Experimental Approaches from a "Forward Looking" Laboratory:

Polymer and Coatings Research at the *NIST Combinatorial Methods Center*

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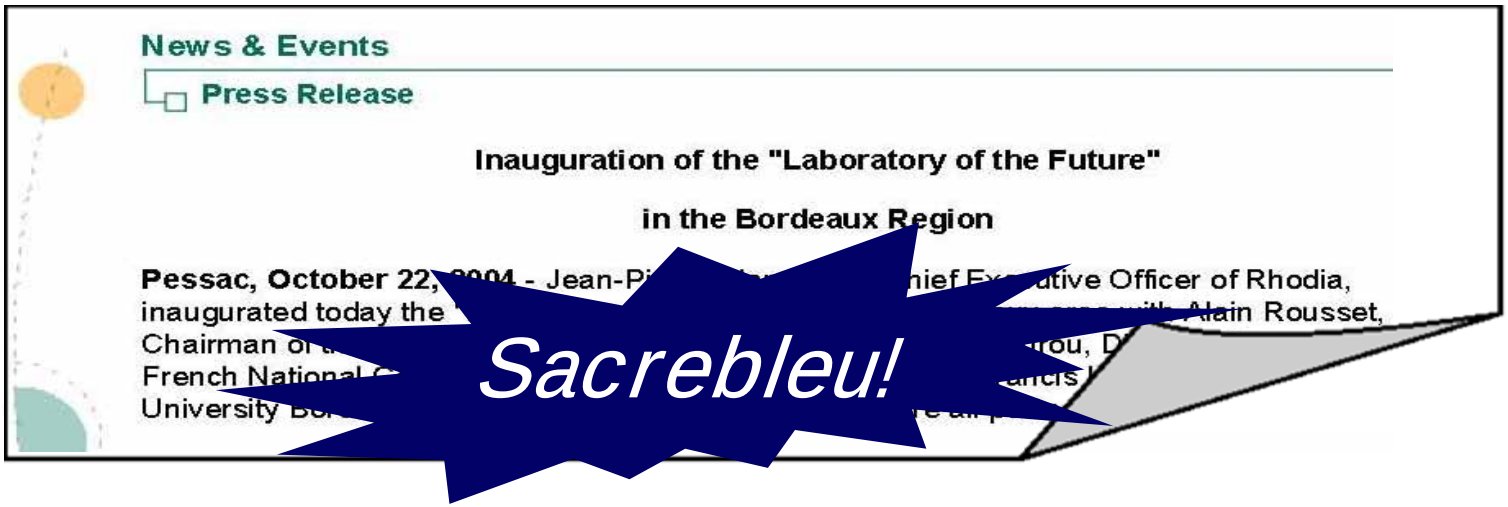
FAQ: "Forward Looking" Laboratory?

Bob suggested a great title: "The Lab of the Future"

Unfortunately, we've been scooped by Rhodia:



C'est la vie, mais…

Laissez les bons temps rouler!

Les bons temps ce matin*

Introduction to NIST

Notes from a "forward looking" laboratory

An brief overview of the ideas that drive the NIST Combinatorial Methods Center (NCMC)

*French text translation courtesy of Google; poor pronunciation courtesy of Mike Fasolka

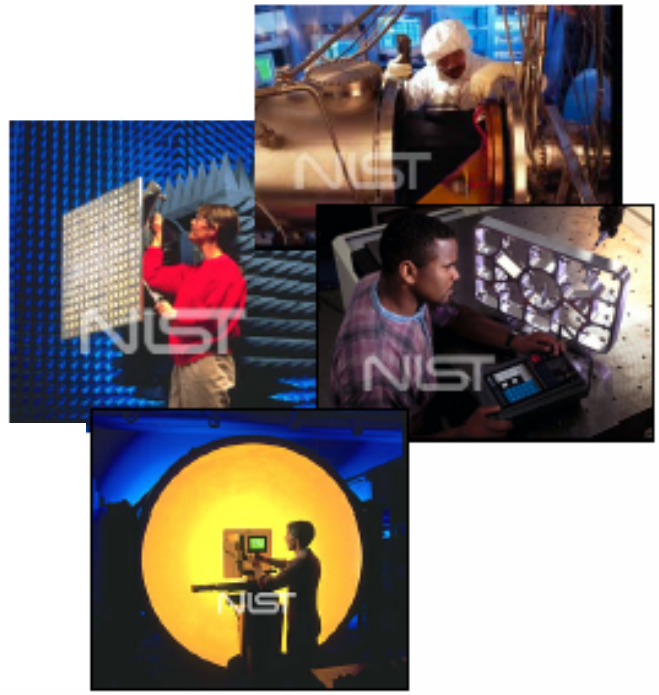
National Institute of Standards and Technology

NIST Mission

Promote U.S. *innovation* and industrial *competitiveness* by advancing measurement science, standards, and technology.

NIST assets include:

- 3,000 employees
- 1,600 guest researchers
- $858 million FY 2005 operating budget

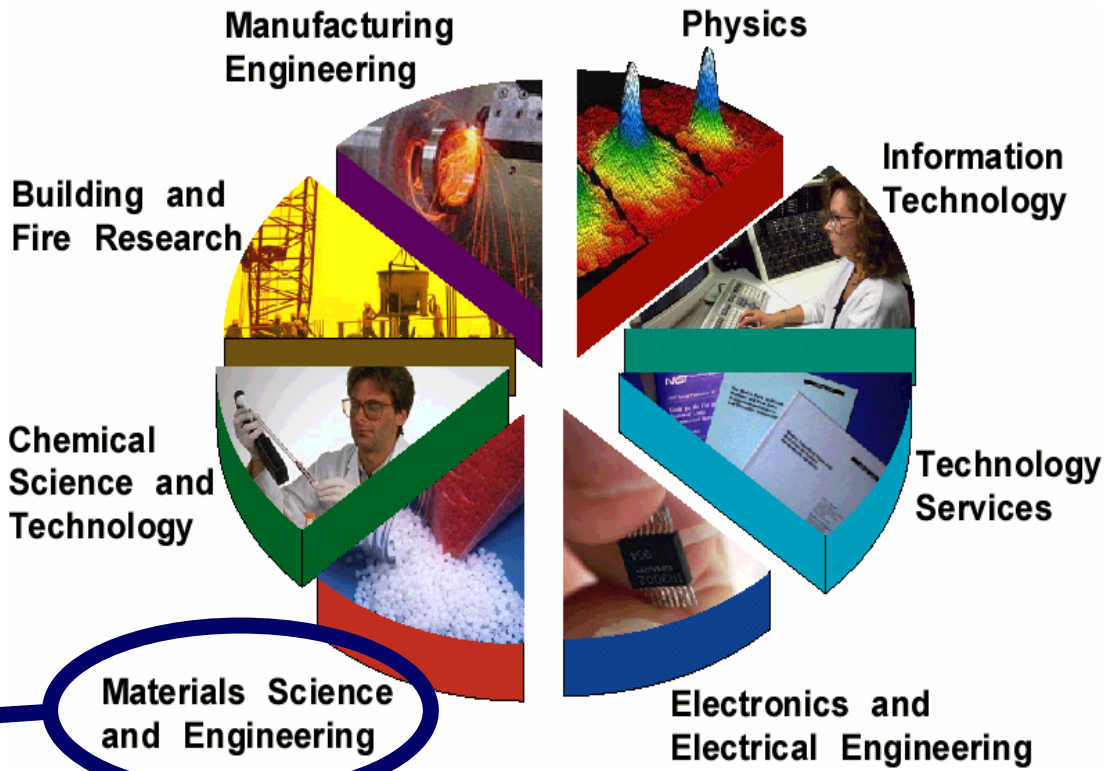


The NIST Laboratories

- Measurement methods research in a wide range of physical chemical, and engineering disciplines
- Respond to measurement needs of industry to continually improve products and services

NIST Laboratories

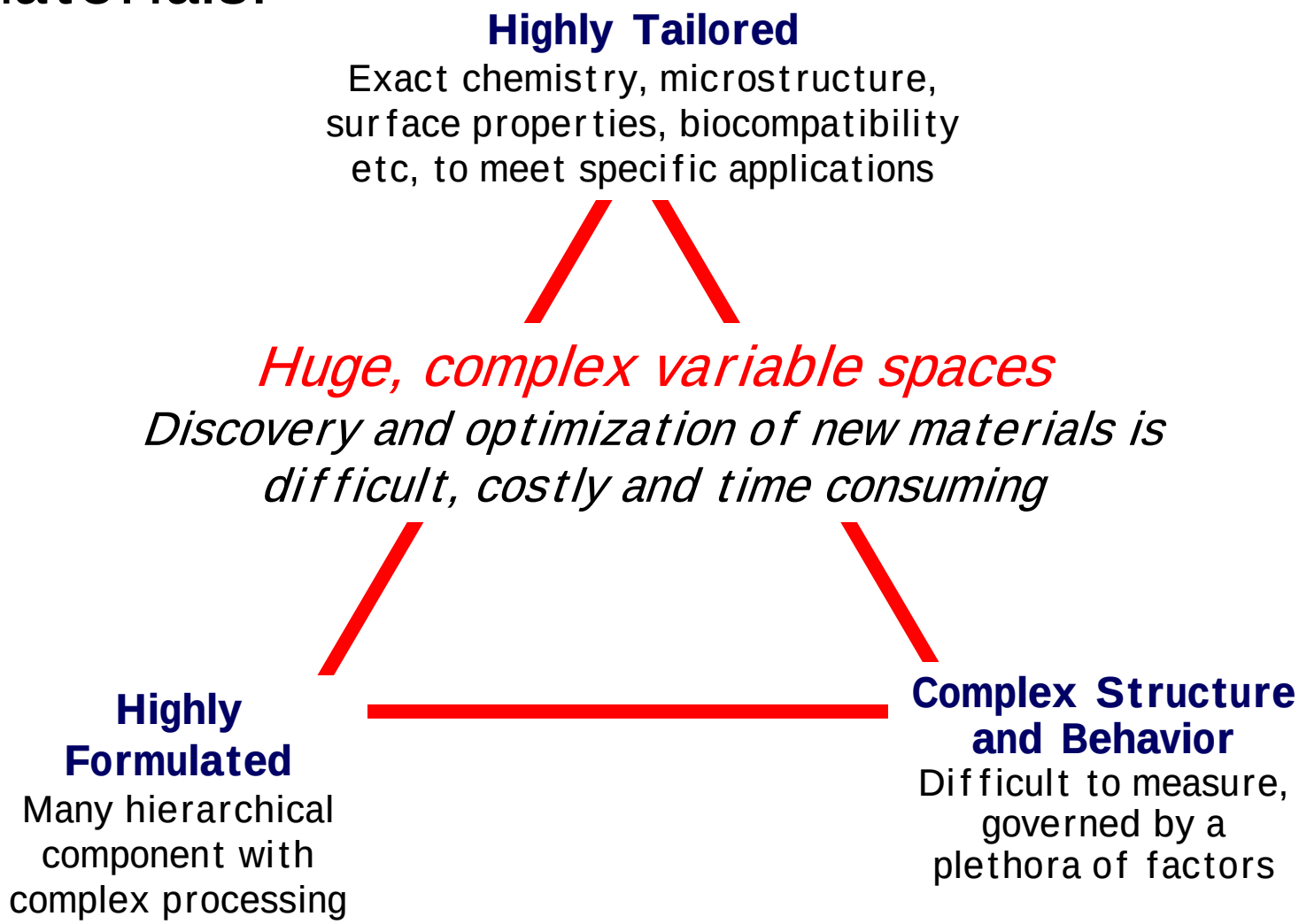
Highly leveraged measurement and research capabilities that support trillions of dollars in industry products and services



Works with industry, standards bodies, universities, and other government laboratories, to improve the nation's measurements and standards infrastructure for *materials*

Challenges to Innovation in Materials

New materials:

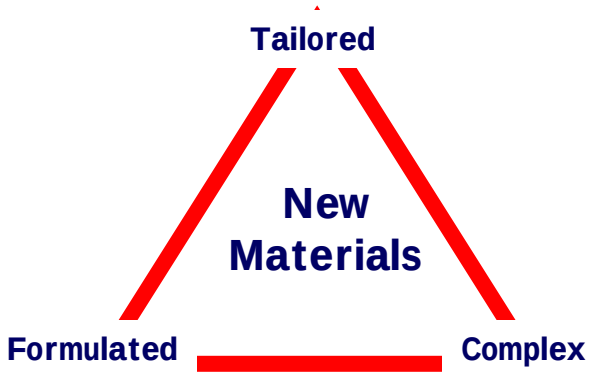


NIST Combinatorial Methods Center

Mission

Advanced *measurement* methods that accelerate the discovery and optimization of new materials

Combinatorial and High-Throughput (C&HT) measurement methods for materials research

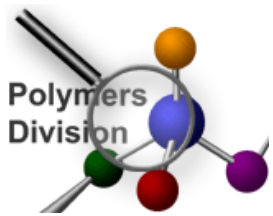


Philosophy

- Lower implementation barriers to C&HT methods
- Present alternatives to existing C&HT paradigms
- Publish everything we do

Focus Areas

- Polymer Formulations
- Polymer Coatings and Thin Films
- Adhesion and Mechanical Properties
- Polymer Nanomaterials and Nanometrology



Notes from a "forward looking" laboratory

Note #1

Spaces not Points

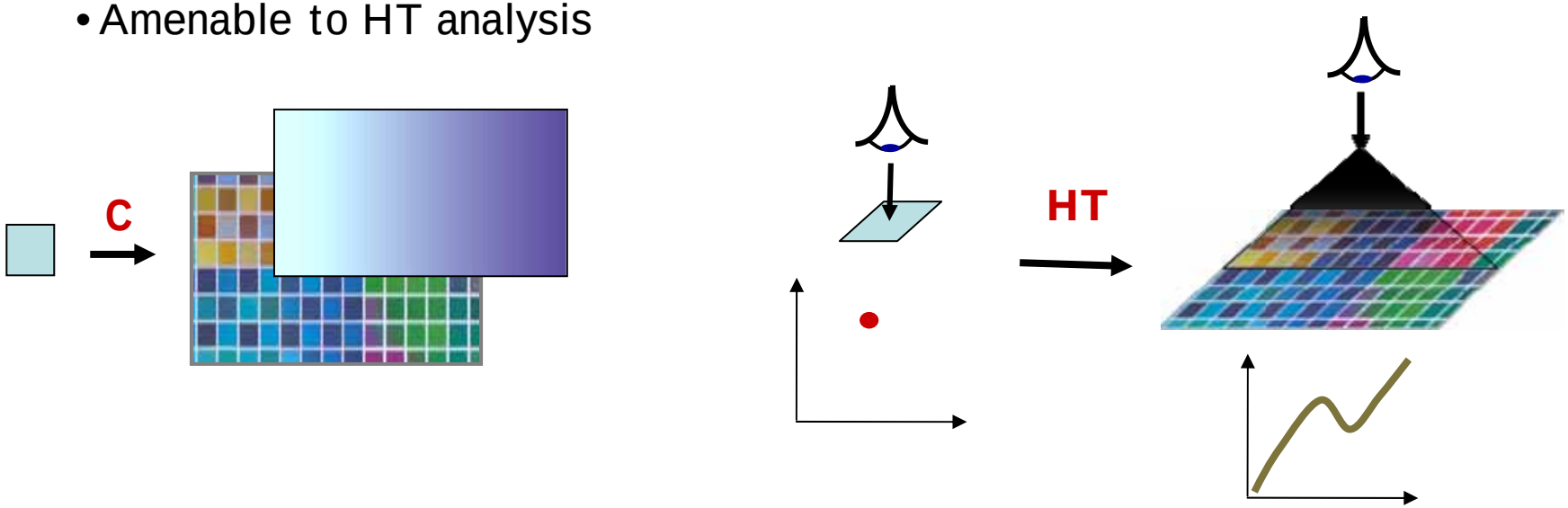
As a matter of *general practice*, NCMC researchers approach problems from a combi perspective.
How can we make this measurement combi?
How can we make it more rapid?

Combinatorial Library Fabrication

Multivariate libraries are the foundation of the combi approach

C&HT approaches to materials hinges on the ability to create appropriate libraries

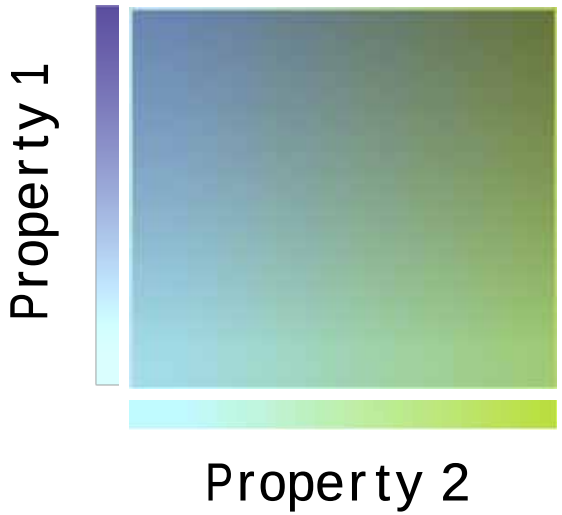
- Express a large number of materials and/or processing factors…
- …for the system of interest
- Amenable to HT analysis



NCMC Researchers think about these issues *a lot.*

Continuous Gradient Libraries

Single specimens that cover large parameter space



- Excellent for behavior or structural mapping
- Property optimization
- Critical phenomenon
- Thin geometry – Films and Coatings
- Easy to implement
- Low-cost infrastructure

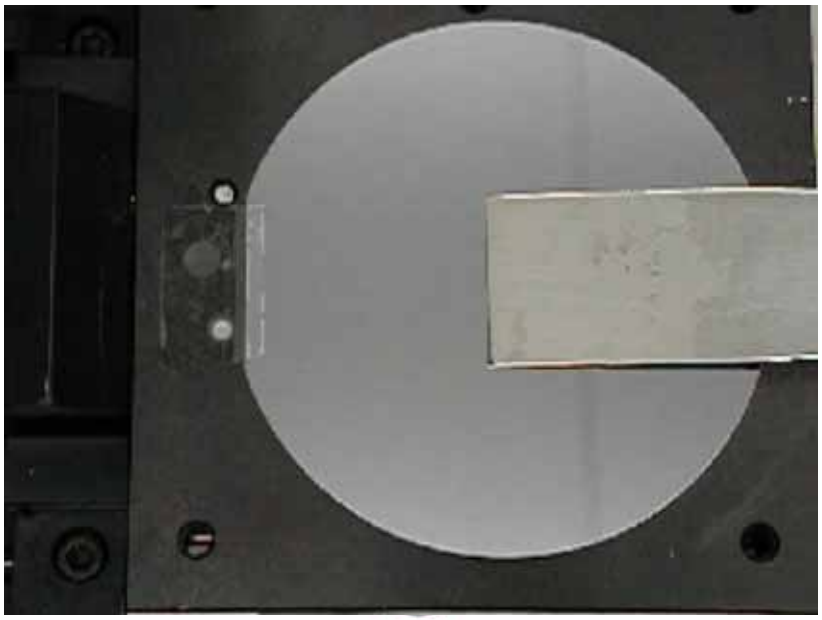
Challenges

- Fabrication in soft materials, organic coatings
- Reproducibility
- Well behaved for quantitative studies

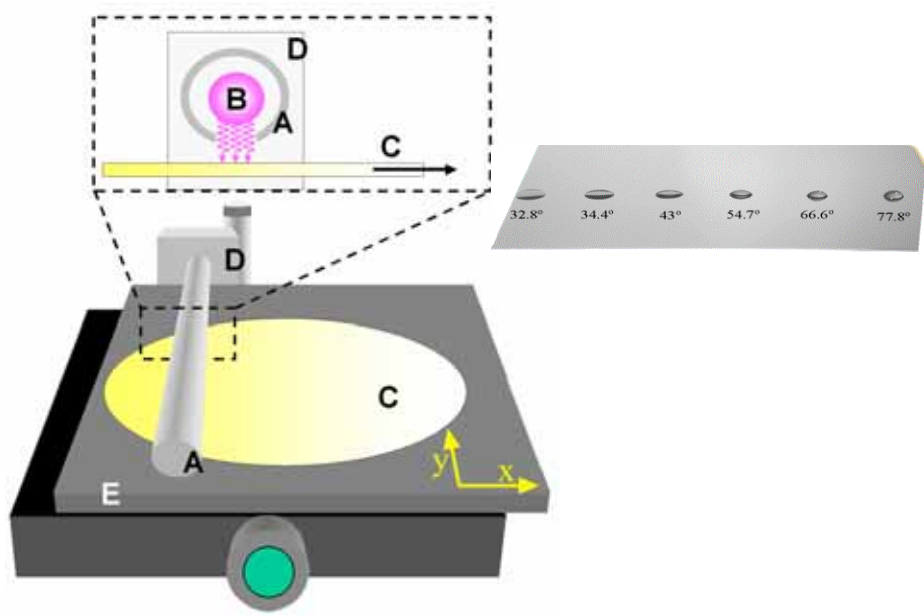
The "accelerated source" method

- A single motion stage with computer control
- A source of material, light, etc.

Film Thickness Gradient



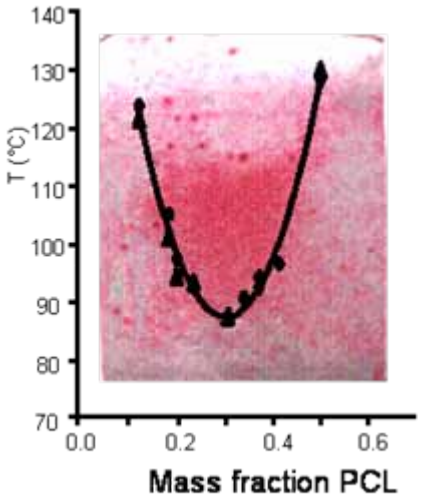
Surface Energy "Hydrophobicity" Gradient



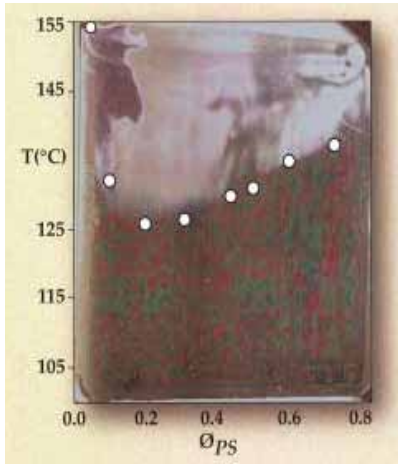
Similar approaches for x-link density, film composition, U.V. curing, roughness and modulus gradients.

Powerful Mapping in a Single Specimen

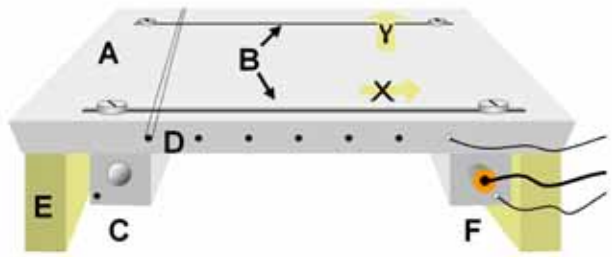
Biocompatibility



Blend Phase Mapping



Gradient Hot Stage



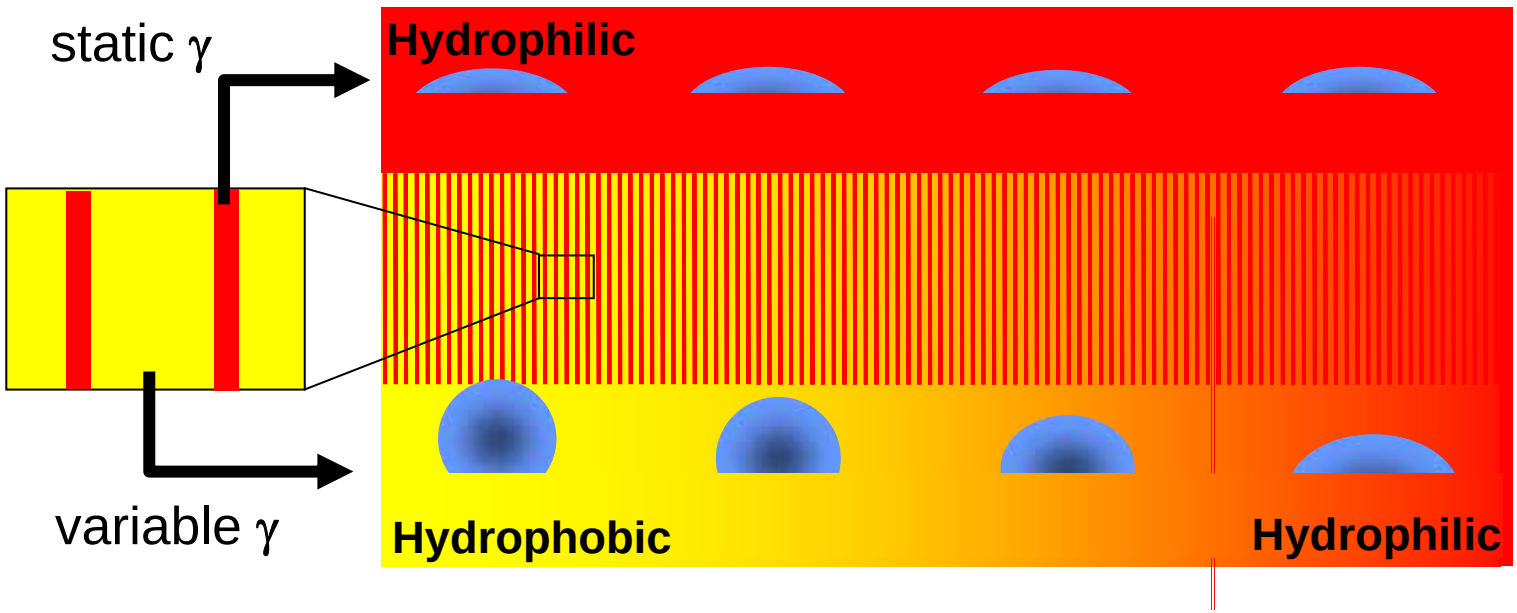
Block Copolymer Film Assembly

- Polymer film wetting and stability
- Blend phase behavior
- Self Assembly and Nanomaterials
- Polymer crystallization kinetics
- Biocompatibility and cell assays
- Photoresist development
- More…

More advanced gradient libraries

Combining micropatterning and gradient design

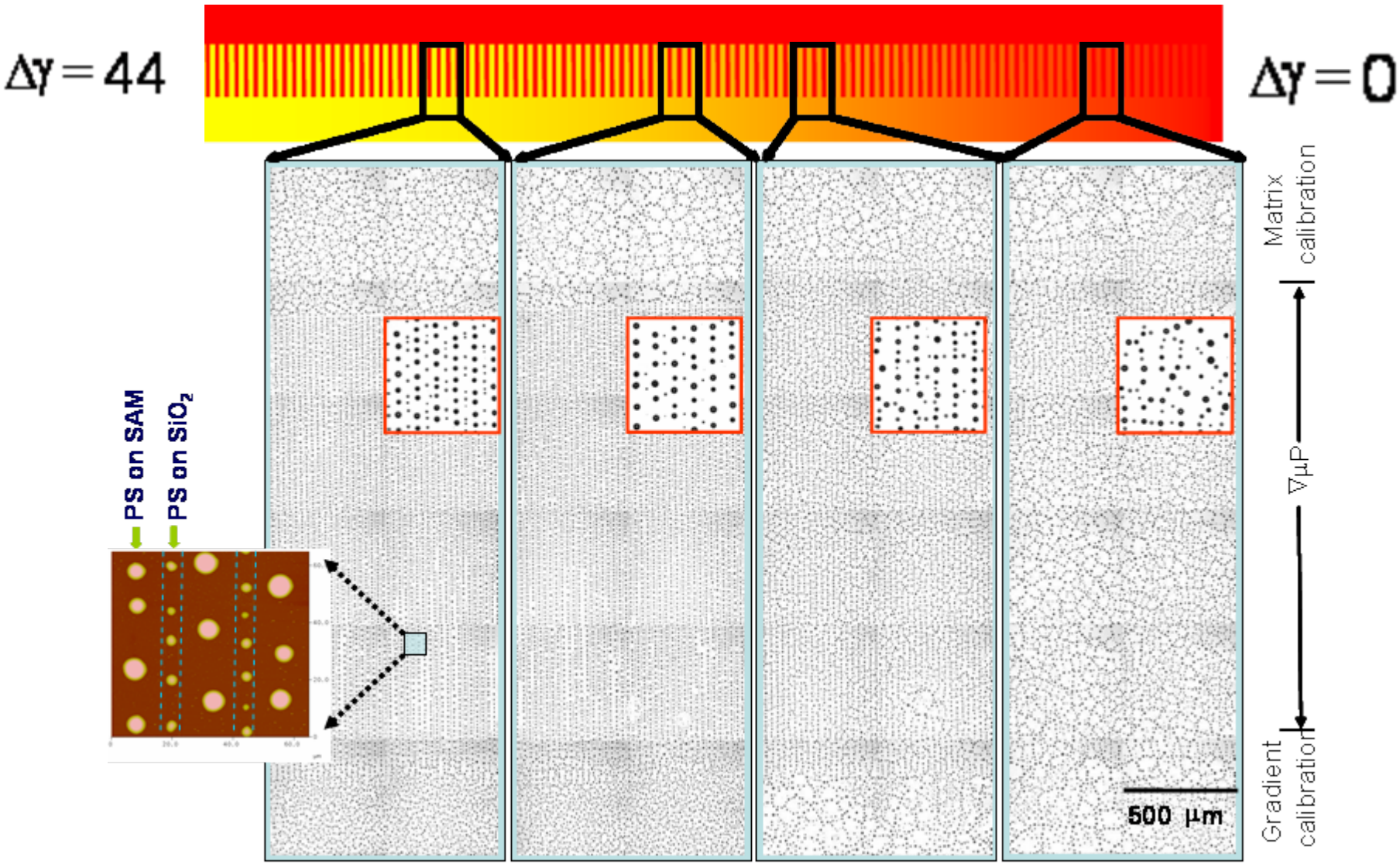
Calibrated gradient in "Chemical Contrast" ($\Delta\gamma$)



A library of chemical heterogeneity "strength"

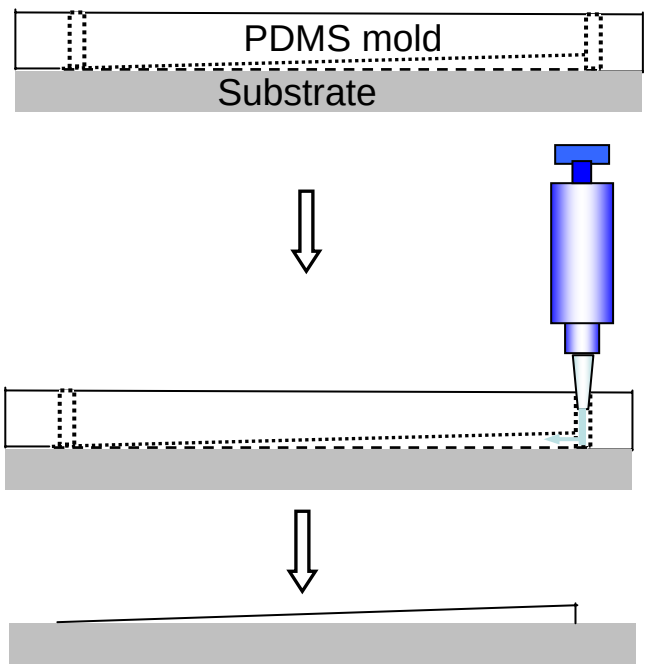
Julthongpiput, D.; Fasolka, M. J.; Zhang, W.; Nguyen, T.; Amis, E. J.; *Nano Lett.* **2005**, *5*(8): 1535.

Example: PS Film Dewetting vs "Chemical Contrast"

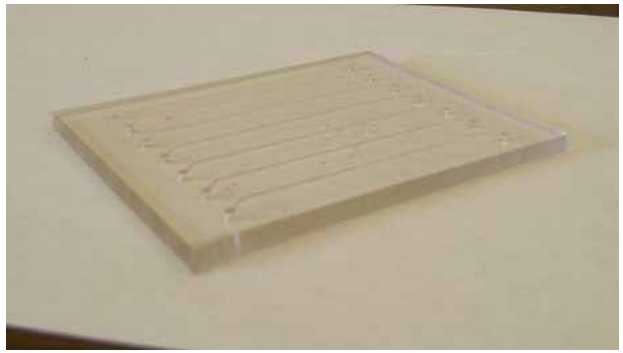


Channel Template Methods

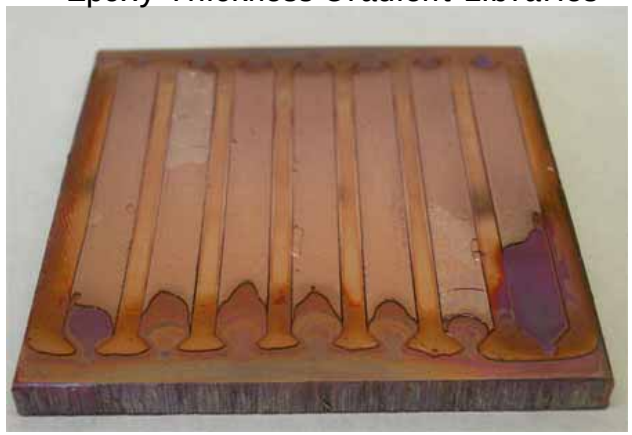
Removable channels (elastomer or glass) deliver specimen to a substrate in a controlled manner.



A series of elastomer channels



Epoxy Thickness Gradient Libraries



When the channel is removed, a gradient library is left on the substrate.

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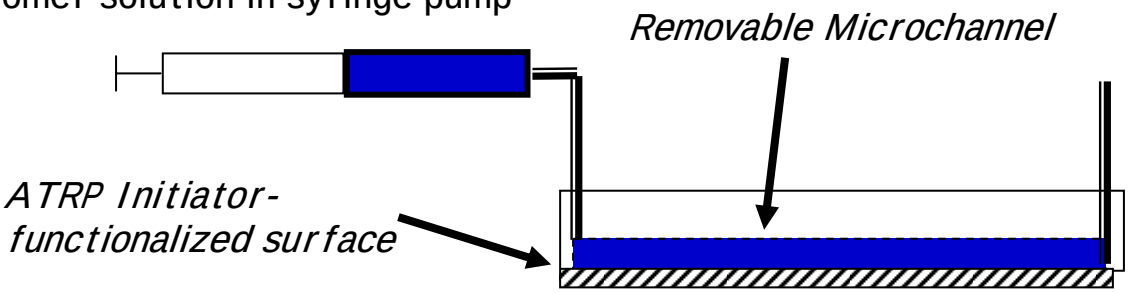
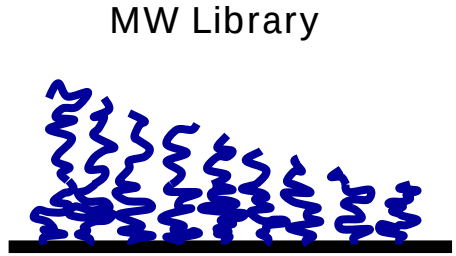
Microchannel Confined Surface Polymerization

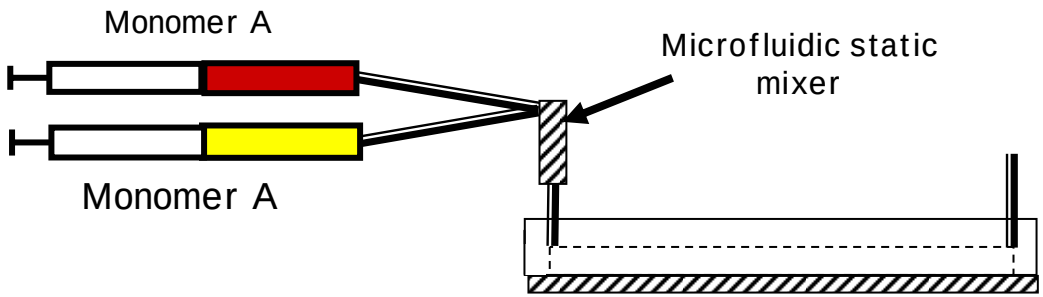
1)

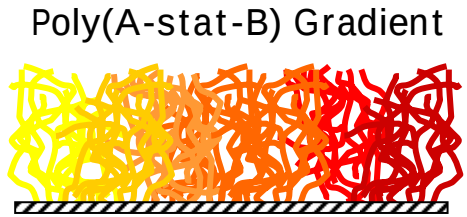




Xu, Wu, Mei, Drain, Batteas, Beers *Macromolecules 38 (1):* **2005,** 6-8.

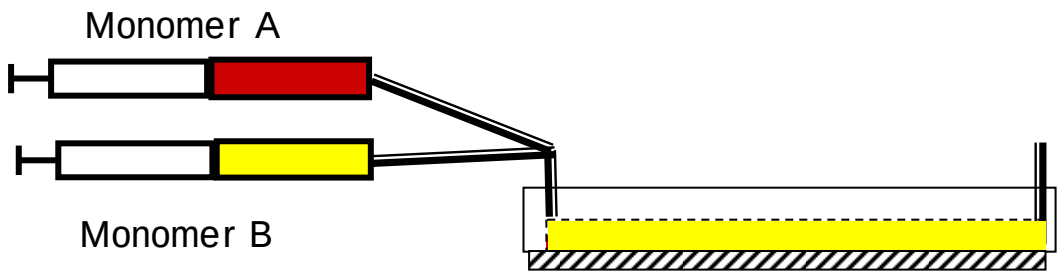
2)

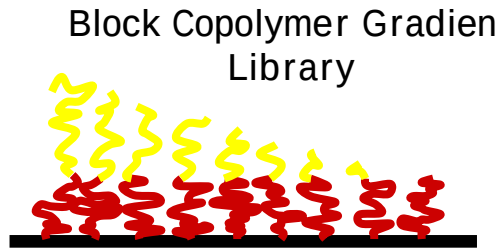




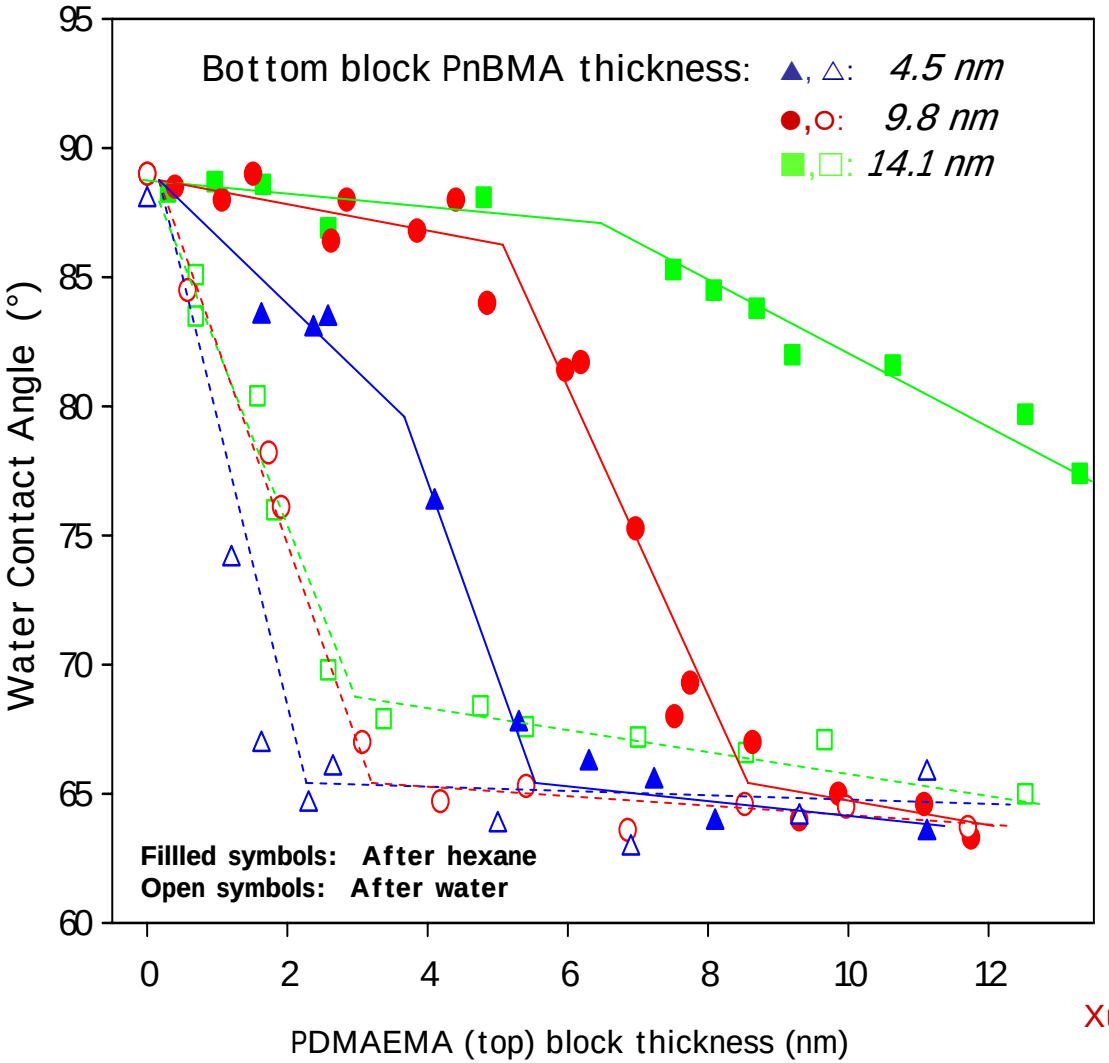
Xu, Wu, Beers et al, *Advanced Materials 2006 (accepted).*

3)

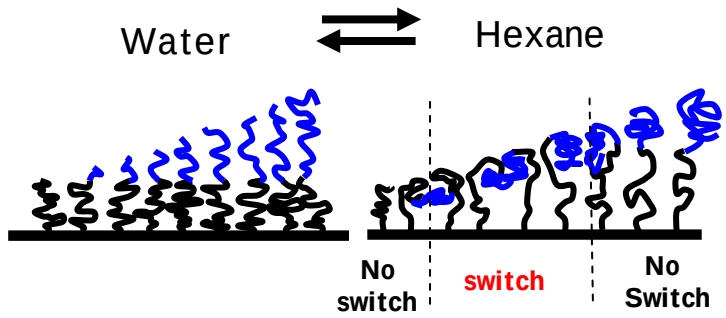




Screening Solvent Responsive BC Coatings



Xu, Wu, Fasolka, Beers



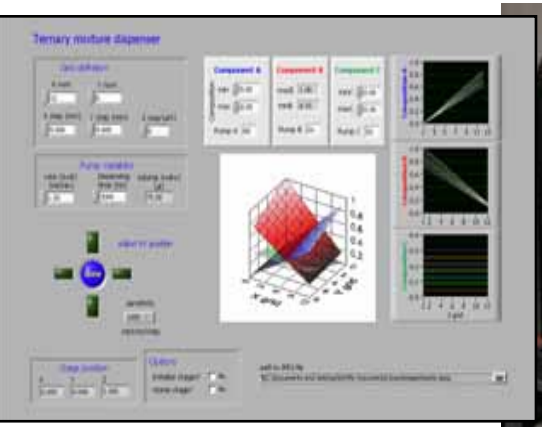
- Gradients illuminate narrow optimal response windows
- Long PDMAEMA blocks suppress switching behavior
- Long PnBMA blocks enhance switching behavior

Xu, Wu, Batteas, Drain, Beers, Fasolka, **2005**, *Applied Surface Science (accepted).*
Xu, et al., **2006**, *Macromolecules (accepted).*

Robotics has its place ☺

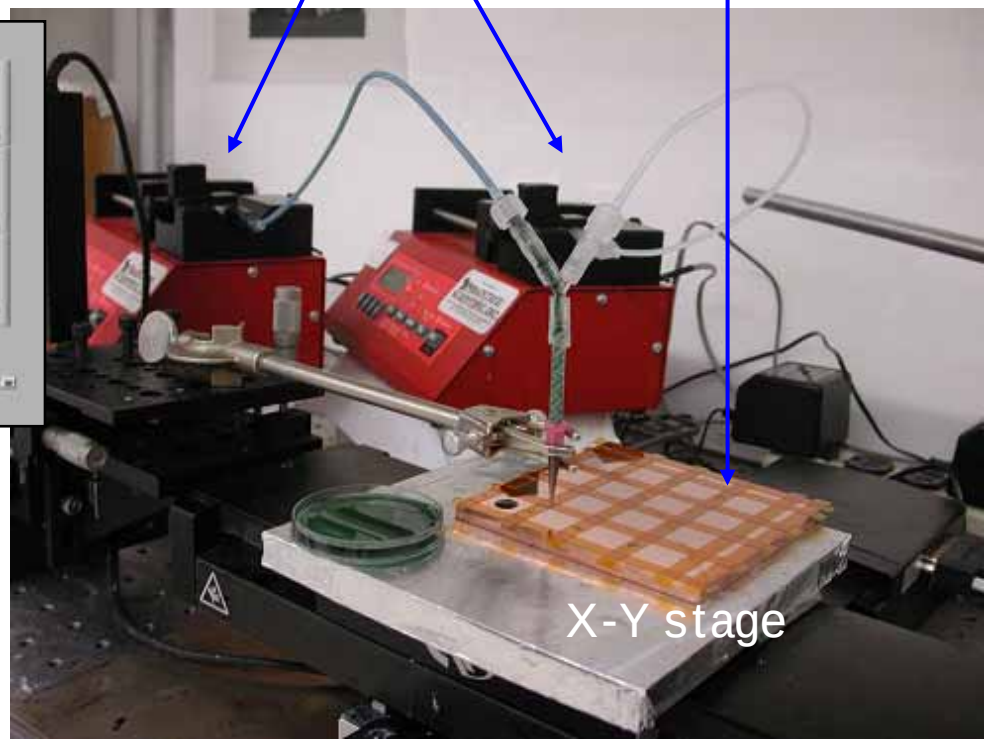
When needed, we build them (you can too!)

Labview Control

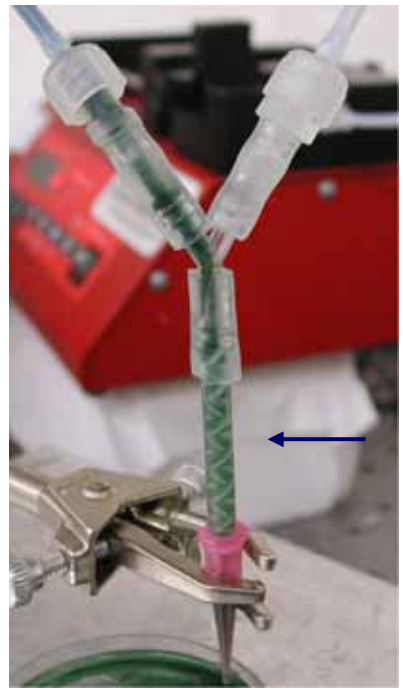


Syringe pumps

Library substrate



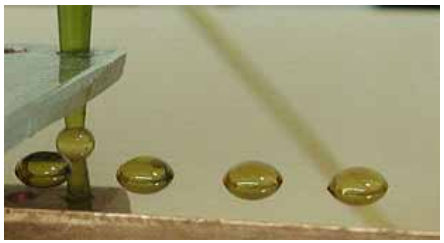
Static mixer



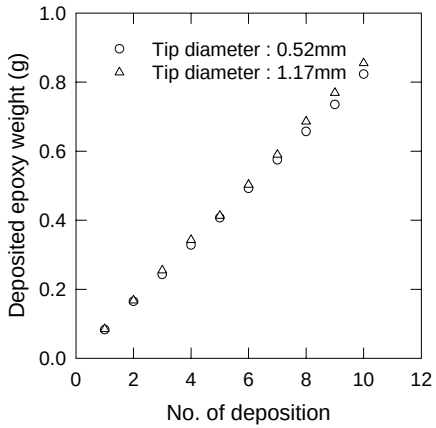
Discrete Library Fabrication

Library validation and calibration is essential for quantitative studies.

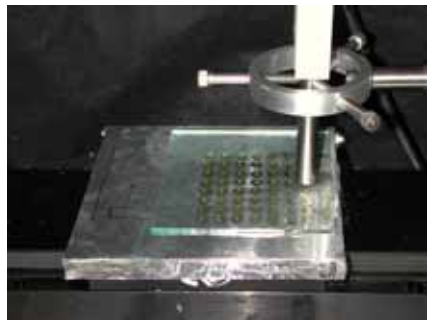
Epoxy formulations on a copper substrate

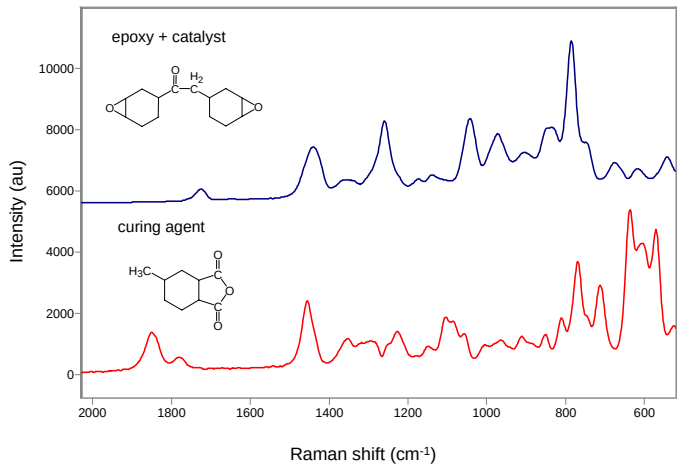


Mass calibration of library



Fiber Optic Raman Spectroscopy





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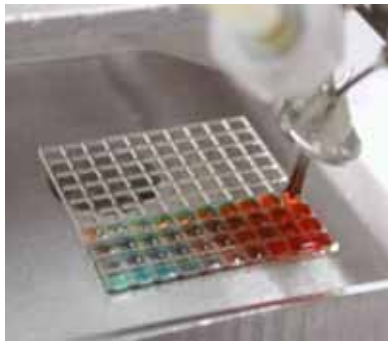
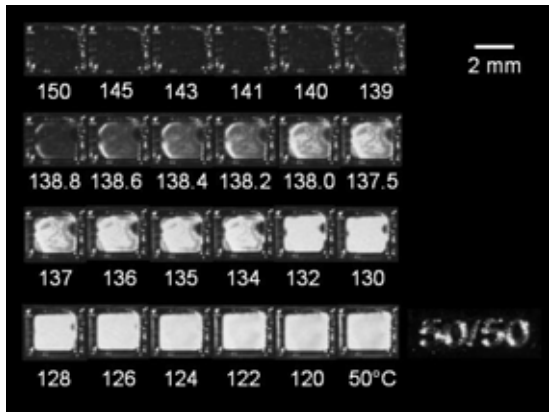
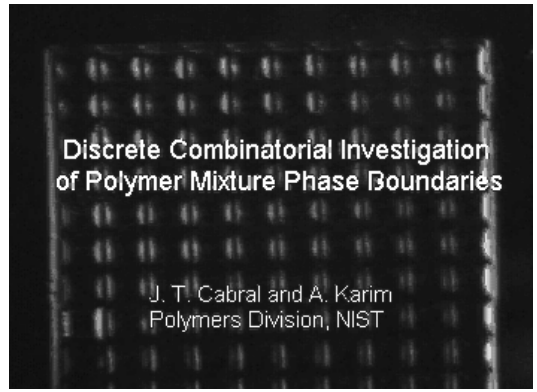
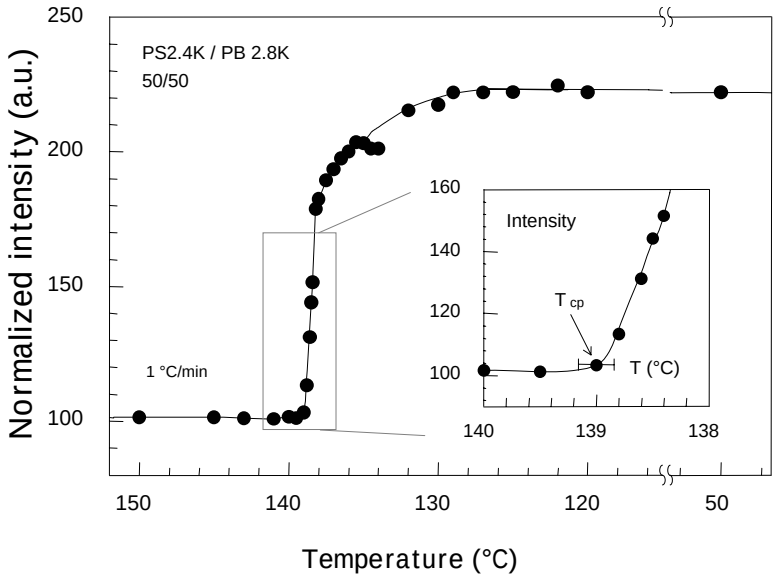
Example: Parallel Cloud Point Mapping

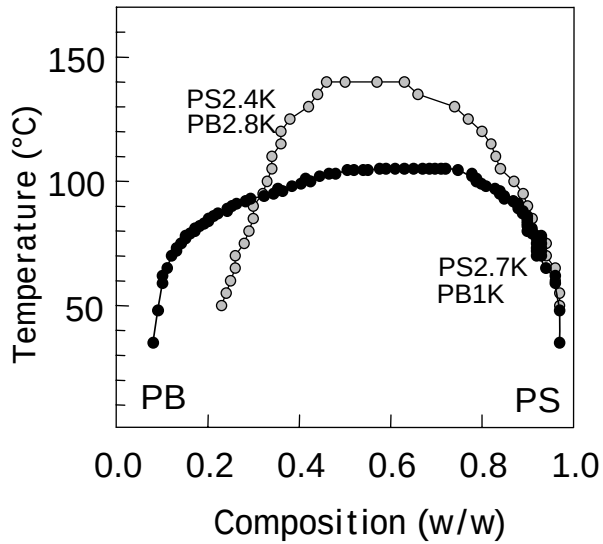
Discrete Polystyrene/Polybutadiene Blend Libraries











Cabral et al *Meas. Sci. and Tech. 2005; 16: 191)*

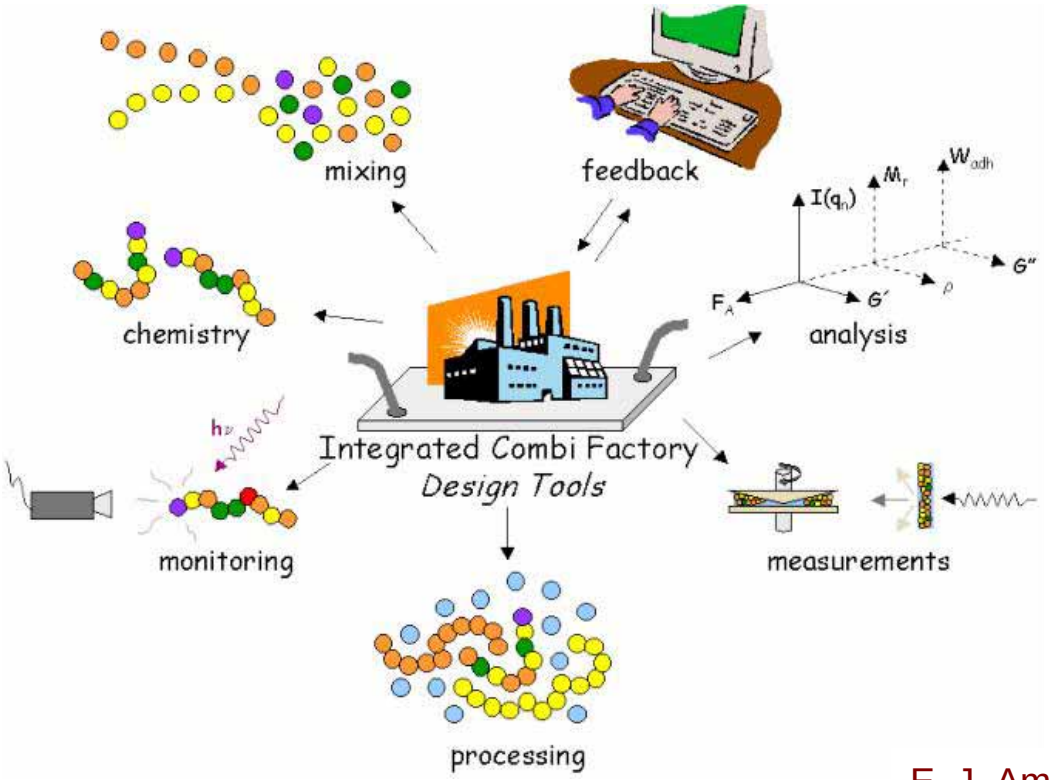
Note #2

Leverage Emerging Technologies, Creatively

There are plenty of opportunities.
Proper adaptation is the key.

Integrated Combi Factory for Formulations

- The NCMC is creating C&HT measurement framework for developing and optimizing formulated products
  - Coatings and paints, personal care, food, fuels etc.
- Our platform leverages *microfluidic technologies* to fabricate, process and measure organic formulations on chip devices

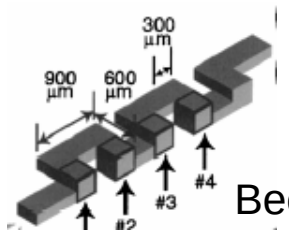


E. J. Amis, *Nature Mat.*, **2004**, *2*, 83.

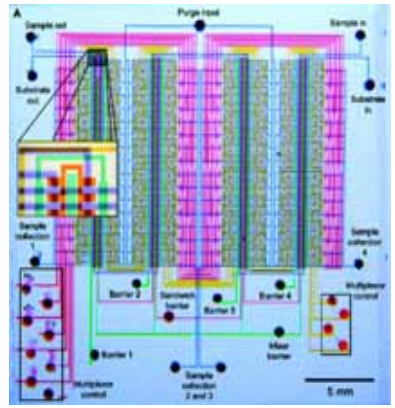
Microfluidic Technologies

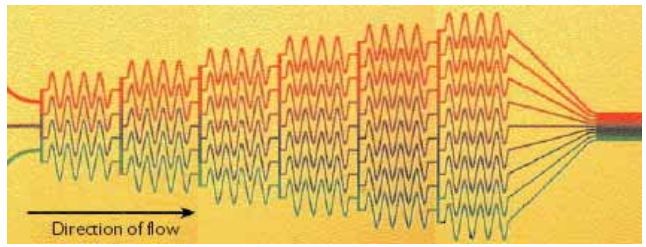
In principle, ready made for C&HT formulations science…

- Small sample volume
- Complex processing / fluid handling
  - Pumps, valves, in & outlets
  - Flow control / mixing
  - Microreactors: Library Fabrication
- Integrated Analysis
  - Electrophoresis
  - PCR
  - Fluorescence analysis



Beebe

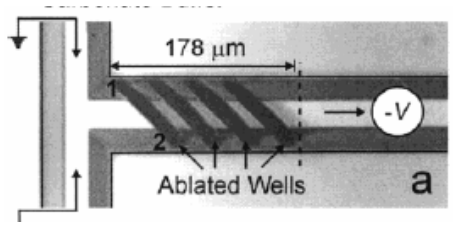

Quake



Whitesides

However:

- Current microfluidic technology is built for biotechnology, i.e. *water*
- Channel materials (e.g. PDMS) are not stable in organic fluids
  - Poor for industrial carrier solvents and monomers
- Current fabrication routes can be slow and expensive
  - Poor for rapid prototyping and design testing



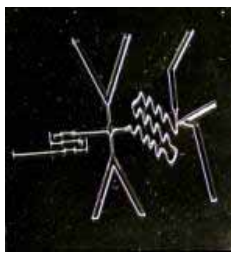
Locascio

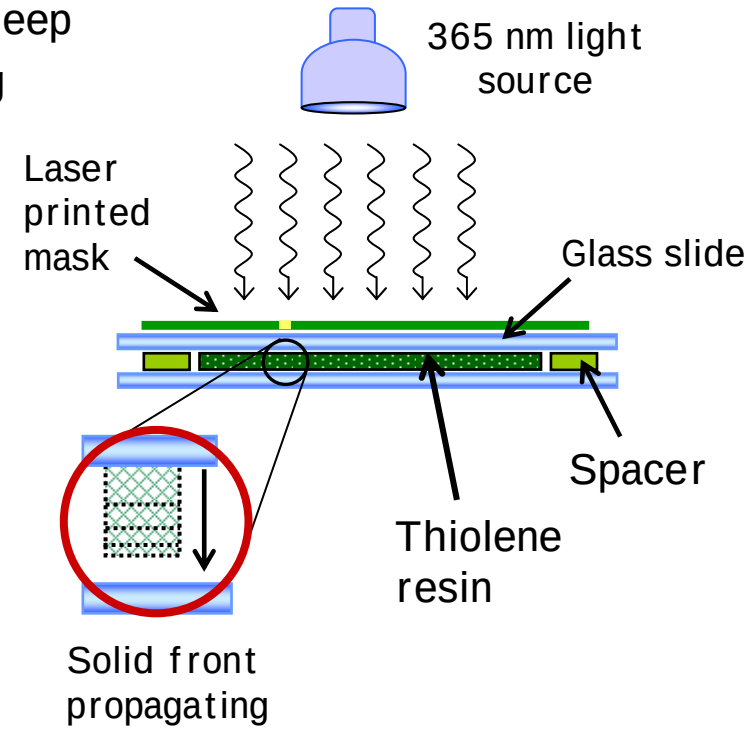
Proper adaptation is the key

Thiolene-based device fabrication technology (UV-curable optical adhesive)

- Enhanced solvent stability: hexanes, benzene, toluene, monomers
- Rapid prototyping: 3 hours from design to device
- Inexpensive
- Meso-Scale Channels: 50mm wide, 50mm - 1mm deep
- Precise channel dimension control and structuring

Cabral et al, Langmuir 20, 10020 (2004)



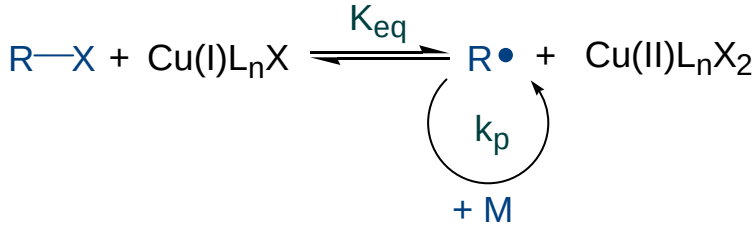


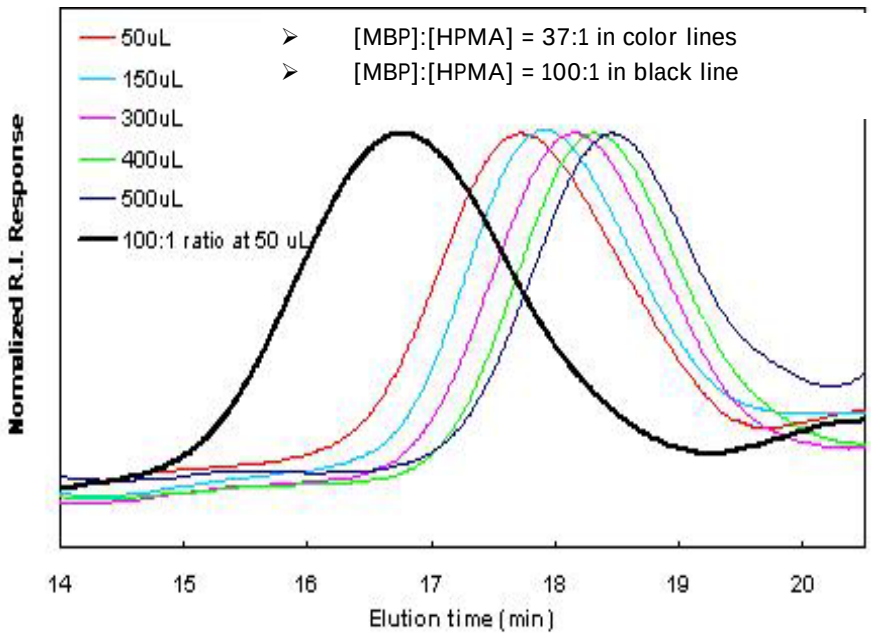
Harrison, C.; Cabral, J. T.; Stafford, C. M.; Karim, A.; Amis, E. J. J. Micromech. Microeng. 2004, 14, 153-158

Controlled Radical Polymerization Chip

- Continuous polymer libraries in a single synthesis, with quality as good as in flask
- RT, solution polymerization
- *Homopolymers, Graft Polymers and Block Copolymers*

Atom Transfer Radical Polymerization (after K. Matyjaszewski)





Hydroxyproplymethacrylate (HPMA)

Flow Control of Architecture:

- Flow rate ↑: residence time, conversion, molecular weight ↓
- Library scope determined by relative rates of input streams
- Library is fabricated by ramping the flow rates

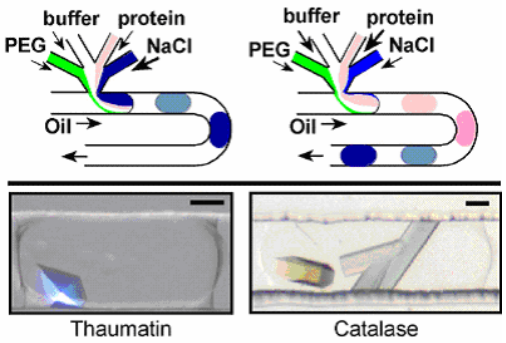
Macromol. Rapid Commun., **2005**, *26*, 1037.
T. Wu et al, J. Am. Chem. Soc., **2004**, *126*, 9880.

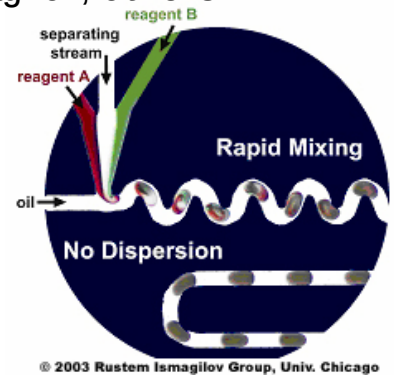
Polymer droplet libraries on a chip

Droplets allow

- Individual, small volume samples
- Higher viscosity/ solid specimens
- Sophisticated sample sorting, mixing and handling

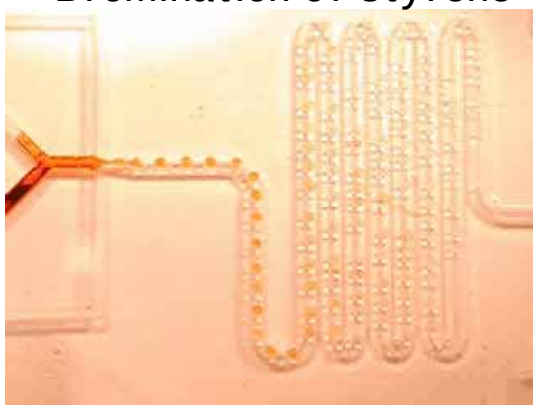
Lit examples: Pine, Ismagilov, others



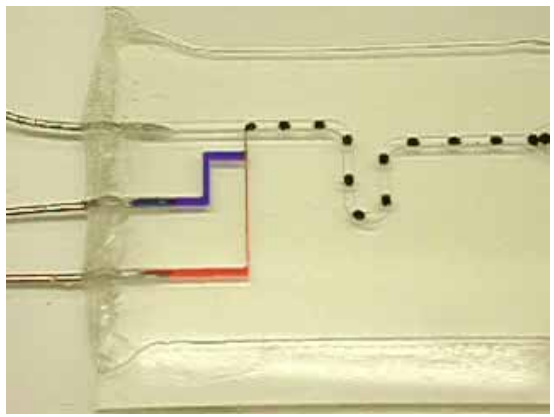


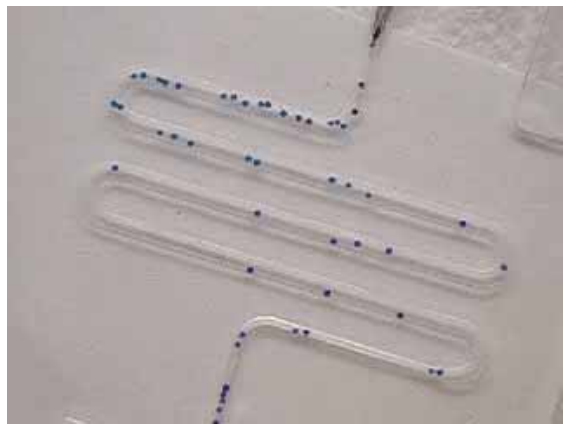
Our adaptation: Droplets as combinatorial organic microreactors for creating libraries of solid polymer droplets

Bromination of styrene



Co-monomer composition libraries





Cygan, Z. T.; Cabral, J. T.; Beers, K. L.; Amis, E. J. *Langmuir,* **2005**, *12,* 3629-3634.

Integrated analysis of polymer droplets

Barnes, Beers, Cygan

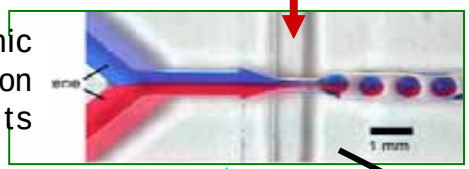
Example: Methacrylic Dental Composite Formulations

benzyl methacrylate and dimethacrylate crosslinker, 1 mol % Irgacure 819 photoinitiator

Monomer droplet library formation

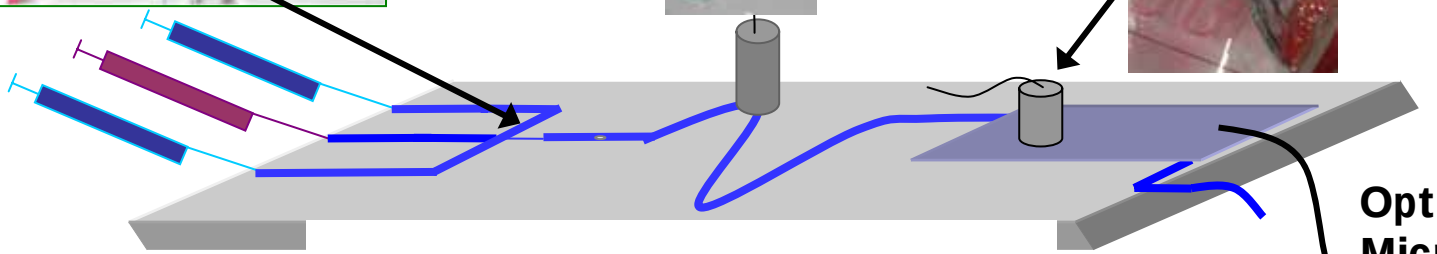
Water and surfactant

Organic reaction components

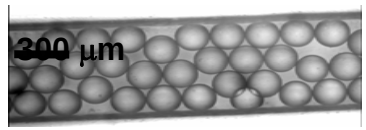


Photopolymerization

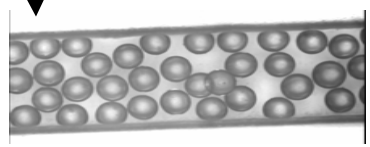
Fiber optic Raman spectroscopy



Optical Microscopy

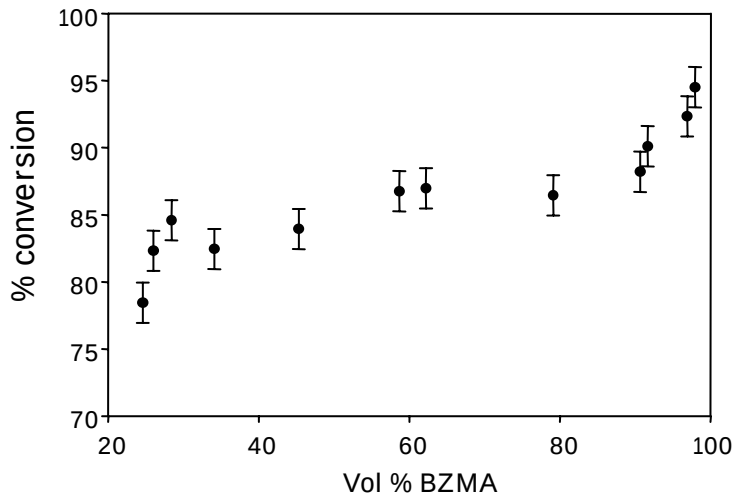


Shrinkage after UV



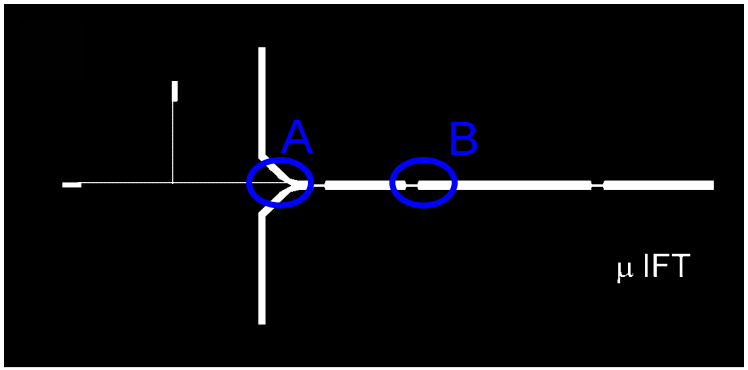
Key Engineering Criteria

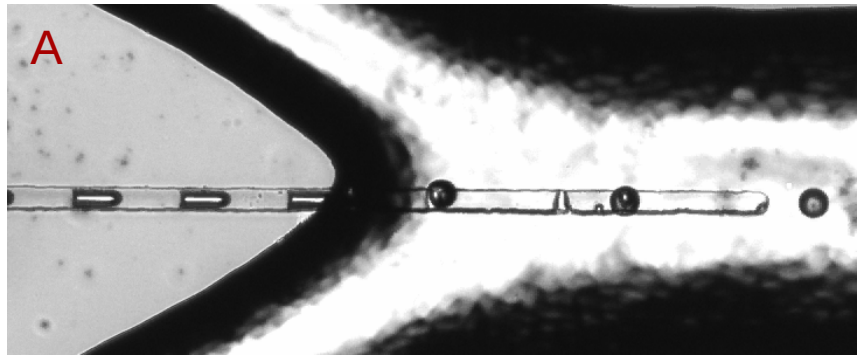
- % Conversion
- Shrinkage

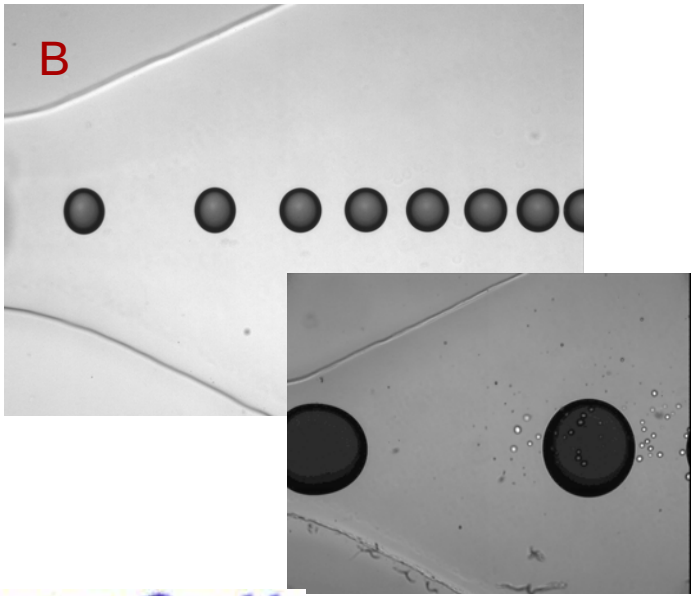


Cygan, ZT; Barnes, SE et al. Submitted

A Microfluidic Interfacial Tensiometer







Interface	σ (mN/m)	σ (lit)
Ppms500/pdms1000	2.52 ±0.27	
Surf. solution/pdms1000	12.7 ±0.4	
Air/pdms1000	23.8 ±1.0	21.2
Air/pdms10000	22.9 ±1.5; 22.6 ±2.1	21.5
	20.8 ±1.5	
H_2O/pdms1000	41.2 ±1.1; 41.5 ±1.6	41.4
	41.0 ±2.8; 41.7 ±3.0	
Air/ppms500	24.2 ±1.3	28.5
Air/glycerol	59.8 ±2.5; 58.5 ±2.7	59.2

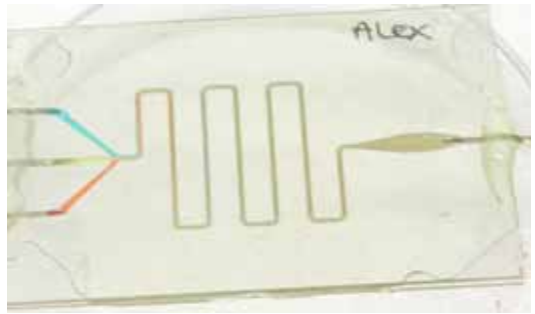
Procter&Gamble

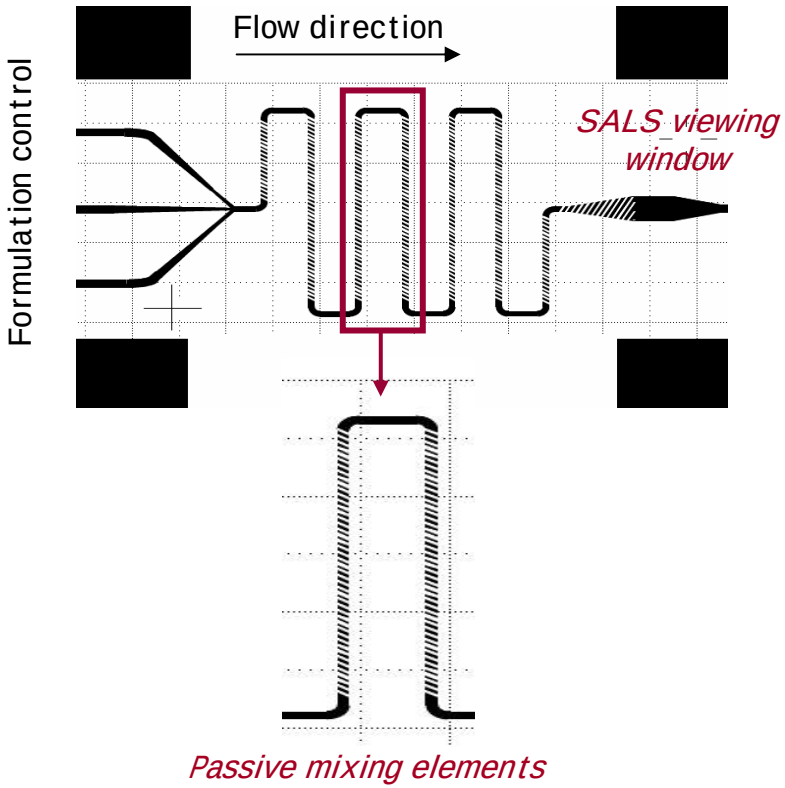
National Starch & Chemical ICI
A member of the ICI Group

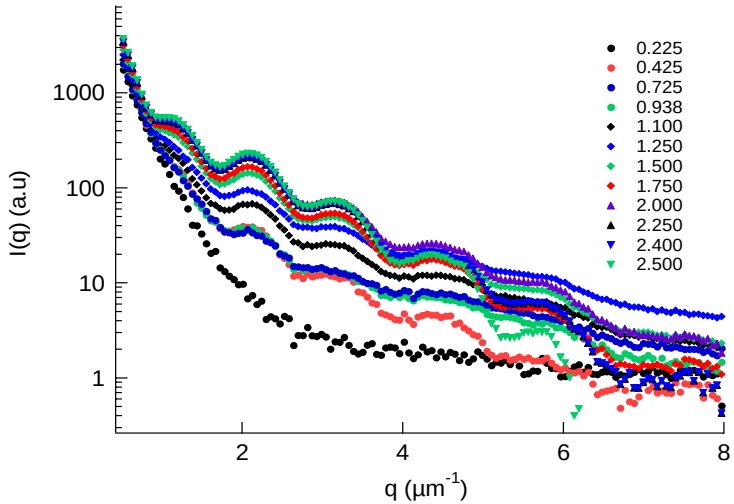
Husdon et al, Appl. Phys. Lett., **2005**, *87*, 081905.

Microfluidic Small Angle Light Scattering

- Rapid analysis of dispersed particles, droplets and emulsion structure
- Systematic, continuous composition changes
- Temperature control in progress







- Validation: mixtures of Polystyrene microbeads
- Future work: polyelectrolytes, emulsions, micelles and particle dispersions

Norman, Chastek, Barnes, Beers

Notes from a "forward looking" laboratory

Note #3

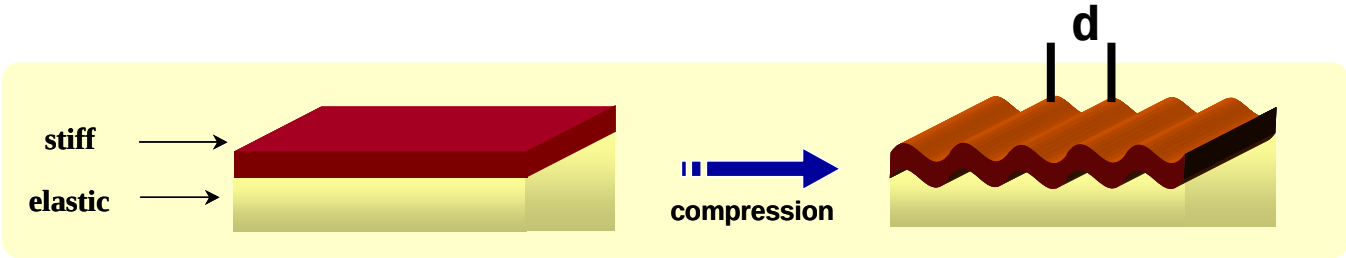
*"To measure is to know."**

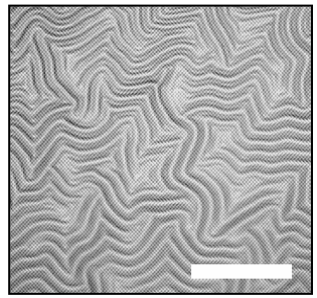
The greatest potential of C&HT is accelerated *knowledge* generation. NCMC researchers strive to develop techniques that are both rapid and *quantitative.*

***Lord Kelvin, 1883**

HT Measurements of film modulus

Idea: leverage a buckling instability in laminates to assess modulus



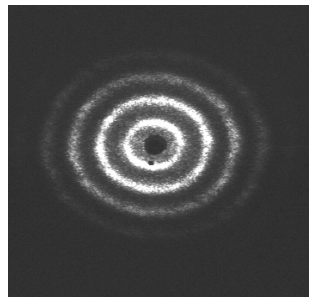


Analytical Solution

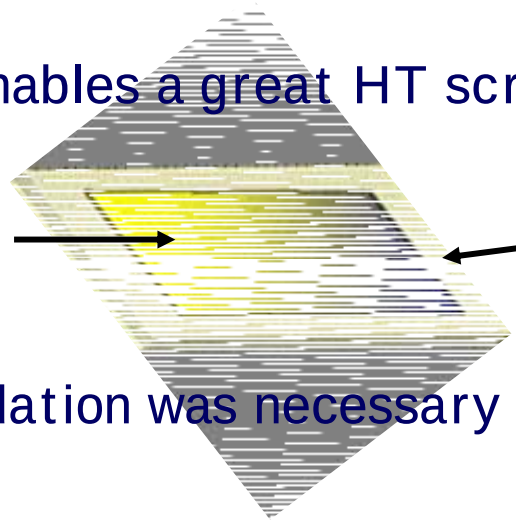
$$d = 2\pi h \sqrt[3]{\frac{(1-\nu_s^2)E_f}{3(1-\nu_f^2)E_s}}$$

Metrology Equation

$$\frac{E_f}{(1-\nu_f^2)} = \frac{3E_s}{(1-\nu_s^2)}\left(\frac{d}{2\pi h}\right)^3$$



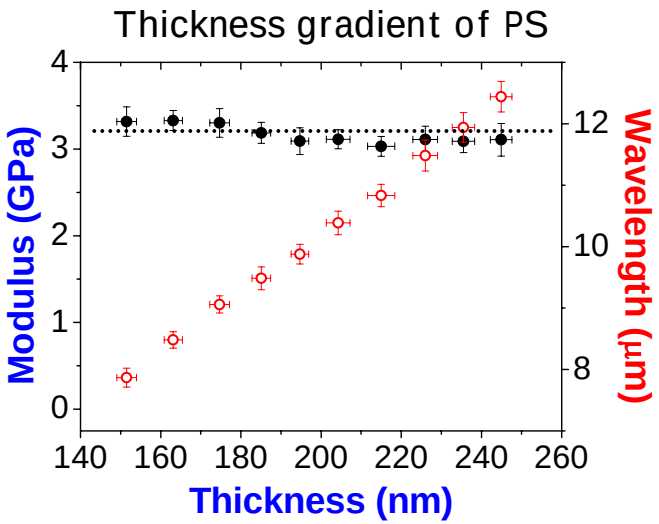
Light scattering enables a great HT screen (1-2 seconds)



But extensive validation was necessary to make it a *HT metrology*

M.A. Biot, *J. Applied Mechanics* **4** (1937) A1.
A.L. Volynskii, *et al.*, *J. Material Science* **25** (2000) 547.

Validation of buckling metrology

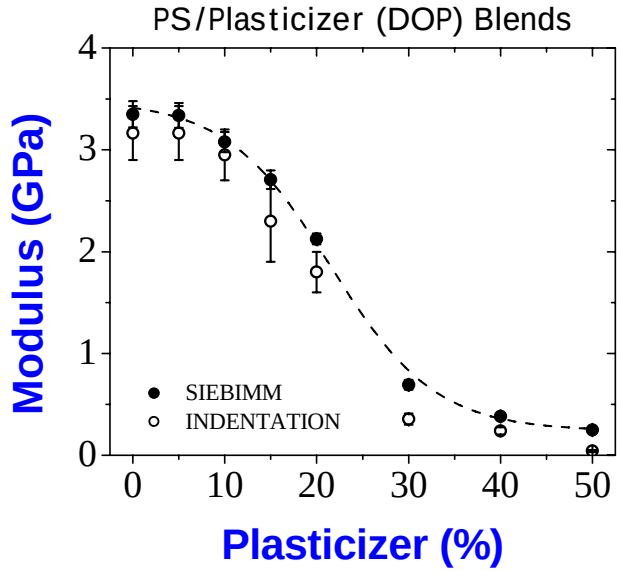


Test governing equations

Internal consistency

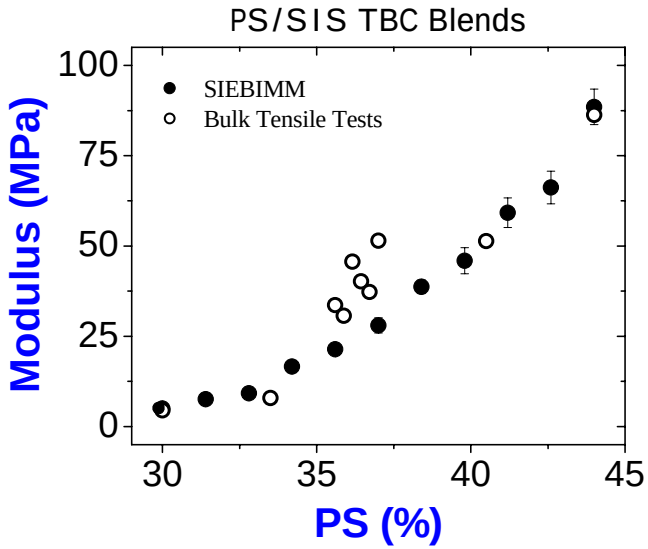
Agreement with known cases

Use of gradients (C&HT)



Comparison with other bulk and thin film tests

Industry relevant (heterogeneous) systems



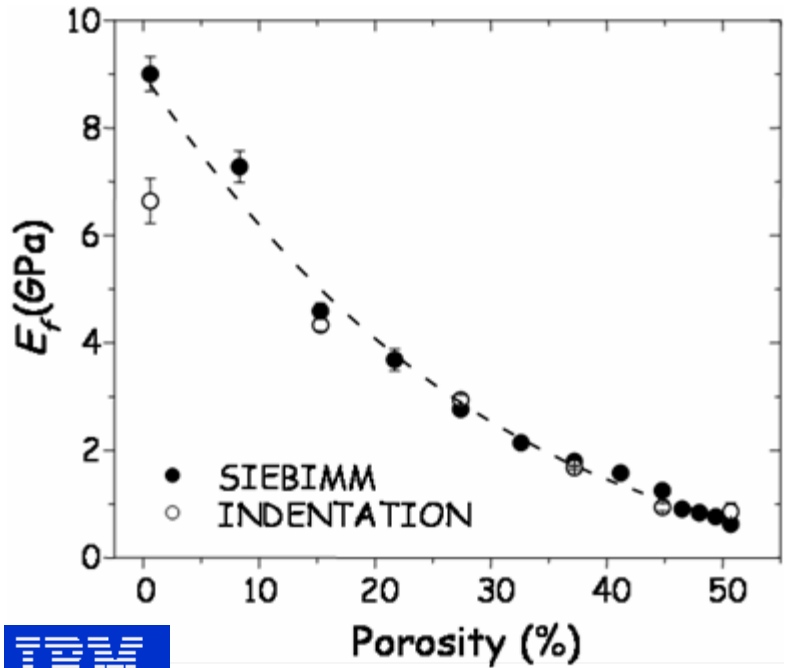
Determination of
Precision: 5%-10%
Reproducibility: 3%
Thickness range: 5nm → 10 μm
Modulus Range: 10 GPa → 4MPa

Stafford, et al., *Nat. Mater.* **2004**, *3*(8), 545.

Knowledge generation in challenging systems

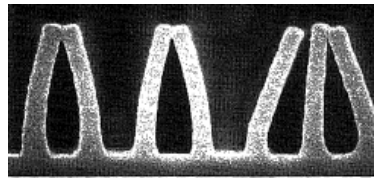
Nanoporous low-K films

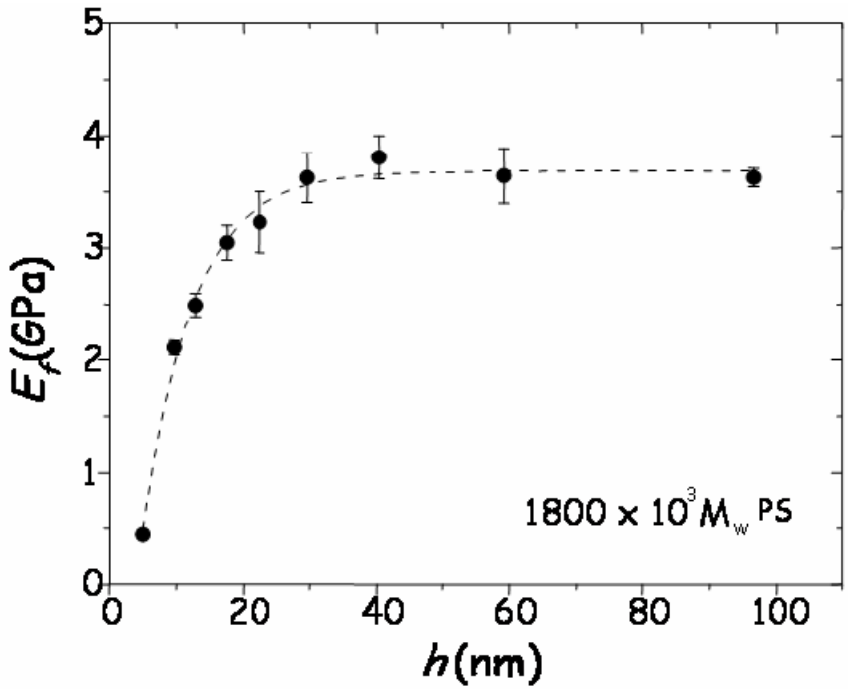
- critical for sub-100 nm electronics applications
- Mechanical properties determine resilience to CMP/planarization



Ultrathin polymer films

Integral part of emerging nanotechnologies (MEMS, NEMS, NIL)

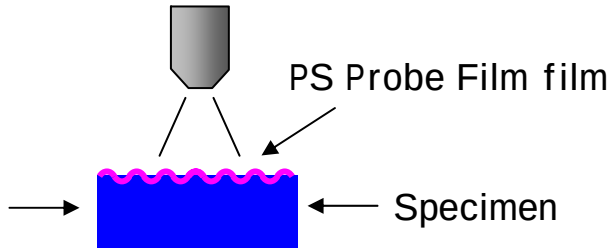


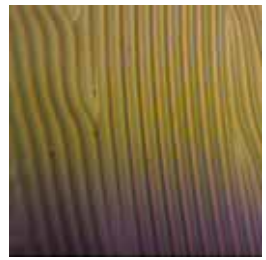


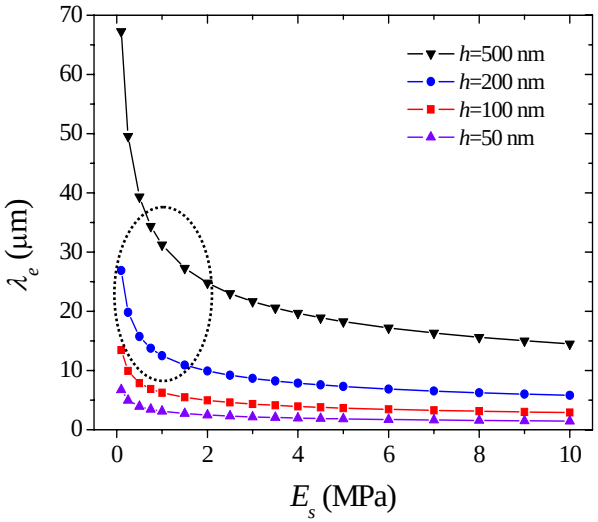
Extension to "reverse" metrology

Known "sensor" film is used to measure modulus of unknown substrate
A new HT metrology for ultra-soft materials: elastomers, gels, hydrogels…

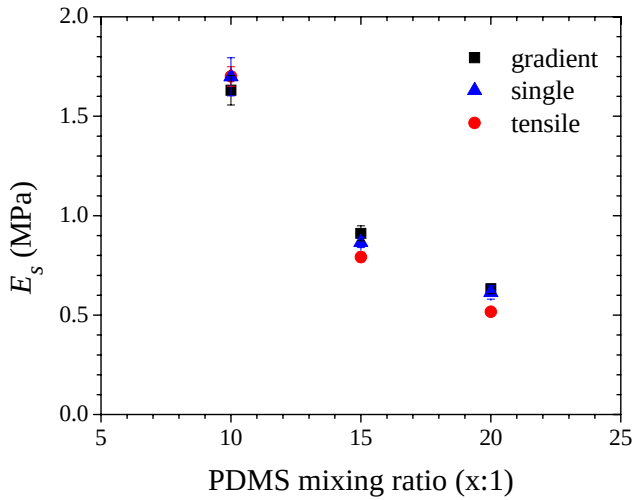
$$\overline{E}_f = 3\overline{E}_s\left(\frac{\lambda_e}{2\pi h_f}\right)^3 \rightarrow \overline{E}_s = \frac{\overline{E}_f}{3}\left(\frac{\lambda_e}{2\pi h_f}\right)^{-3}$$



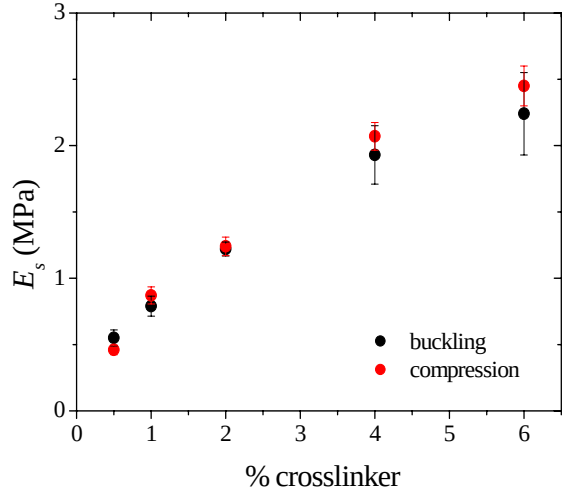




Determination of optimal sensor film thickness for soft materials



Validation against traditional tests for various silicone elastomer formulations



Measurement of *hydrated* PHEMA hydrogel formulations

Summary

The notes from a "forward looking" laboratory

- *Spaces not points*
- *Leverage emerging technology*
- *To measure is to know*

Thanks to the NCMC Members

Currently 18 institutions from industry and academia
A broad cross section of the materials research sector

Insight
High throughput technologies

Boston Scientific

ARKEMA

intel

PPG

The University of Southern Mississippi 1910

Air Products

L'ORÉAL

Veeco

Honeywell

DOW

World Leader in Nanomechanical Test Instruments
Hysitron Incorporated

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ICI

BASF

Rhodia

ExxonMobil

Bayer

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AKZO NOBEL

The Gillette Company

3M

Air Force Office of Scientific Research
United States Air Force

bp

Sealed Air

EASTMAN

MICHELIN

Rohm and Haas

Contacts and the NCMC Team

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Ask for a CD!

Or visit our website at www.nist.gov/combi.

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Nanomaterials and Nanometrology:

Mike Fasolka, Mai Julthongpiput, Kirt Page, Thomas Epps

"The people of NCMC are viewed as "clever folks" who are developing elegant innovative screens. Its a good outfit to be hooked up with. I think we're getting more than our money's worth." *–M. S. Vratsanos, Air Products, NCMC member*