NSTI Nanotech 2007: Polymer Nanotechnology

Combinatorial Methods for Nanostructured (Polymer) Materials

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Technology Administration, U.S. Department of Commerce

NIST Combinatorial Methods Center

www.nist.gov/combi

Outline

- Combinatorial and Hi-Throughput Methods
- Nanostructured Materials Applications
  - Block Copolymer Thin Films
  - Surface Grafted Polymers
  - Microfluidics: Solutions and Particles

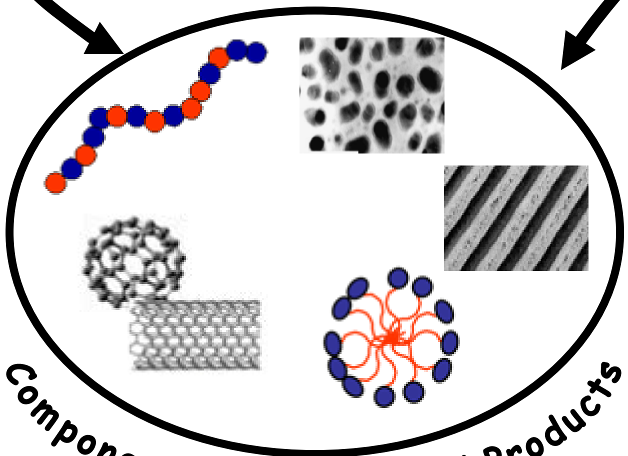
The Potential of Polymer Nanotech

Hierarchical Molecular Design

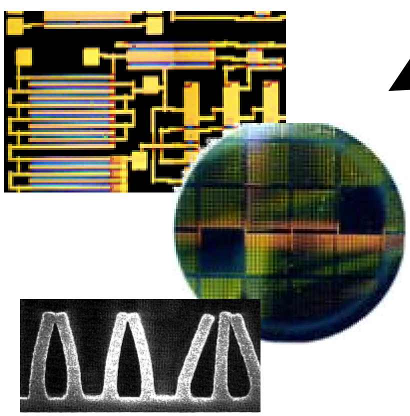
Monomer type
Monomer distribution
Polymer composition
Polymer architecture

Unique Physics & Chemistry

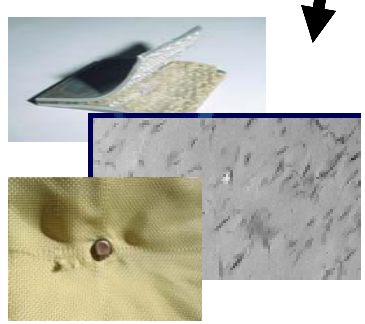
Low-temperature phase behavior
Self Assembly
Solution/Fluid Properties
Specific Bioactivity



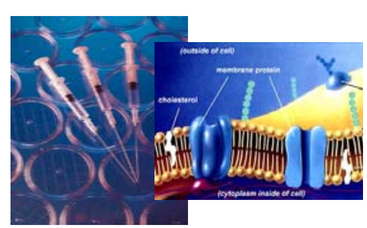
Components for Advanced Products



Opto-Electronics
MEMs, NEMs



Adhesives, Composites
Textiles

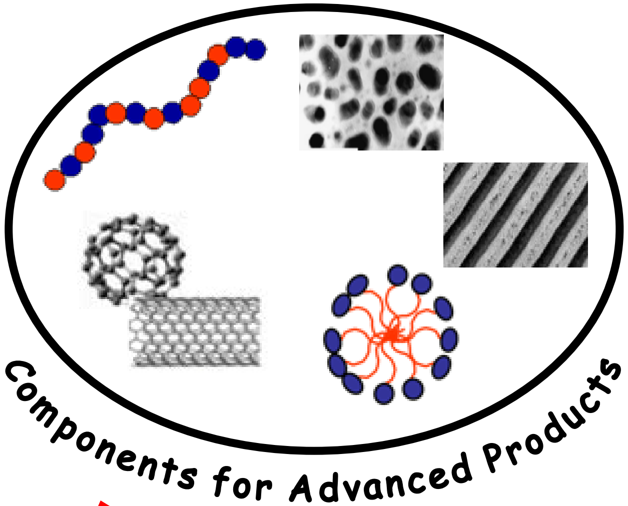


Biotechnology
Biomedical

Coatings and
Paints

Personal Care
Cosmetics, Food

The (Huge) Problem with a Huge Palette



Discovery
Formulation
Optimization

New Materials for New Technologies

Tailored
Exact structure and properties to meet specific applications

Large, complex variable spaces
Huge number of experiments

Formulated
Many components, complex processing

Complex Structure and Behavior
Difficult to measure

The discovery and development of *one* new material can cost $20M and 2-10 years of research…

A Great Idea for Complex Systems

Combinatorial and High-throughput Methods

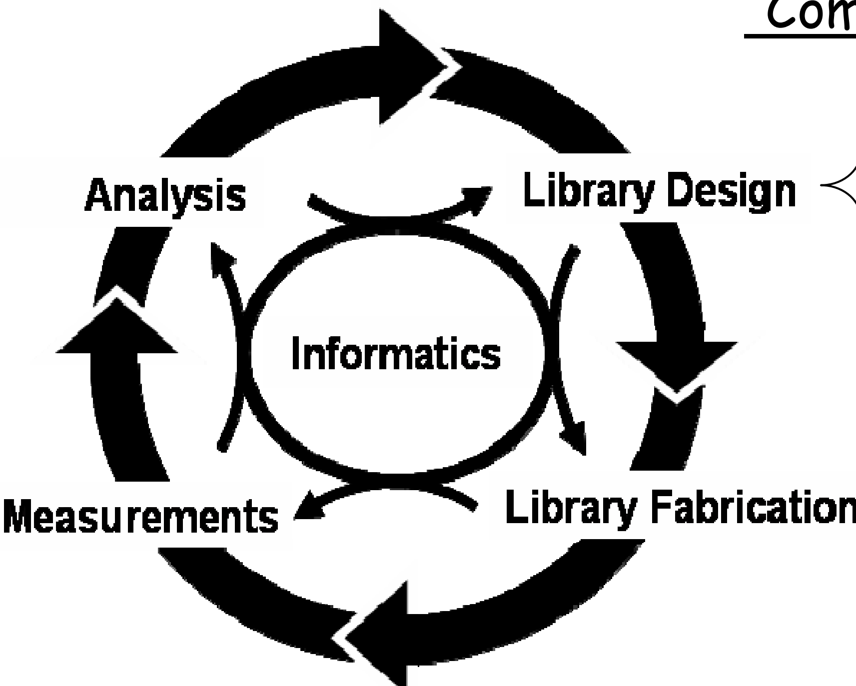
- Revolutionized genomics and drug discovery in the 90s
- *Now, "Combi" is doing the same for materials research*
- Faster discovery and optimization of complex new products
- Increased research productivity
- Reduced waste, reduced use of expensive specialty components

"The train is leaving the station. You are either on board, or will be left behind." - Richard Gross, VP for R&D, Dow Chemical

" 70% of the worlds 30 largest chemical companies have substantial investment in combi programs" – Peter Cohen, Symyx

A New Way of Doing Experiments

Combinatorial Methodology



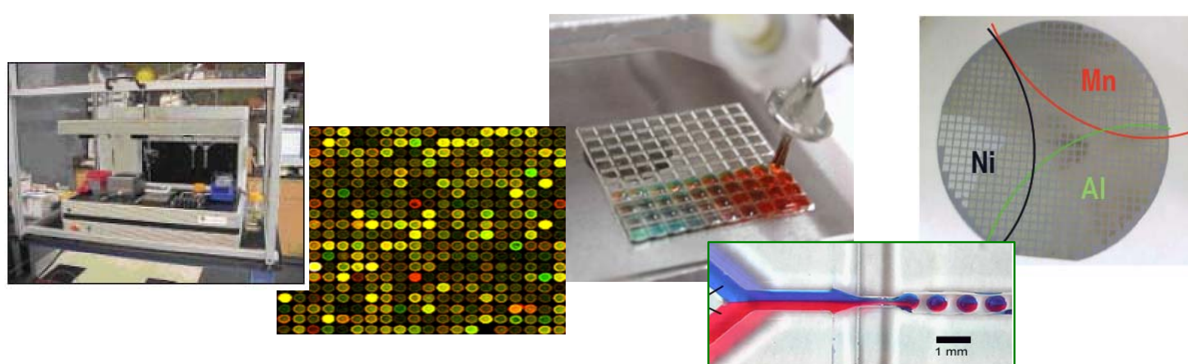
Traditional Route: *Single Hypothesis*
Single Case Specimens

<u>"Combi" Route</u>

- "Space" hypotheses
- Akin to traditional DOE
- ID governing parameters

- Physical realization of library design
- Clever fabrication/synthesis
- Automation
- Miniature sample arrays

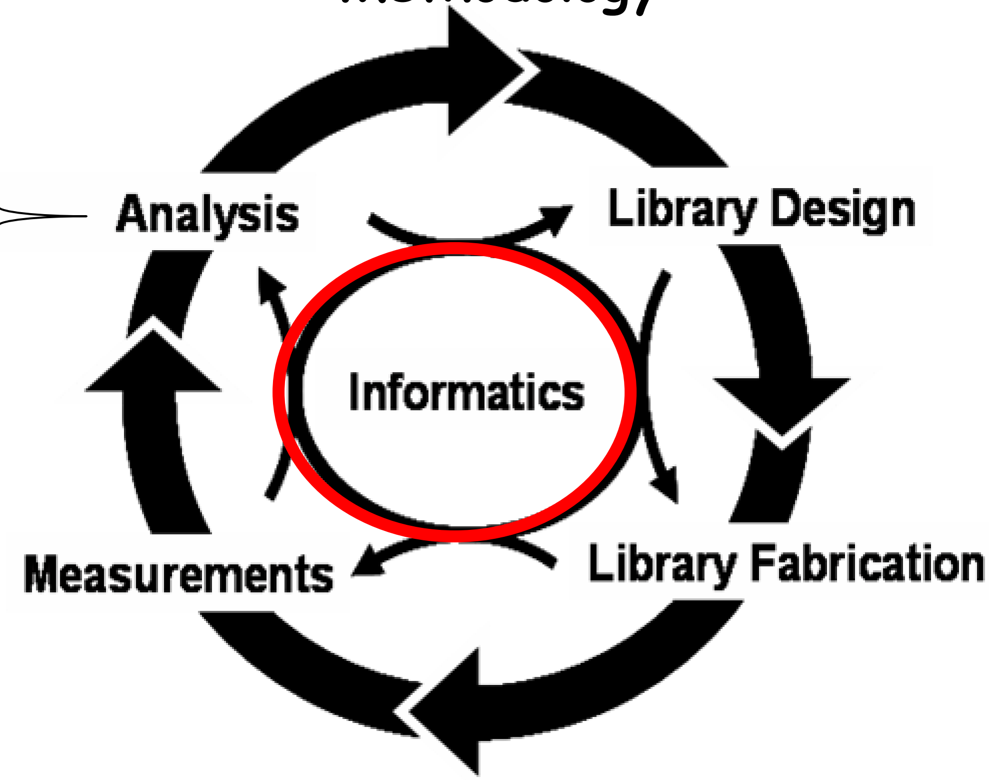
Thorough exploration of huge parameter spaces…



A New Way of Doing Experiments

Traditional Route: *Single Measurement*
Single Conclusion

Combinatorial Methodology



"High-throughput" Route

- Ultra rapid data assessment
- Datamining/Image analysis
- New routines often needed

- Ultra rapid assessment of structure and properties
- Leverages Library Design
- New devices often needed

"Informatics"

- Computational infrastructure for automation in each step
- System integration: Central database, data coordination between steps
- "Closing the combi loop": datamining for conclusions and refinement…

NIST Combinatorial Methods Center

Mission

Combinatorial and High-throughput *measurement solutions* that accelerate the discovery and optimization of new materials

Research Products

- Library designs and high-throughput measurement platforms
- New methods for emerging systems
- Driven by customer needs
- "Open Source" Consortium

Polymer Focus Areas

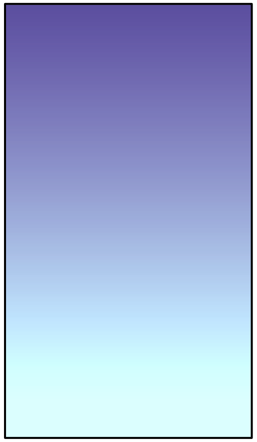
- Adhesion and Mechanical Properties
- Fluid Formulations
- Nanomaterials and Nanometrology
- Testbed: Films and Coatings

LEARN MORE: www.nist.gov/combi

Continuous Gradient Methods

An approach to combi library fabrication

Continuous Gradient Specimens

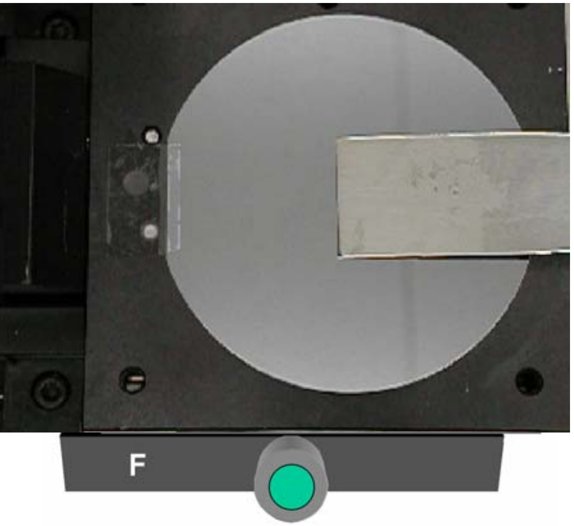


Crossed-Gradient Combinatorial Libraries

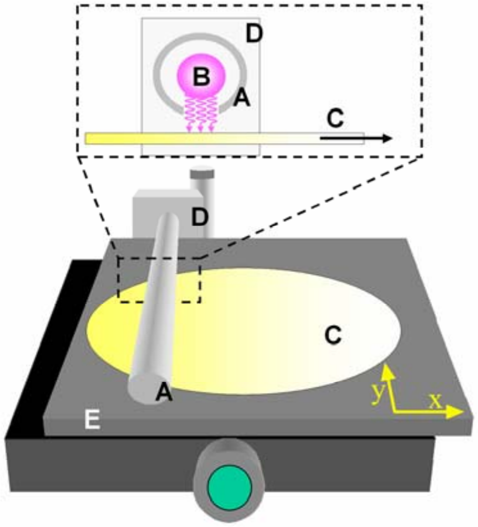
- Entire "spaces" rather than single "points"
- Unparalleled property mapping
- Illuminate of critical phenomena

NIST Gradient Library Toolbox

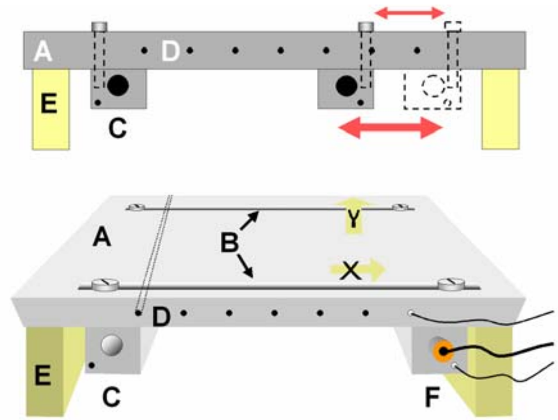
Predictable, reproducible fabrication of gradients in properties of interest to materials researchers



NIST Gradient Film Flow Coater



NIST Gradient Light Exposure Device



NIST Gradient Temperature Stage

Film Thickness

Blend Composition

Modulus

Surface Energy

Cross-linking Density

Surface Topography (Roughness)

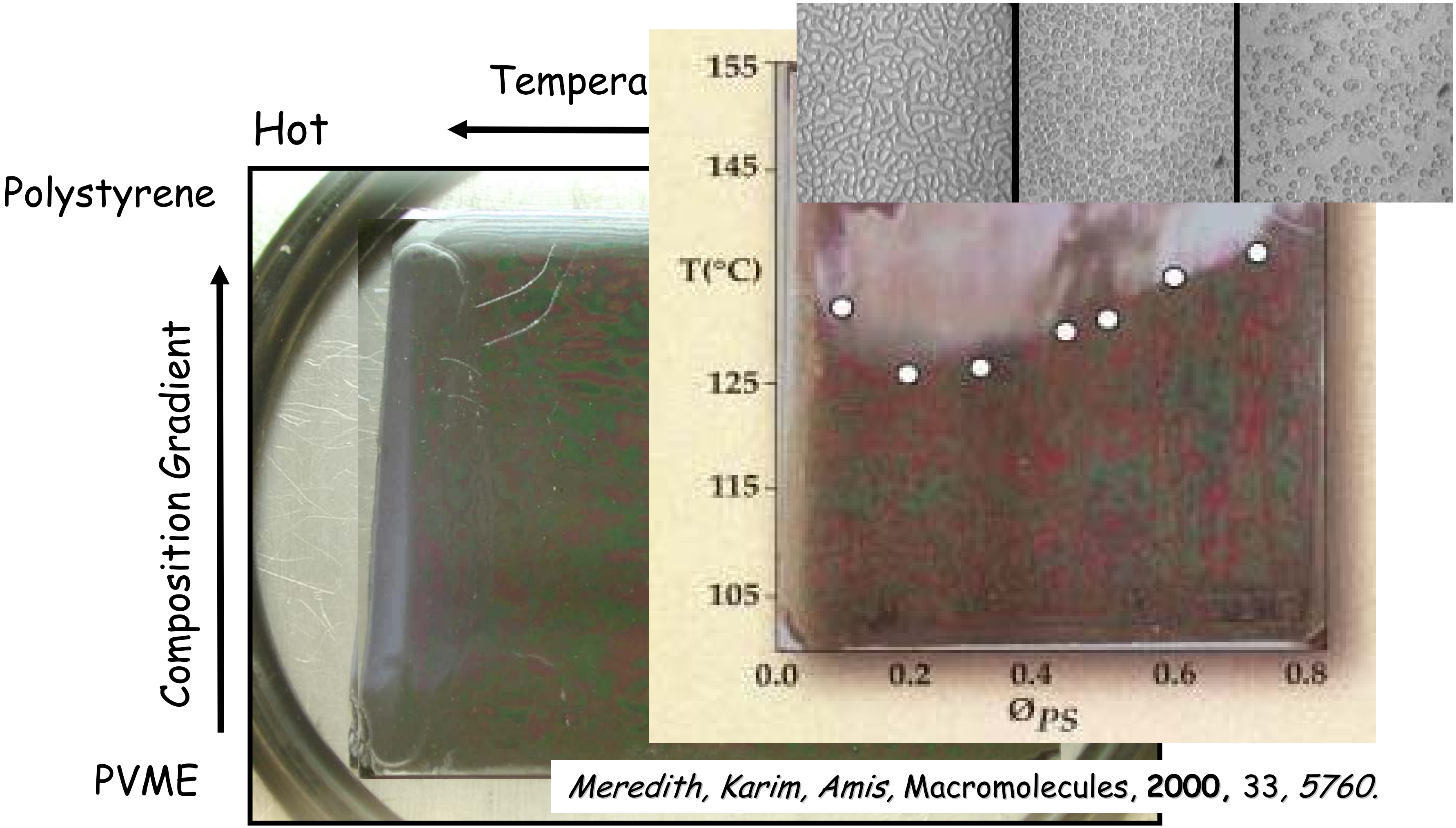
Processing Temperature

Photopolymerization

Surface Functionalization

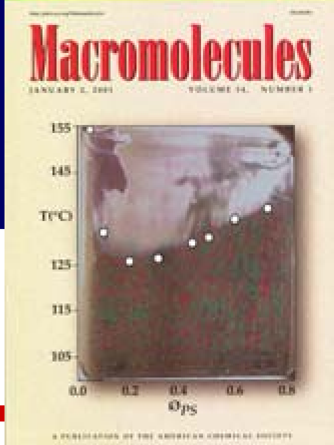
Combi Polymer Blend Phase Diagrams

Conventional method: Many experiments, Weeks of effort
Combinatorial method: One experiment, complete in 1 day



Meredith, Karim, Amis, Macromolecules, **2000**, 33, *5760.*

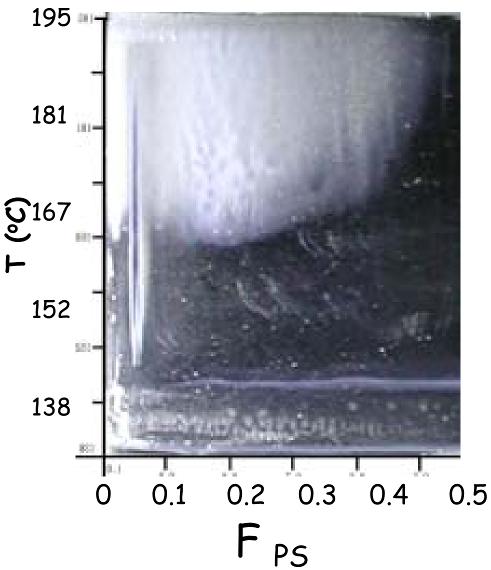
Extension of Combi Phase Diagrams



Low-effort phase diagrams enable rapid, comprehensive research of complex systems…

Additives

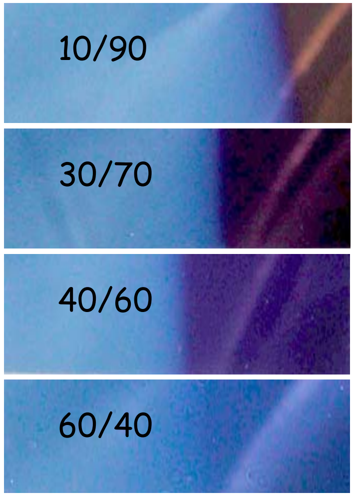
nanofillers



dPS/ PVME/ 2% Closite
(Southern Clay)

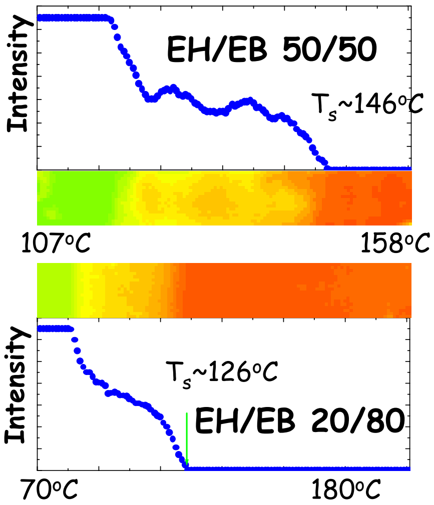
Engineering Materials

advanced photo-resists



PHS/PBOC films
(IBM)

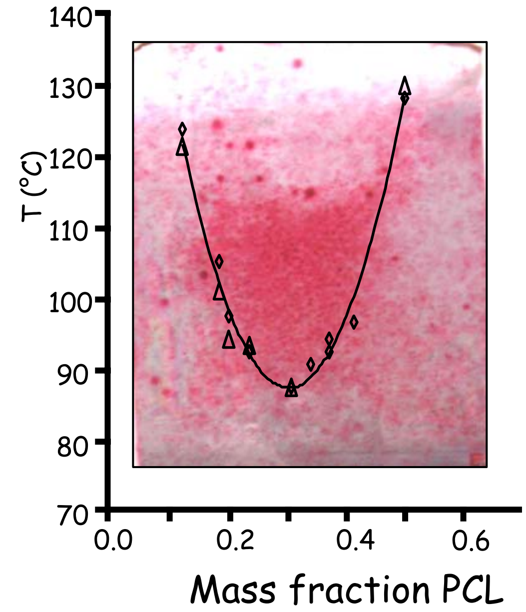
polyolefins



EH/HB Thick Films
(Exxon)

Biocompatibility

Cell assays



Meredith, Amis, Karim, Han, Lenhart, Sehgal

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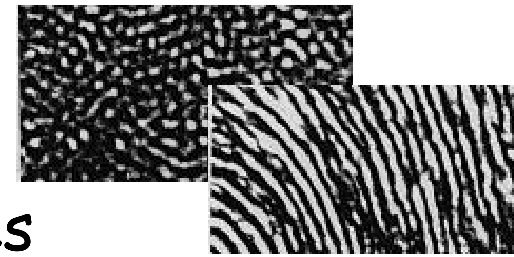
  - Surface Grafted Polymers
  - Microfluidics: Solutions and Particles

Theme: Importance of interfaces

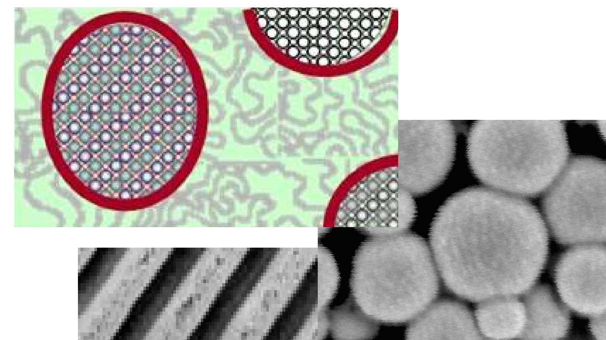
Nanostructured materials are "all interface"

Nanostructured Fluids



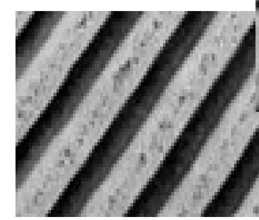
- Management of structure, stability
- Performance of surfactants/additives

Nanoparticle Composites



- Management of flocculation
- Targeted dispersion/activity

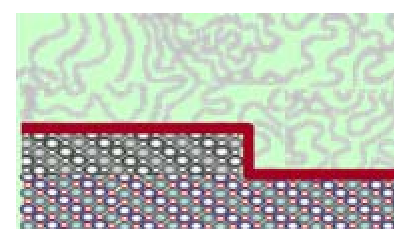
Polymer Self-Assembly



Kramer et al, Advanced Materials 2005 17(21) 2618.

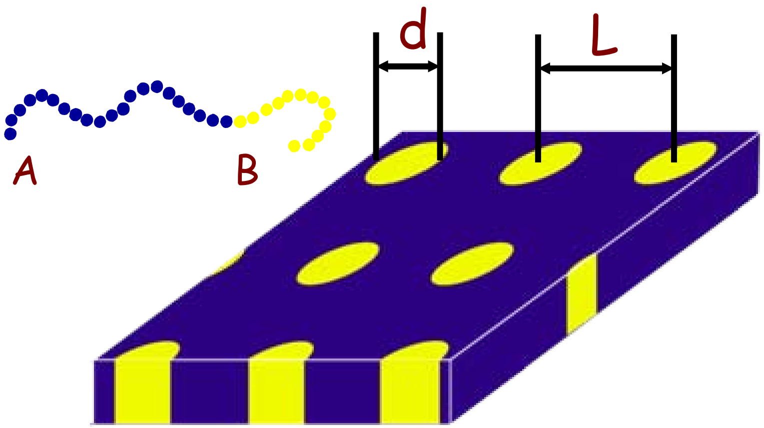
- Driver for microphase separation

Films and Coatings



- Management of adhesion, wetting, nanostructure and particle orientation

Block Copolymer Nano-lithography

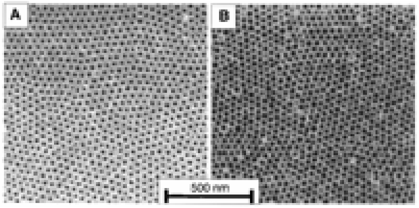


- Self-assemble into nano-arrays with highly regular domain size (d) and period (L).
- Array dimensions are tailored via molecular architecture (M = molecular weight):

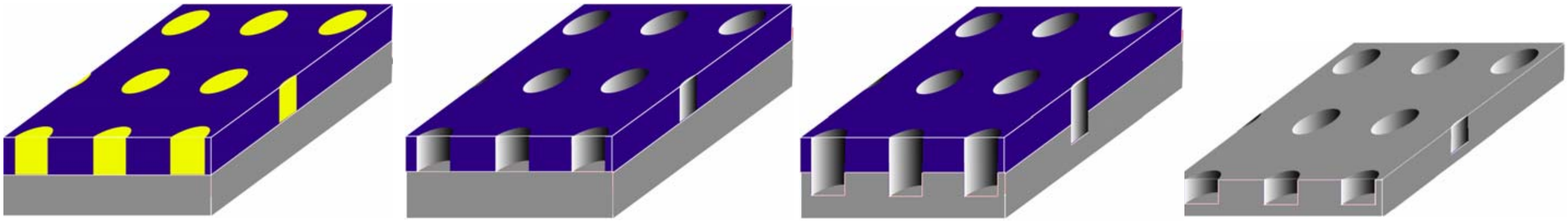
$L \sim (M_A+M_B)^{2/3} \rightarrow$ (20nm – 60 nm)

$d \sim M_B/(M_A+M_B) \rightarrow$ (7 nm – 20 nm)

BC Lithography Scheme



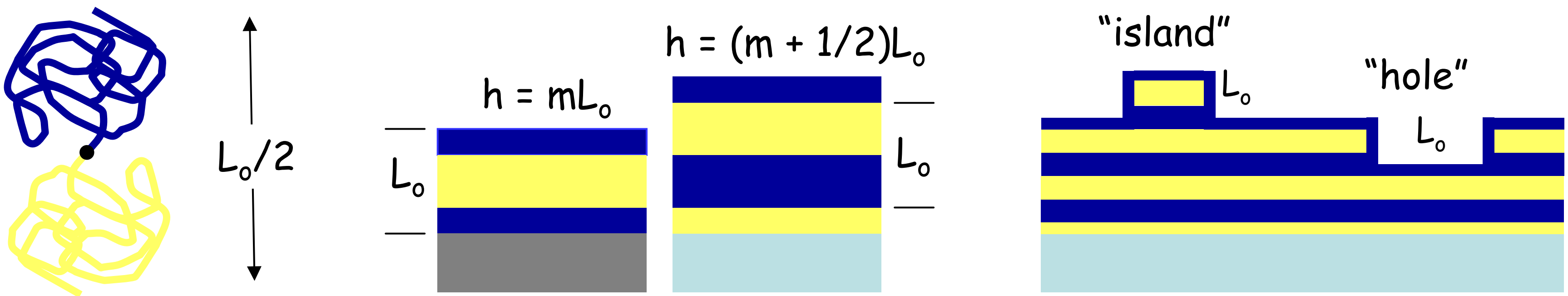
Mansky et al. Science **1997**, *275*, 1458.
Huang *et al. Macromolecules* **1998**, *31*, 7641
Park et. al. Science 1997, *276* 1401-1404



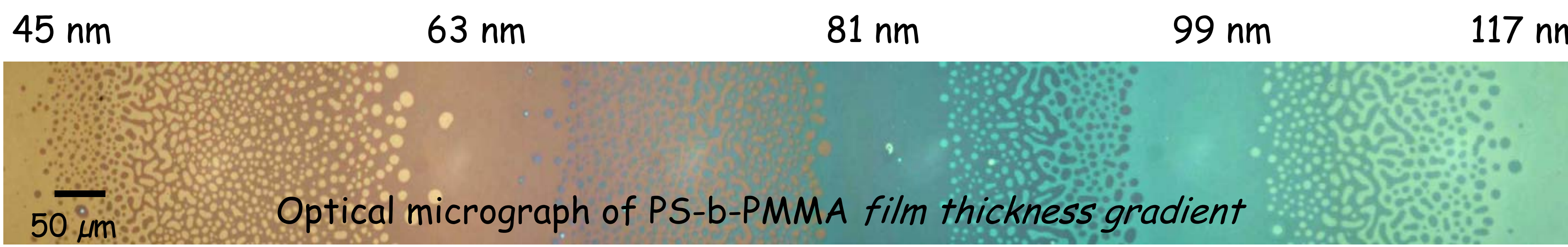
1. Deposit BC
2. Selective BC etch
3. Etch Substrate
4. Remove Polymer

Block Copolymer Film Behavior

Effect of thin film confinement



Film thickness determines surface relief structure



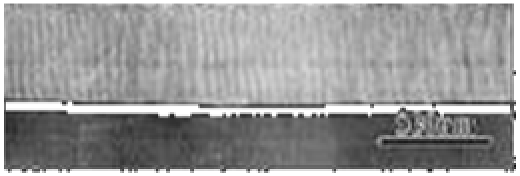
Optical micrograph of PS-b-PMMA *film thickness gradient*

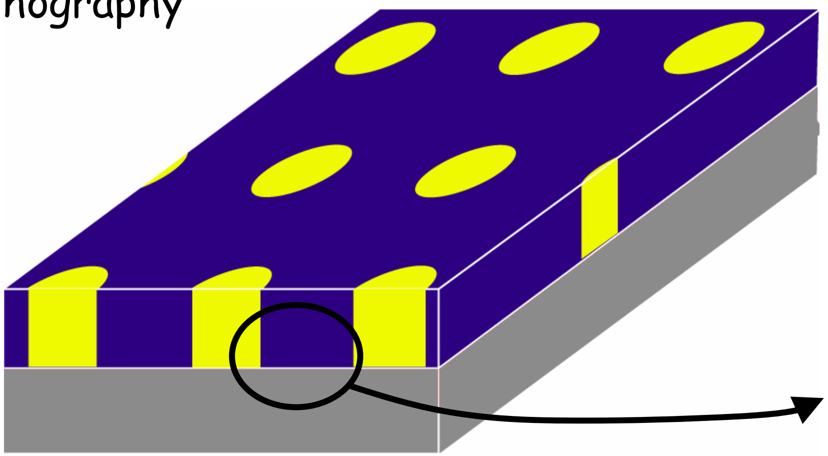
Smith, Douglas, Meredith, Amis, Karim, Phys. Rev. Letts., 2001, 87, *015503*
Smith, Douglas, Meredith, Amis, Karim, J. Polym. Sci. Polym. Phys., 2001, 39, *2141*

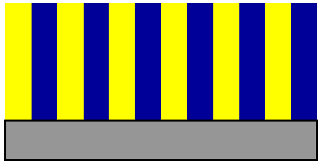
Importance of Interfacial Energy

Substrate determined by application:

- Typically an oxide, like SiO_2
- Preferential wetting of one block
- Not useful for lithography



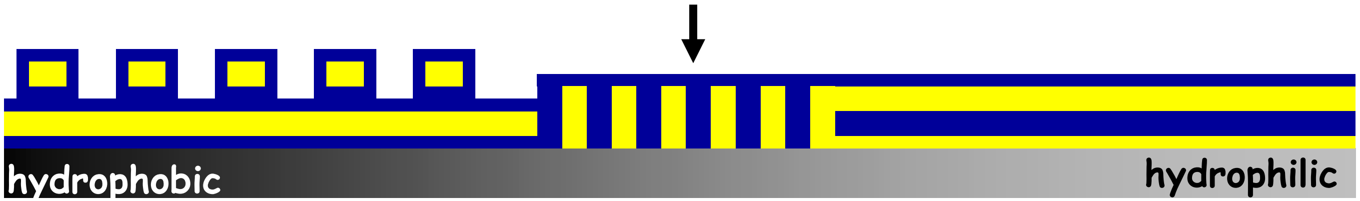




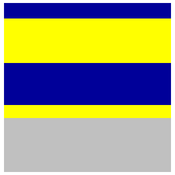
Useful orientations require interface engineering

Target: "Neutral Surface" - ⊥ domains

Symmetric wetting

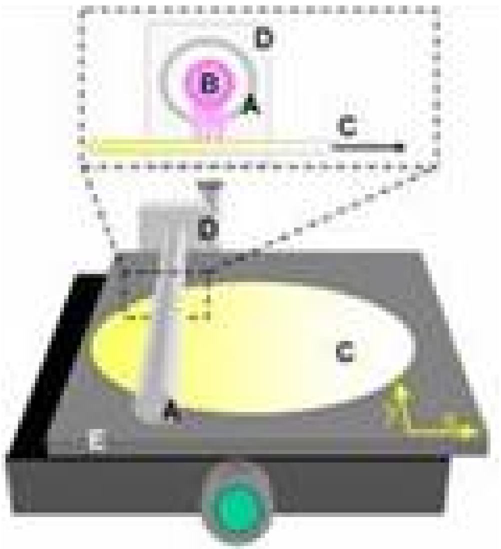


Anti-Symmetric wetting

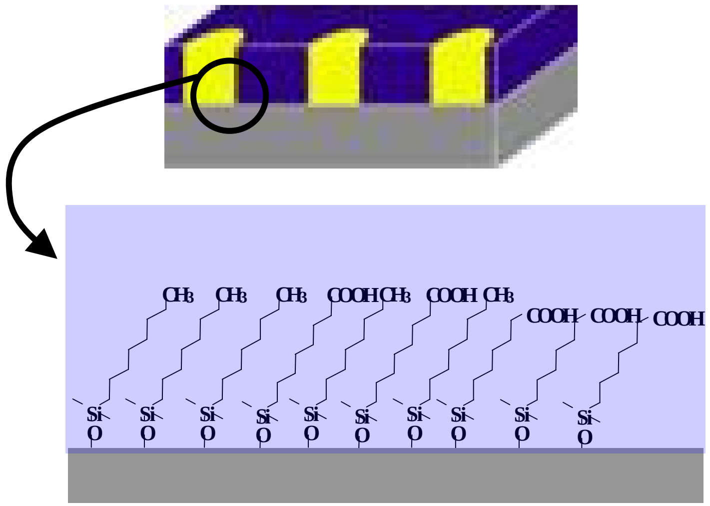


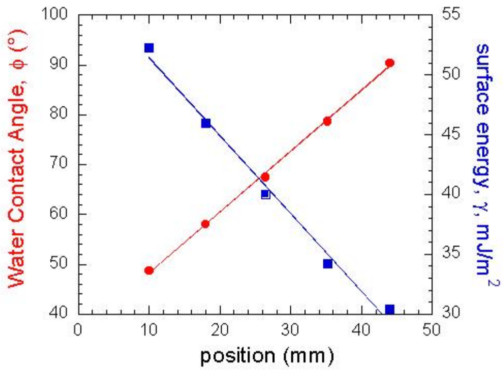
Combi approach to interface engineering

Surface Energy Gradient Library

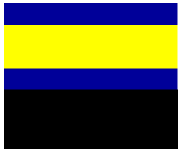


NCMC UV-Ozone Gradient Device





Symmetric wetting



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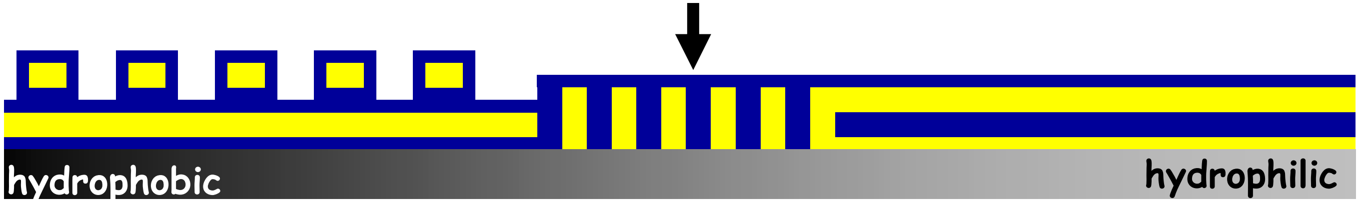
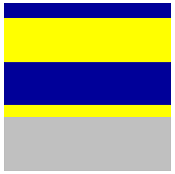
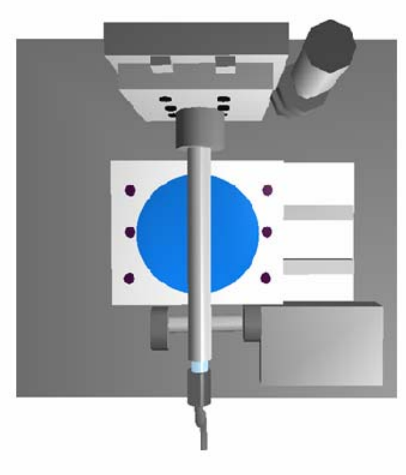


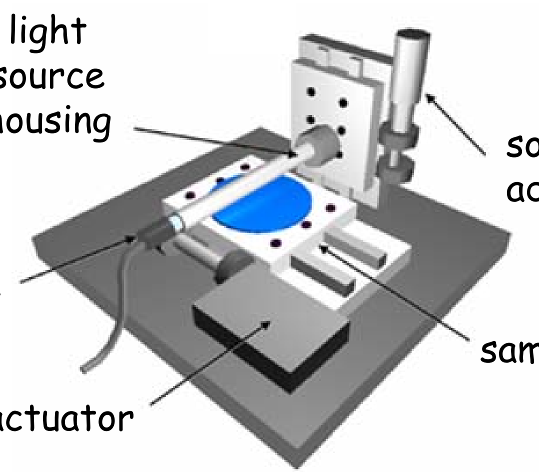
Anti-Symmetric wetting



Light exposure gradients

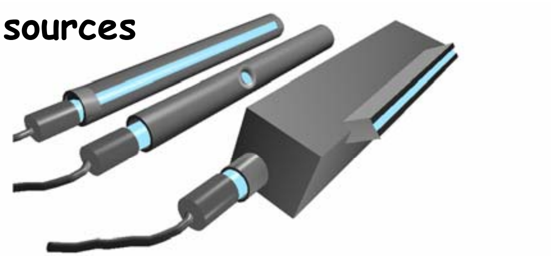
NIST Gradient Light Exposure Device





Light source appliances

For wand sources

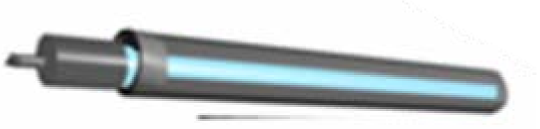


For flood sources

- Can shape a variety of light sources
- A variety of libraries:
  - **Surface energy/hydrophobicity**
  - Bio-functionality
  - Photopolymerization
  - Photo-aging and degradation
  - Photoresist processing

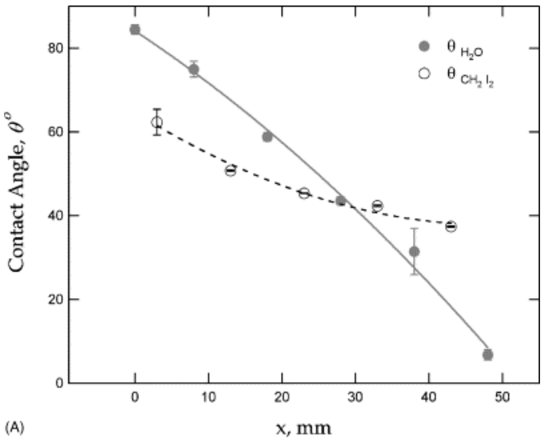
Berry, Stafford, Pandya, Lucas, Karim, Fasolka, Review of Scientific Instruments 2007 (in press)

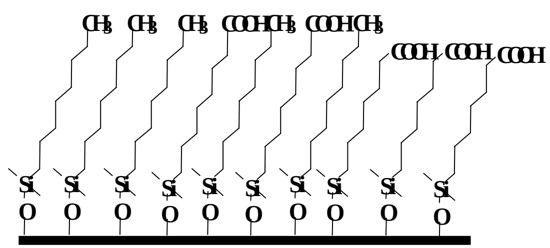
Surface Energy Gradient

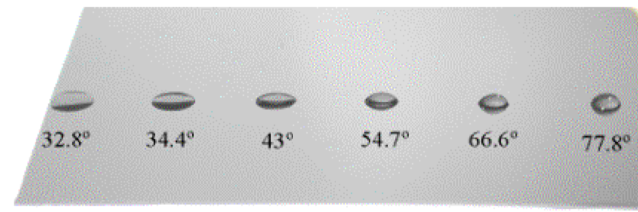


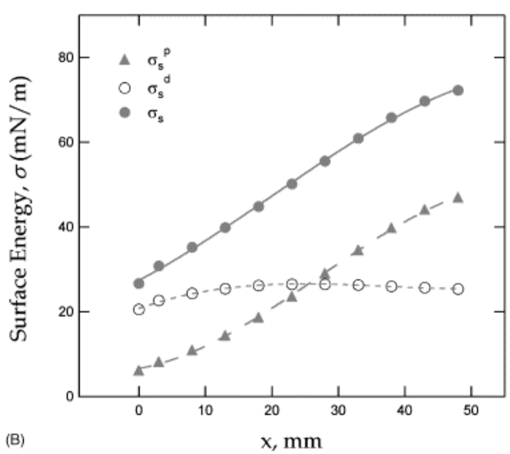
192nm wand source in slit aperture housing

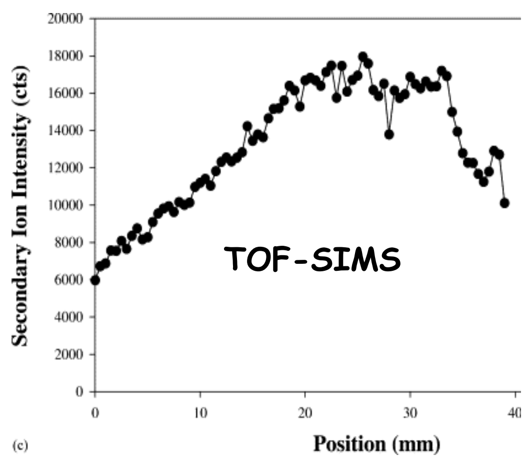
Library Range:
20-78 mJ/m^2

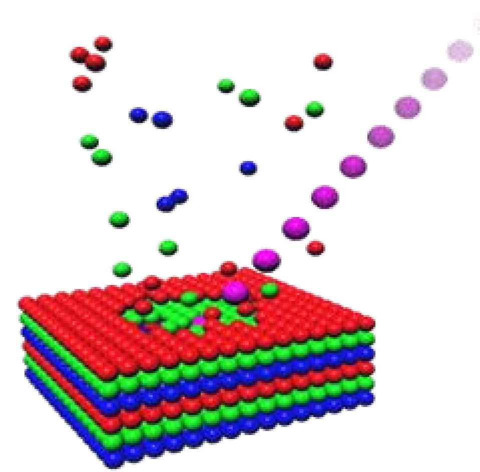








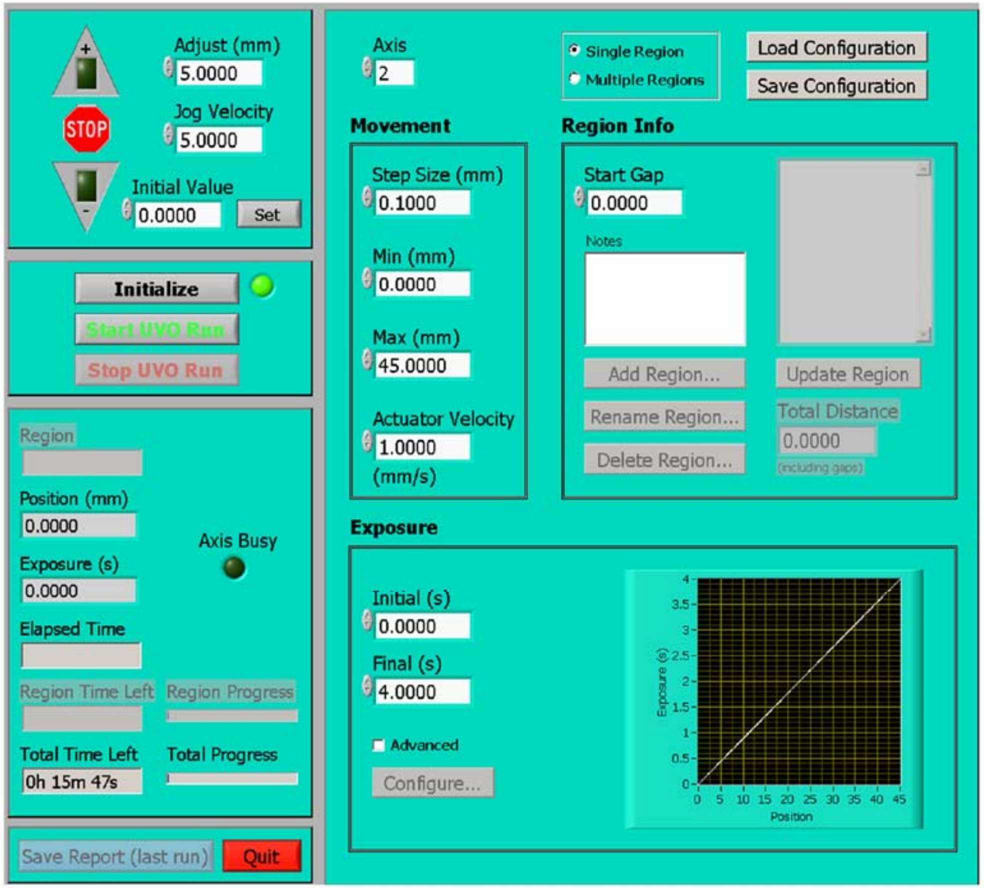


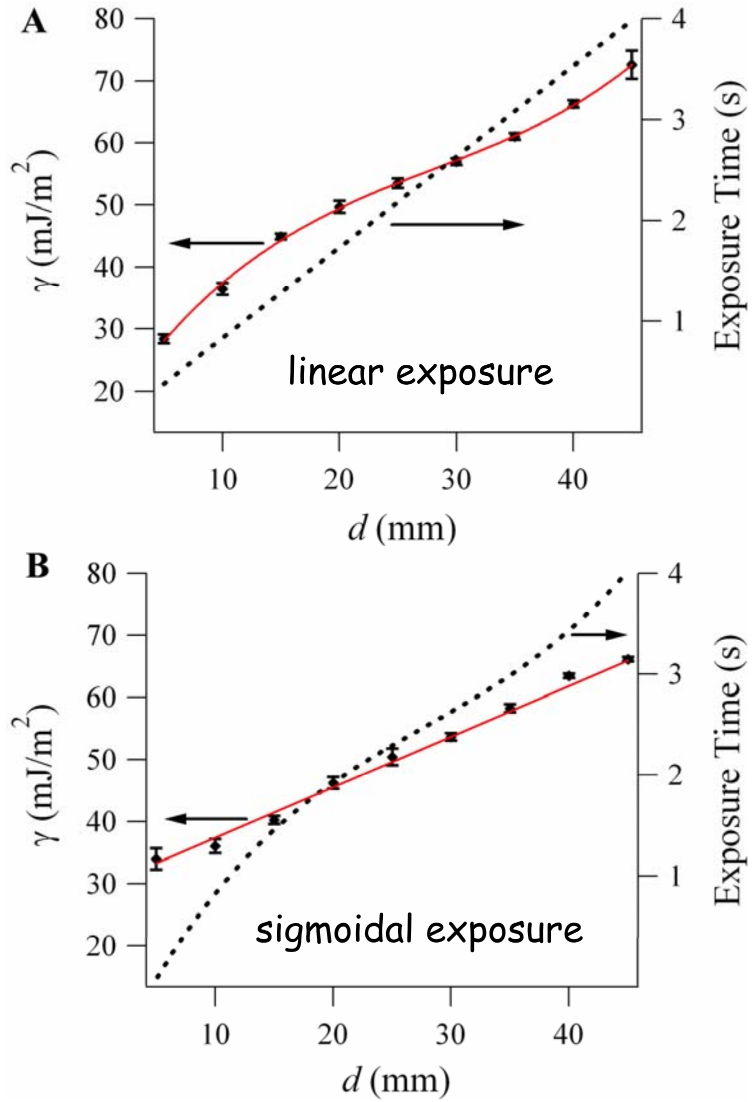


Roberson, Fahey, Sehgal, Karim, Applied Surface Science **200**, (2002)

Ashley, Karim, Douglas, Langmuir, 21, (2005)

Instrument automation





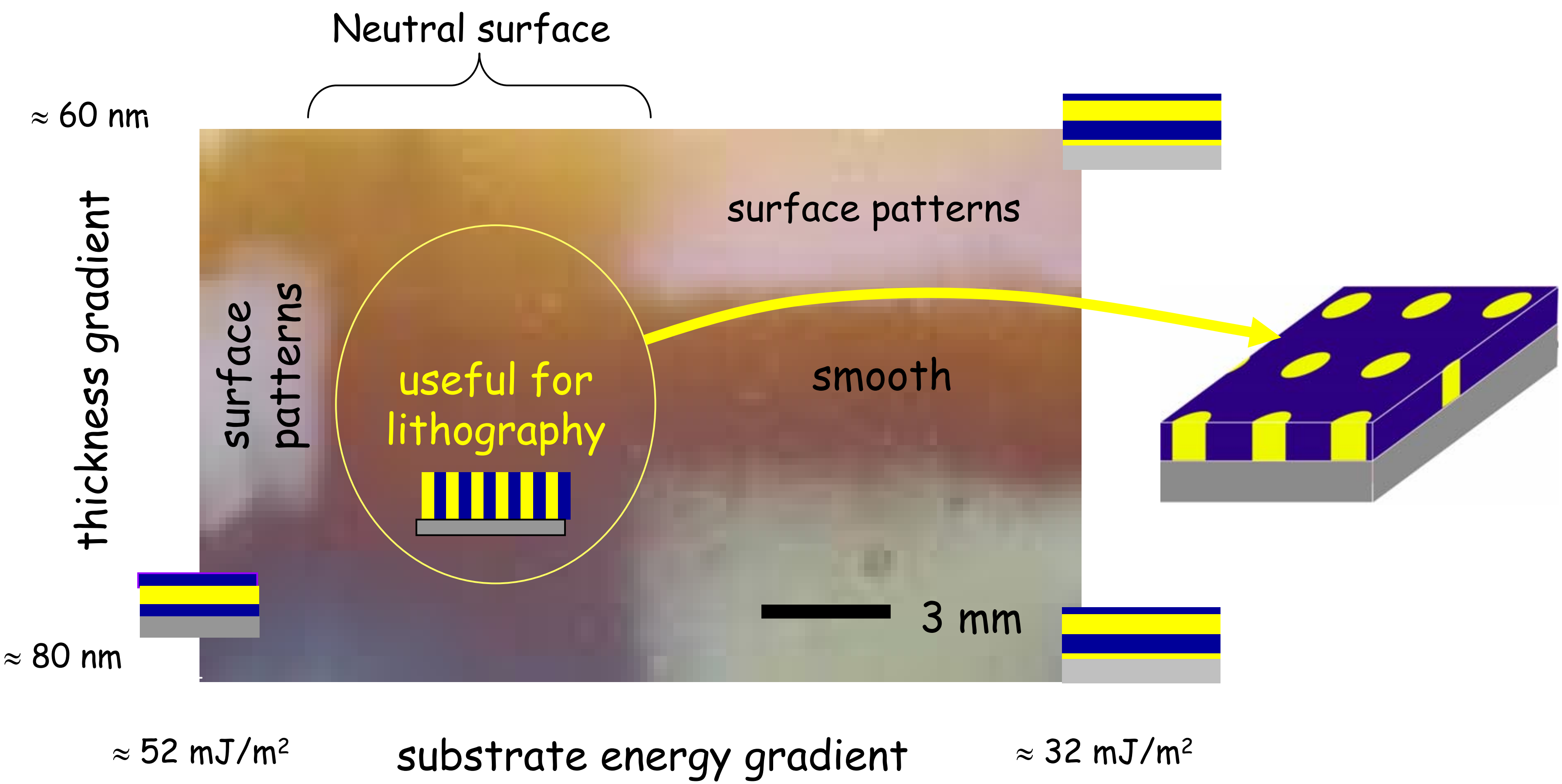
User defined exposure functions:

- Flexible library design
- Rectification of complex behaviors into well behaved libraries

Berry, Stafford, Pandya, Lucas, Karim, Fasolka, Review of Scientific Instruments 2007 (in press)

Gradient Optimization of Surface Energy

Gradient library illuminates range of surface energy for proper BC morphology



A.P. Smith et al, Macromolecular Rapid Communications 2003; 24(1): 131

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Grafted Polymer "Brushes"

End-grafted polymers are a robust means to functionalize surfaces
- Covalent bonding
- Enhanced surface coverage
- Enhanced end group expression

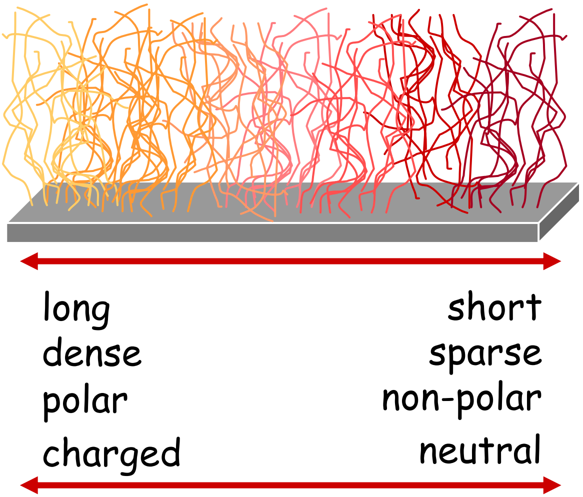
} "Brush Effect": volume exclusion, elongated coils

S. T. Milner, *Science* 251, 905 (1991)

New controlled synthesis routes enable grafted polymer with designed chemistry and architecture

Matyjaszewski, et al, *Macromolecules*, 1999
Huang, *et al*, *Macromolecules*, 2002

Brushes enable:
- Tailored surface functionlization
- Particle functionalization
- Intelligent surfaces and Sensors



Combi gradient brush libraries:
- design and optimization of grafted polymers

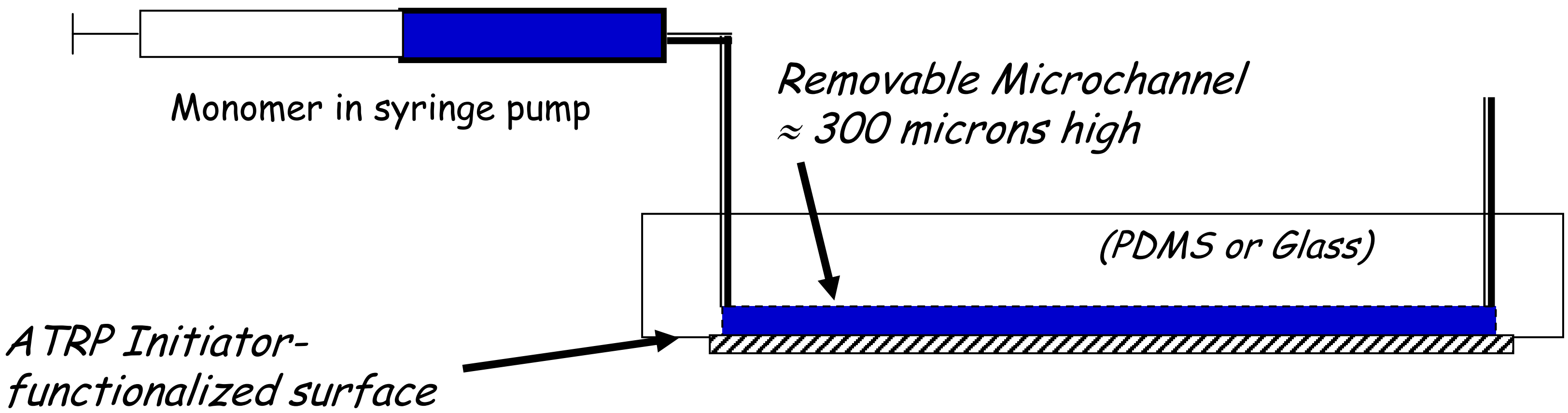
See also: Tomlinson, M. R.; Genzer, J. *Macromolecules* **2003**, *36*, 3449-3451.

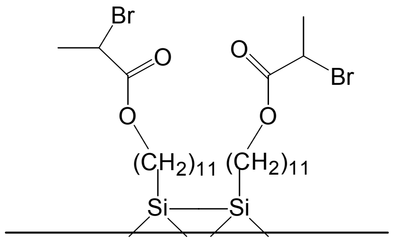
Wu, Xu, Beers, Mei, Fasolka

Microchannel Confined Surface Initiated Polymerization (μSIP)


Kathryn Beers

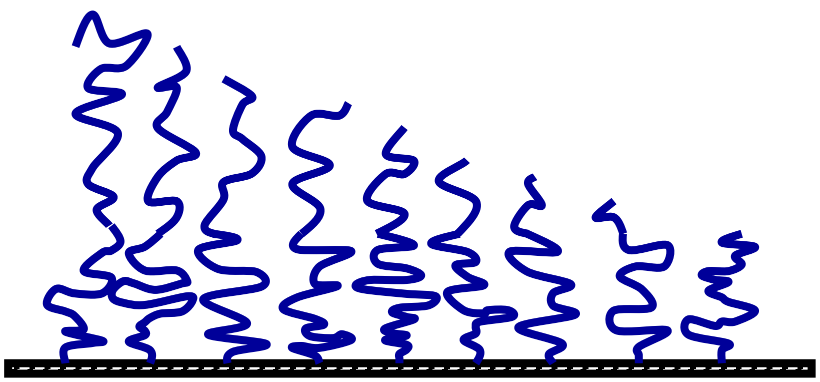
- Microchannel confines monomer solution at surface
- Flow Control: Tailor reaction time at the surface (chain length thickness) or the reaction medium/surface exposure





Matyjaszewski, et al, *Macromolecules*, 1999
Huang, *et al*, *Macromolecules*, 2002

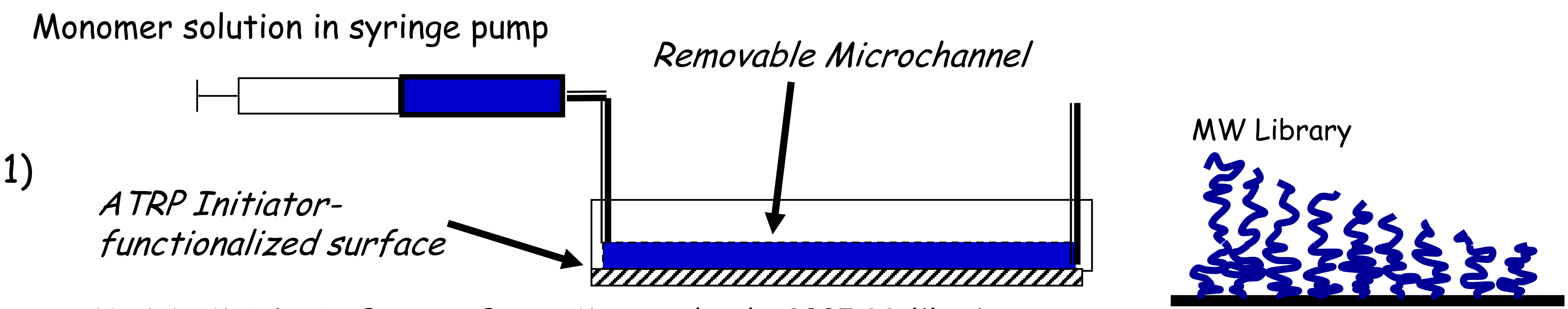
Xu, Wu, Mei, Drain, Batteas, Beers
Macromolecules 38 (1): **2005**, 6-8.



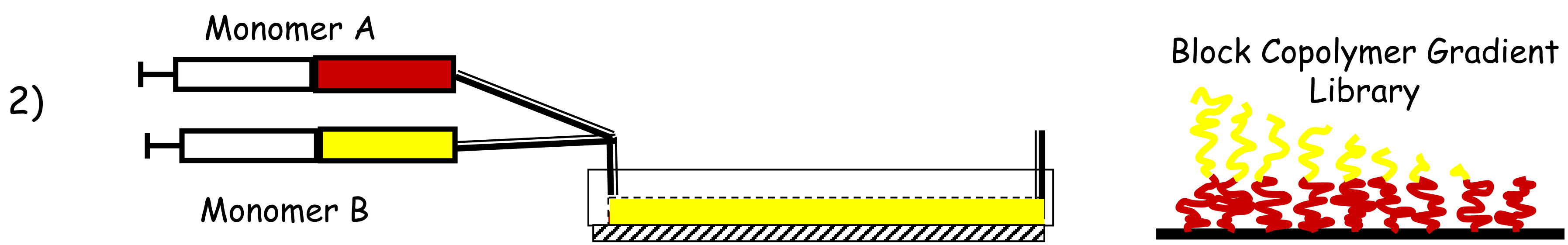
T. Wu
C. Xu
K. Beers

Simplest Case: Molecular Weight Gradient Library

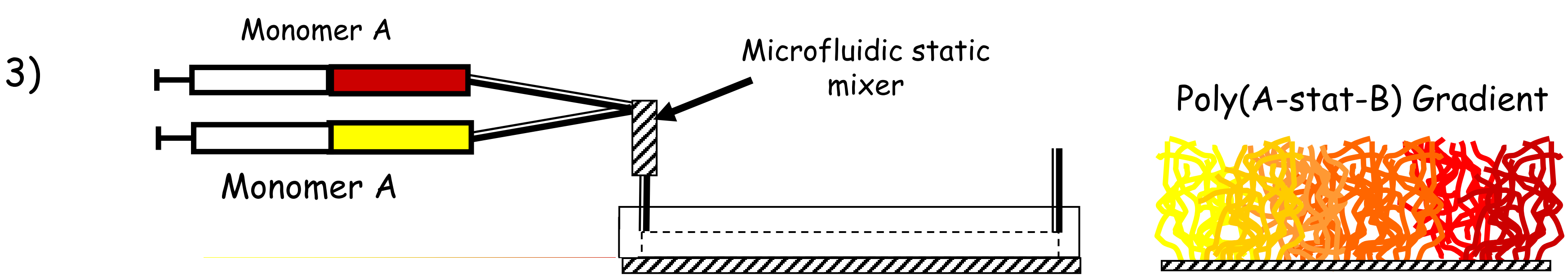
Flexible library fabrication



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



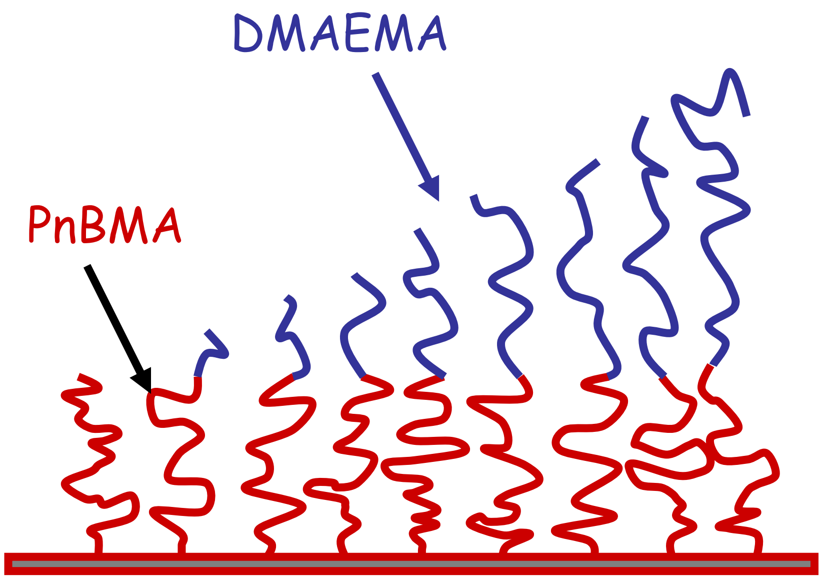
Xu, Beers, Fasolka et al, *Macromolecules* 2006, 39 (9), 3359 & *Applied Surface Science* 2006, 252 (7), 2529.



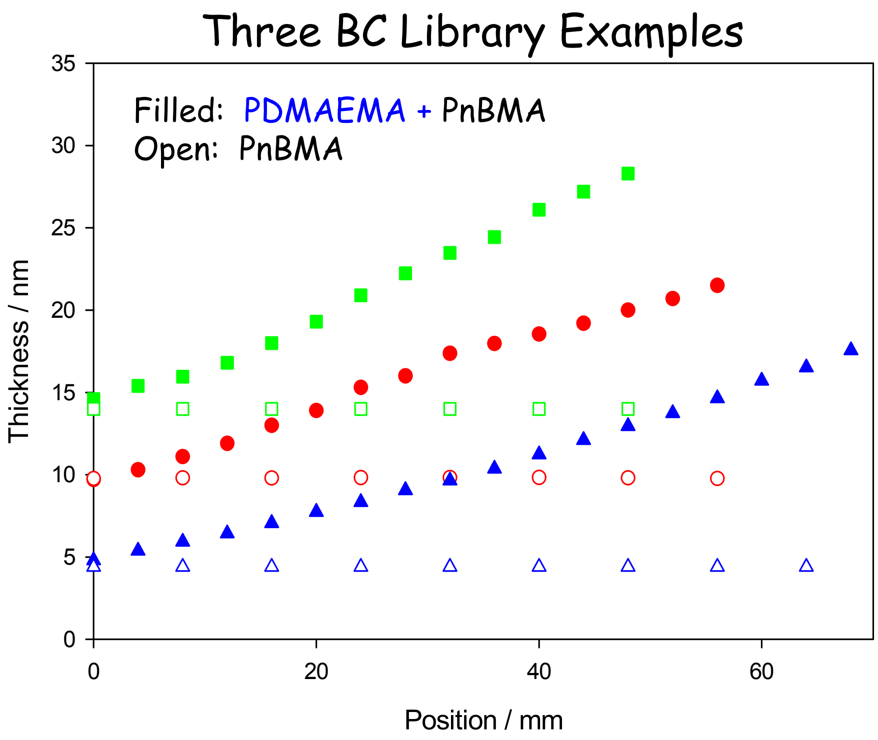
Xu, Wu, Beers et al, *Advanced Materials* 2006, 18 (11), 1427.

BC Gradient Example

- Uniform Poly(n-butyl methacrylate) (PnBMA) bottom layer
- MW gradient of poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) grown from PnBMA layer
- Library of "environment-responsive" grafted polymer surfaces

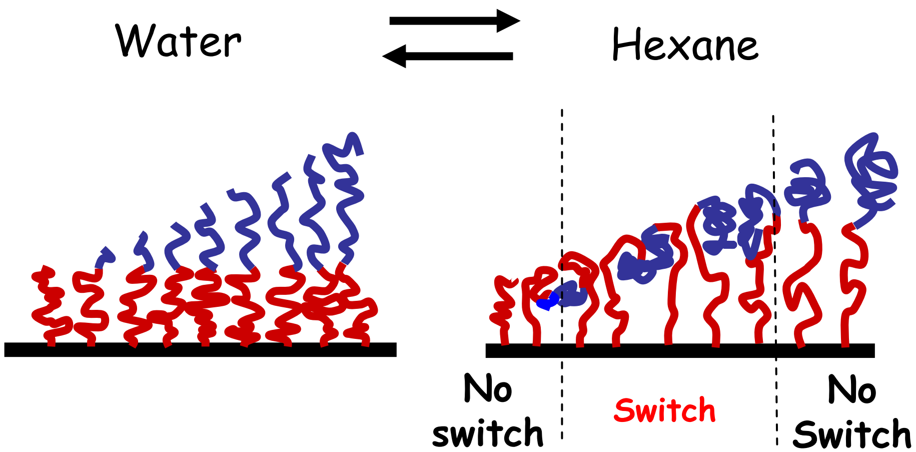


Applied Surface Science **2006**, 252, 2529.

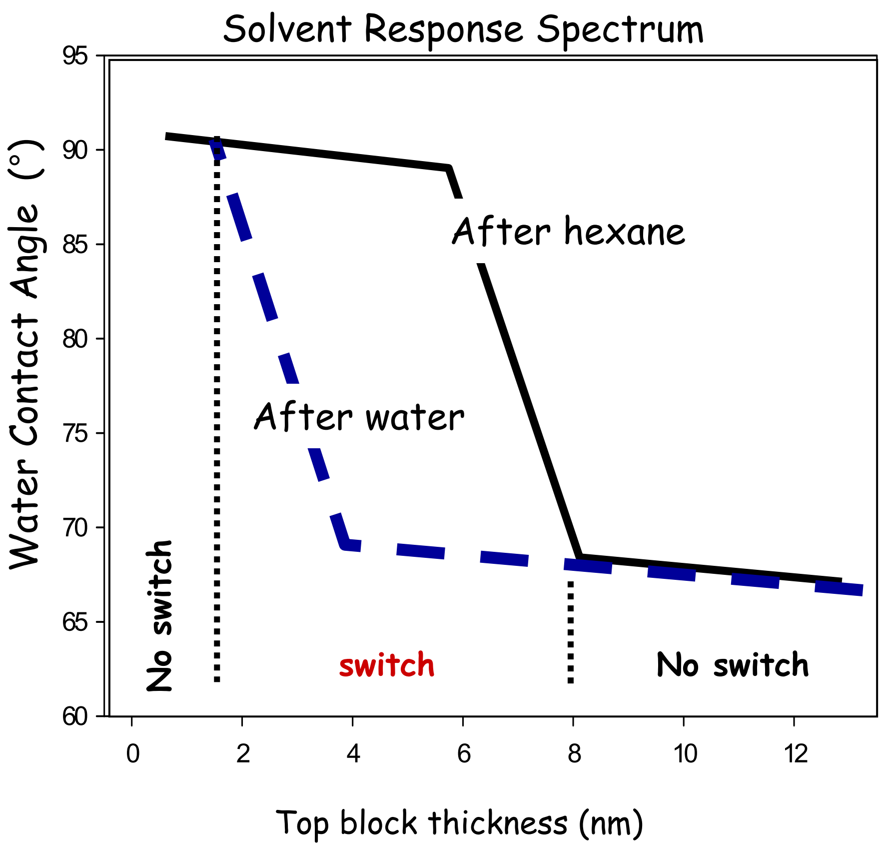


Solvent Response Screening

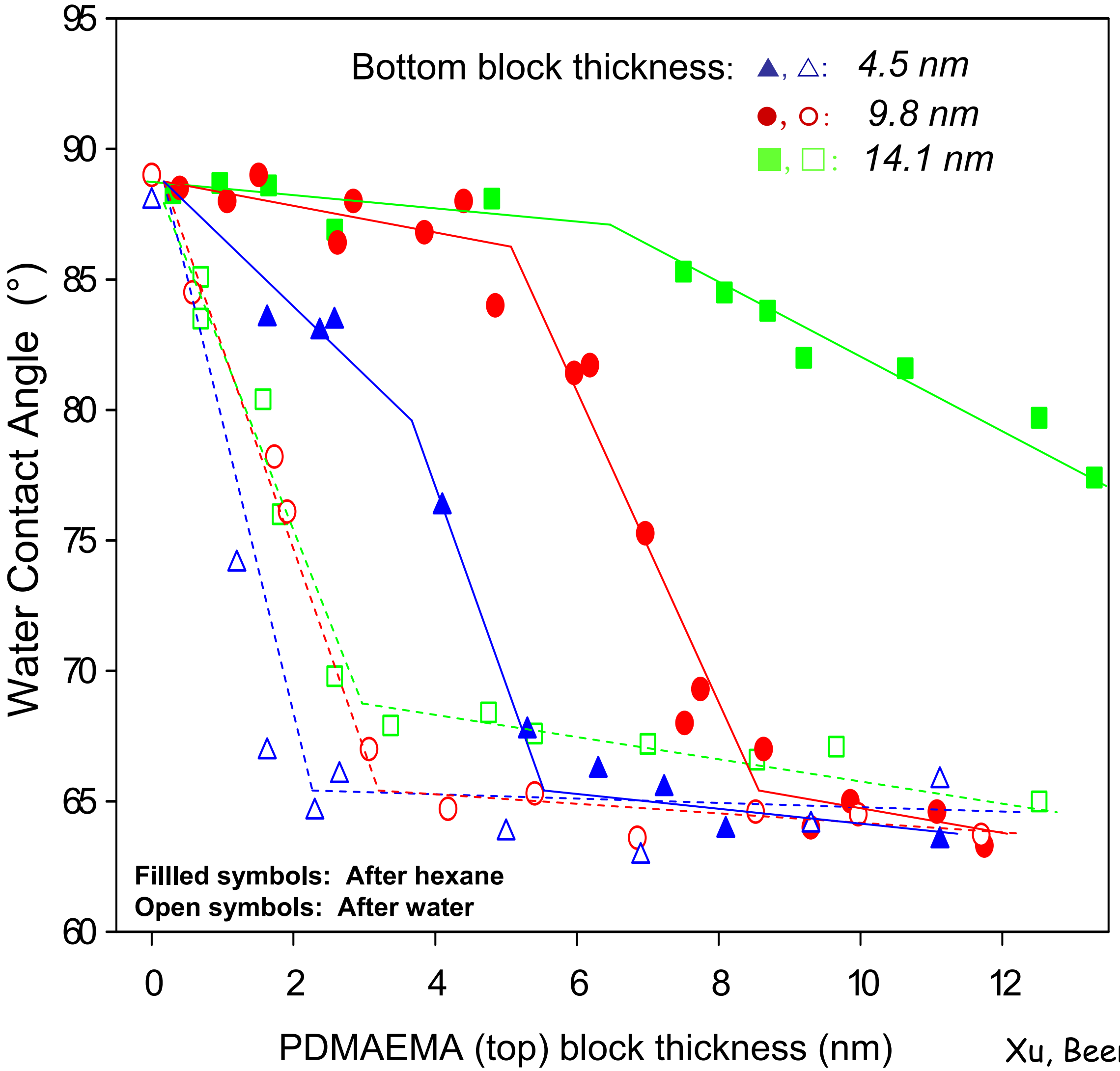
- Gradient libraries *map* BC restructuring in response to solvent exposure
- Gradient libraries *illuminate* molecular parameters (block lengths) that maximize (or minimize) environmental response

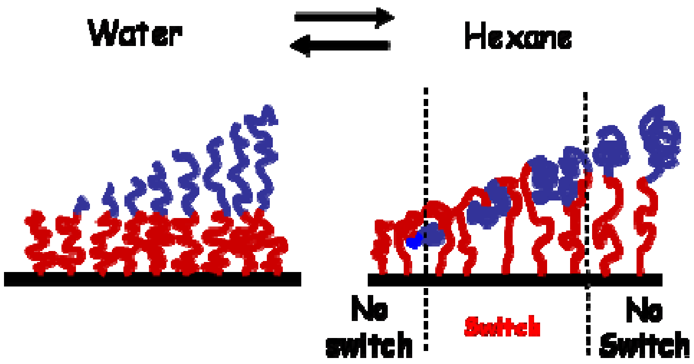


- Libraries screened with selective solvents: water (PDAEMA) and hexane (PnBMA)
- Automated water contact angle measurements gauge brush response over library after solvent exposure



Solvent Response Screening

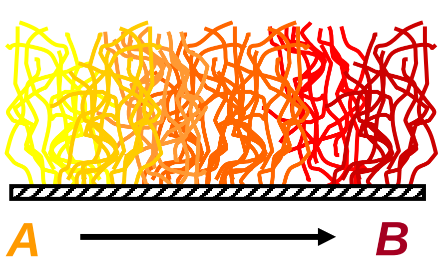


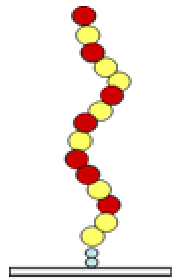


- Gradients illuminate narrow optimal response windows
- Long PDMAEMA blocks suppress switching behavior
- Long PnBMA blocks enhance switching behavior

Xu, Beers, Fasolka et al, *Macromolecules* **2006**, 39, 3359

Statistical Copolymer Gradients



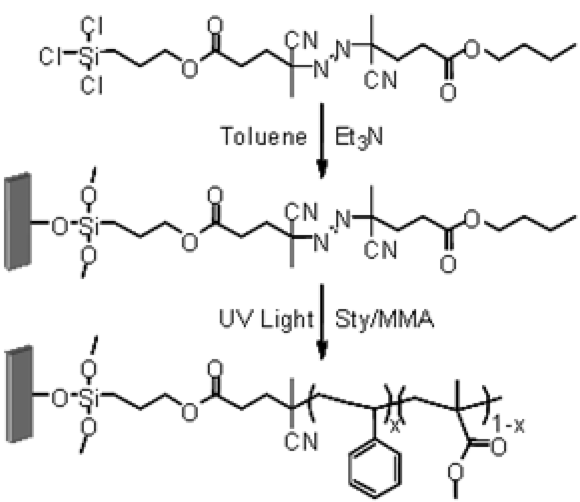


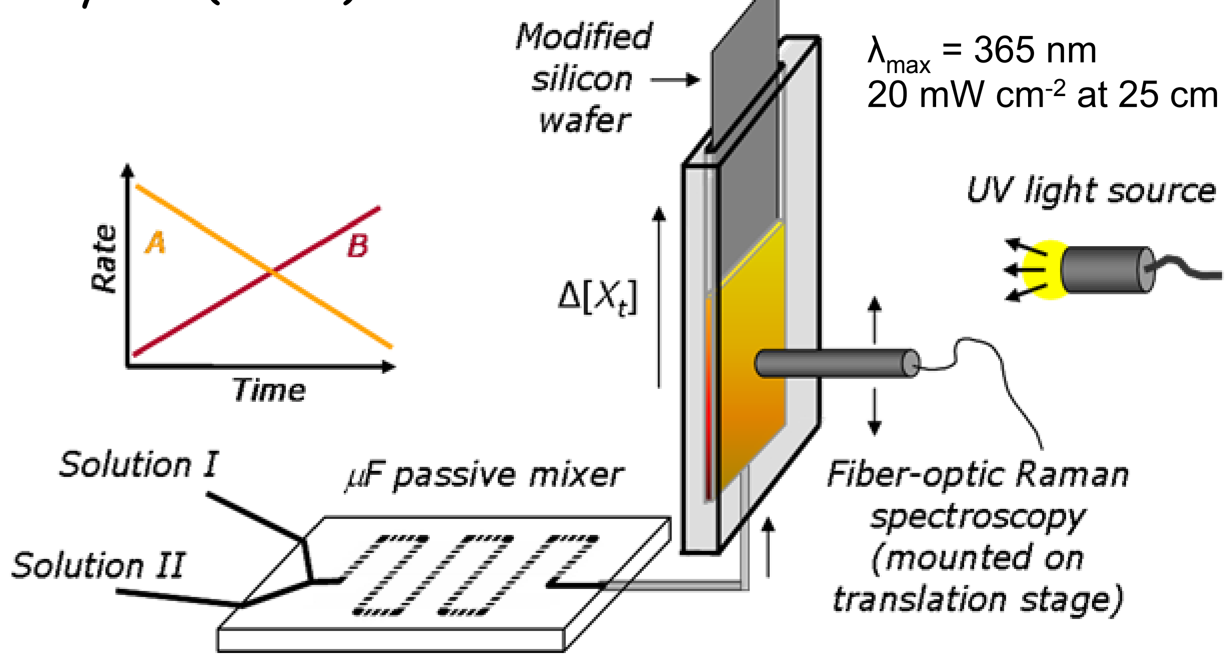
- Tailored functionality w/o segment segregation
- Stable expression of complex chemistries
- A better surface energy library

<u>Demonstration System</u>

Monomer A: Styrene (Styr, PS)

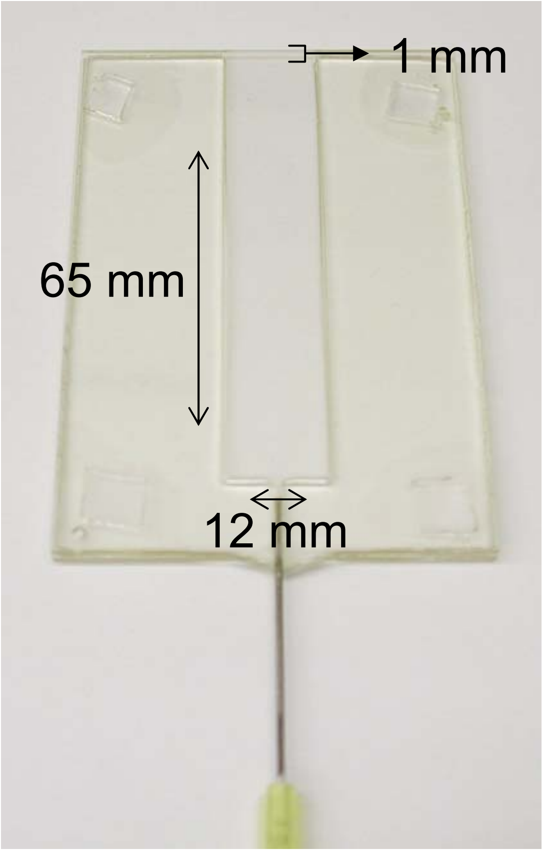
Monomer B: Methyl methacrylate (MMA)

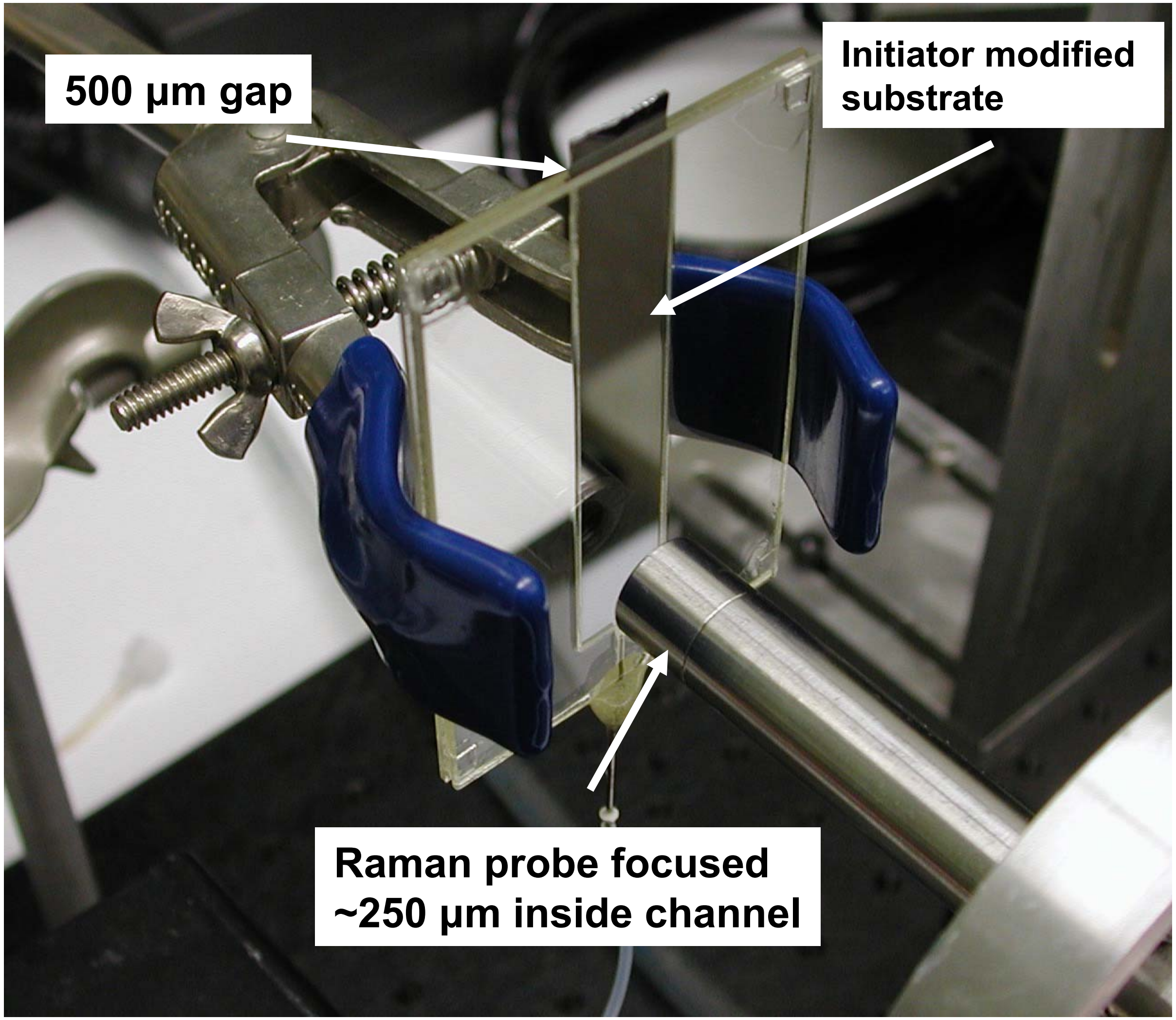




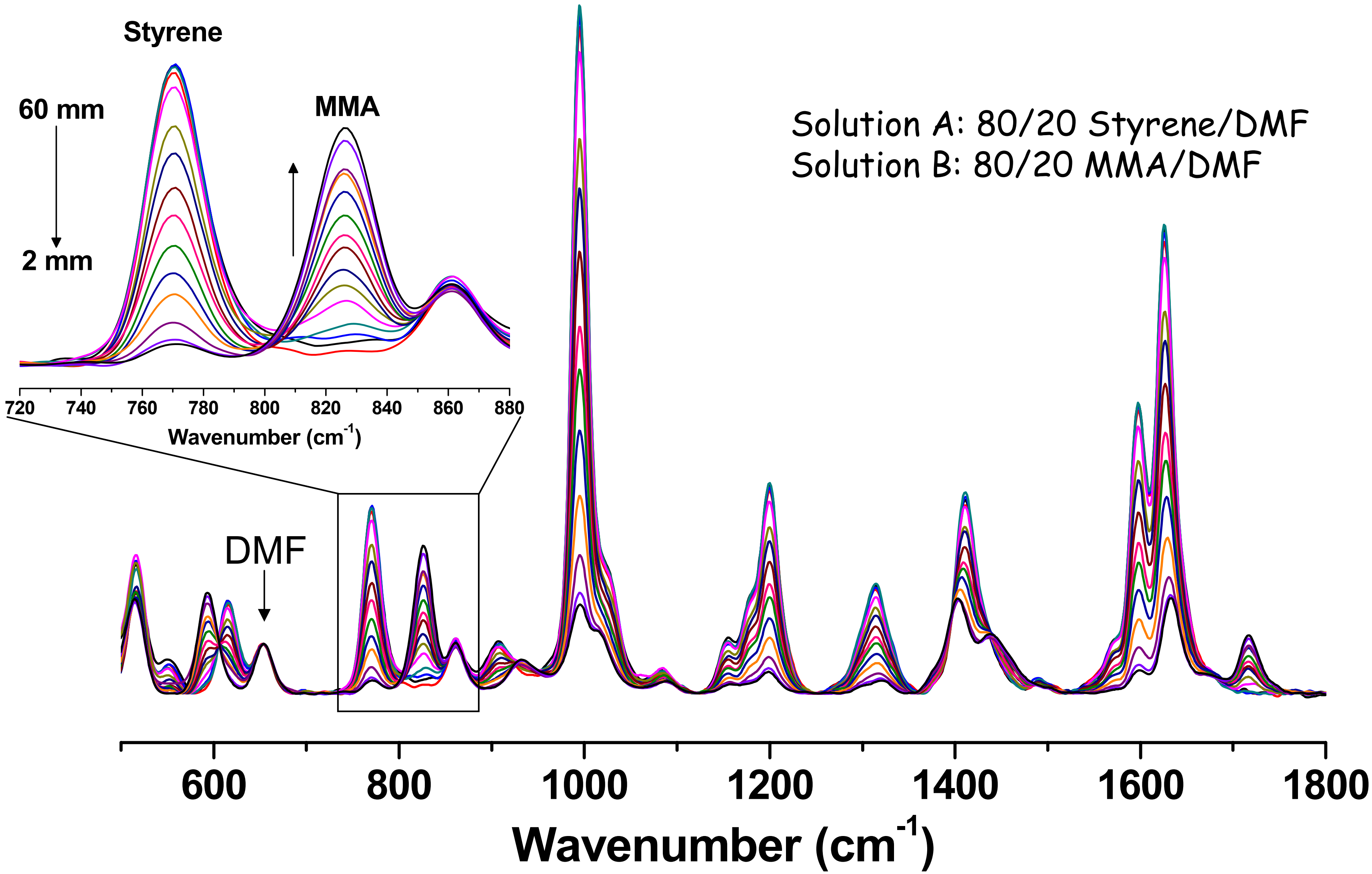
Microchannel Device

Thiolene resin and glass microchannel



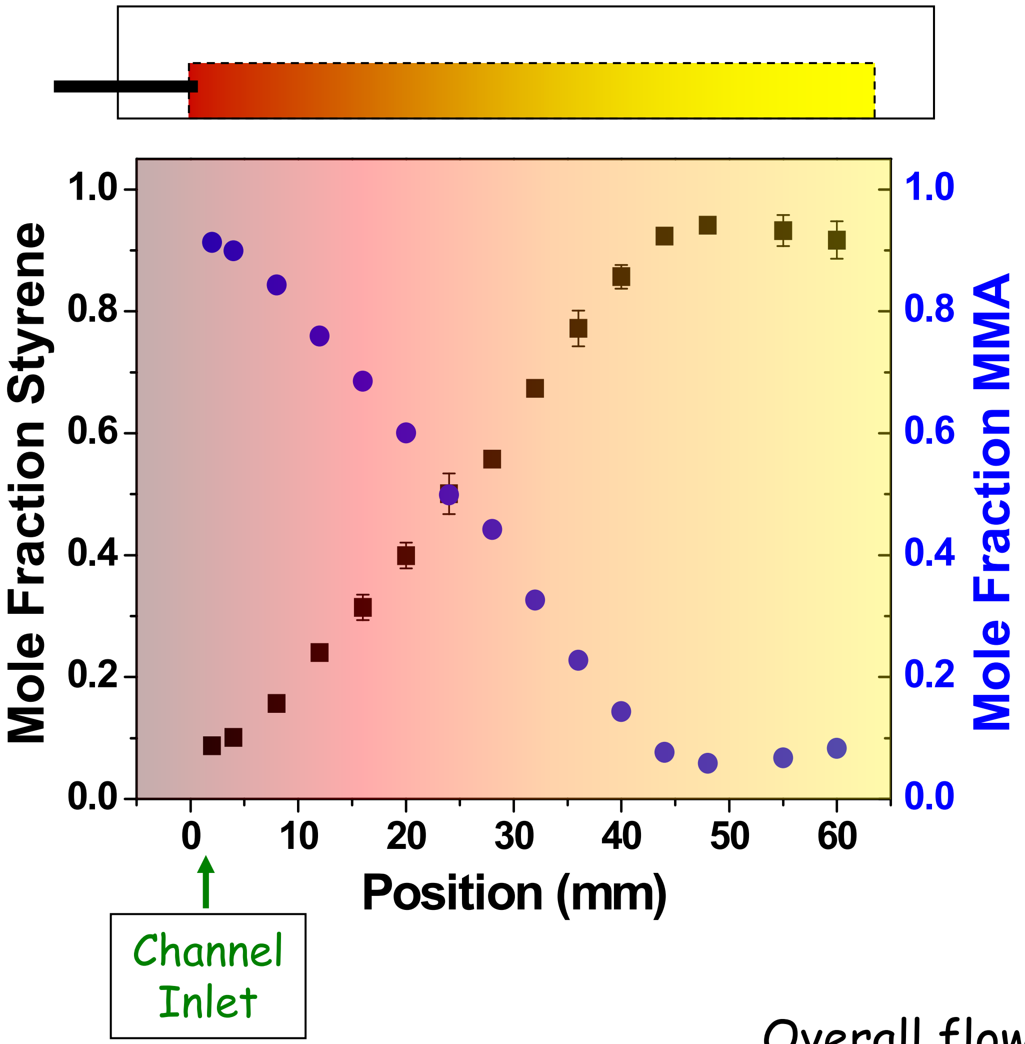


Raman Spectroscopy of Solution Gradient



Background/Baseline Corrected

Solution Gradient Library



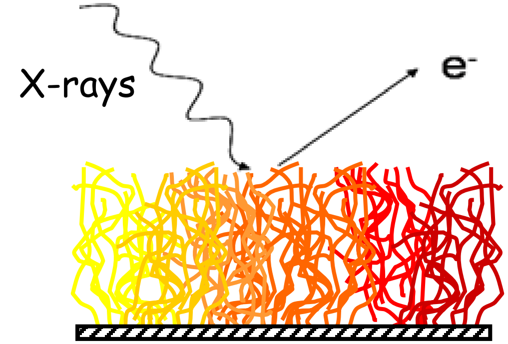
- Gradient spans Sty to MMA composition space
- Solution gradient is confined in microchannel
- Gradient is maintained more than 2 hours
- Typical reaction time is 20 minutes

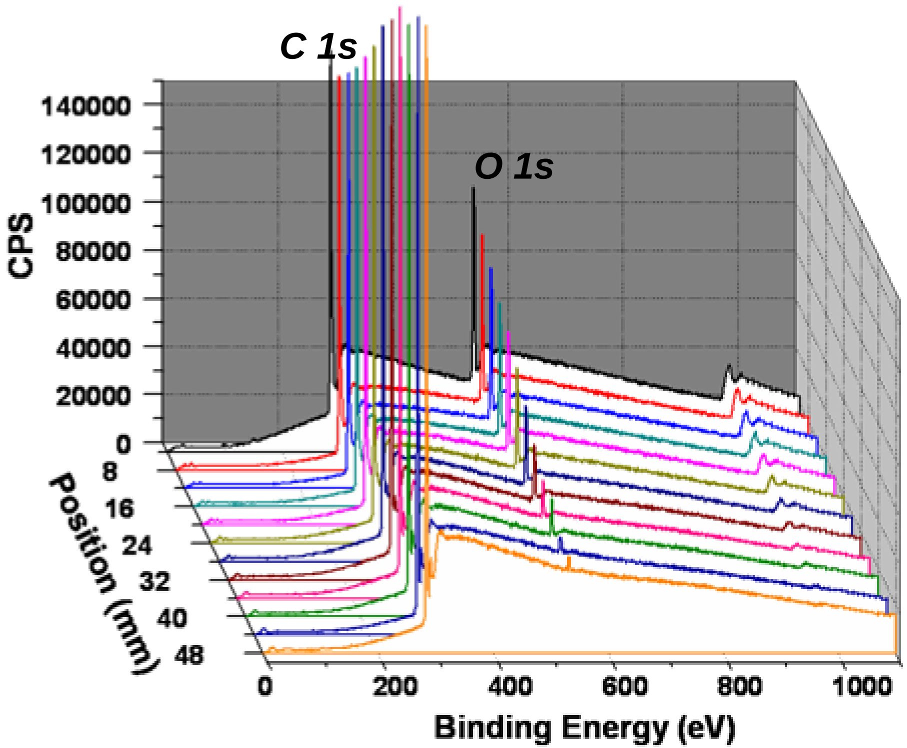
Overall flow rate: 0.2 mL/min

NIST

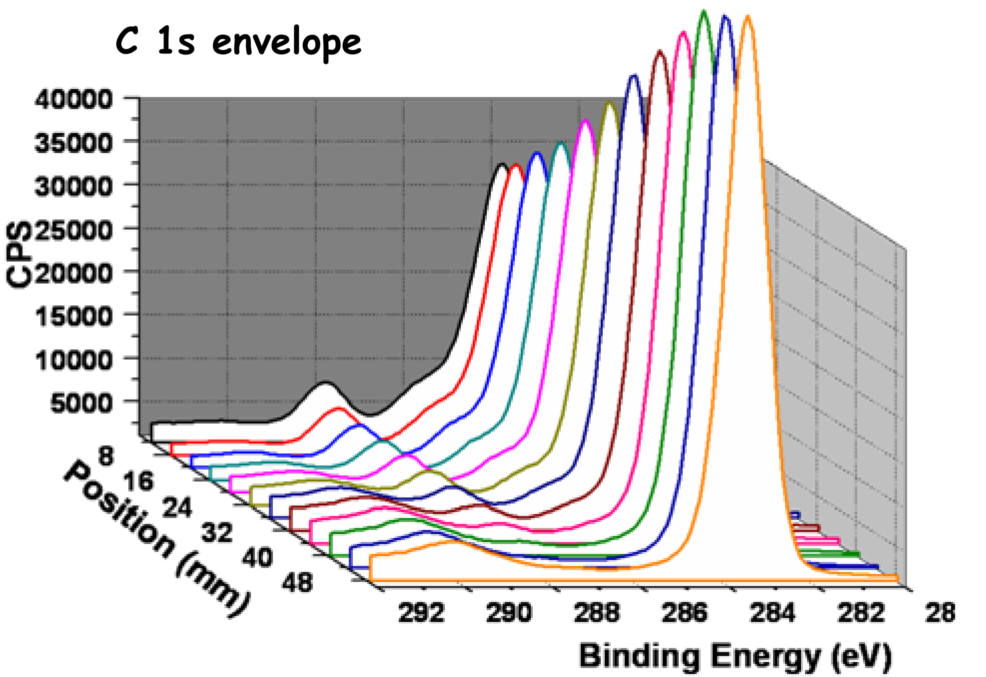
XPS – Copolymer Composition Gradient

- Automated X-ray photoelectron spectroscopy (XPS) maps composition in the gradient library



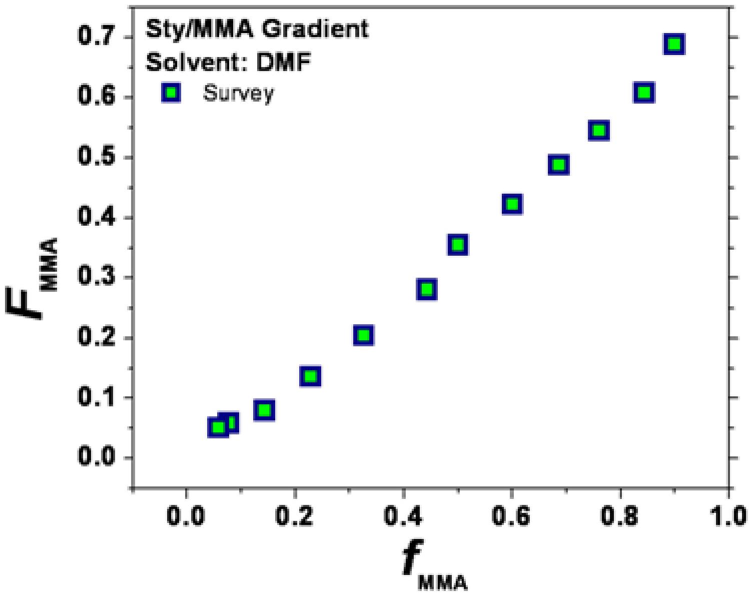


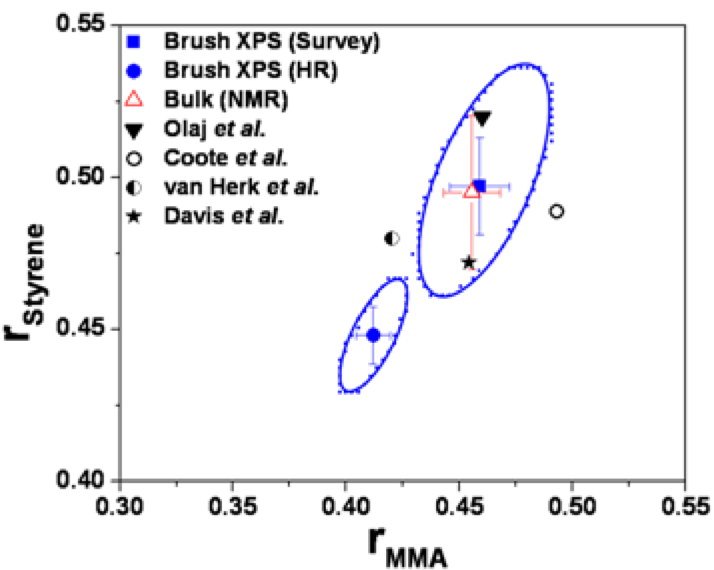
Survey Spectra



High Resolution Spectra

Combi Screening of Reactivity Ratios



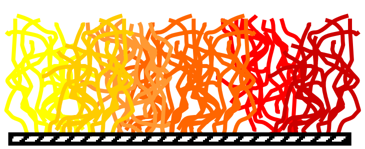


Reactivity Ratios (r)

- Relate monomer solution composition (F) to copolymer composition (f)
- Key design parameter for tailoring copolymer chemistry
- Difficult and time consuming to measure by traditional methods

Grafted Combi Libraries:

- Yield reactivity ratios in a single specimen

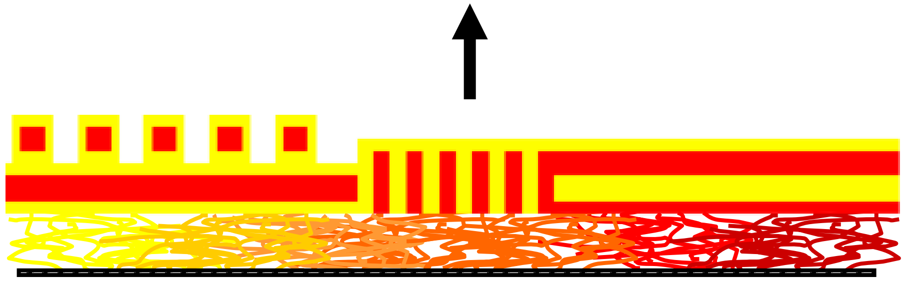


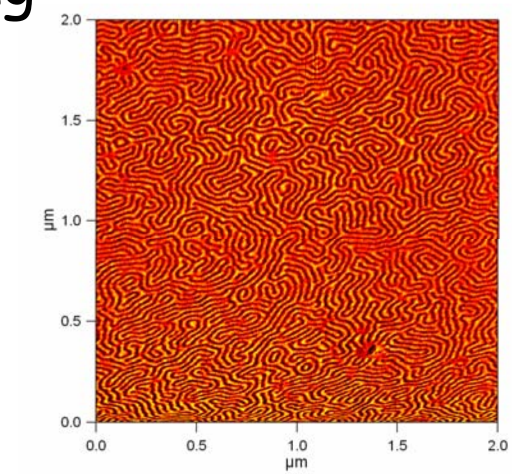
Patton et al. Macromolecules 2007 (submitted)

Combi Tuning of Interfaces

Example: Film Self-Assembly Engineering

PS-*stat*-PMMA Brush (58 mol % PS), 5 nm thick
PS-b-PMMA BC thin film, 24 nm thick

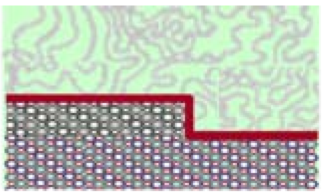


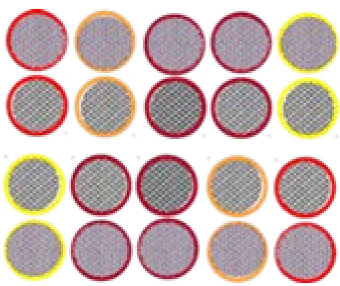


Huang *et al.*
Macromolecules
1998, *31*, 7641

Huge number of potential applications:

- Organic electronic materials/devices
- Adhesion and wetting management
- Biocompatibility/Biofunctionalization
- Nanoparticle functionalization libraries





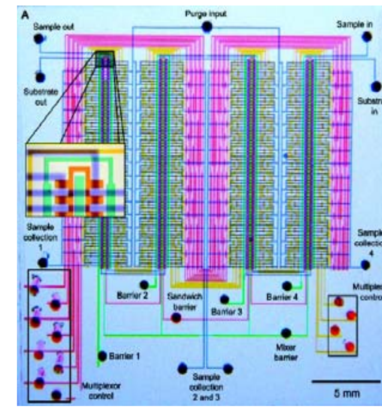
Outline

- Combinatorial and Hi-Throughput Methods
- Nanostructured Materials Applications
  - Block Copolymer Thin Films
  - Surface Grafted Polymers
  - Microfluidics: Solutions and Particles

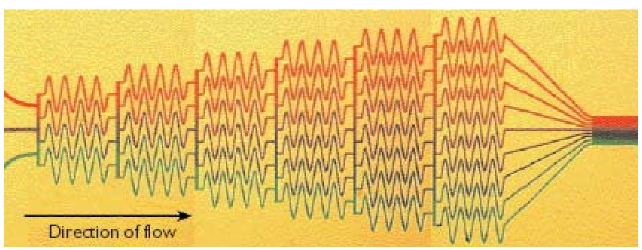
Microfluidic Technologies

Huge potential for Combi analysis of nanostructured fluid formulations

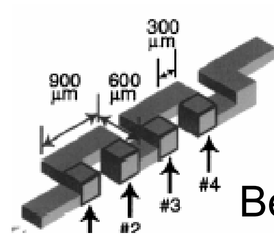
- Small sample volume
- Library Synthesis, processing and handling
- Integrated analysis of products



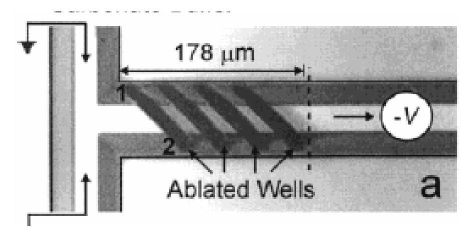
Quake



Whitesides



Beebe

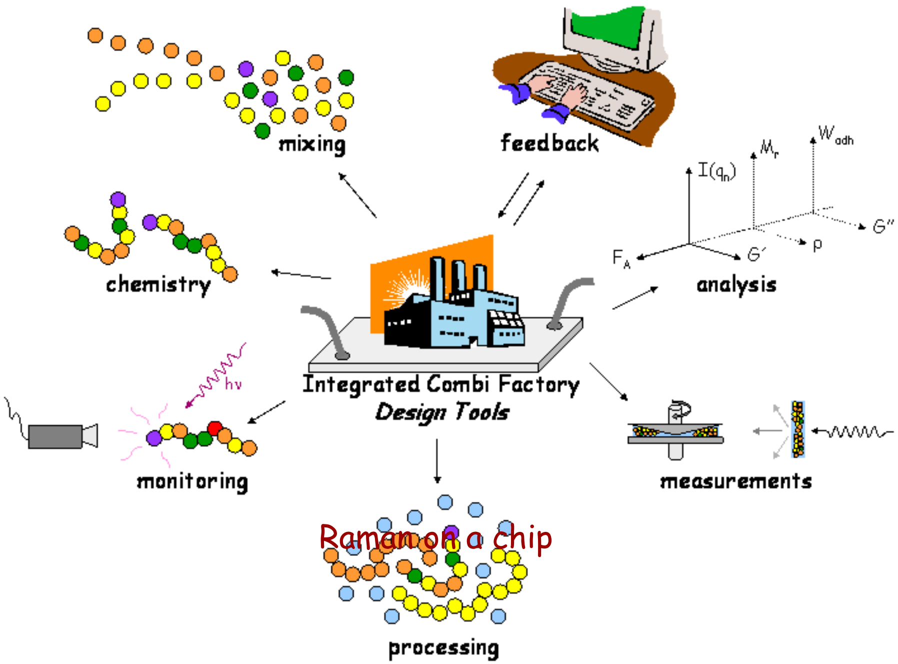


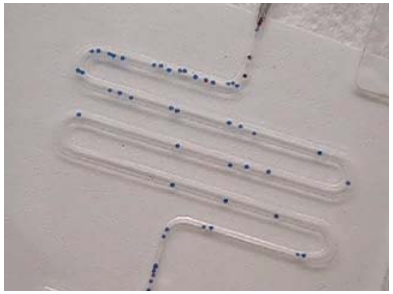
Locascio

However:

- Most microfluidic technology is geared for biotechnology, i.e. *water*
  - Incompatible with organic solvents and, thus polymer synthesis
  - Low temperature

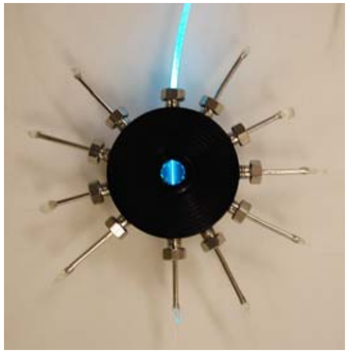
Microfluidics for Polymer Materials





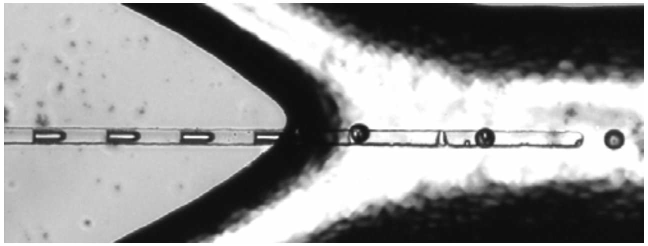
Continuous materials library synthesis in channels

- Organic solvents
- *Polymer and Particle Synthesis*
- Controlled high-temperature



Microfluidic Dynamic Light Scattering

Fluid Interfacial Tension on a chip

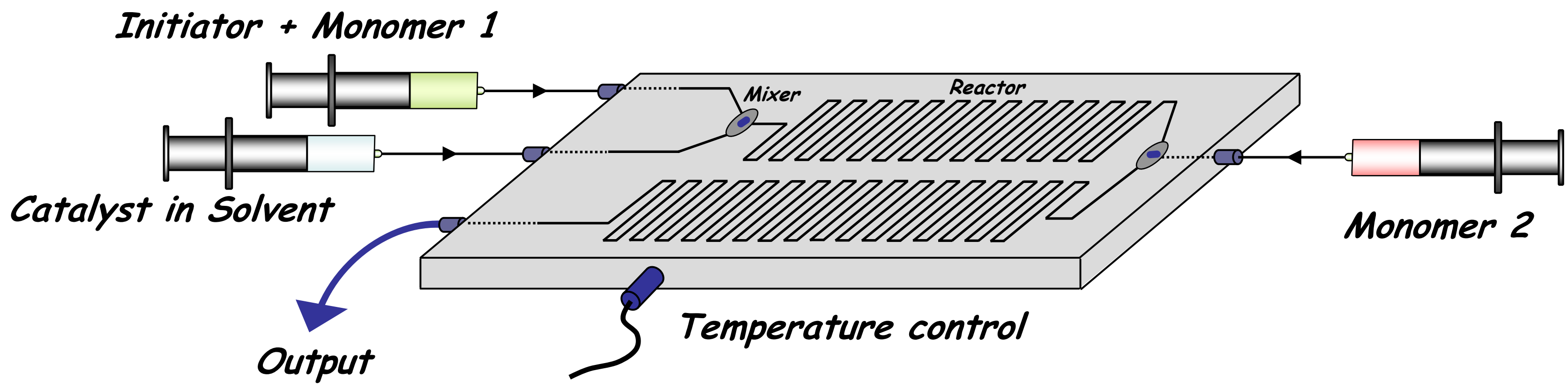


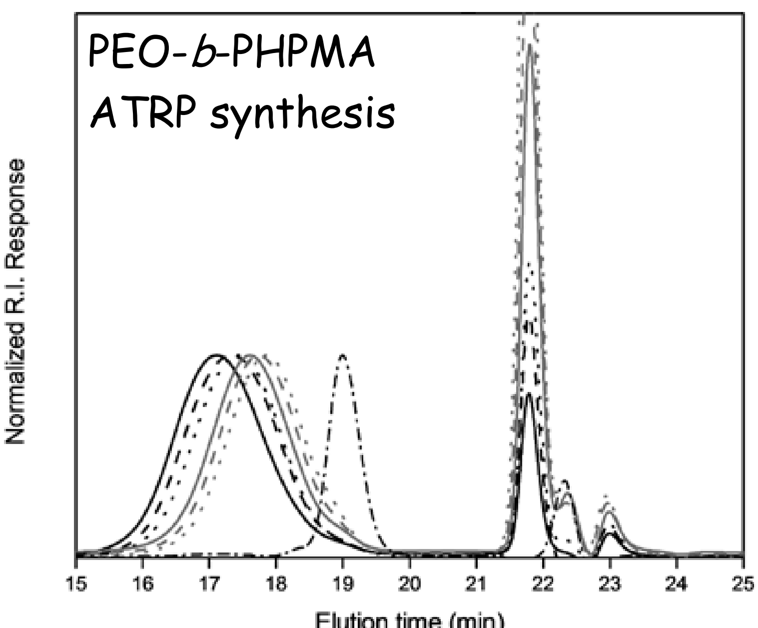
Integrated measurements

- Spectroscopy
- *Solution behavior*
- *Particle Size*
- Interfacial tension
- Rheology

Continuous Polymer Synthesis on a Chip

Solvent resistant metal or thiolene microfluidic synthesis platform



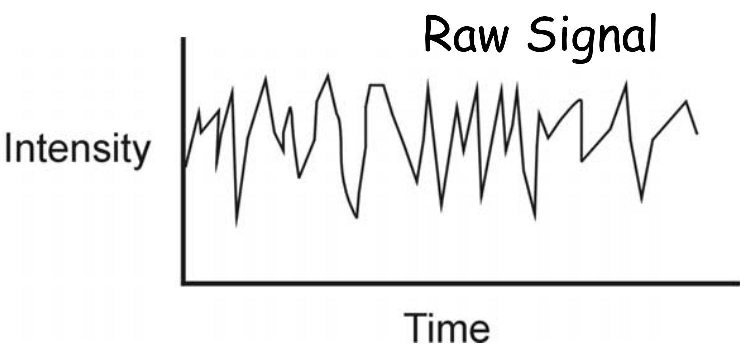


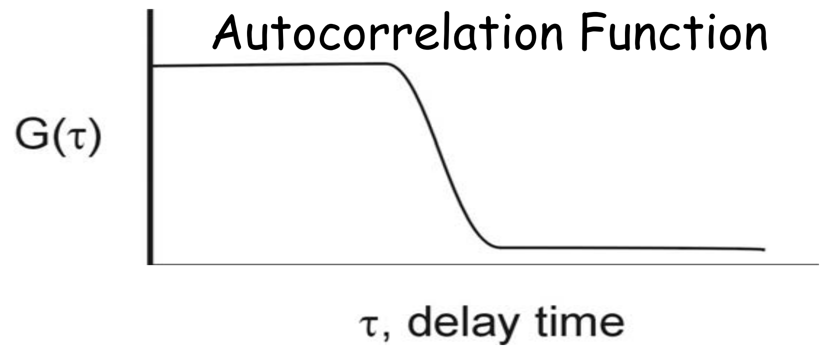
- Homopolymers, block copolymers, graft copolymers…
- Flow rate control: MW, composition
- Continuous, systematic series of polymers
- MW and PDI often better than flask!

Wu, Beers et al. Macromol. Rapid Commun., **2005**, *26*, 1037.
T. Wu et al, J. Am. Chem. Soc., **2004**, *126*, 9880.
Chastek, Iida and Beers (in Preparation)

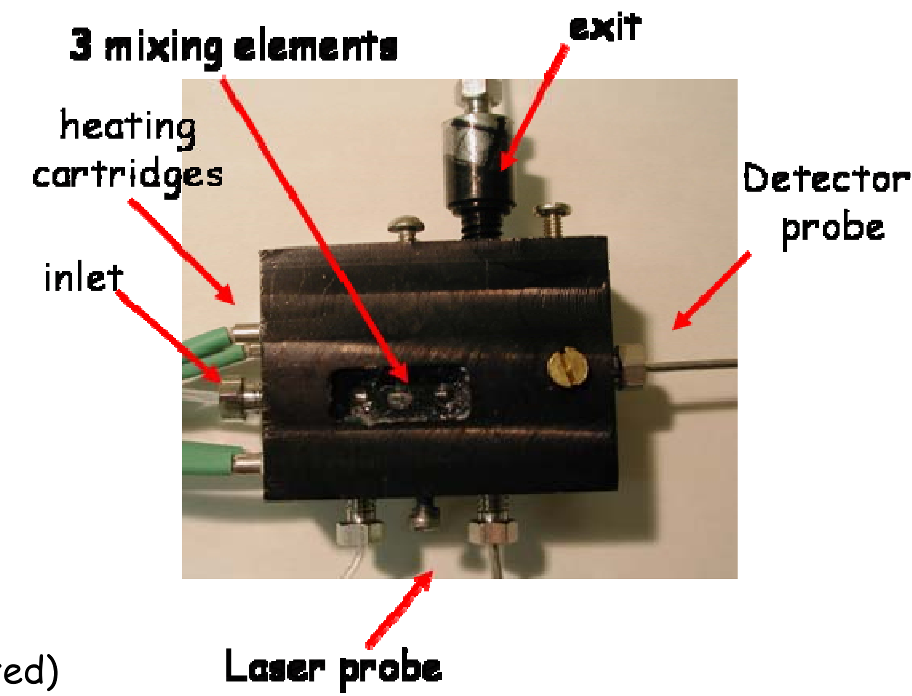
Microfluidic Dynamic Light Scattering

Dynamic Light Scattering (DLS) from particles in solution





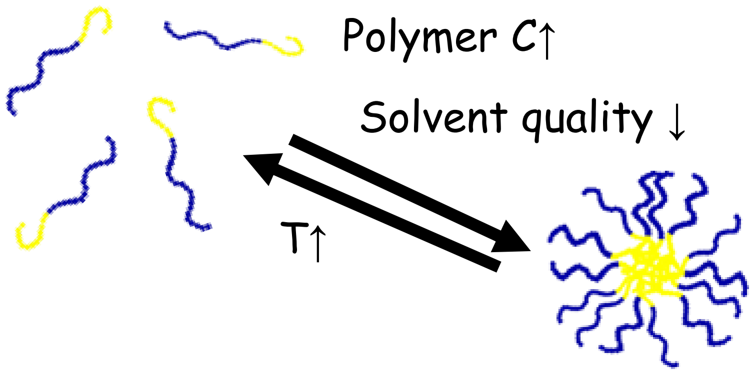
- G(τ) → diffusion coeff. → particle size
- Ideal for 20-500 nm particles
- 5% precision in a few seconds
- Easily integrated into microfluidic devices



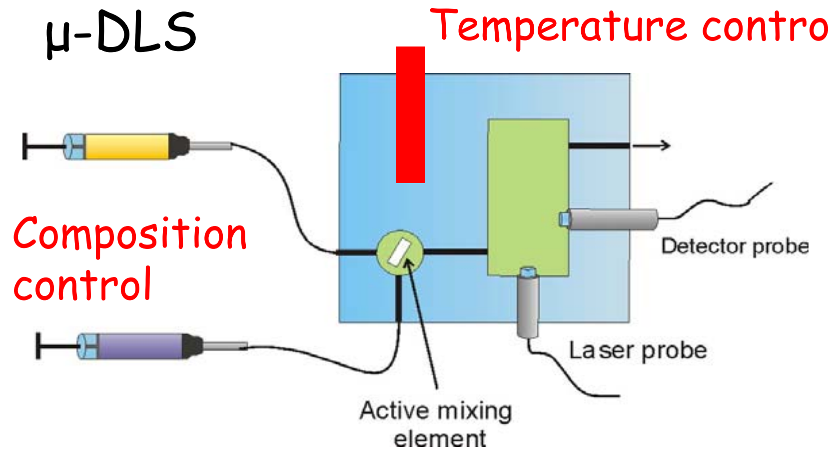
Chastek, Beers et. al. *Rev. Sci. Instrum.* 2007 (Accepted)

HT Screening of Fluid Nanostructures

Block Copolymer Micelles in Solution

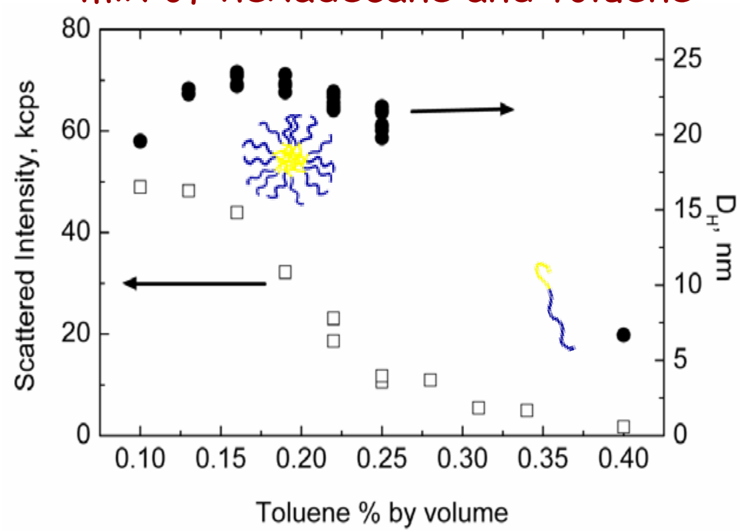


μ-DLS



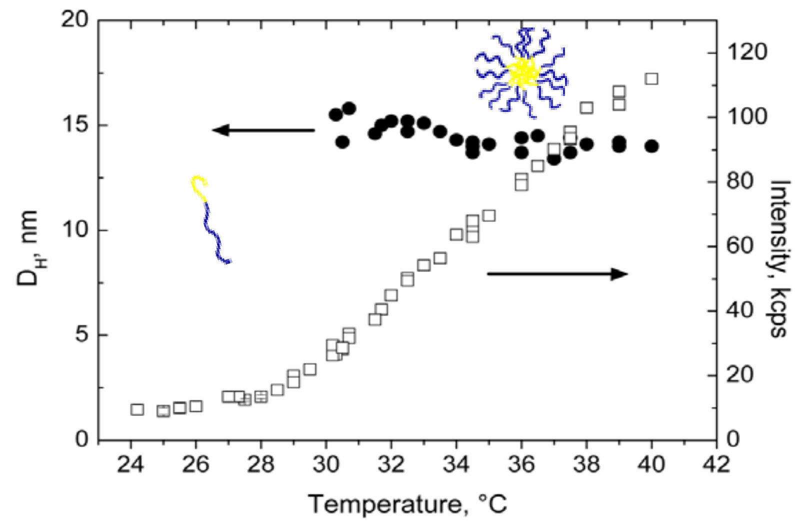
Mapping solvent quality

poly(styrene-b-isoprene)
mix of hexadecane and toluene

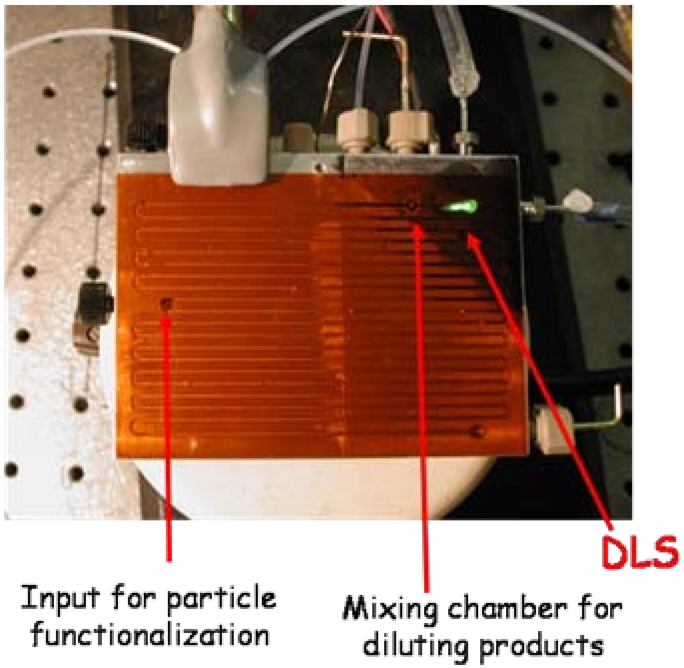


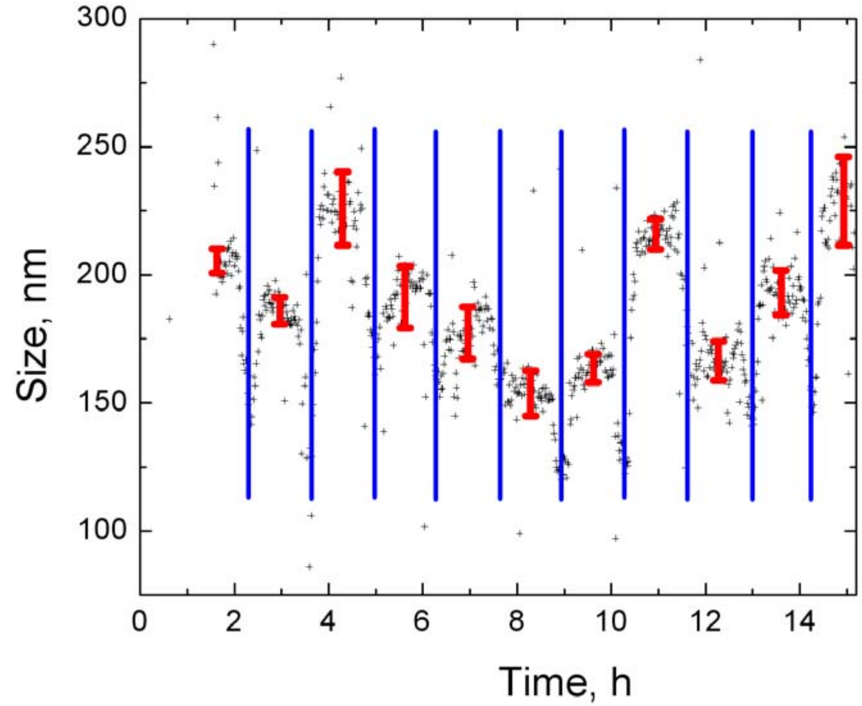
Mapping Temperature

PEO-b-PPO-b-PEO
in water



Integrated Particle Synthesis and DLS





Demo: Stöber Method

Ethanol Water Ammonia

Tetraethyl orthosilicate (TEOS)

Size determined by reagent ratios and temperature.

Silica nanoparticle μ-reactor

- Fully Automated
- Continuous library synthesis and online DLS
- Real time mapping of product size with reaction conditions

W. Stöber, A. Fink, E. Bohn, J. Coll. Int. Sci., 26 (1968) 62.

Outline

- Combinatorial and Hi-Throughput Methods
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  - Block Copolymer Thin Films
  - Surface Grafted Polymers
  - Microfluidics: Solutions and Particles

Acknowledgements

NCMC Development Team:

Carol Laumeier, Kathryn Beers, Chris Stafford, Alamgir Karim, Eric J. Amis

Polymer Formulations Team:

Thomas Chastek, Kathryn Beers, Tao Wu, Chang Xu, Steve Hudson, Kalman Migler

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Mechanics of Complex Interfaces Team:

Chris Stafford, Jun-Young Chung, Adam Nolte, Heqing Huang, Jae Hyun Kim, Martin Chiang

Funding and Partnerships

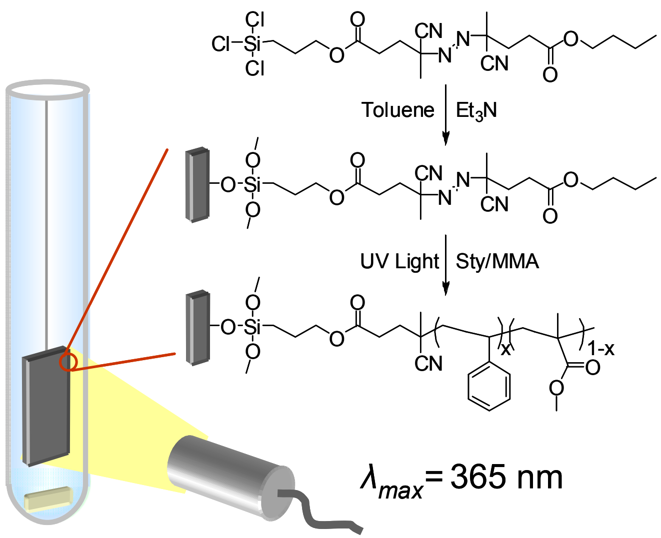
- NCMC Consortium Members
- NIST Advanced Technology Program

Learn More about Combi and High Throughput Methods

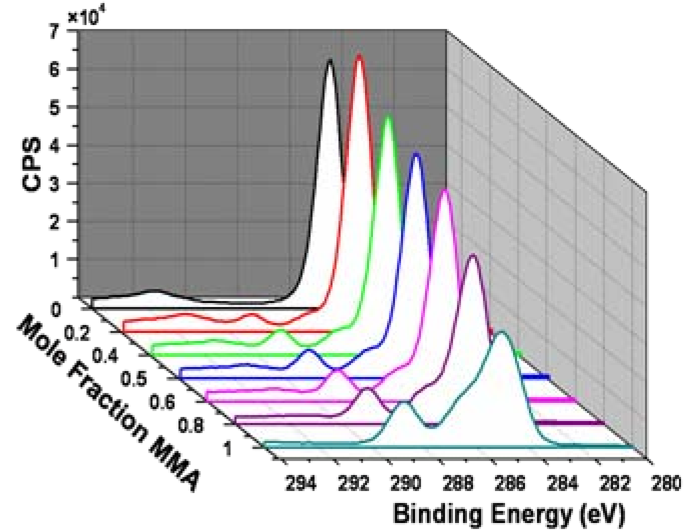
NCMC Website: www.nist.gov/combi

Ask For a CD!

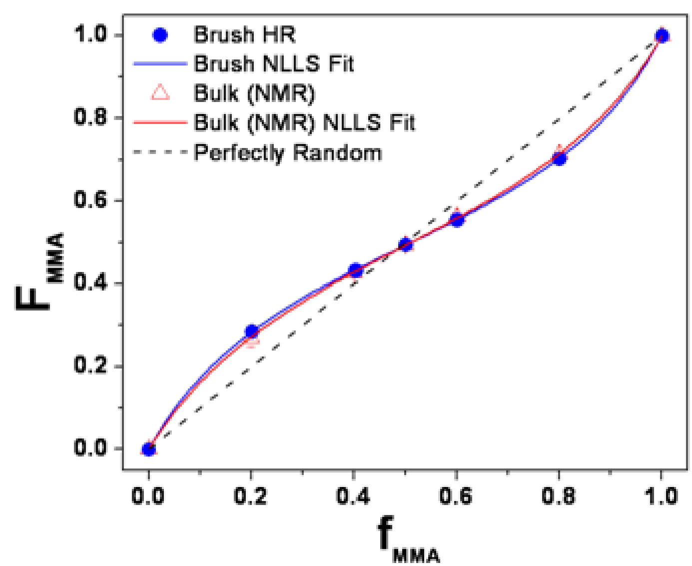
SIcP - Route to Reactivity Ratios



Copolymer brushes prepared at various monomer feeds



Data fit to copolymer equation by NLLS



- Average monomer conversion: 0.56 ± 0.05 % (based on gravimetric analysis of "free" polymer in solution)
- Average brush thickness: 24 ± 3 nm
- Copolymer composition measured using XPS (survey and high resolution methods)
- Composition data fit to the copolymer equation using a NLLS optimization