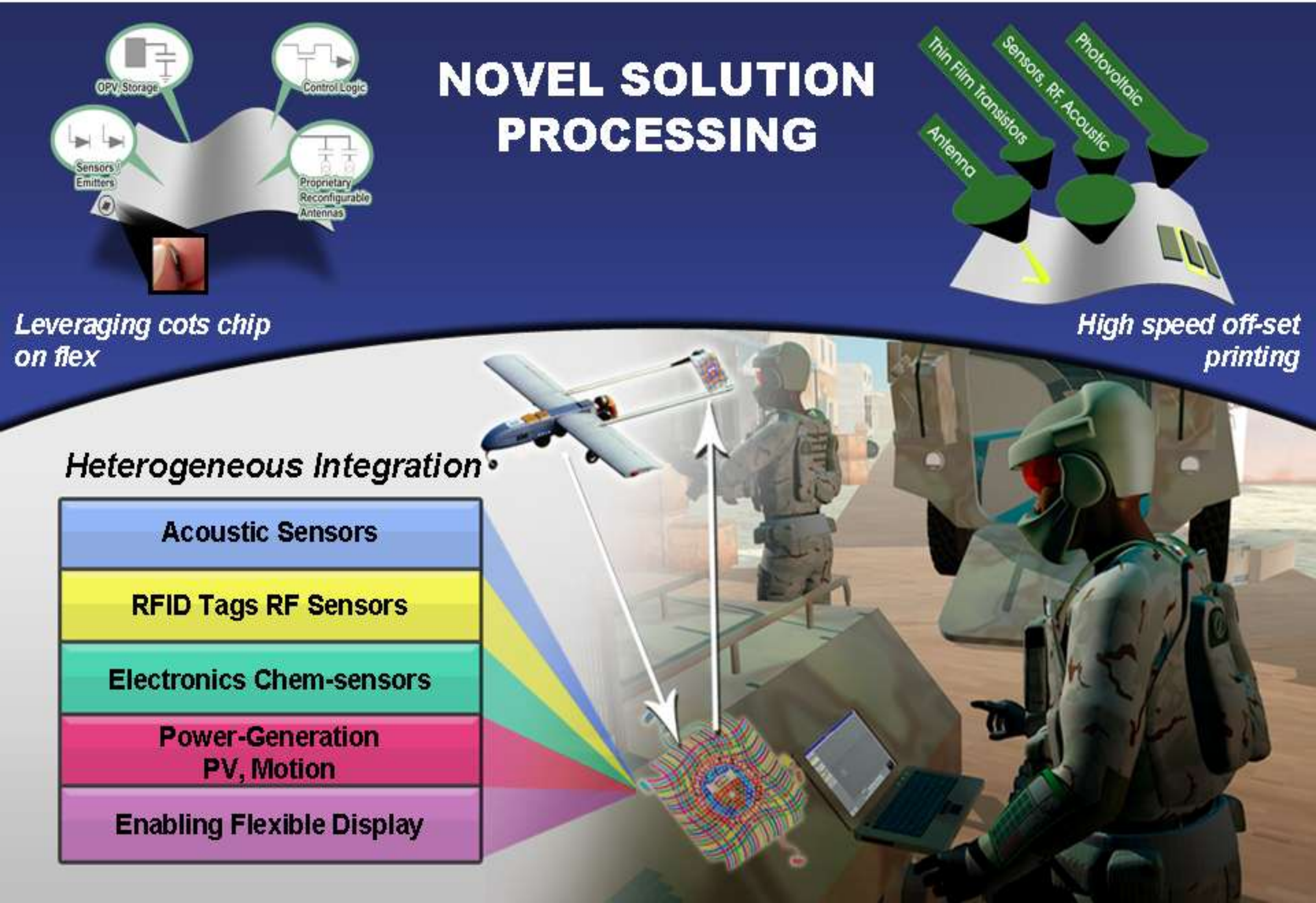
- BS in Computer Science from UT Dallas in 2005
- MS in Intelligent Systems from UT Dallas in 2006
  - Advisor: I. Hal Sudborough
  - Thesis: "Pipeline: A software tool to improve the pancake problem upper bound“
- PhD in MSE from Georgia Tech in 2009
  - Advisor: Ken Gall
  - Thesis: “Optimization of mechanical properties and manufacturing techniques to enable shape-memory polymer processing”
- Founder and CTO of Syzygy Memory Plastics in 2007
  - 2 filed provisional patents, 1 patent-pending
  - >$1,000,000 raised (private investment + grant money)
  - Commercial launch of *PremEar Plugs*™ in Q4 2011



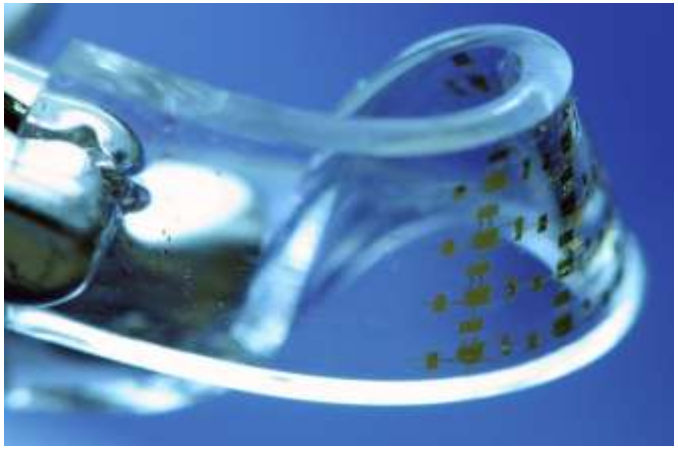
Overview

- Why Flexible Electronics? Why UT Dallas?
- Shape Memory Polymers
  - Radiation Processing
  - Thermomechanics
  - Biological Response
- Neural biotechnology
  - Multi-electrode Arrays
  - Cortical brain probes
  - Nerve cuff electrodes

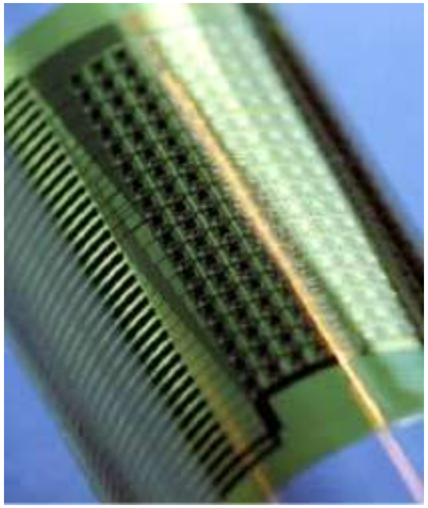
Why Flexible Electronics ?



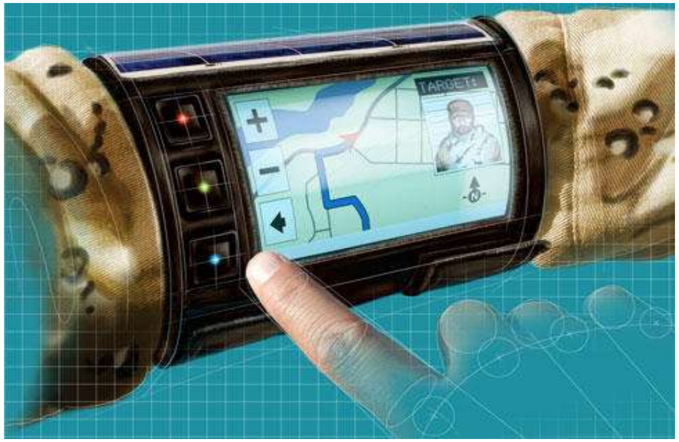
Motivation



Measure athletic performance



Accurately map electrical signals in the heart and brain



Lightweight integrated systems

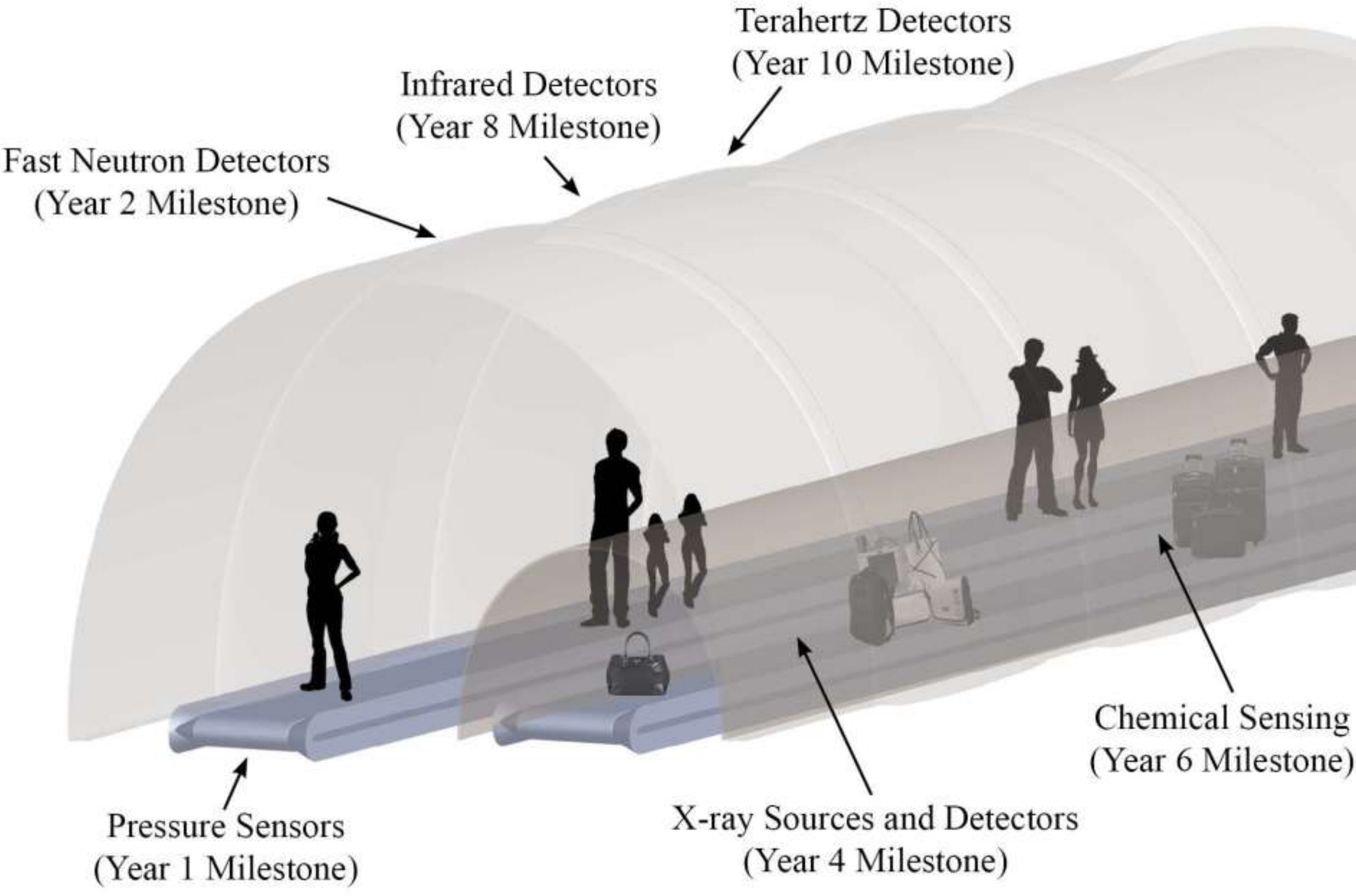
E-newspaper displays

Proposed NSF NanoSystems Emerging Research Center for

Conformable Large-Area Sensors and Systems

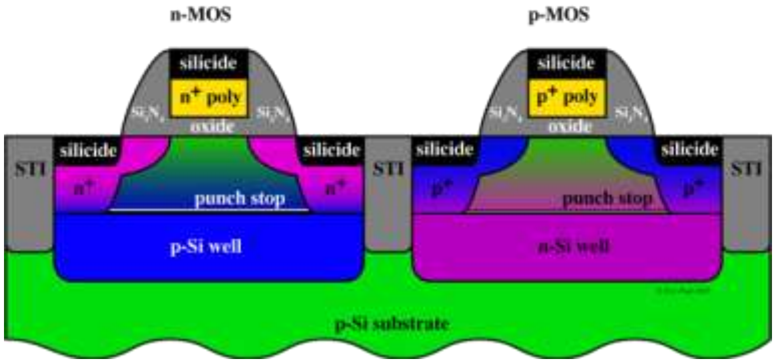
- **Utilize** the unique properties of nanostructured materials to enable macroelectronic systems with unprecedented functionality
- **Demonstrate** high performance macroelectronics as a transformative technology enabling a broad range of new industries
- **Integrate** sensors, actuators, supporting electronics, and communications on large, flexible sheets that can integrate seamlessly with their applications environment

Tunnel of Truth Concept: Testbed #1

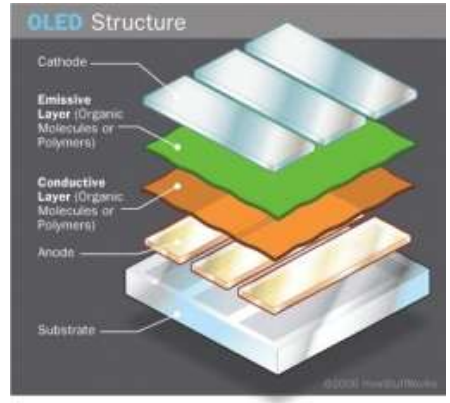


Materials and Interfaces Define Device Performance

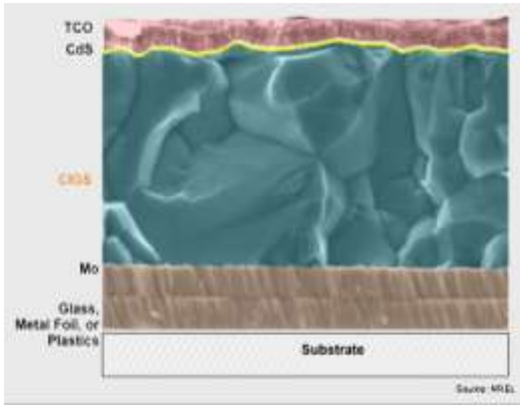
Inorganic CMOS



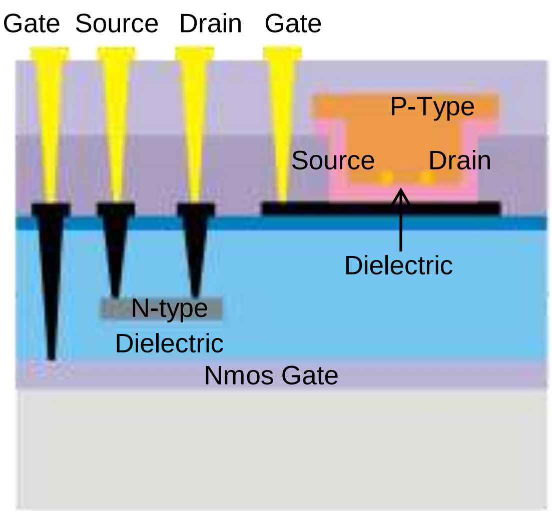
OLEDs



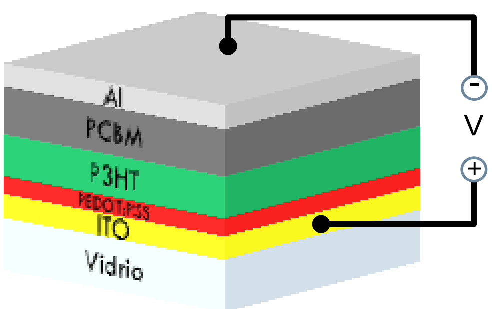
Inorganic Solar Cells



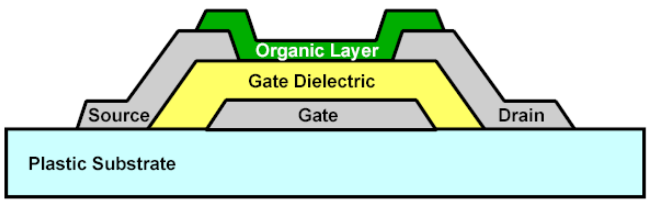
Hybrid CMOS



Organic Solar Cells



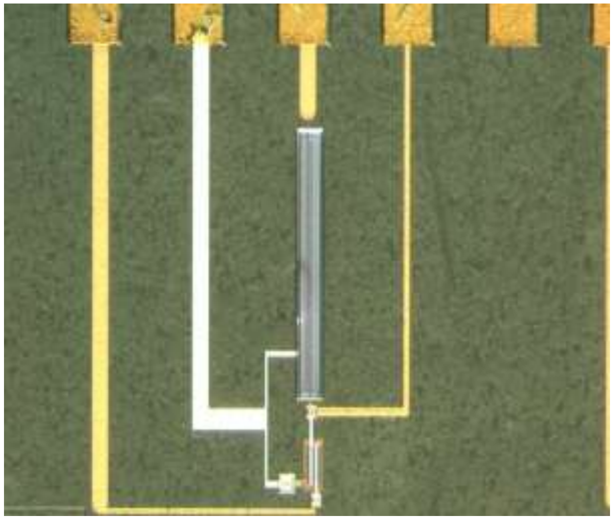
TFTs

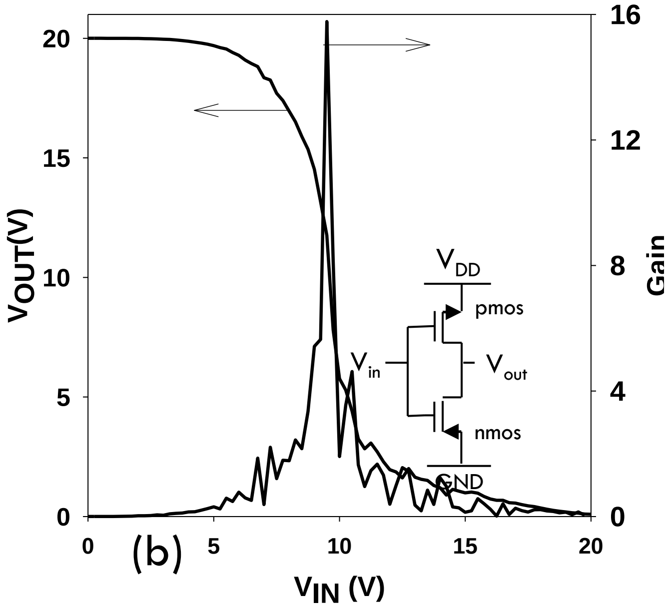


Film structure, Interface and surface defines device performance and reliability → *UT Dallas' mission is to investigate these issues*

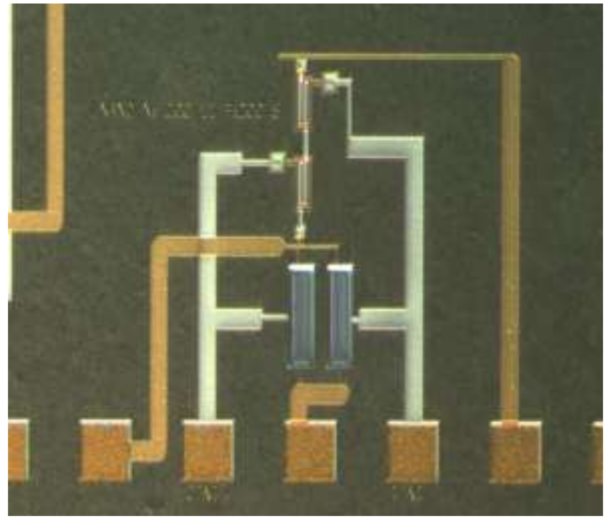
CMOS Devices Processed

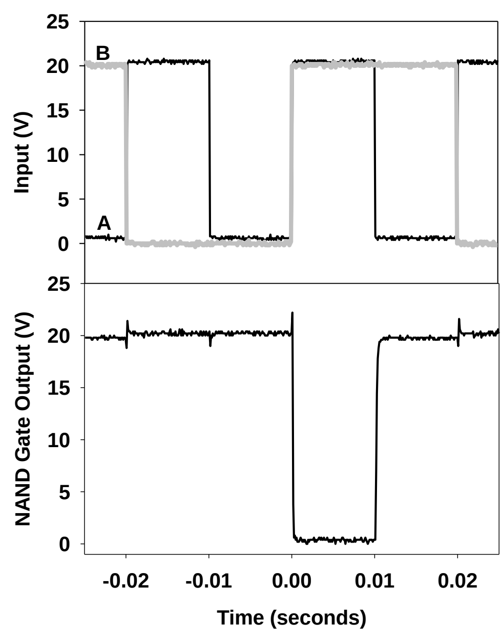
Inverters



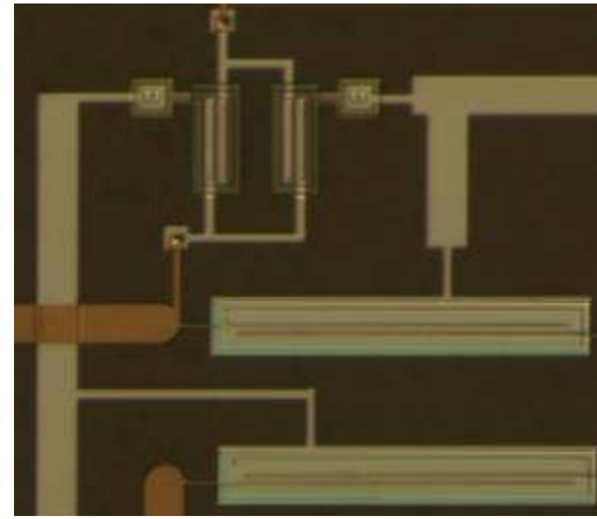


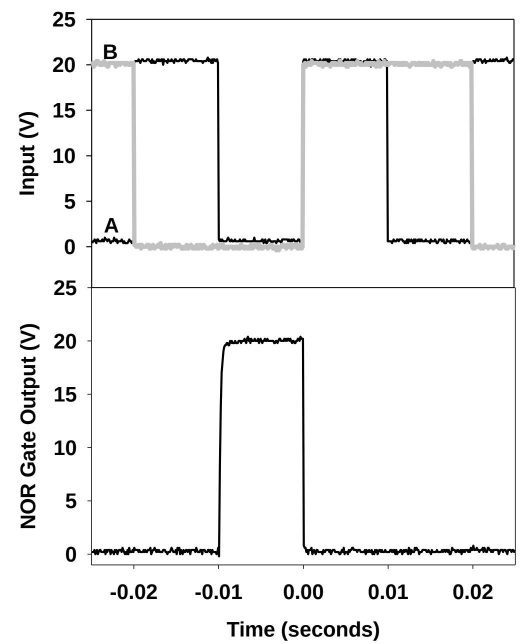
NAND Gates





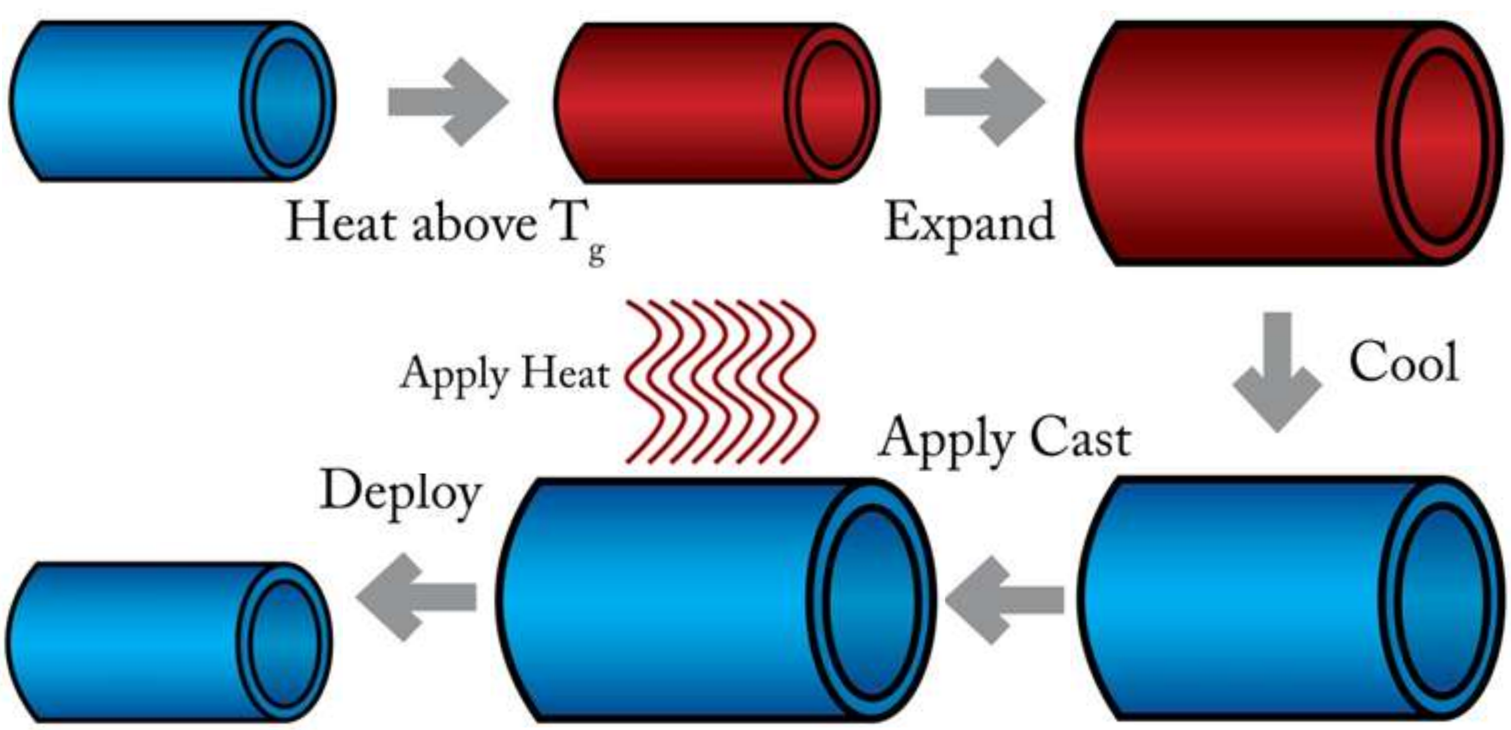
NOR Gates





Shrink Wrap to Shape Memory

Shape-memory polymer (SMP) orthopedic cast



Background – Engineering Materials (1)

- "Materials themselves affect us little; it is the way we use them which influences our lives." [1]
- *Vulcanization*, named after the Roman god of Fire, utilizes sulfur and heat to crosslink natural rubber (polyisoprene) [2]
- Targeted irradiation of thermoplastic precursors such as polyethylene can lead to grafting and the creation of a network polymer which resembles chemical crosslinking [3]

1. Epictetus, *Discourses, Book Chapter 5*, Athens, Greece **50 A.D.**
2. Goodyear, C. *Gum-Elastic and Its Variety, with a Detailed Account of Its Applications and Uses, and of the Discovery of Vulcanization*, Vol. I; New Haven, CT, **1855**
3. A. Charlesby, *Nature* **1953**, *4343*, 167

Background – Engineering Materials (2)

- Studies have been undertaken on the effect of e-beam radiation on synthetic acrylic *elastomers* [1]
- Studies have been undertaken on the effect of e-beam radiation on synthetic acrylic *rubbers* [2]
- Some acrylate SMPs have independently tunable T_g and E_R and show biocompatibility [3]

1. I. Banik, A. K. Bhowmick, *Radiation Physics and Chemistry* **2000**, *58*, 293
2. V. Vijayabaskar, S. Bhattacharya, V. K. Tikku, A. K. Bhowmick, *Radiation Physics and Chemistry* **2004**, *71*, 1045.
3. C. M. Yakacki, R. Shandas, D. Safranski, A. M. Ortega, K. Sassaman, K. Gall, *Advanced Functional Materials* **2008**

Mnemosynation™

SMP mass-manufacturing technique that combines:

1.) tunable thermoplastic polymer synthesis,

2.) crosslinker blending,

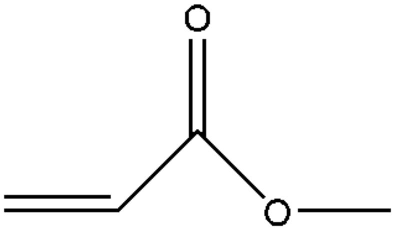
3.) plastic molding and

4.) high-energy radiation

5.) to control final thermo-mechanical properties

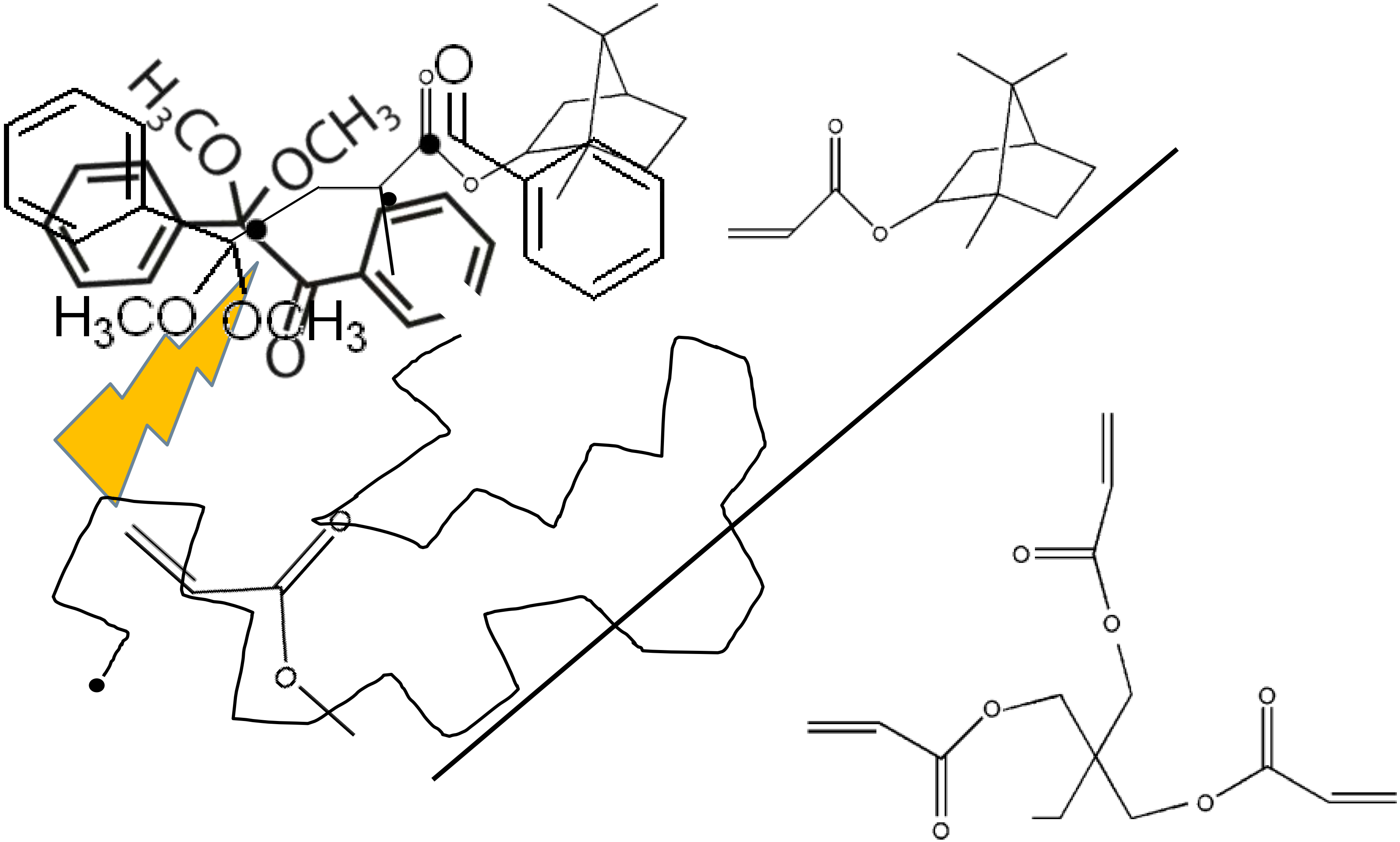
6.) in a custom device.

Monomers

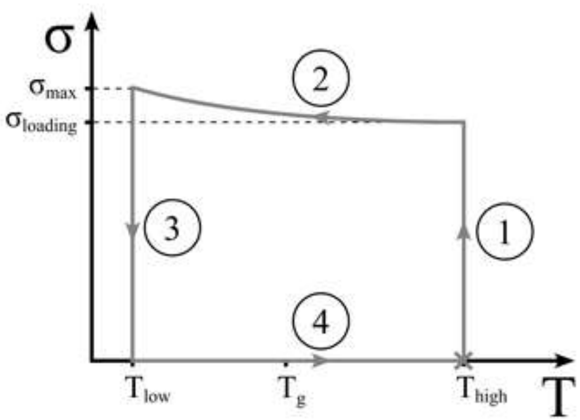


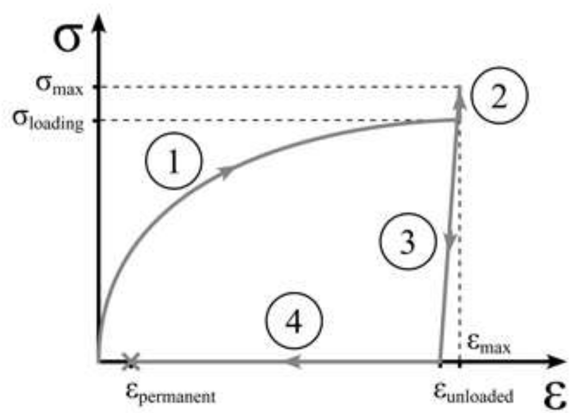
- *Methyl acrylate (MA)
- Butyl acrylate (BA)
- Isobornyl acrylate (IBoA)
- Trimethylolpropane triacrylate (TMPTA)
- Triallylisocyanurate (TAIC)
- *4-tert*-butylcyclohexyl acrylate (TbCHA)
- N-isopropylacrylamide (NiPAAm)
- Acryloylmorpholine (AMO)
- 2-carboxyester acrylate (CXEA) oligomers

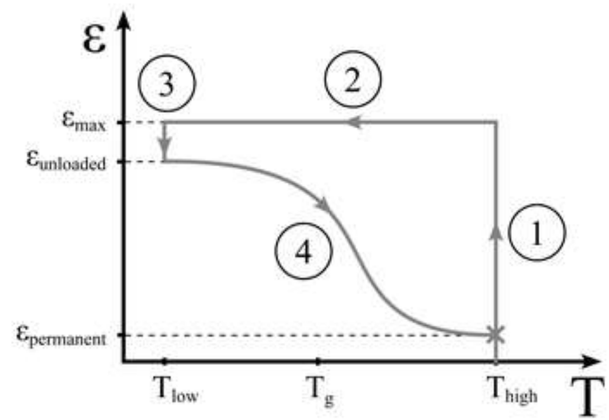
Polyacrylate Polymer Synthesis

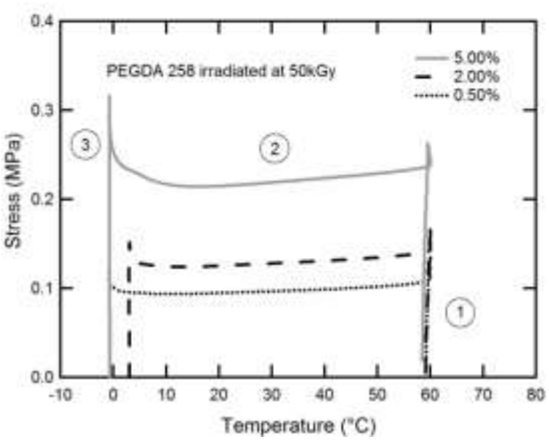


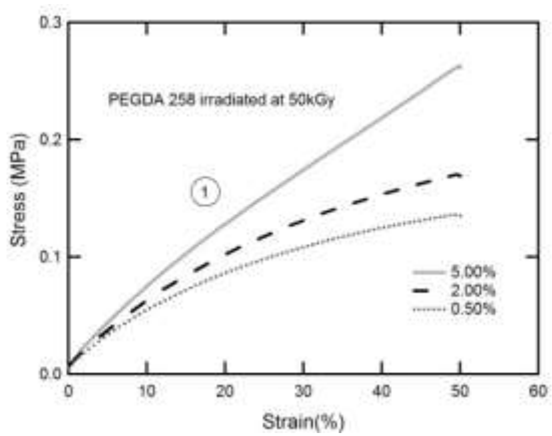
Shape-Memory Cycle

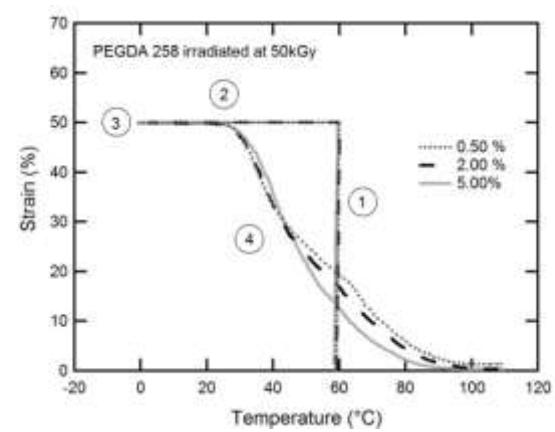




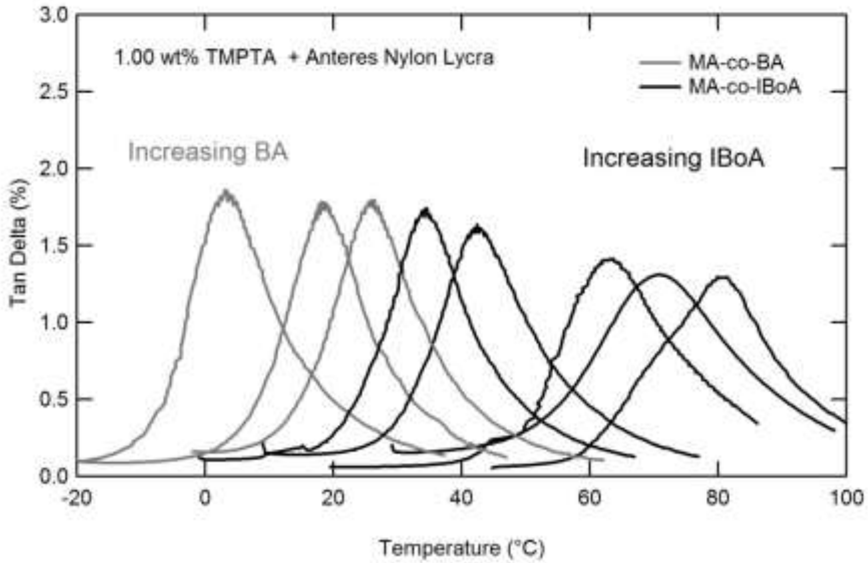


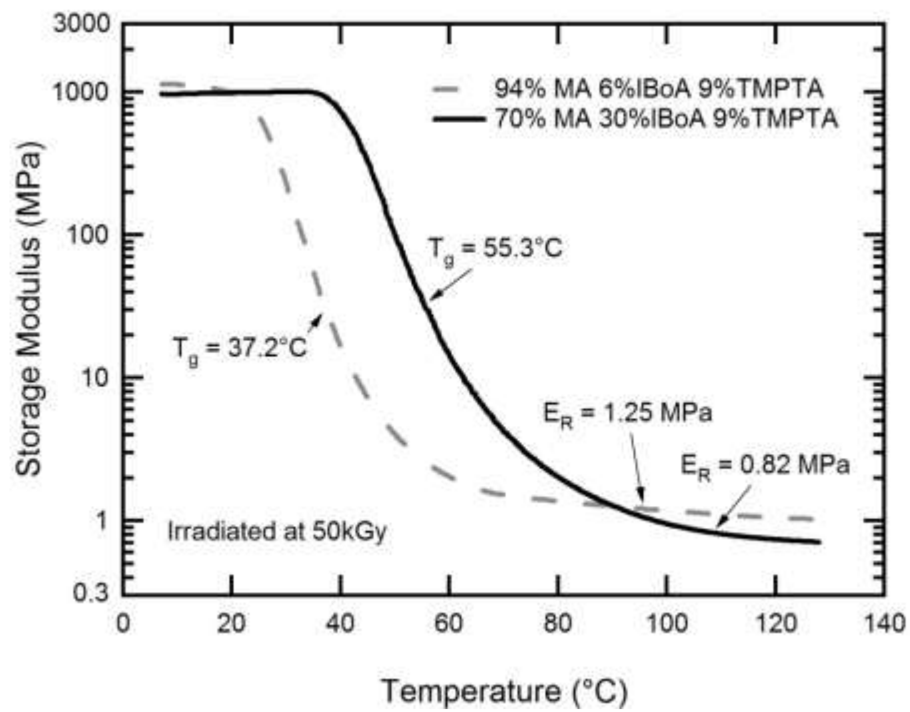






Altering Glass Transition (recovery temp.)





Criticisms of SMP Modeling

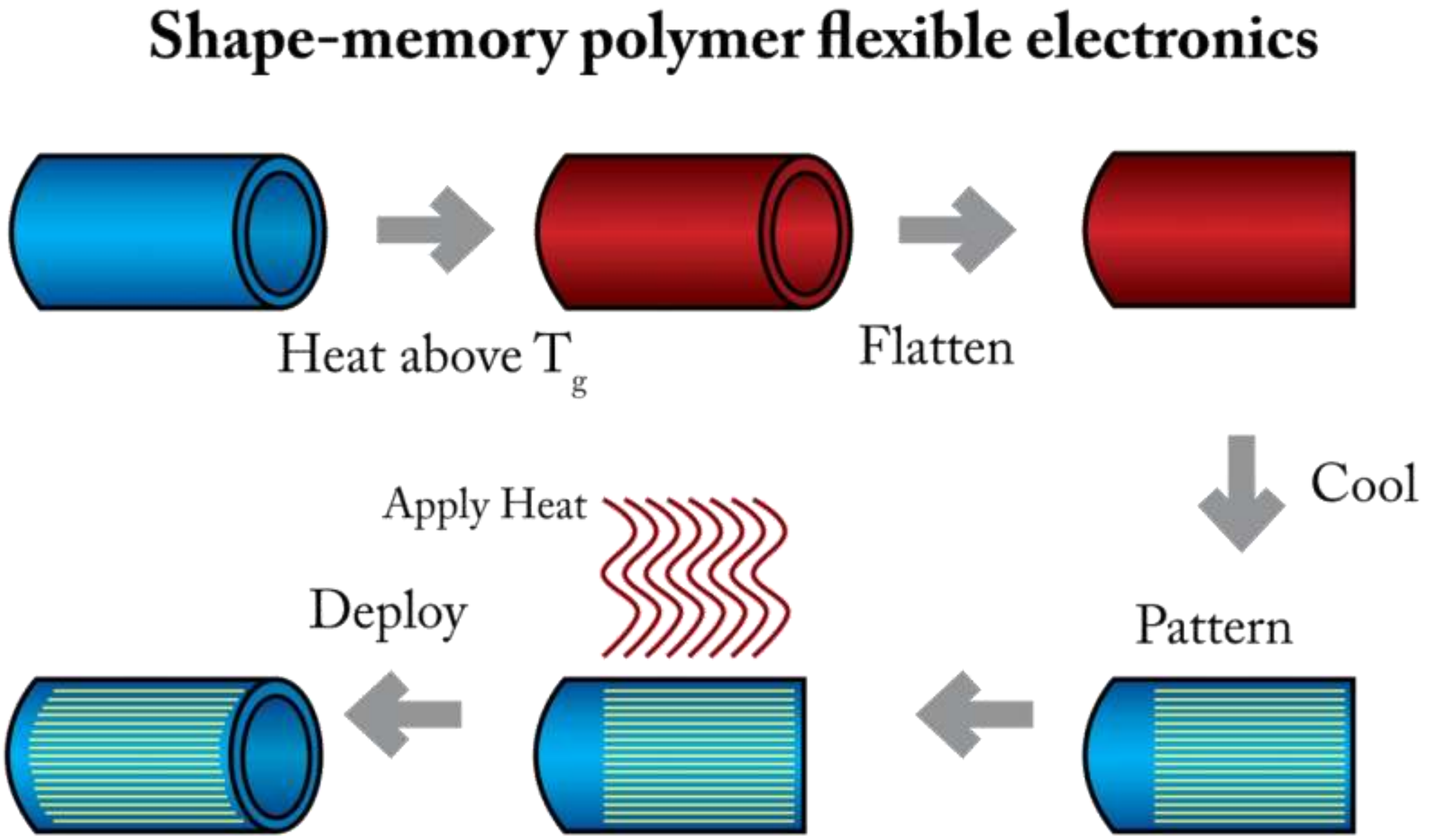
- "the few models that have been developed for shape memory polymers are 1D curve fits based on linear viscoelasticity"
- "[SMP models] are valid only for small strains"
- "models are ad hoc and are not placed within a proper thermodynamic framework"
- "cannot be generalized to account for three-dimensional deformations easily"

2008: G., Barot , I.J., Rao , K.R., Rajagopal

SMPs for Flexible Electronics

How Processing Defines Structure and Properties

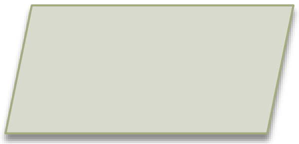
Devices on shape memory polymers



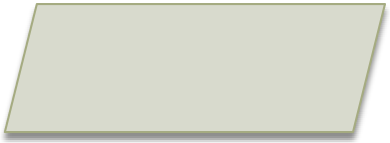
Method 1

Improvement to Method 1

- Synthesize + irradiate SMP substrate

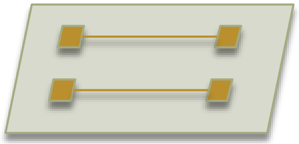


- Heat and stretch



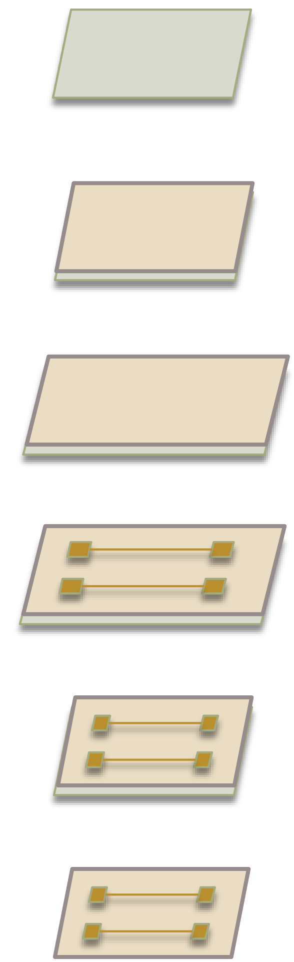
- Deposit gold electrodes

- Heat to enable strain recovery

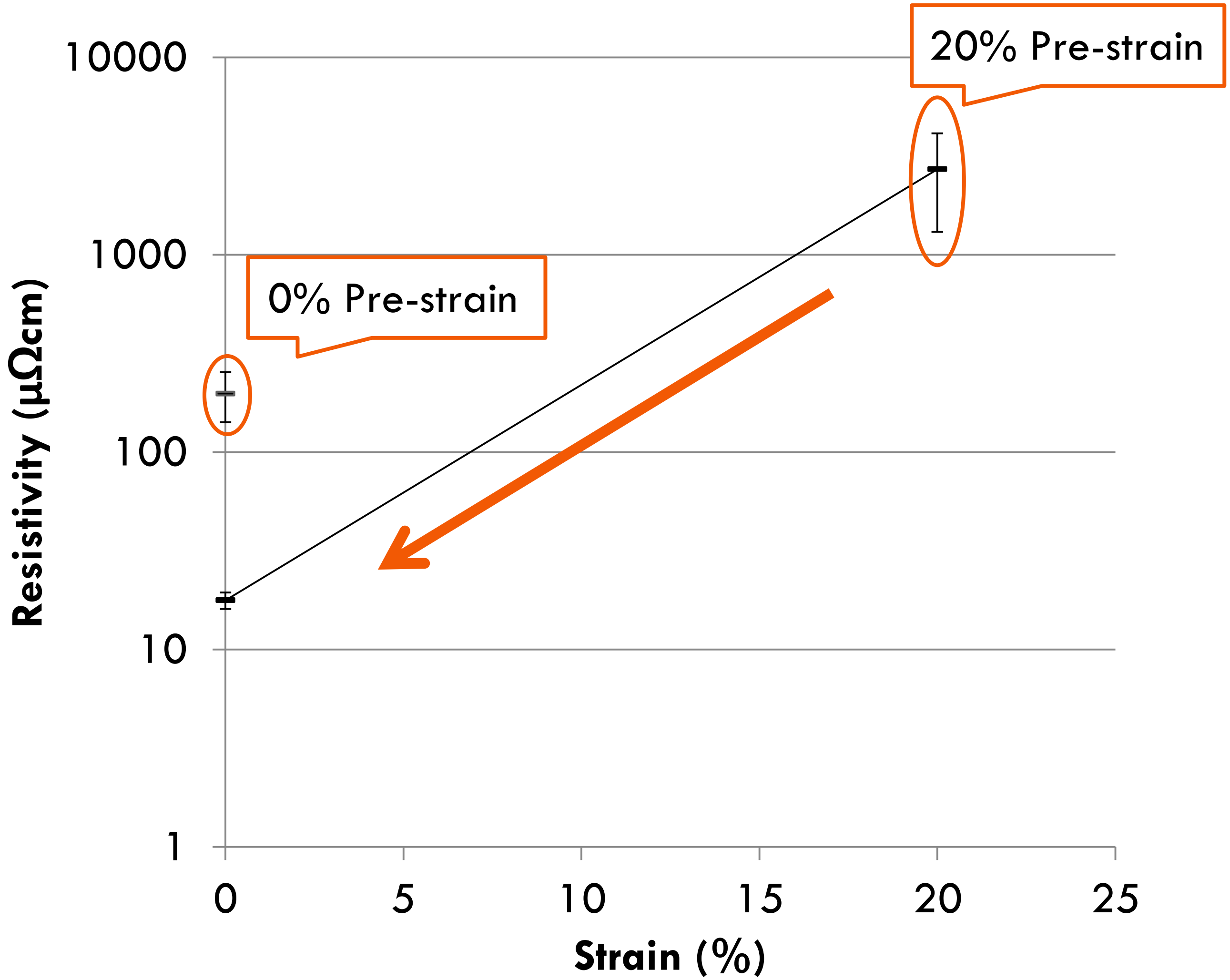


SMP as a Carrier for PDMS (polydimethylsiloxane)

- Synthesize + irradiate SMP carrier
- Spin coat 260µm thick layer of PDMS
- Heat and stretch
- Deposit gold electrodes
- Heat to enable strain recovery
- Peel PDMS from SMP carrier



Resistance Change Following Strain Release

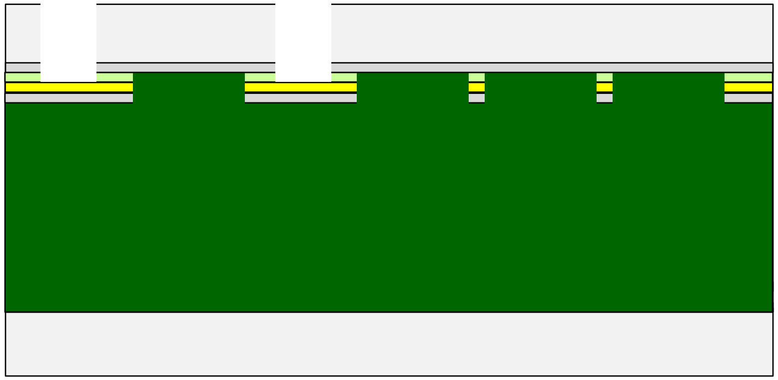


-- Collaboration with Abhishek Raj, Wenzhe Cao and Sigurd Wagner – Princeton University

Improved Processing and Adhesion

Liftoff process:

1. Glass Backing
2. Deposit Parylene
3. Deposit Gold
4. Deposit Chrome
5. Mask + Etch
6. Make Mold
7. Fill with Solution
8. UV Cure at 365 nm
9. Flip + Remove Glass
10. Parylene Coating
11. RIE to Reveal Pads
12. Deform + Irradiate



Method 2

Improved Processing and Adhesion

Liftoff process:

1. Glass Backing
2. Deposit Parylene
3. Deposit Gold
4. Deposit Chrome
5. Mask + Etch
6. Make Mold
7. Fill with Solution
8. UV Cure at 365 nm
9. Flip + Remove Glass
10. Parylene Coating
11. RIE to Reveal Pads
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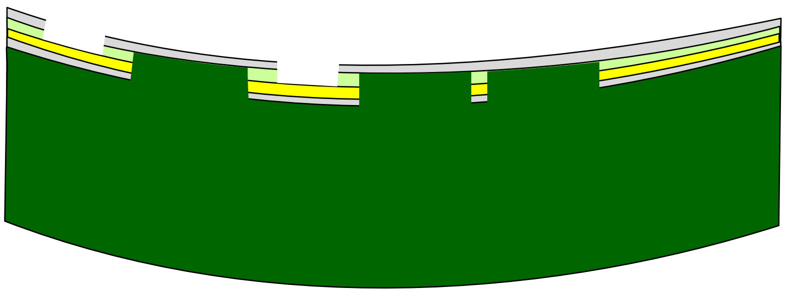


Method 2

Utilize the Shape Memory Effect

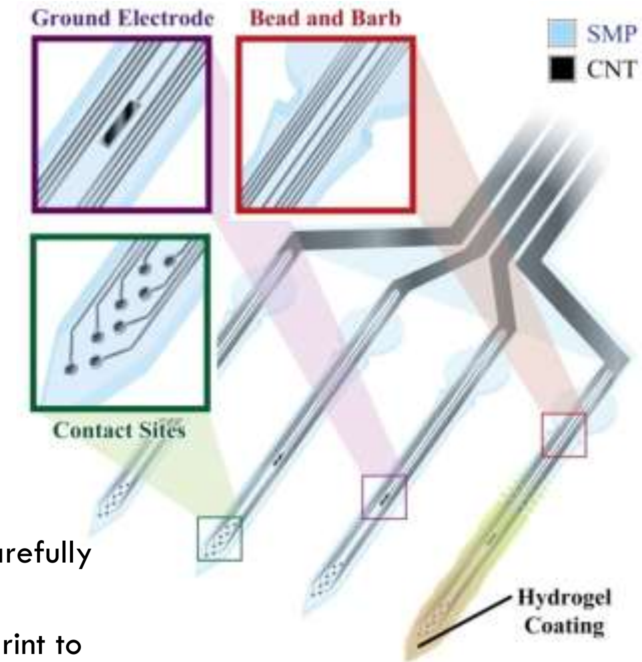
- Use Mnemosynation™ on the device
  - Heat and deform to a new shape (e.g. cylinder) without destroying the electrodes
  - Expose to ionizing radiation to permanently set the new final shape
- Use the SMP cycle
  - Heat, Deform, Cool
  - Heat to Recover
- **Applications:** Neuronal brain probes, cell culture dishes, cochlear implants, TFTs, flexible orthotics and prosthetics

Method 1 or Method 2

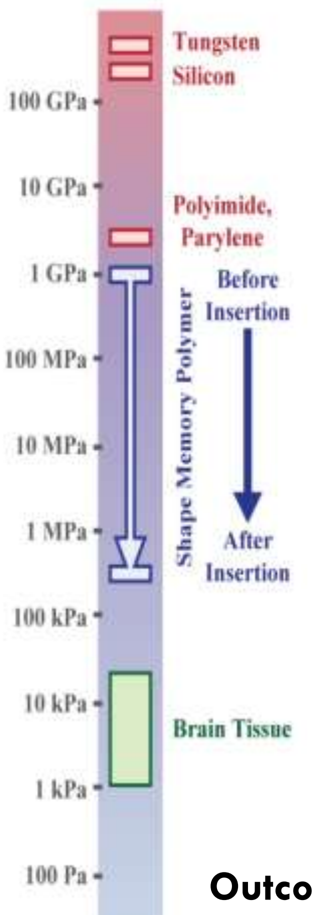
Neural Biotechnology

Nerves of stainless steel, gold, chrome, titanium, nanotubes, graphene or conductive polymers

High Channel Count, Shape Memory Polymer, Carbon Nanotube Electrodes in Degradable Drug-Eluting Hydrogels as Reliable Central Nervous System Interfaces



Goal: Increase chronic reliability of CNS electrodes utilizing advanced photolithography, shape memory polymers, carbon nanotubes and drug-eluting hydrogels in *in-vivo* animal models.



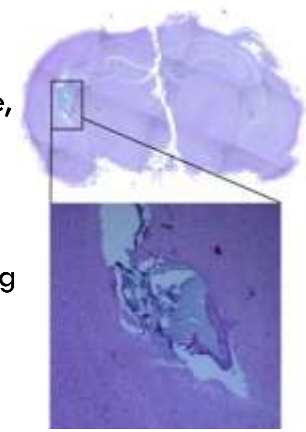
Advanced Photolithography (*top right*) to produce a massively scalable solution with (sub 10 µm) features on both sides of a carefully chosen electrode geometry to meet cost-realism targets.

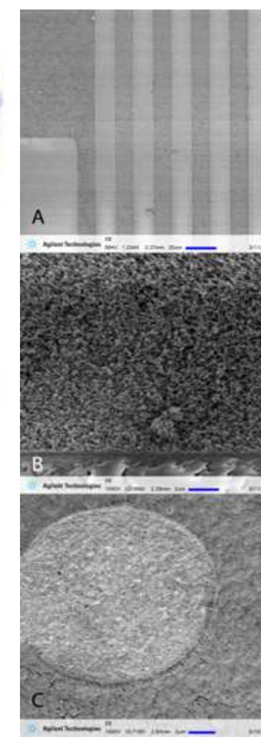
Shape Memory Polymers (SMP) (*left*) to minimize surgical footprint to deliver non-buckling insertion, yet ultra-soft (sub 1 MPa) modulus in brain tissue with the ability to morph into a new shape during use.

Carbon Nanotube (CNT) Electrodes (*bottom right*) to lower impedance, improve strain capacity, increase attachment surface area at the exposed electrode pad, and, with neural growth factor functionalization, promote localized neurite outgrowth.

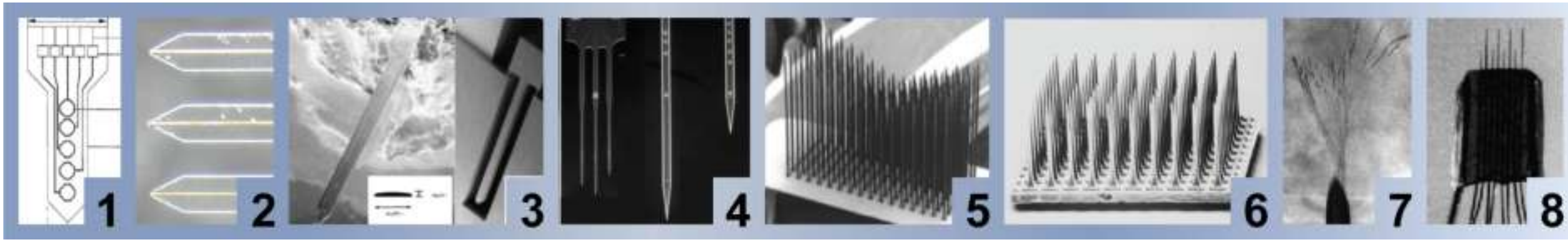
Drug-Eluting Hydrogels (*inside right*) to minimize shearing forces during insertion, and with the timed-release of anti-inflammatory agents, improve tissue response.

***In-vivo* animal models** (rats in Phase I, rats and primates in Phase II) enable recording amplitude and SNR comparisons (whisker deflection paradigm in somatosensory and motor cortex recordings) and histology (quantitative glial response, inflammatory response) at time intervals and with accelerated testing (cyclic deflection of implanted electrode at tethering location).





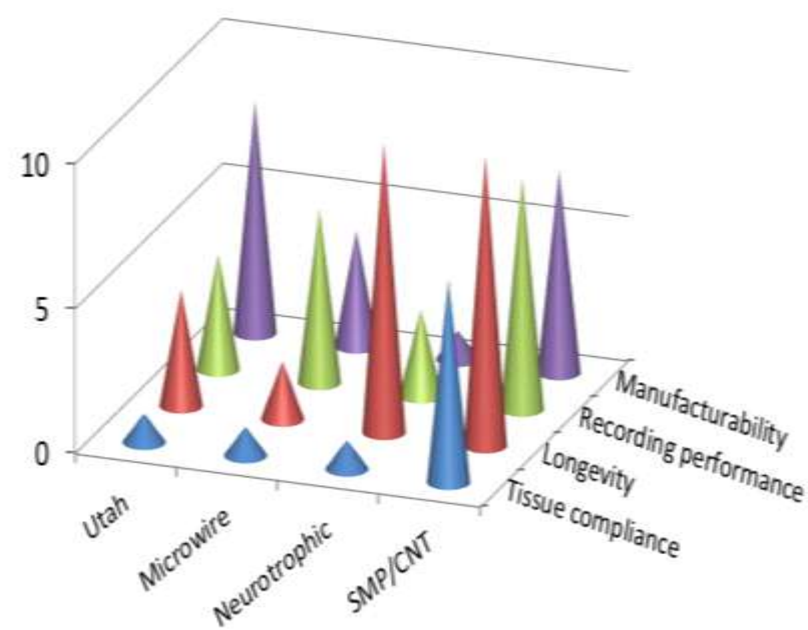
Outcome: Chronic, reliable CNS electrodes to interface with 22 DOF systems



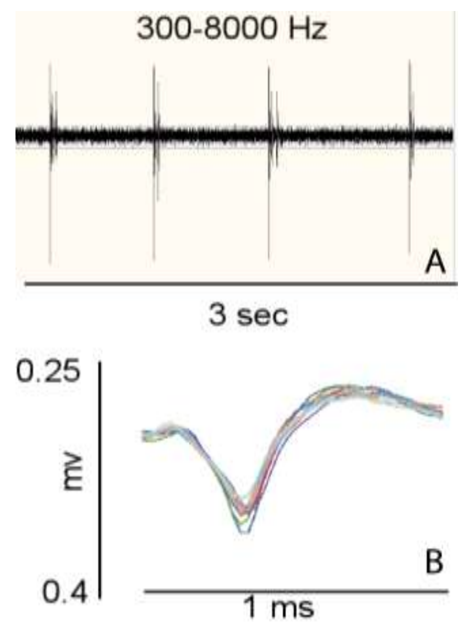
State-of-the-art

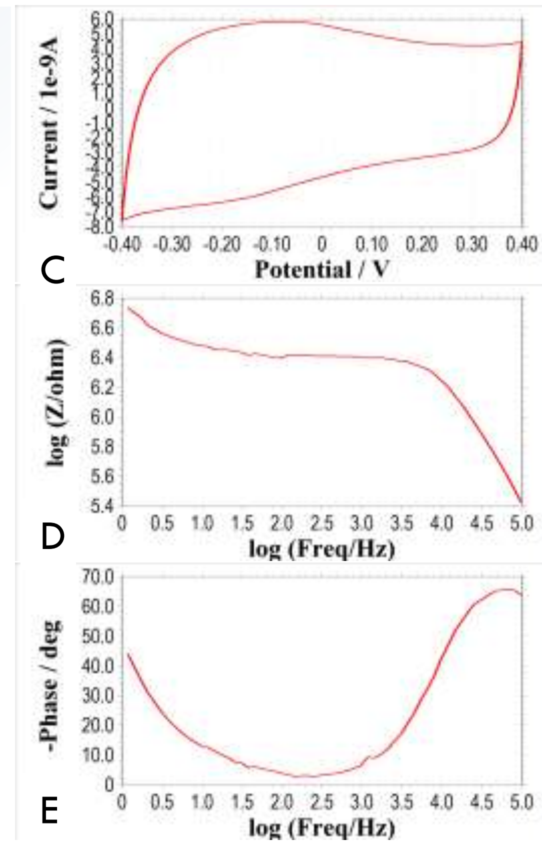
Neuronal probes have been proposed in a variety of geometries and possess similar engineering and commercial challenges to MEA's. Existing probe devices include: (1) multi-lead Si probes [52], (2) multi-prong Si probes [53] (3) various shaped Si probes [19] and (4) polymer-based neuronal probes with embedded 25 μm microwires [54]. Successful neural arrays include: (5) Si probe array [48, 49], (6) Utah array [17] (7) 12.5 μm Ni-Cr-Al microwire array [55] and (8) 100 μm W microwire array [56].

Comparison of CNS interfaces

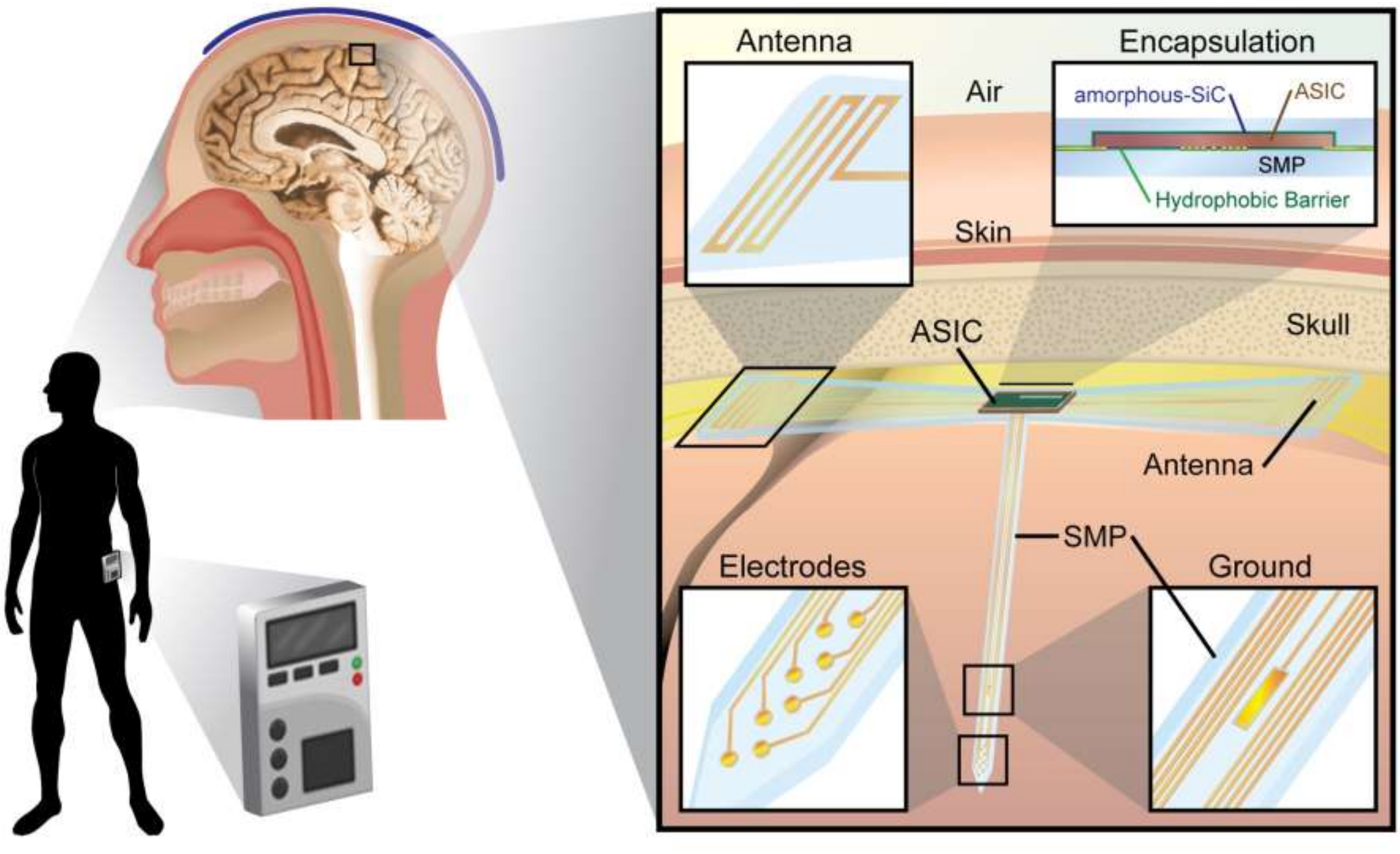


This team's unpublished initial results with SMP electrodes in a rat cortex

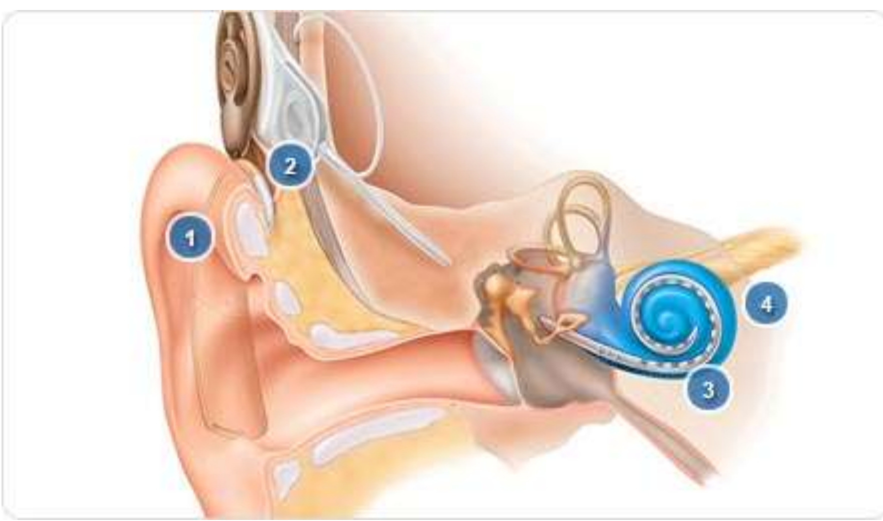


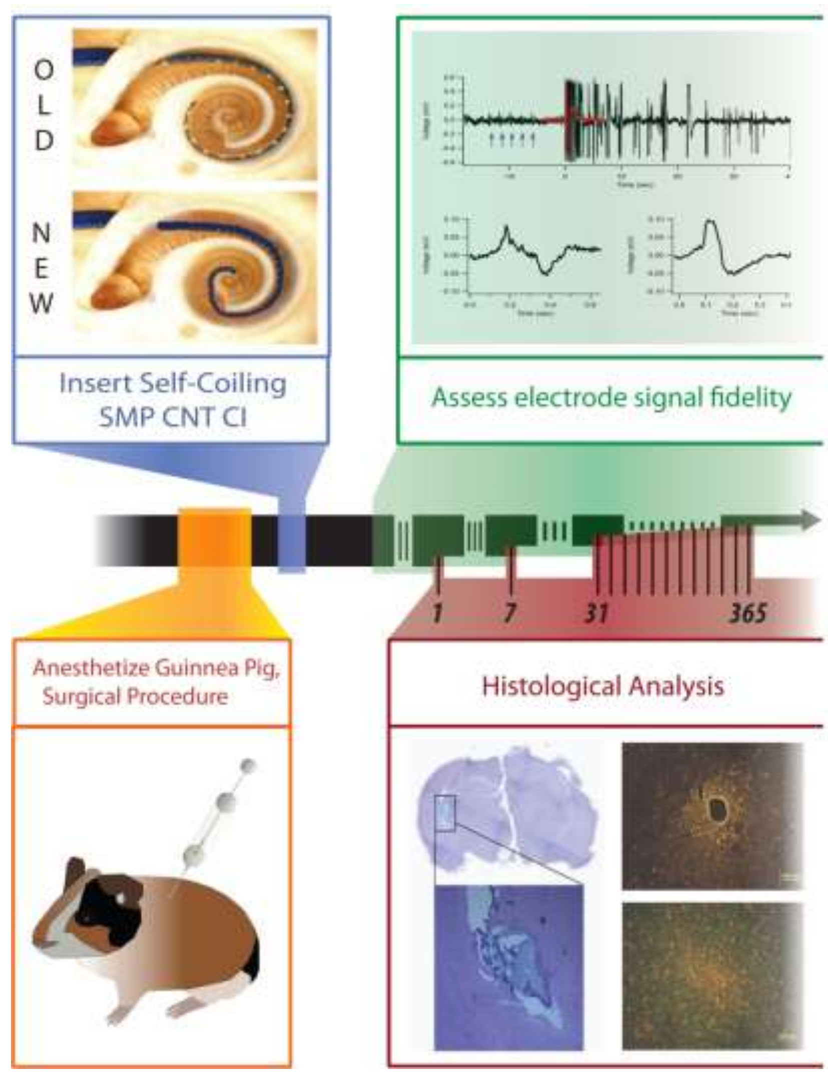


Wireless Brain Probes

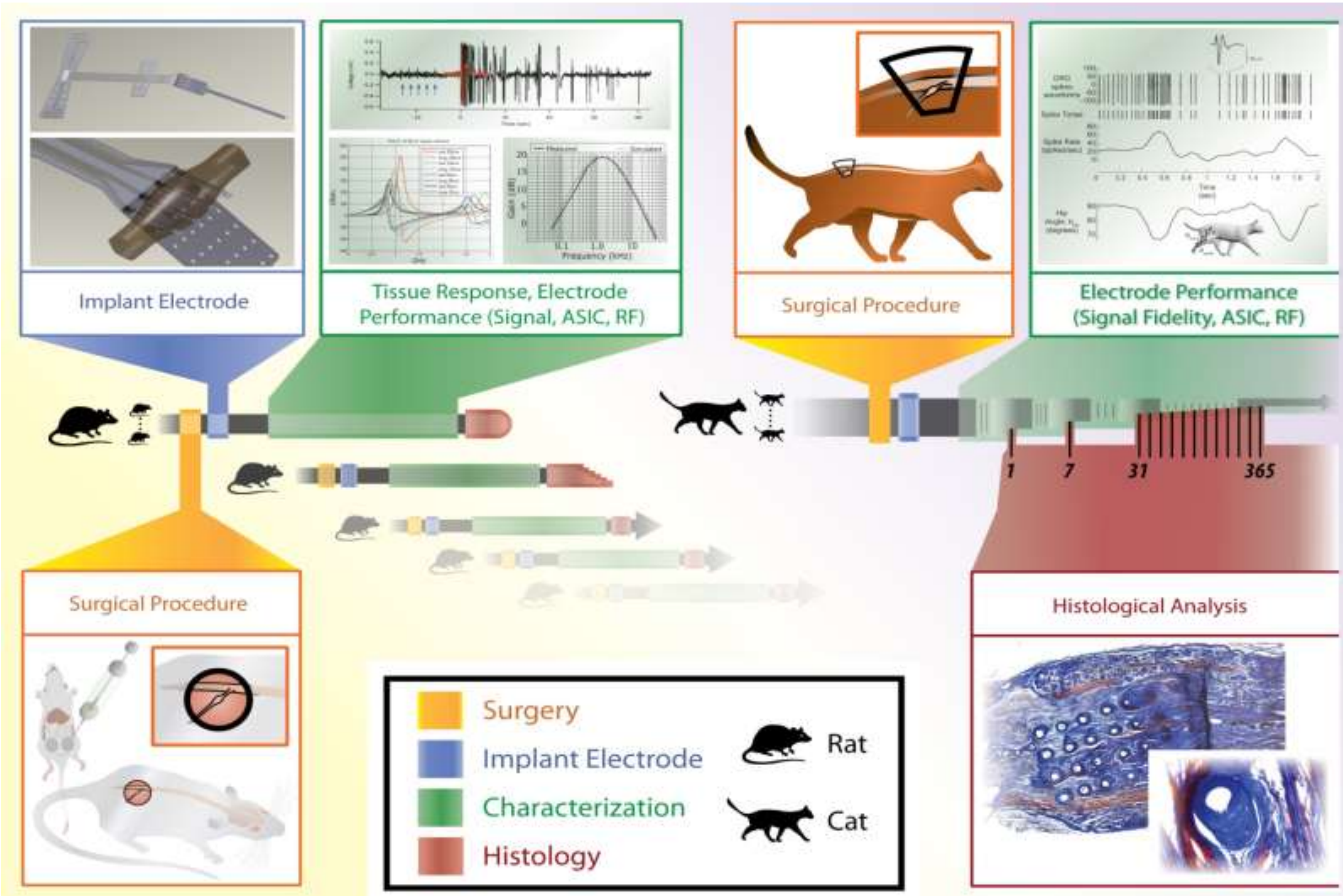


Cochlear Implants



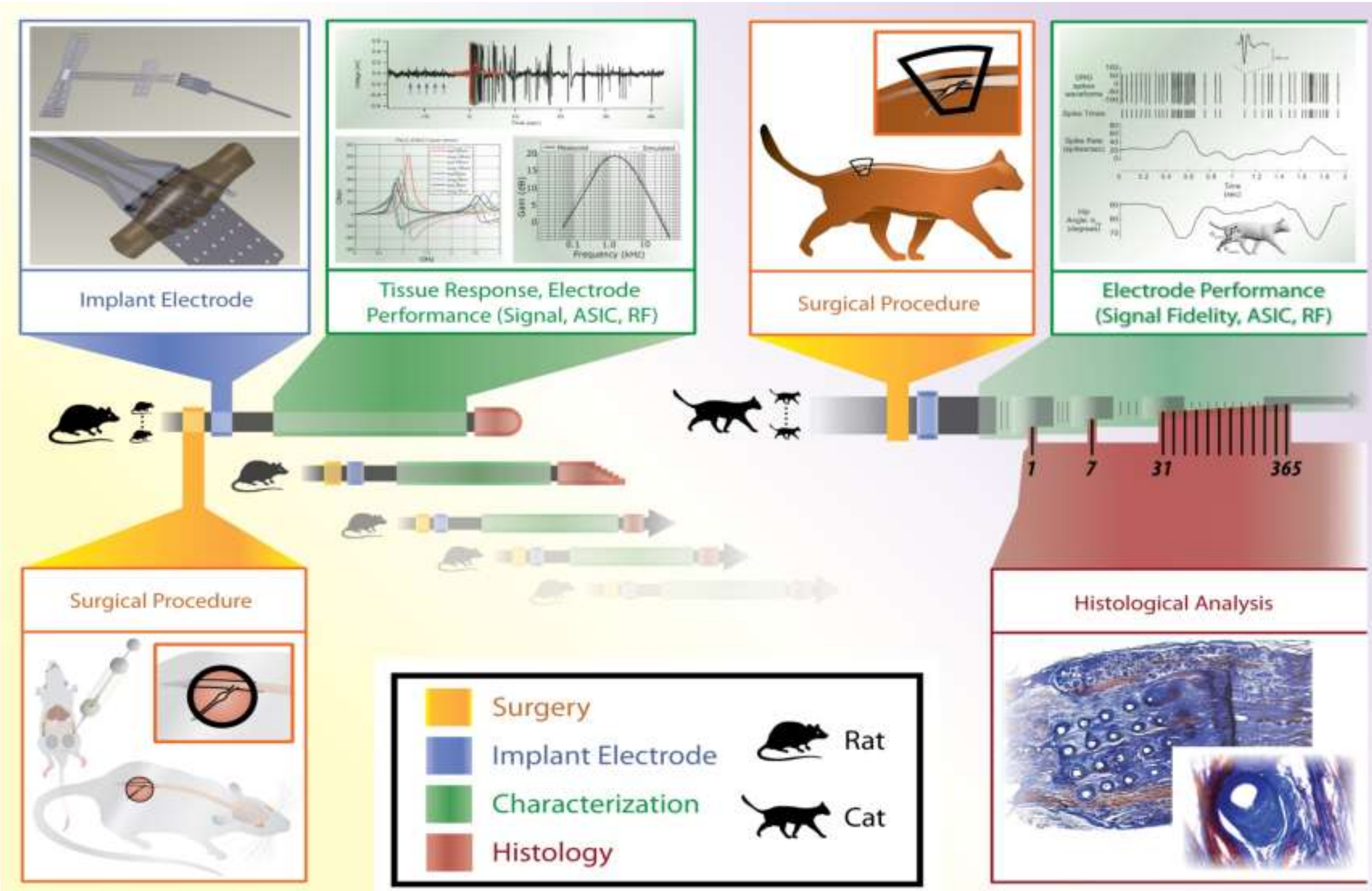


Nerve Cuff Electrodes



Grounded SMP Nerve Cuff

DRG Nerve Cuff Electrode



Conclusions

- Flexible electronics are here, now
- CLASS could help centralize efforts across the world in flexible electronics in Dallas
- SMPs can be used to tailor a substrate's thermomechanical properties
- SMPs can be used cleverly in various processing routes to create complex 3D structures
- Neural technology market predicted to be $8.8 billion in 2012 (cochlear implants: ~$1.6 billion)*

*http://www.neurotechreports.com/pages/marketprojections12.html

Acknowledgements

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- **APRL Undergraduate Researchers**: Abhishek Raj, Sagar Shah, Clive Liu, Ryan Marcotte, Zoe Wilson, Nate Fairbank, Vivek Raman, Courtney Keeler, Wesley Fichera
- **Academic Collaborators**: Drs. M. Quevedo, B. Gnade, S. Wagner, R. Rennaker, E. Keefer, B. Wester, Y. Hanein, J. Elisseeff, A. Blanchard, H. Lu, D.W. Smith, D. MacFarlane, D. McDowell, B. Boyan, R. Dasari, R. Tannenbaum, M. Stefan, S. Marder, S. Barlow, R. Roeser
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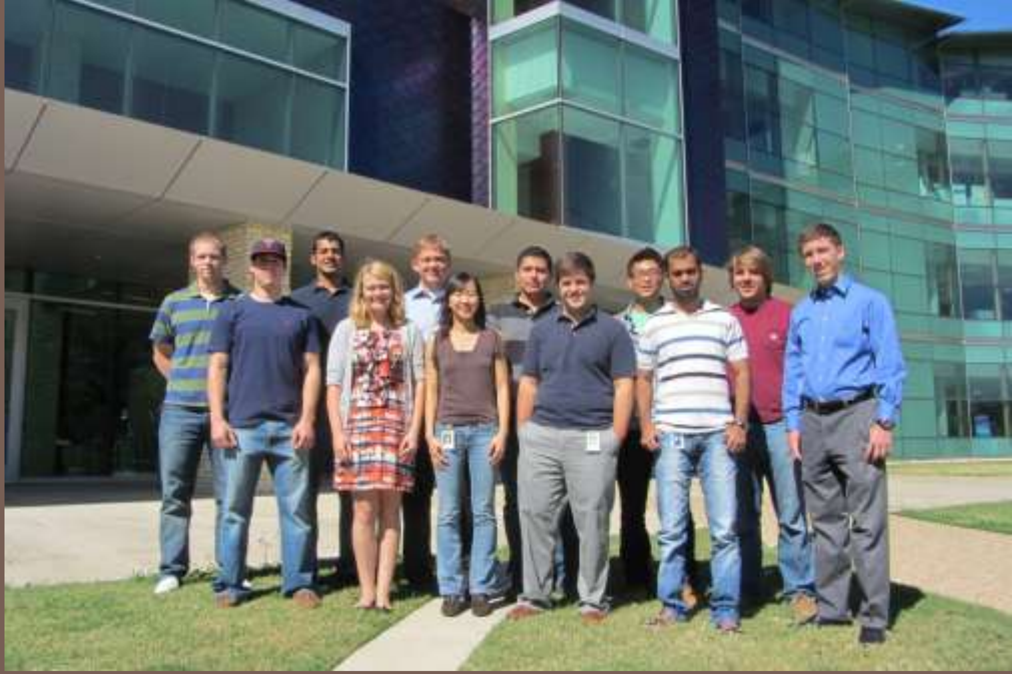
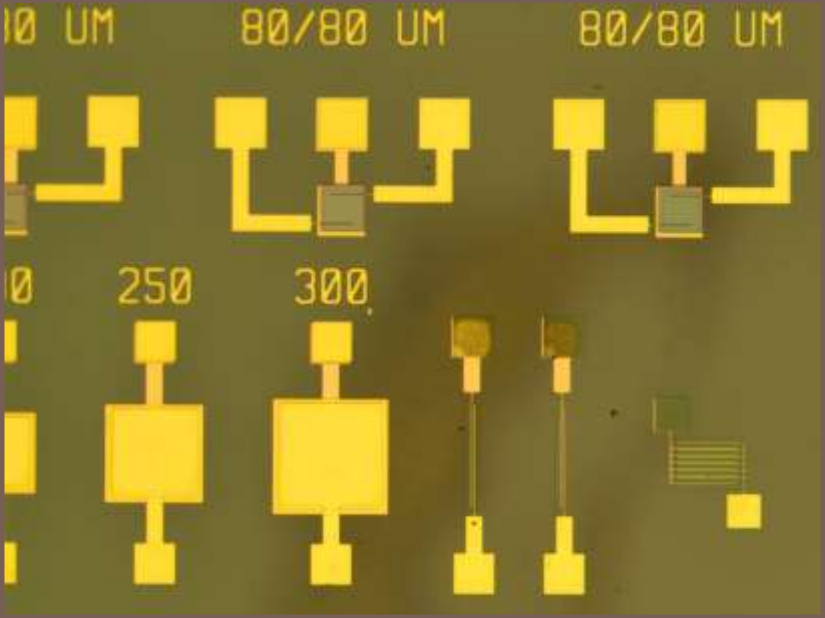
- **CIRMS hosts**

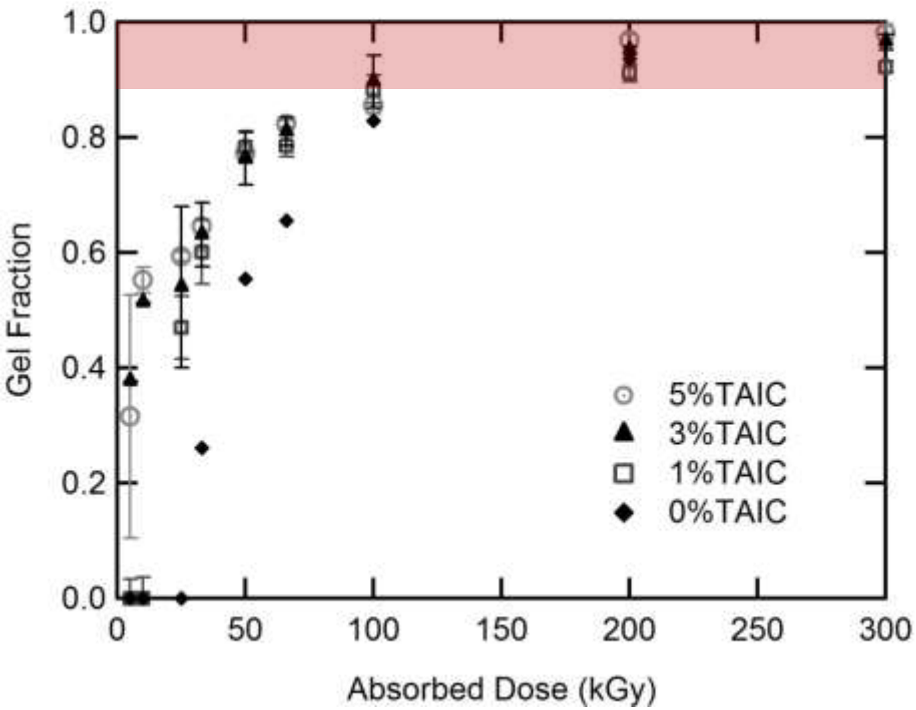


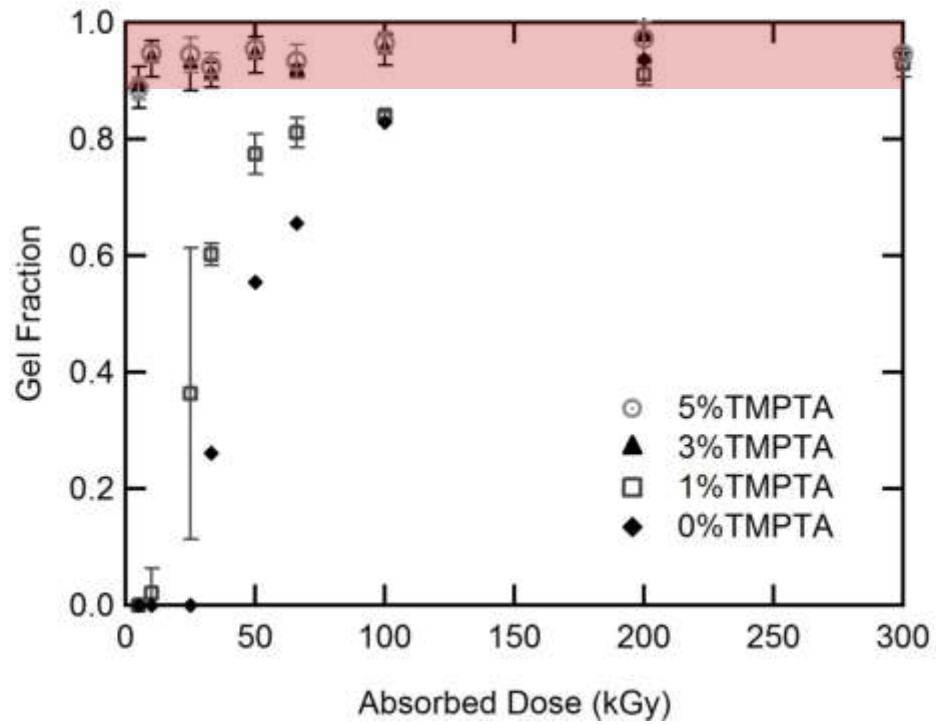


THANK YOU

email questions to walter.voit@utdallas.edu

Effects of Irradiation (processing)





Note: Base polymer is poly(methyl acrylate) (PMA)

Classical Charlesby-Pinner Equation

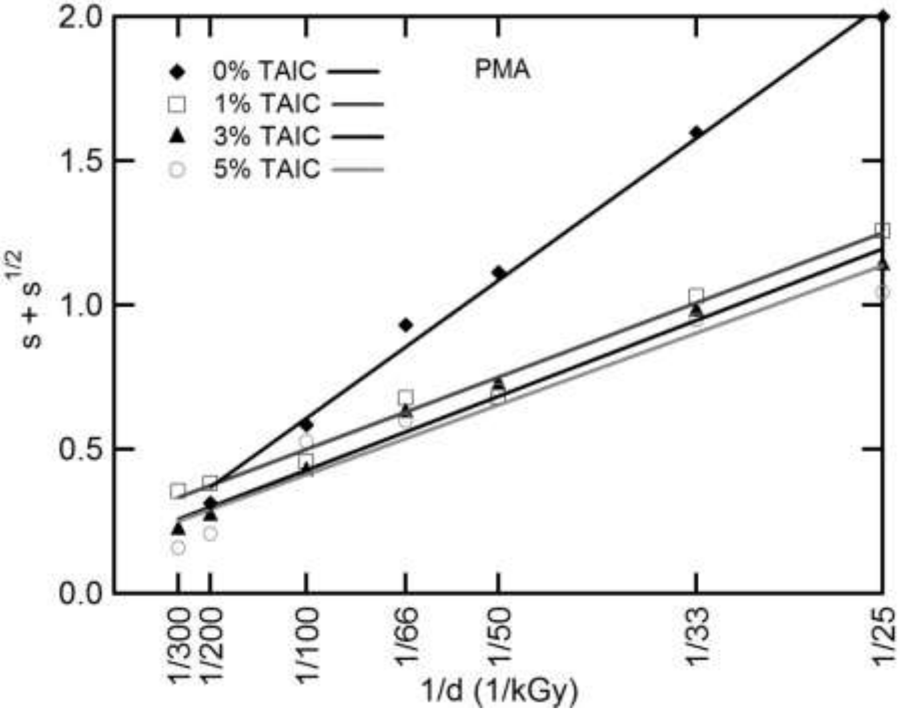
$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 d}$$

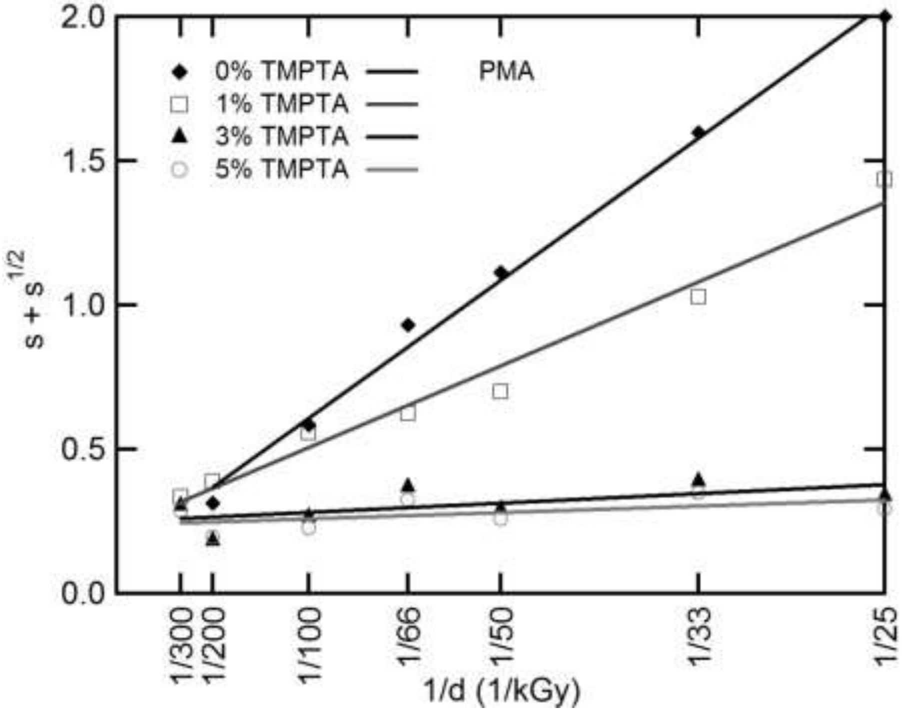
s - sol fraction
p_0 - degradation density
q_0 - crosslinking density
μ_1- initial weight, average degree of polymerization
d - radiation dose

- Linear data set generated plotting $\boldsymbol{s+s^{1/2}}$ vs. $\boldsymbol{1/d}$
- Linear fit yields intercepts at $\boldsymbol{1/d}$ = 0 and $\boldsymbol{s+s^{1/2}}$ = 2
- $\boldsymbol{1/d}$ = 0 intercept is ratio of scission to crosslinking ($\boldsymbol{p_o/q_o}$)
- $\boldsymbol{s+s^{1/2}}$ = 2 intercept is min. dose of gelation ($\boldsymbol{d_o}$)

Analysis

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 d}$$





Notice the very small slope seen with the 3 wt% and 5 wt% TMPTA samples

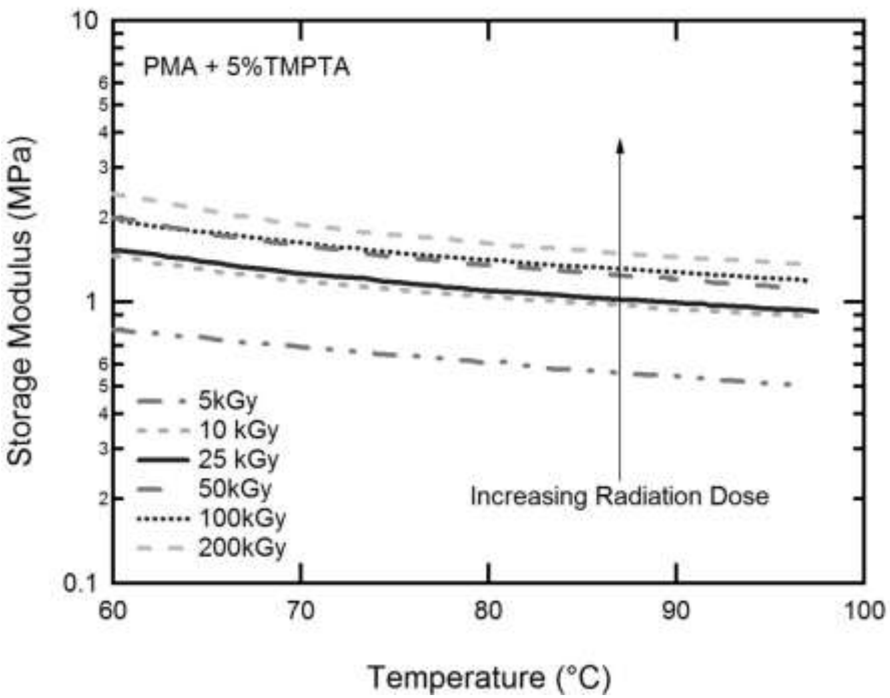
Charlesby-Pinner Metrics

Crosslinker	p_0/q_0	d_0 (kGy)	R^2
0%	.129	25.57	.993
1% TAIC	.248	14.30	.985
3% TAIC	.173	14.00	.982
5% TAIC	.170	13.21	.934
1% TMPTA	.223	15.94	.976
3% TMPTA	.248	**1.836**	**.383**
5% TMPTA	.237	**1.240**	**.300**

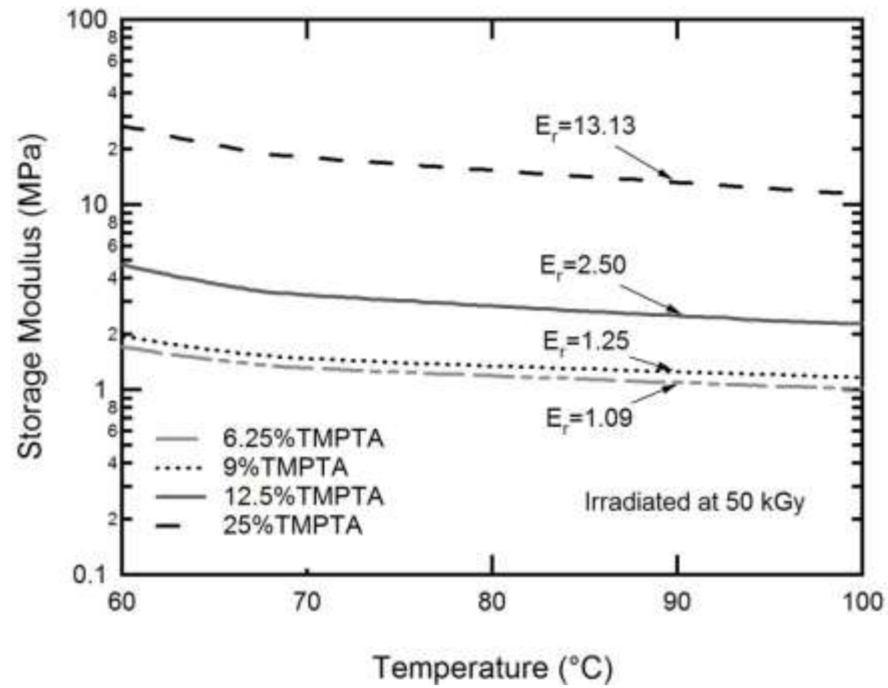
$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 d}$$

p_0 - degradation constant
q_0 - crosslinking constant
d_0 - minimum dose for gelation
R^2 - accuracy of linear fit

Altering Rubbery Modulus (comfort / force)

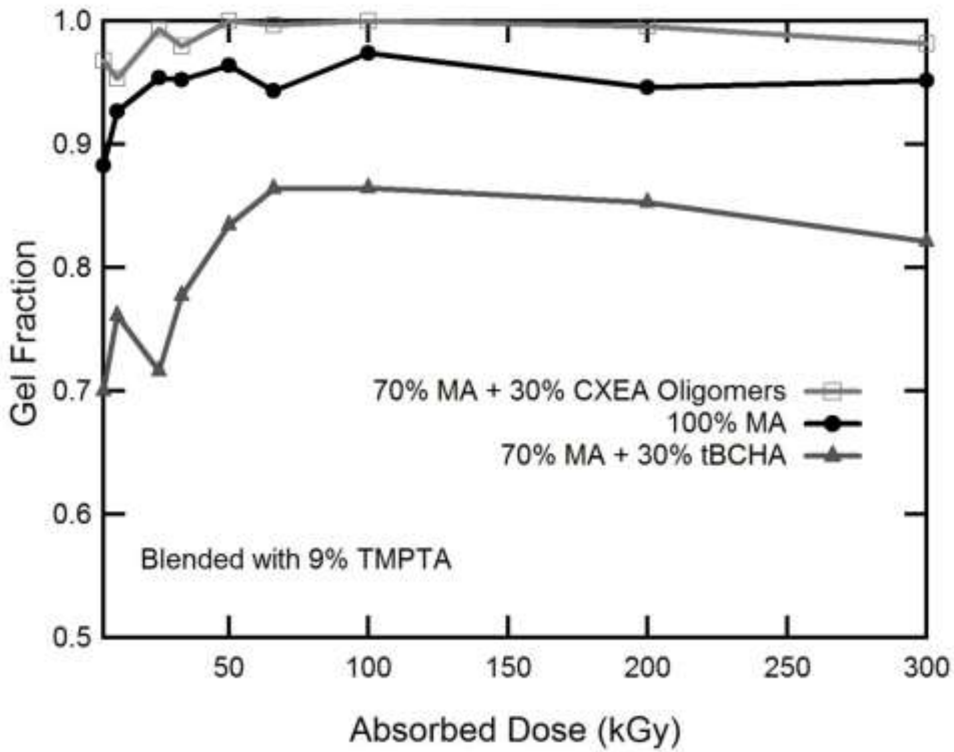


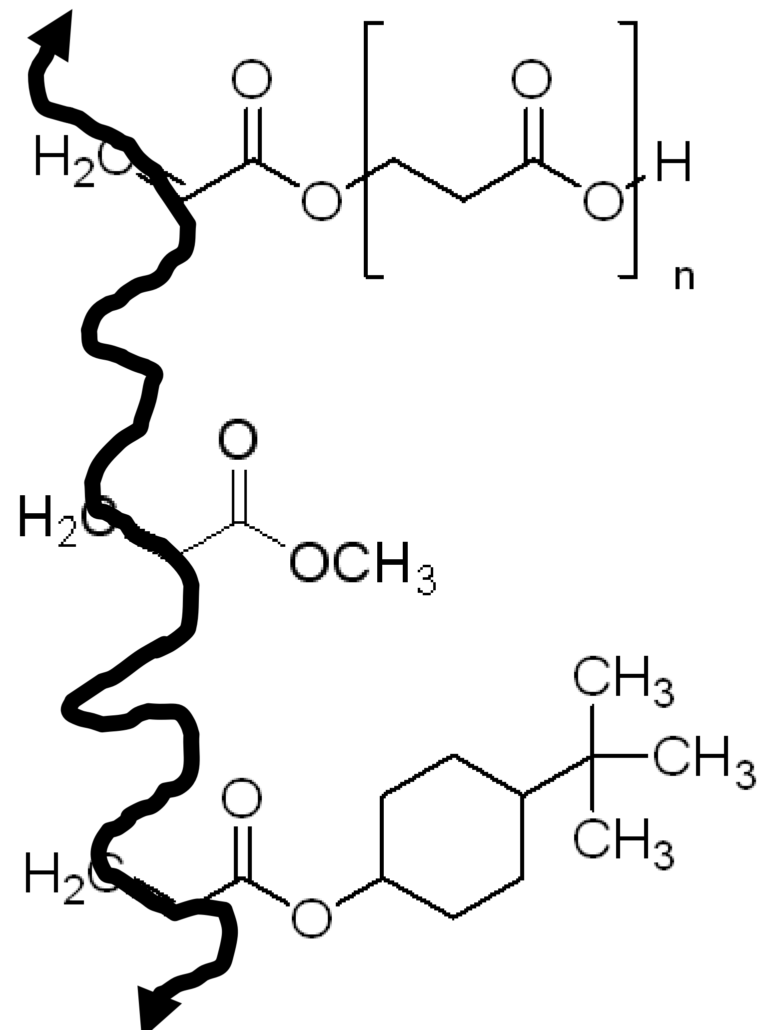
1. Changing dose



2. Changing crosslinker concentration

α - Hydrogen Hypothesis





*Potential for a publication in Radiation Physics and Chemistry