# Combinatorial Studies of Block Copolymer Interactions with Surfaces

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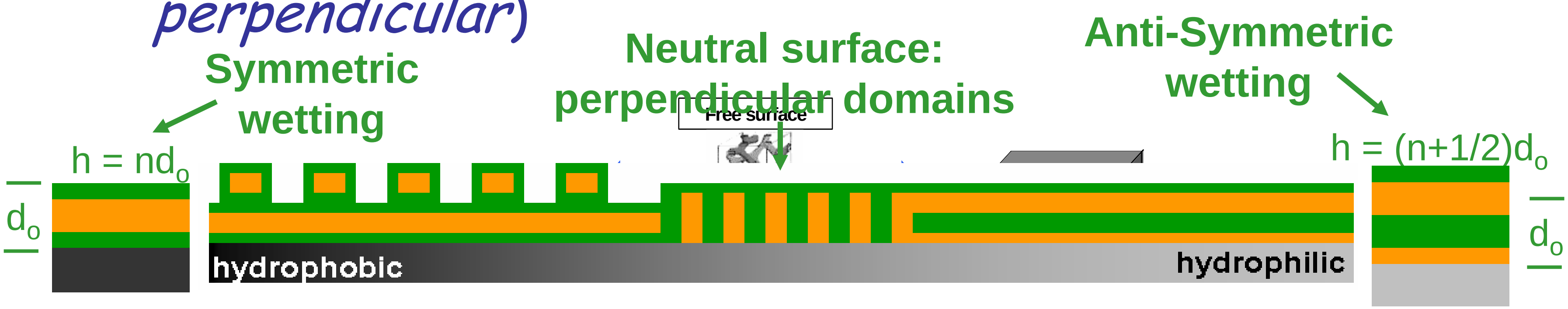
# Polymer Thin Films

- Triblock copolymers potential for designing percolating nanomaterials
- Goal: Explore ability of polymers to accommodate thin film boundary conditions
  - Influence of surface energy on wetting and morphological properties (surface directed structures)
  - Confinement effects on triply-periodic morphologies (absence of preferential alignments: *parallel* or *perpendicular*)




Substrate Surface Energy Gradient

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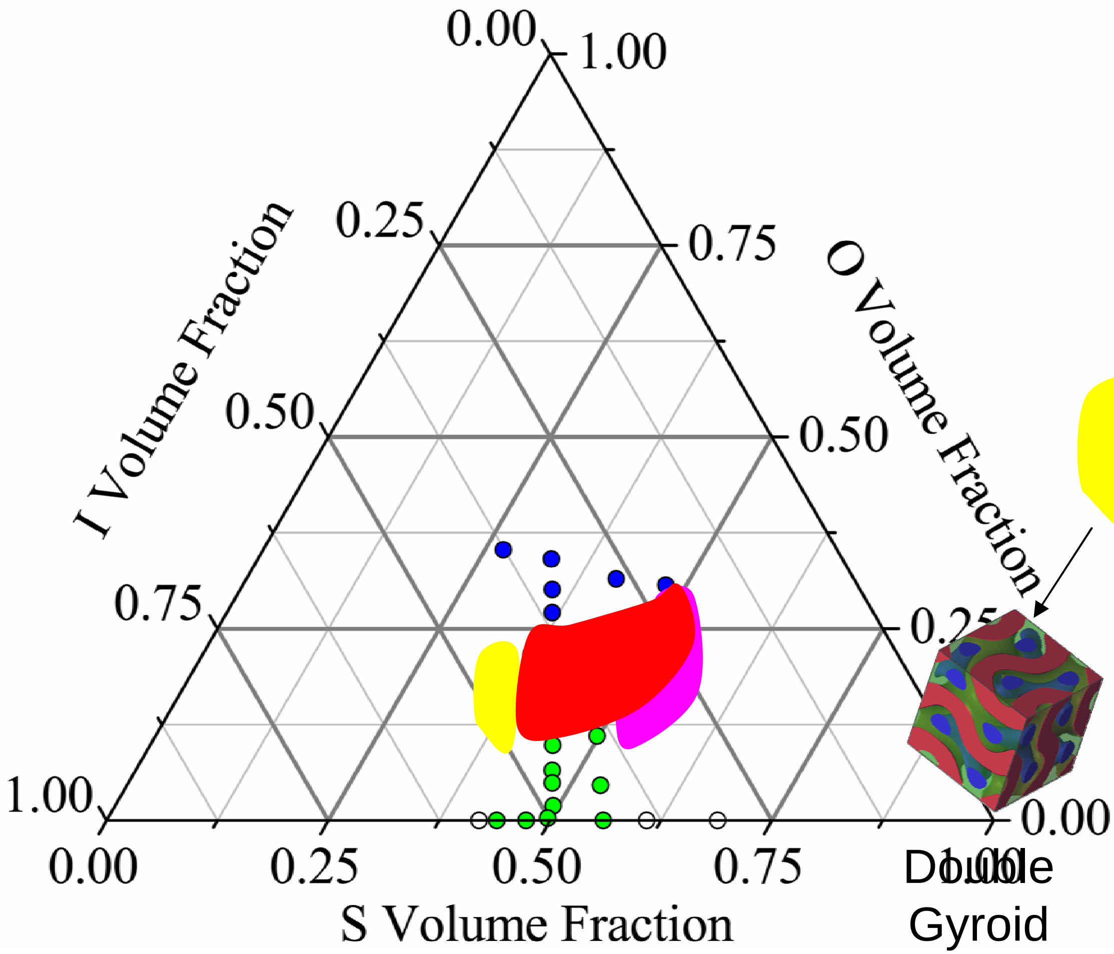
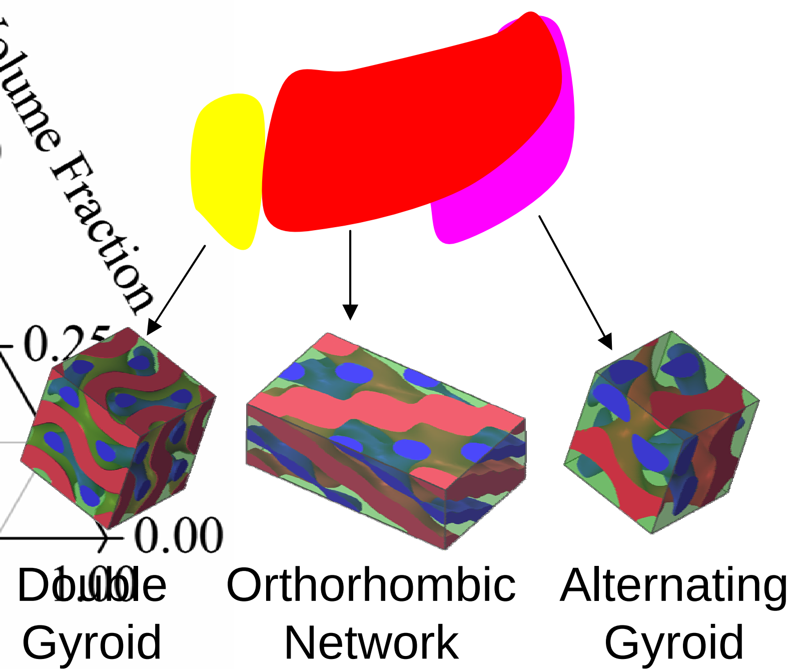
# Polymer System

lene oxide) [ISO]

t network phases



# Network Phases

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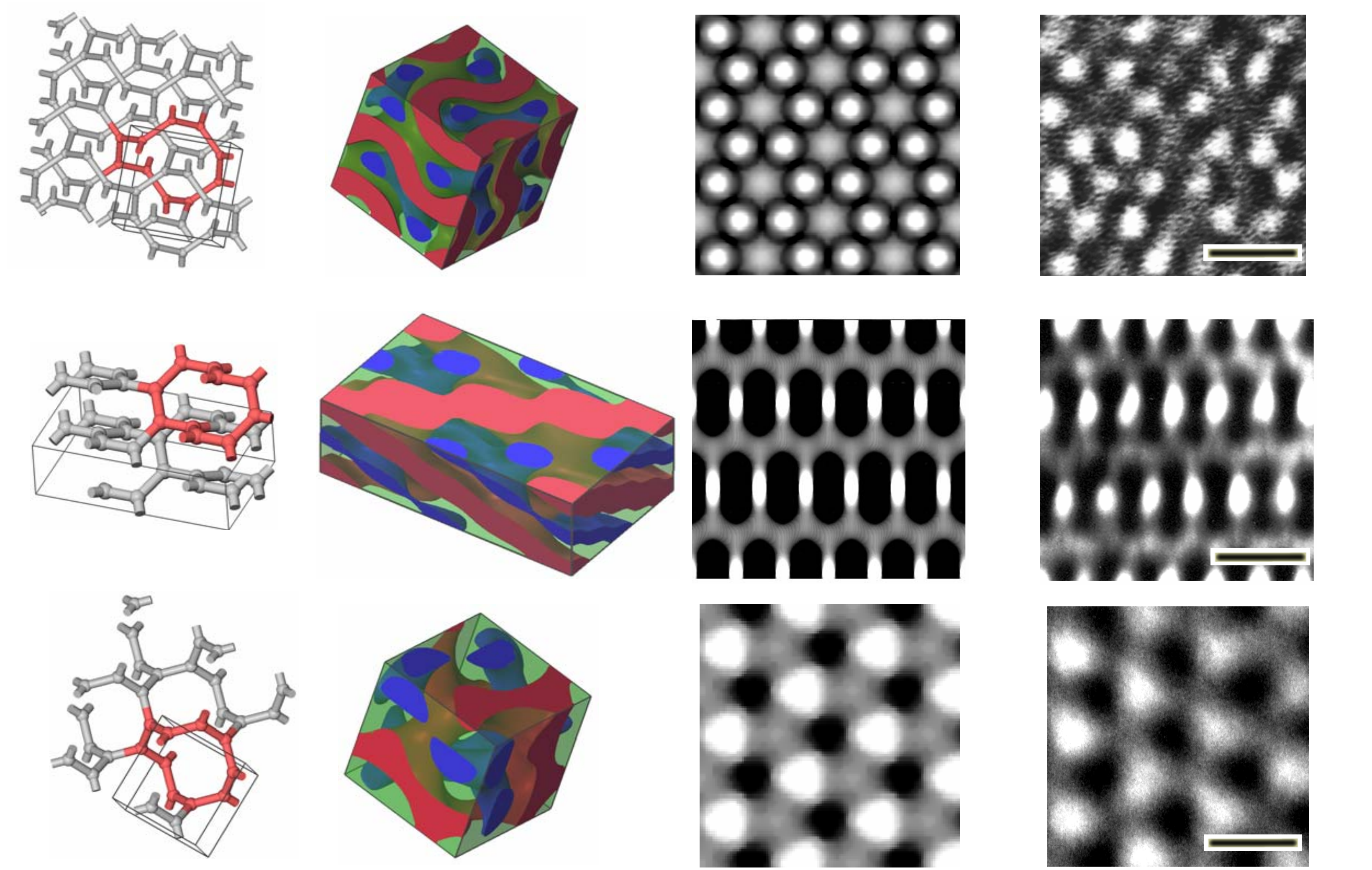
$Q^{230}$ (Ia3d)

$O^{70}$ (Fddd)

$Q^{214}$ ($I4_132$)



Lattice | Morphology | Simulated TEM | Experimental TEM

Cochran, Bailey, and Bates

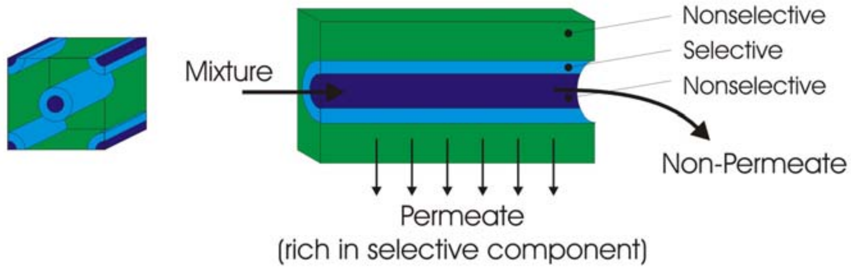
30 nm scale bars

# Potential Applications



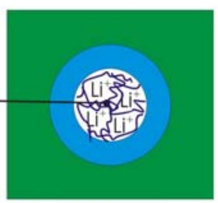
- Separations

ABC Triblocks

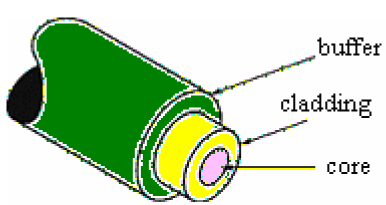



- Ion Conduction
  (fuel cells, lithium-ion batteries)

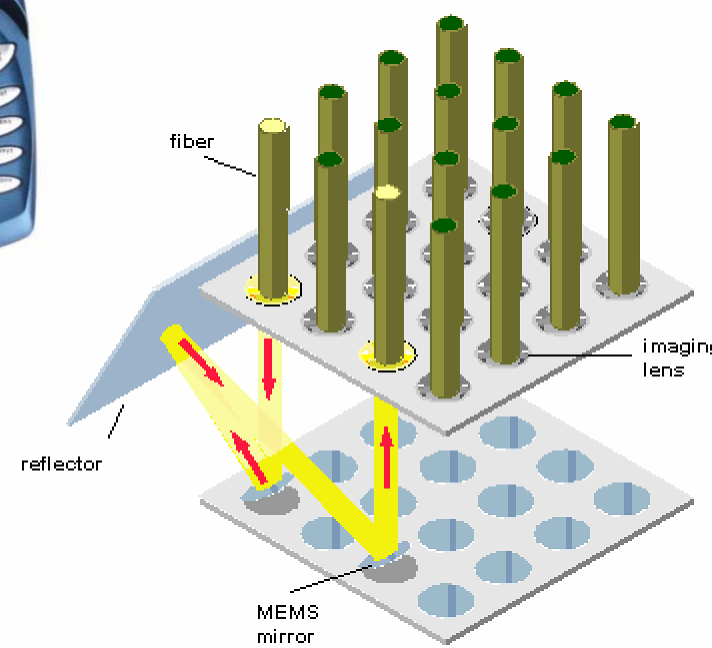
ABC systems containing PEO blocks can be selectively doped with lithium salts



Shell layers and surrounding matrix can be chosen for insulating properties, to reduce PEO crystallinity and to provide mechanical integrity








From Computer Desktop Encyclopedia

# Challenges to Materials Development



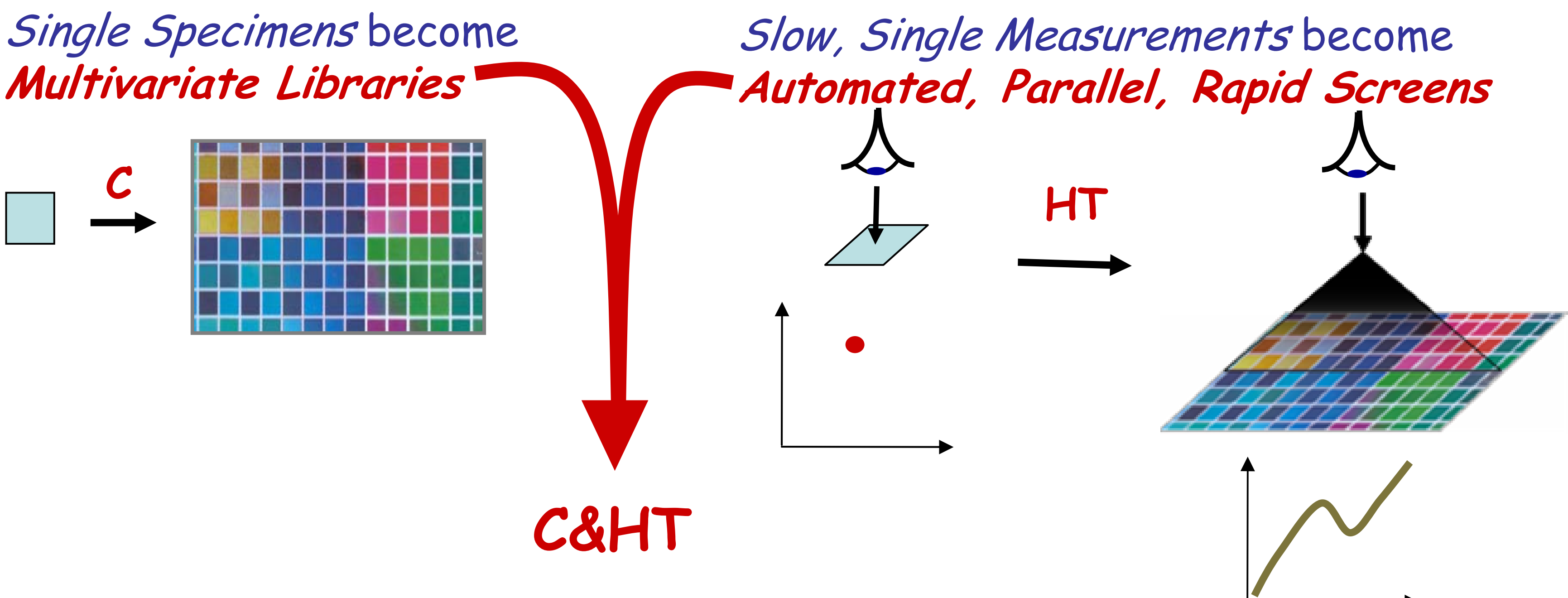
**New materials are:**

- **Highly Tailored:** Optimized to meet a *specific* application.
  - Exact chemistry, microstructure, surface properties, biocompatibility…
- **Highly Formulated:** Include many components on many levels.
  - molecular, mixtures, processed and fabricated structures…
- **Exhibit Complex Behavior:** Properties are governed by a plethora of (often competing) factors.
  - composition, molecular properties, specimen geometry, processing, environmental factors…

*Discovery and optimization of new materials is difficult, costly and time consuming.*

# Combinatorial Methods

Combinatorial and high-throughput **(C&HT)** techniques accelerate the study and optimization of complex systems by launching research beyond the "one-at-a-time" experiment paradigm…




- Thorough exploration of large parameter spaces
- Rapid assessment and optimization of complex systems
- Increased productivity
- Reduced waste, Reduced use of expensive components

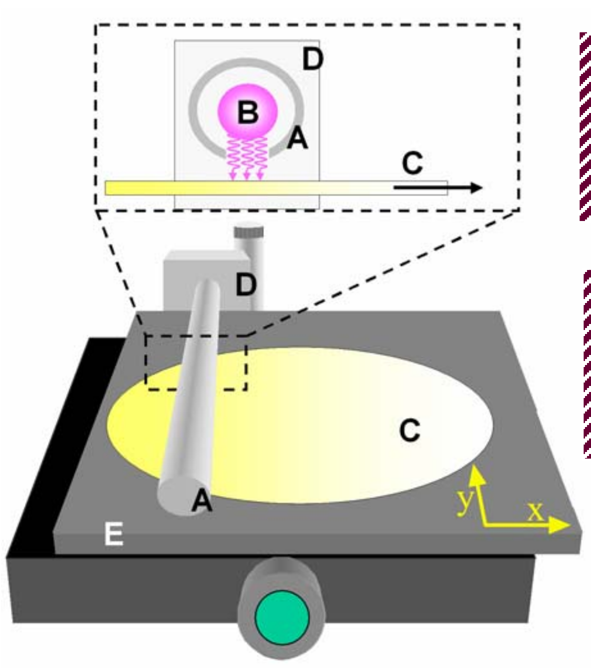
# Interfacial Energy at the Substrate Surface

## Surface Energy Gradients Using SAM's

# Gradient Substrate Formation



chlorosilane (ODS) SAM subjected to UV-ozone (UVO) exposure gradient



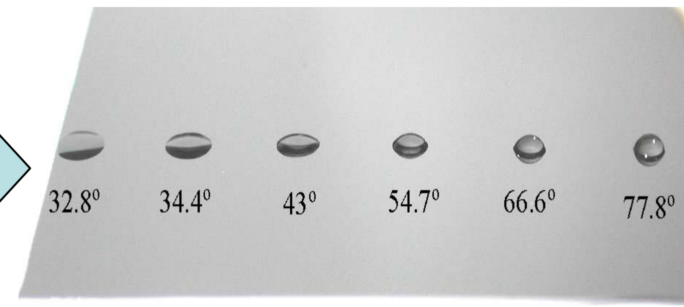

**computer controlled motorized stage**

$CH_3$
$O\text{-}Si\text{-}(CH)_7\text{-}CH_3$
$CH_3$

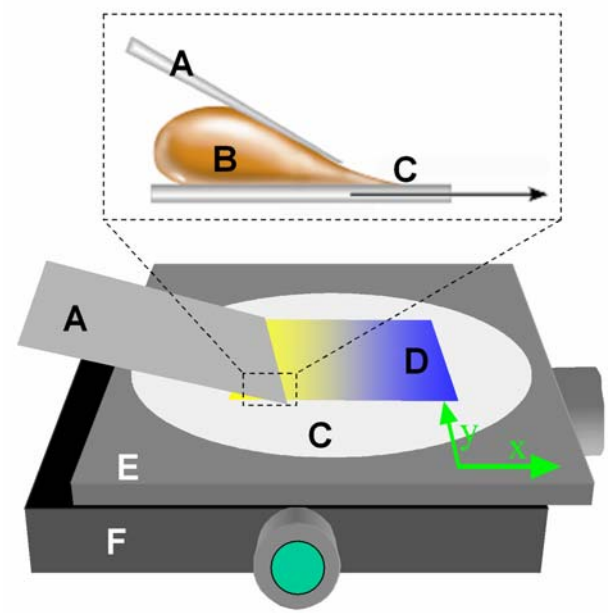
UVO

$CH_3$
$O\text{-}Si\text{-}(CH)_6\text{-}COOH$
$CH_3$

exposure dependent SAM conversion



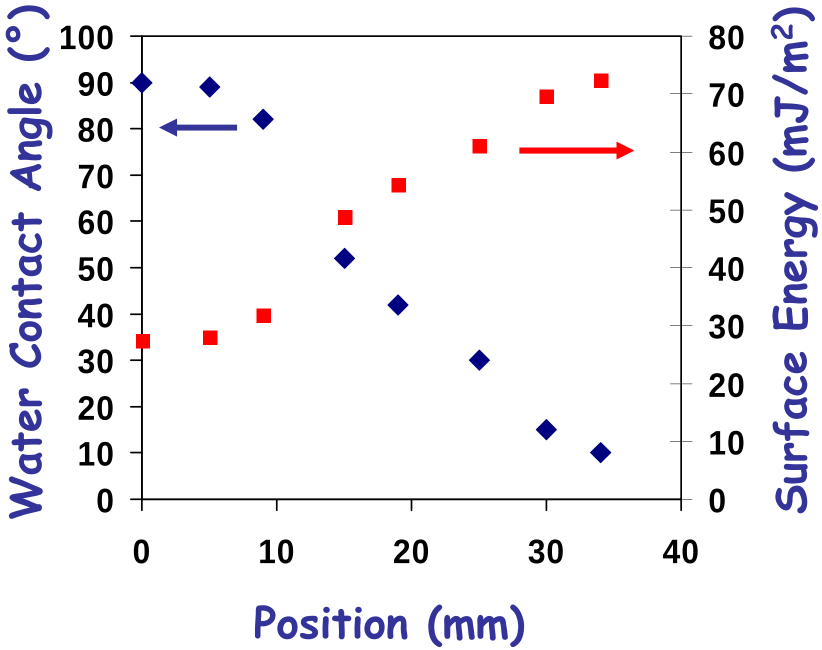

**water contact angle**

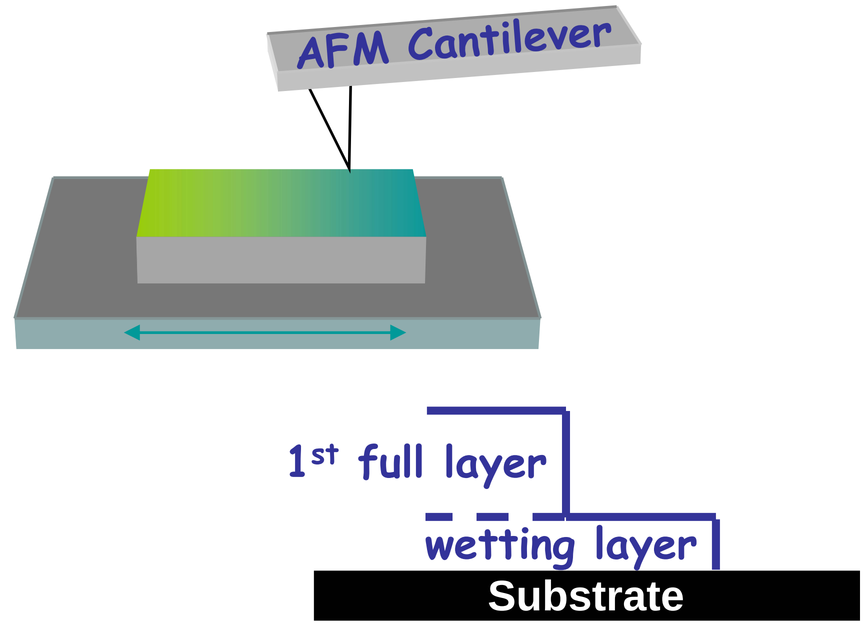



**polymer film flow-coated on substrate**

# AFM of Gradient Sample



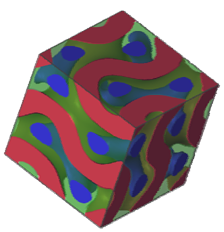
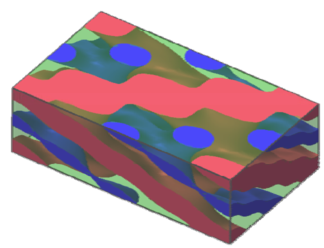
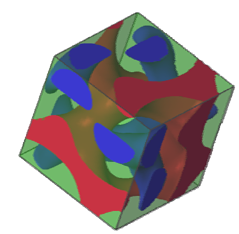


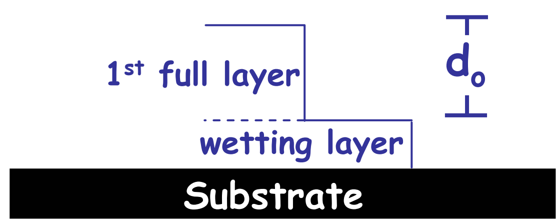

- Film thicknesses tuned for probing wetting layer and first full layer behavior
- Samples annealed at 110 °C (1-12 hours)
- Approximately 6 surface energies examined per sample

# Bulk Data on ISO Polymers

| ISO-2a | ISO-3i | ISO-15a |
|---|---|---|
| $M_n$ = 15.4 kg/mol | $M_n$ = 17.8 kg/mol | $M_n$ = 14.5 kg/mol |
| $f_o$ = 49/36/15 | $f_o$ = 39/40/21 | $f_o$ = 27/56/17 |
| Double Gyroid | Orthorhombic Net | Alternating Gyroid |
| d = 44 nm | d = 22 nm* | d = 22 nm |

**Increasing Poly(isoprene) Content** ←



# Polymer Microstructure using AFM

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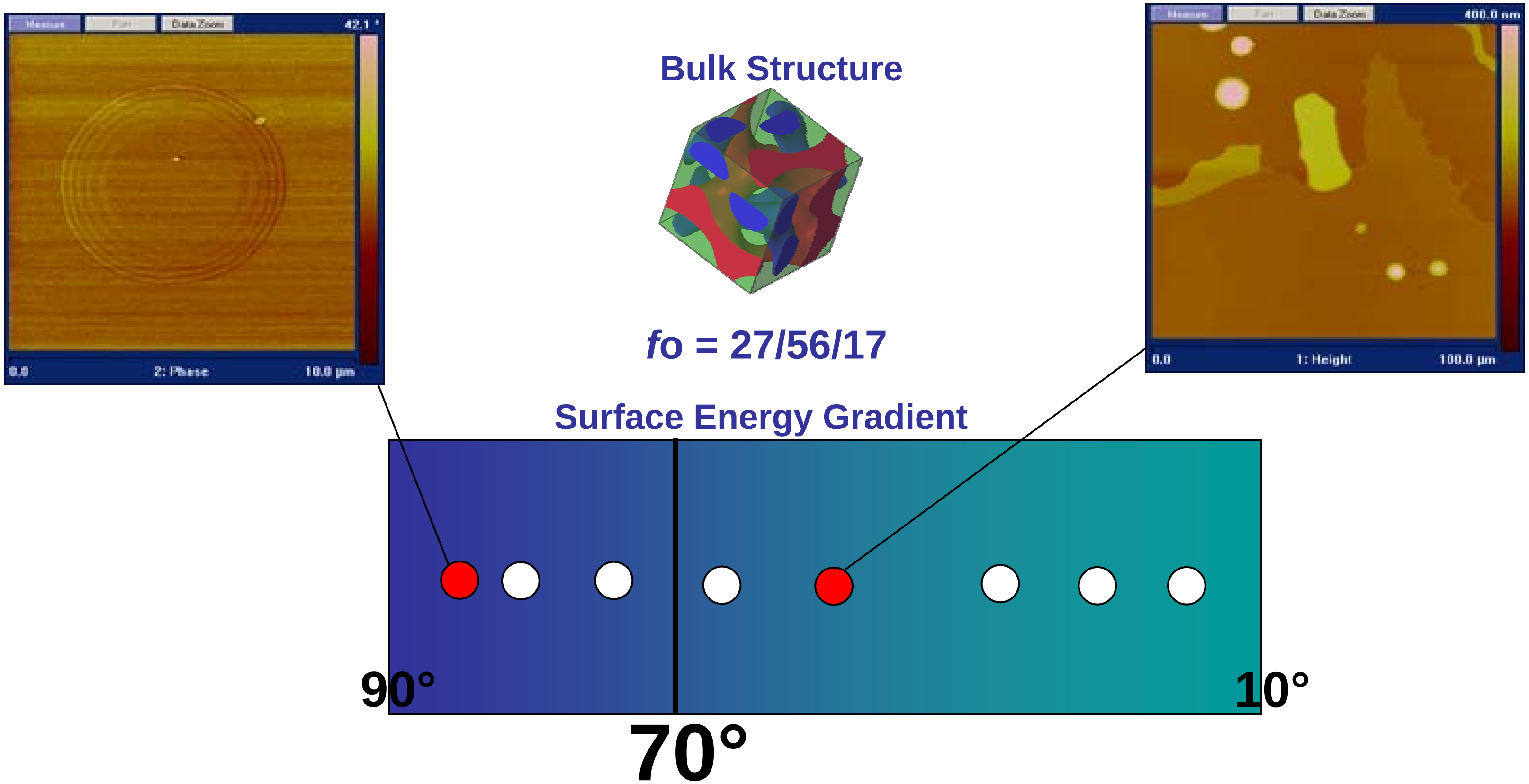



## High Contact Angle

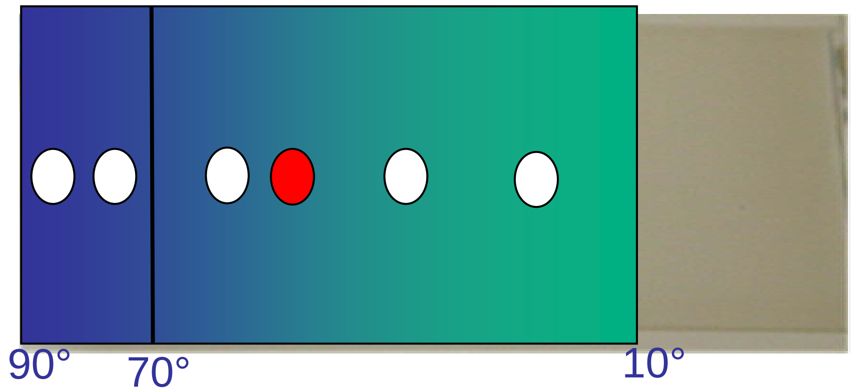
- Half period wetting layer
- Featureless islands and holes
- Likely surface parallel lamellae
- d = 16 nm (scratch test)

## Low Contact Angle

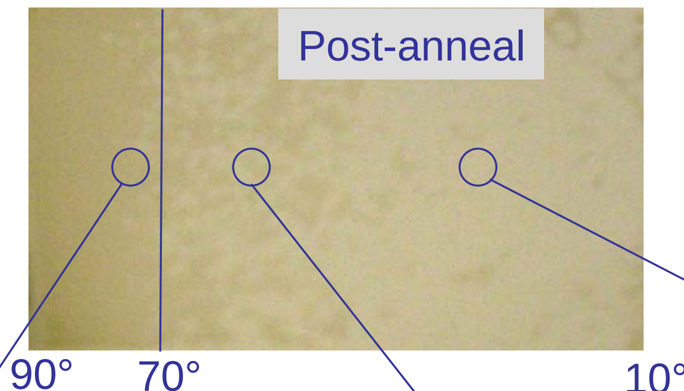
- Dewetting, droplet formation
- Half period wetting layer
- Featureless islands and holes
- d = 16 nm (scratch test)

# Dewetting of Polymer Film

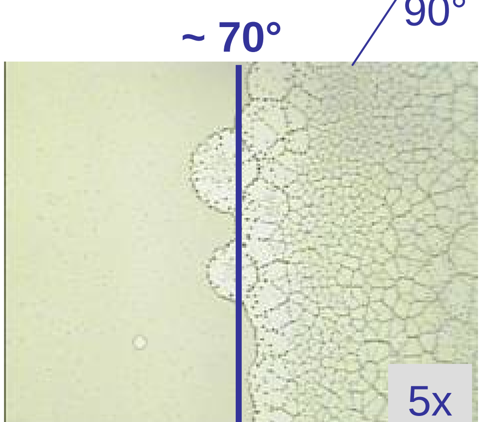
No Dewetting in Pre-Anneal Sample

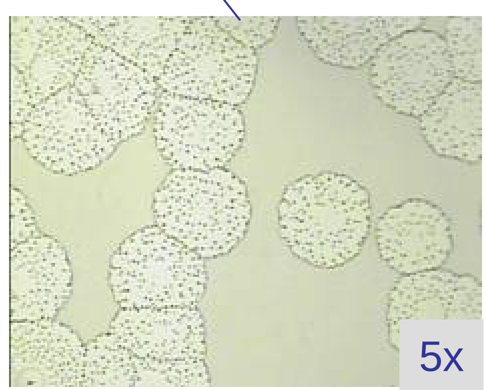


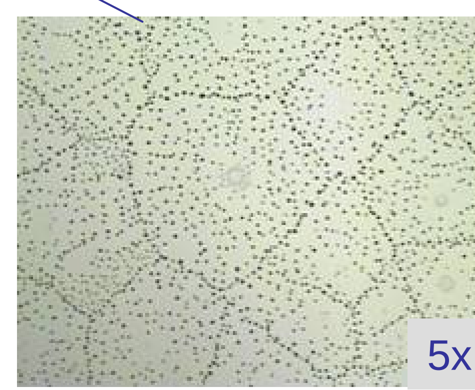

Dewetting Observed After 2 Hours Annealing




90° Contact Angle Reference Region

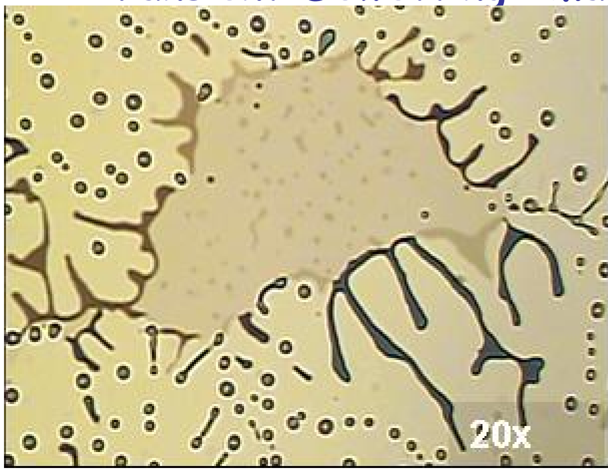


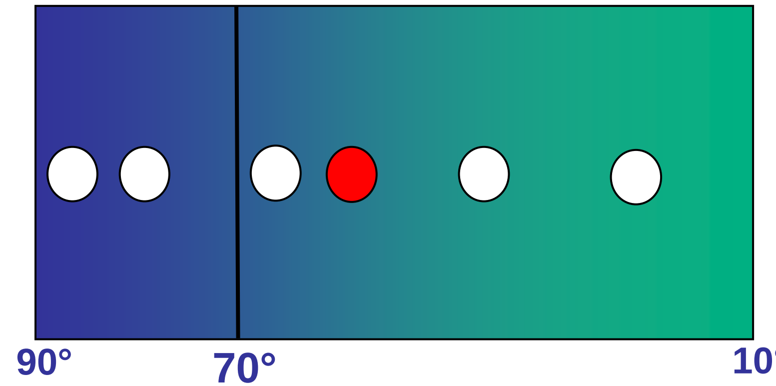



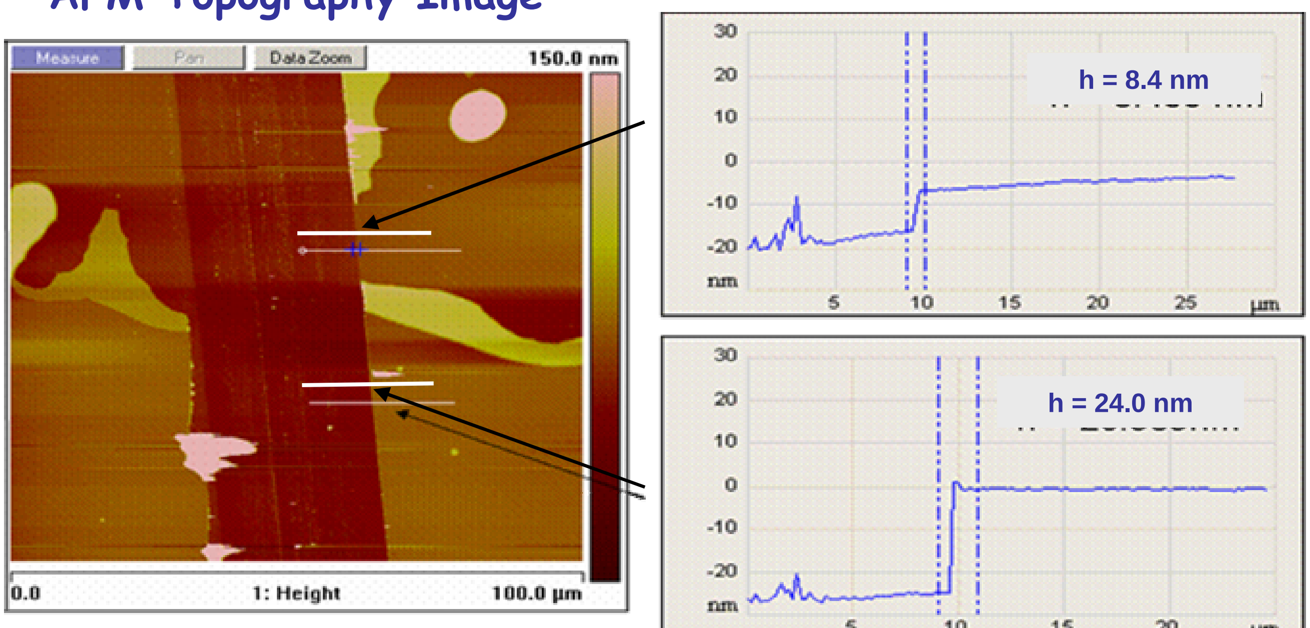
# Autophobic Dewetting ?

Transient Dewetting Image




AFM Topography Image



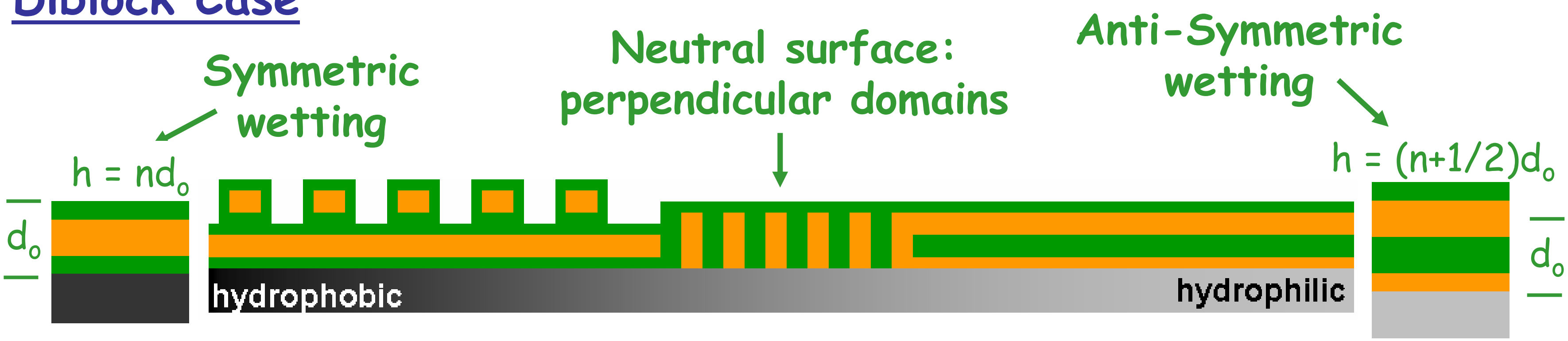

Wetting Layer
½ $d_o$ ~ 8 nm

Domain Spacing
$d_o$ ~ 16 nm

# Wetting Layer Composition Analysis



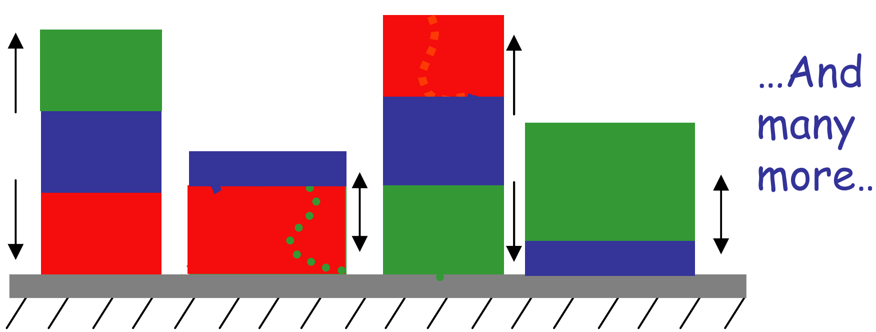
## Diblock Case




## Triblock Case

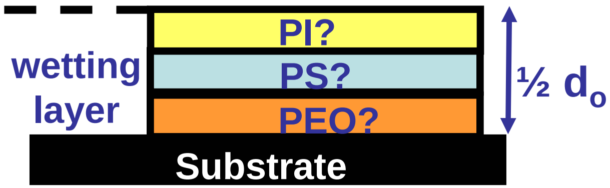
- Surface energy determines wetting layer composition profile
- Almost always asymmetric wetting layer
- Wetting layer influences polymer thin film structure

Sample Triblock Wetting Layer Composition Arrangements

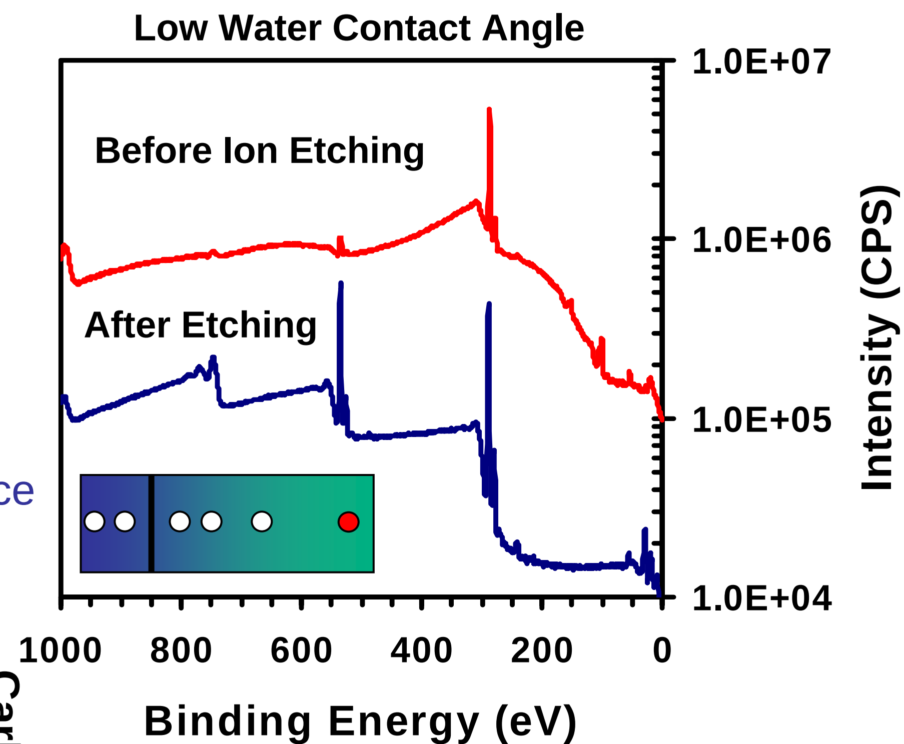


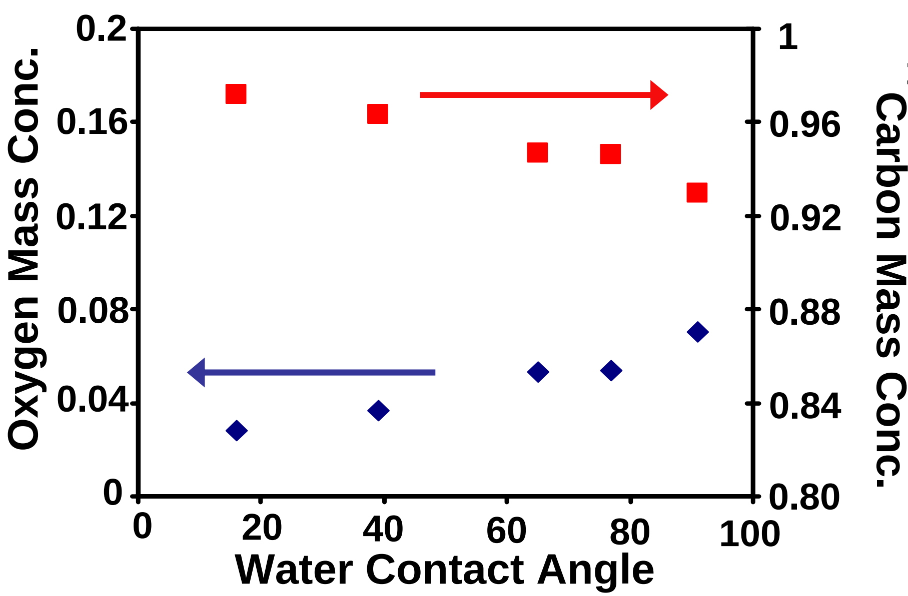

Much more complicated than diblock case!

# XPS - Top Surface



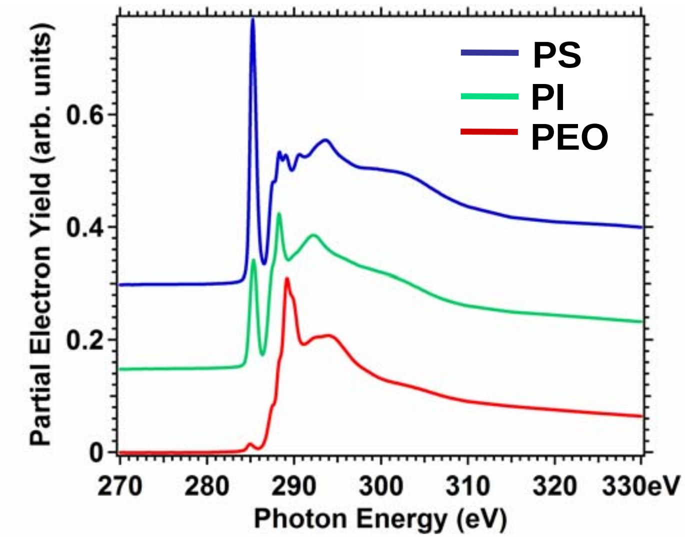

- Before etching - hydrocarbon surface
- After etching - oxygen rich surface
- PEO block preferential interaction with $SiO_2$ substrate
- Not all carbon accounted for at bottom surface



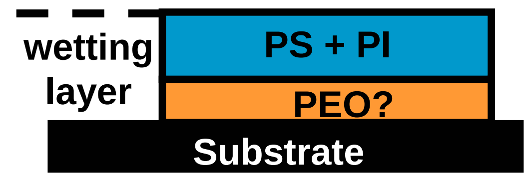



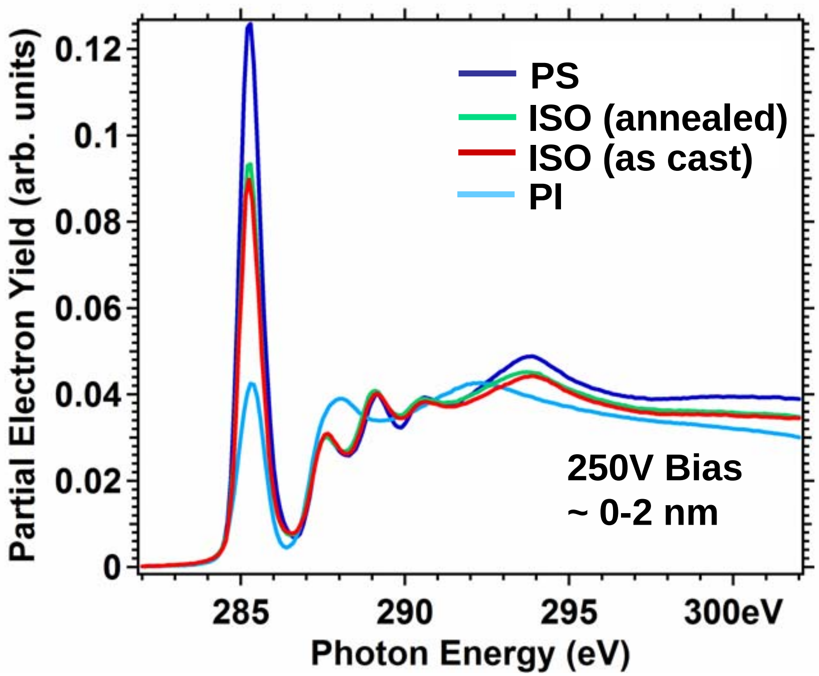

- Top surface carbon concentration decreases as water contact angle of bottom surface increases
- Top surface oxygen concentration increases as water contact angle increases
- Conclusion – more poly(ethylene oxide) at bottom surface at lower contact angles

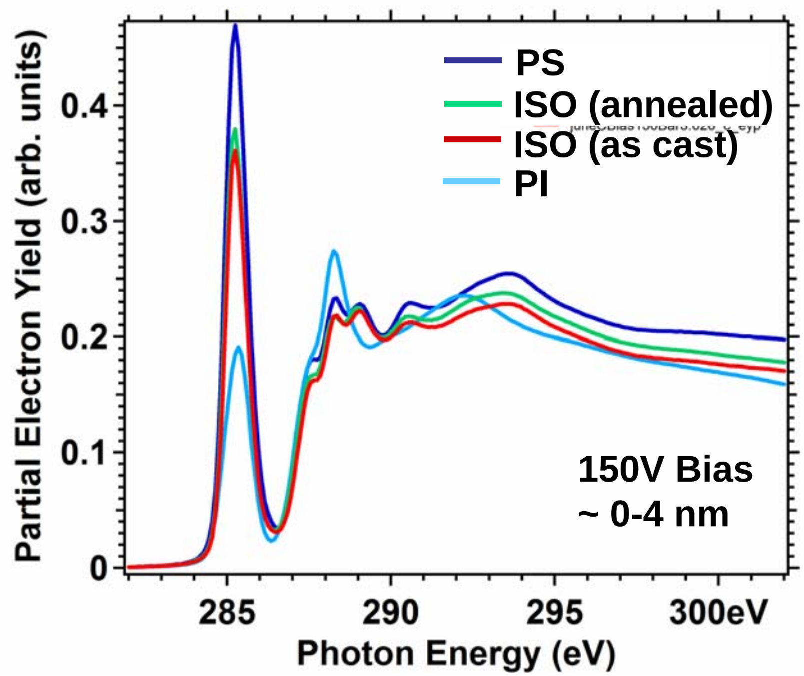
# NEXAFS - Top Surface




- Examined film containing only wetting layer (low contact angle)
- Mixed PS/PI layer
- Minimal PEO detected down to ~6 nm



# Bottom Surface Analysis

# Sample Preparation

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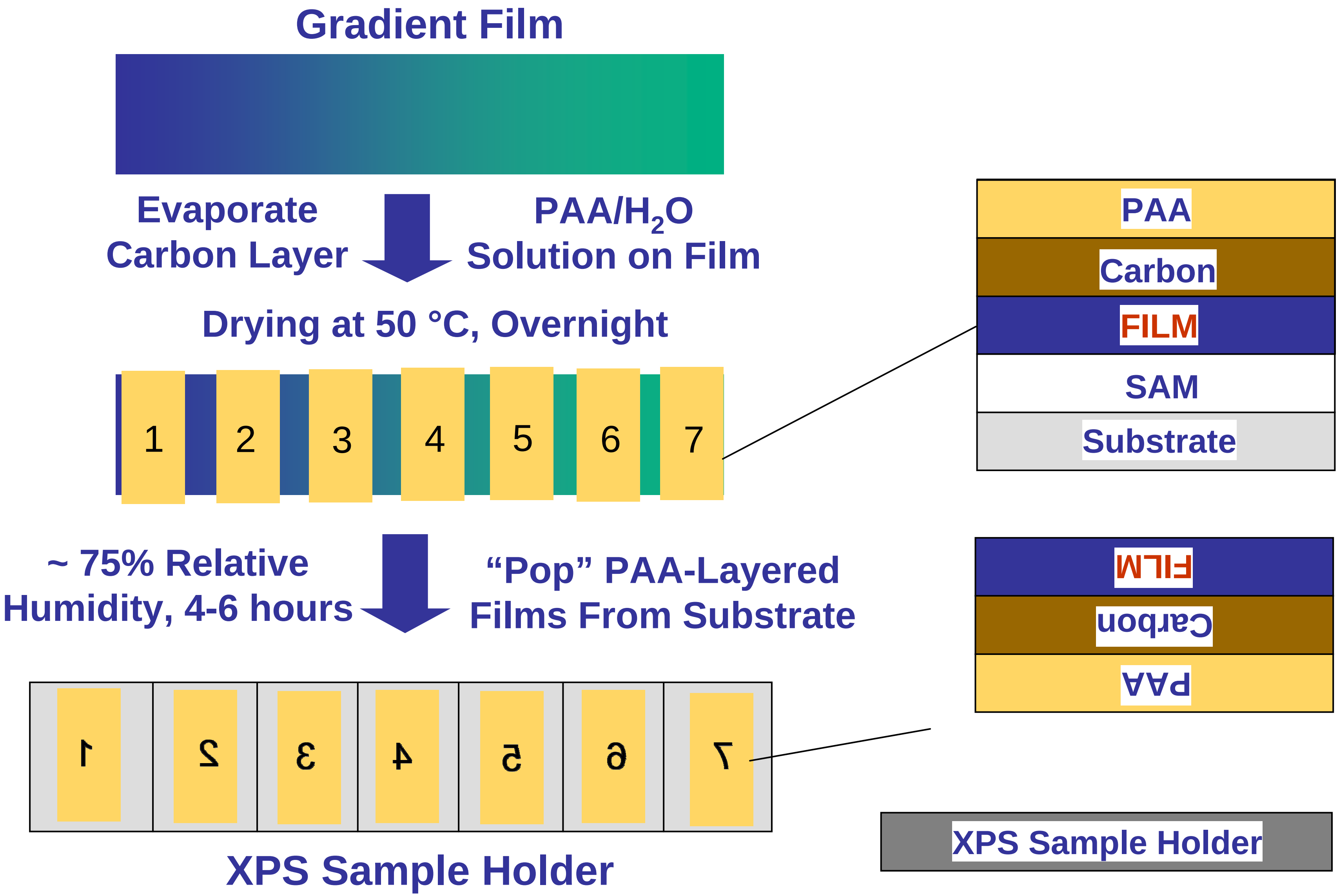


# Bottom Surface Analysis

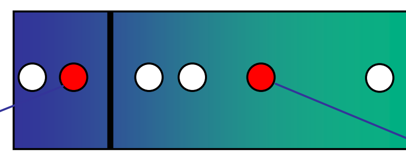


## TOF - SIMS

- PS and PEO detected at surface
- No PI detected at surface
- No SAM on surface (SAM remained on substrate)
- Significant PS content (poor etching behavior using $SF_5^+$ sputtering)

## XPS

- PEO and unsaturated hydrocarbon detected
- Relative compositions determined using oxygen atomic concentration as basis
- Layer composition affected by surface energy



**XPS**

Atomic Conc. (O) = 5.2%

Carbon:Oxygen Ratio = 18.3:1 ~ 18:1

Surface PS:PEO Mole Ratio = ~ 2:1

**XPS**

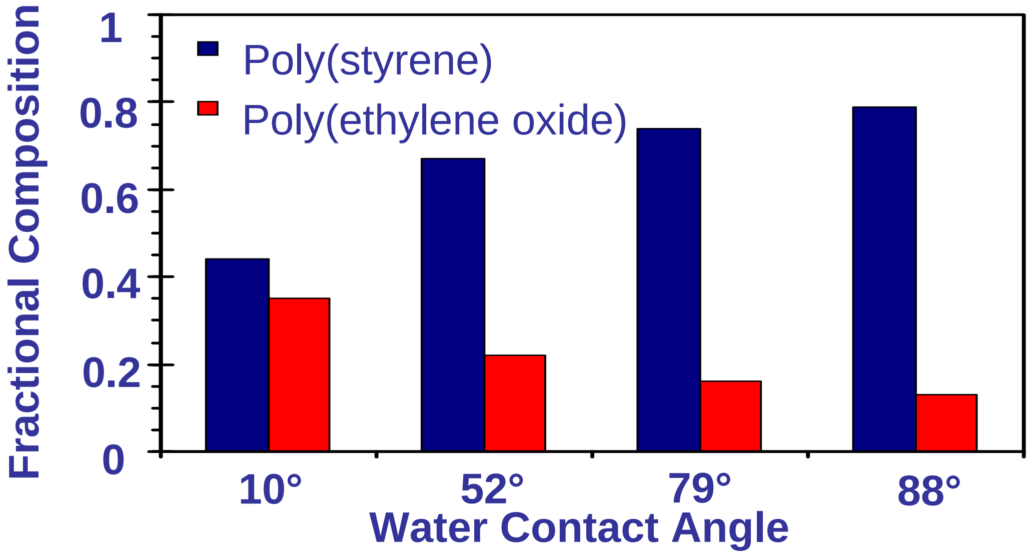
Atomic Conc. (O) = 9.5%

Carbon:Oxygen Ratio = 9.6:1 ~ 10:1

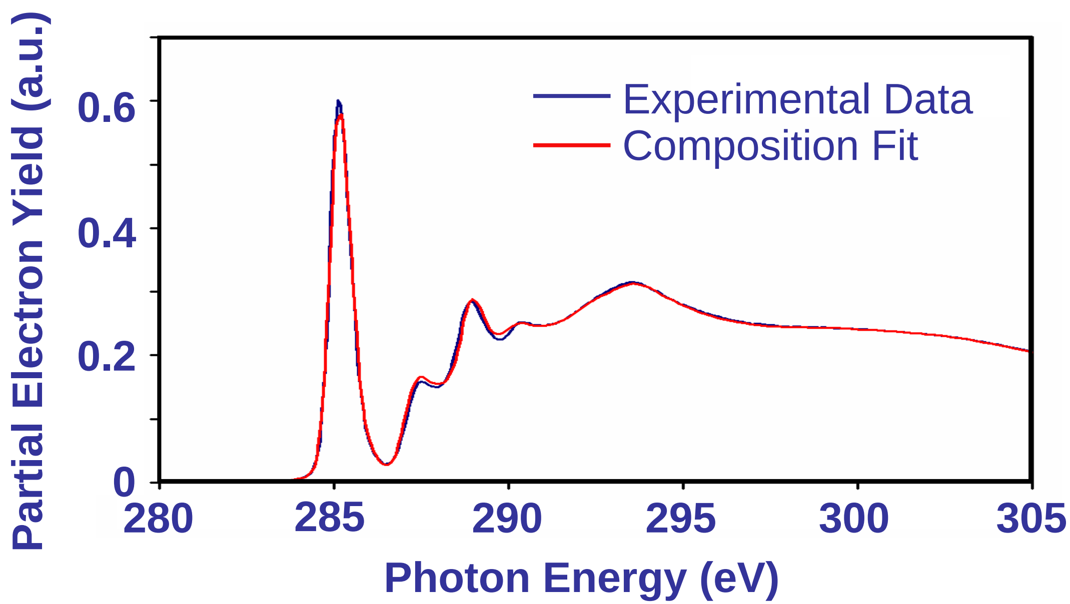
Surface PS:PEO Mole Ratio = ~ 1:1

# NEXAFS – Bottom Surface





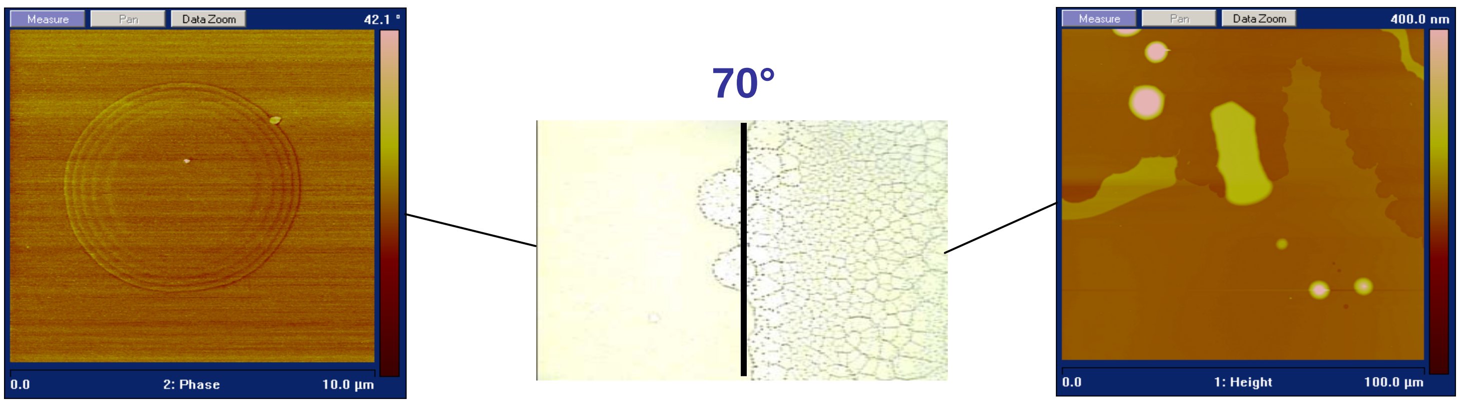

- Poly(styrene) content increases as hydrophobicity of substrate (water contact angle) increases
- Poly(ethylene oxide) content decreases as hydrophobicity increases
- Minimal poly(isoprene) content at bottom surface

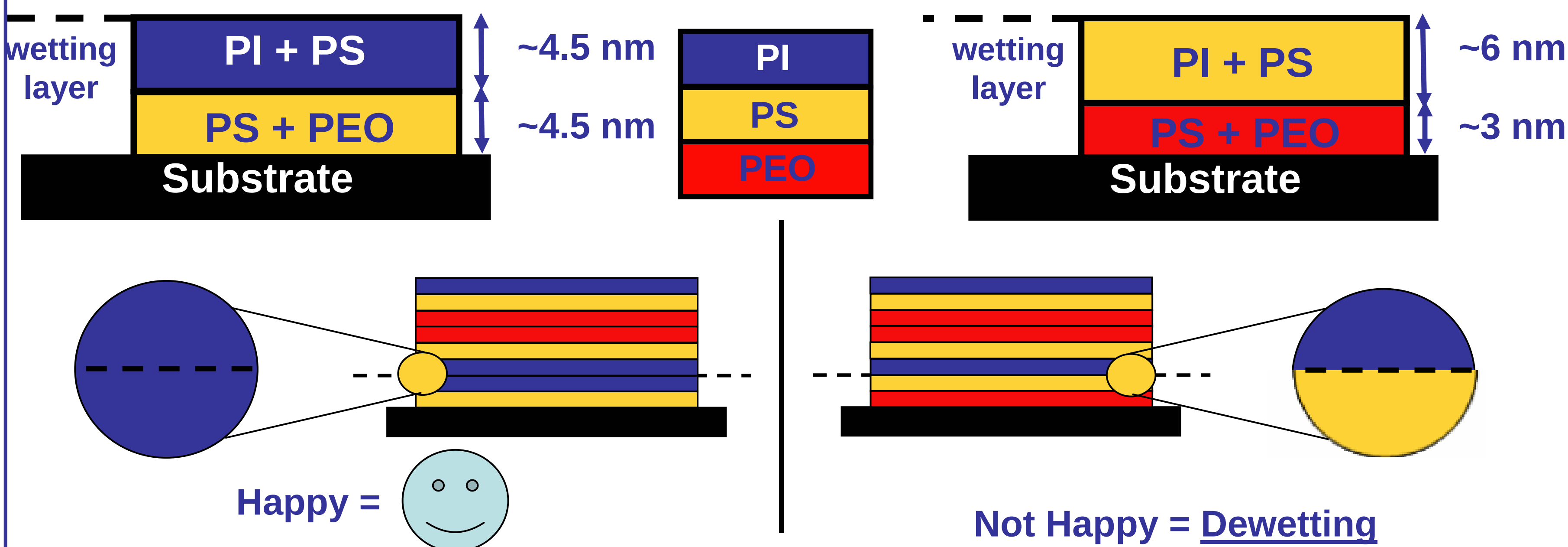



- Distinct differences in PS, PI, and PEO homopolymer carbon spectra
- Linear combination of spectra used to estimate sample compositions
- Good fit achieved in all cases

# Wetting Layer / Substrate Effects

## Low PI Content (27/56/17) [ISO]



# Summary Part I

- Composition of wetting layer a governing factor in film behavior
  - Wetting layer chemical expression is controlled by substrate surface energy
- Film morphology is dependent upon substrate surface energy
  - Motif shift away from bulk morphology
  - Anti-symmetric wetting layer found in all cases
  - Autophobic dewetting found at certain combinations of volume fraction and surface energy
- All films studied exhibit a morphological transition at ~70° substrate contact angle (~40 $mJ/m^2$)

Polymers Division

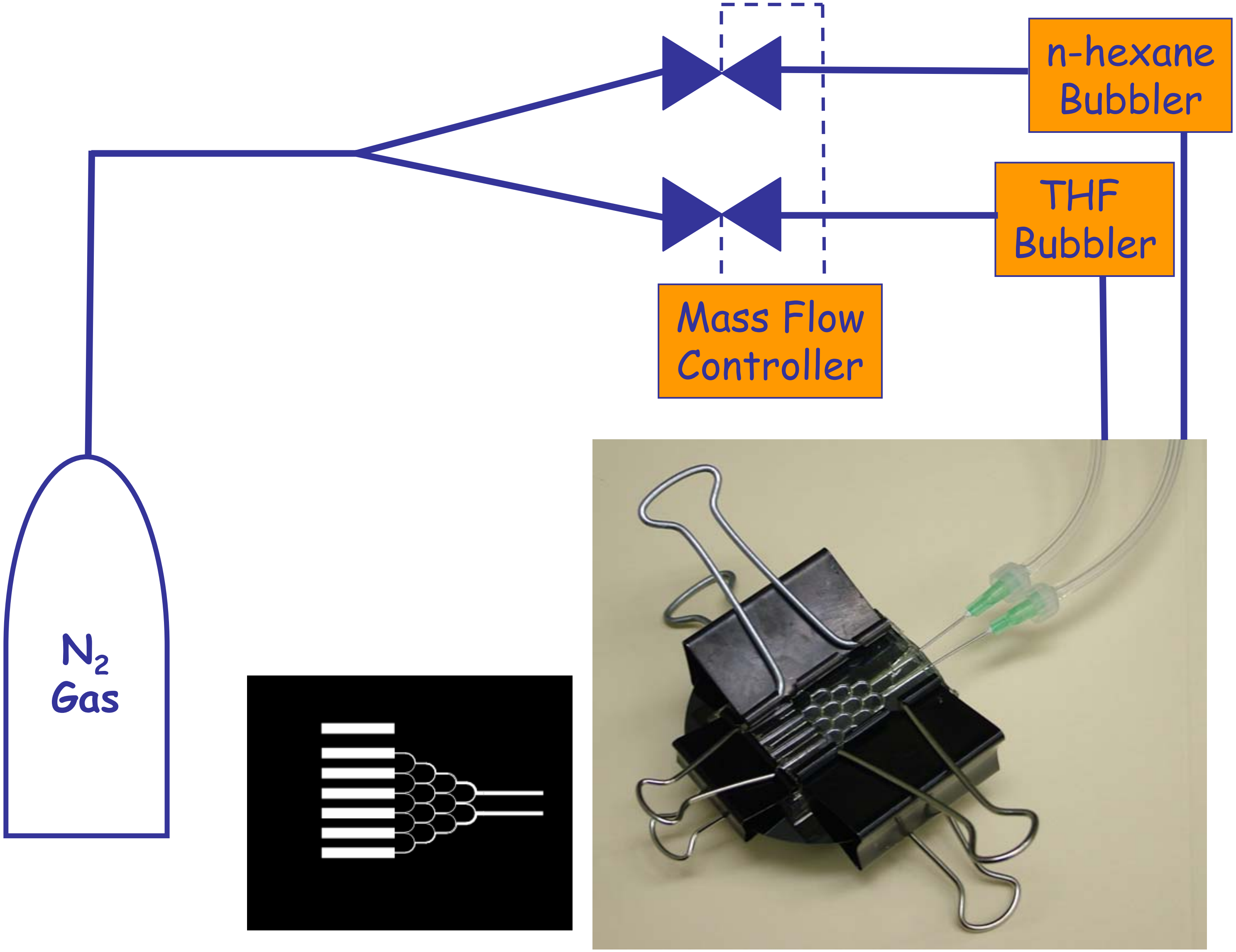
# Interfacial Energy at the Free Surface

## Solvent Vapors

# Solvent Vapors

- Control of free surface (non-substrate) interfacial energy of important
- Method to influence structure of pre-made polymer films
- Option for directed self-assembly
- Typical experiments performed in “bell jars” at long annealing times (days)

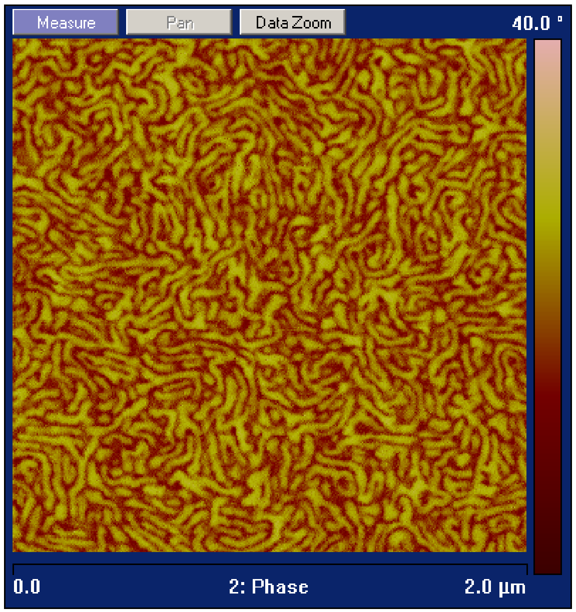
# Solvent Vapor Device
# Discrete Gradient



# Control "Bell Jar" Experiments



24 hour exposure time

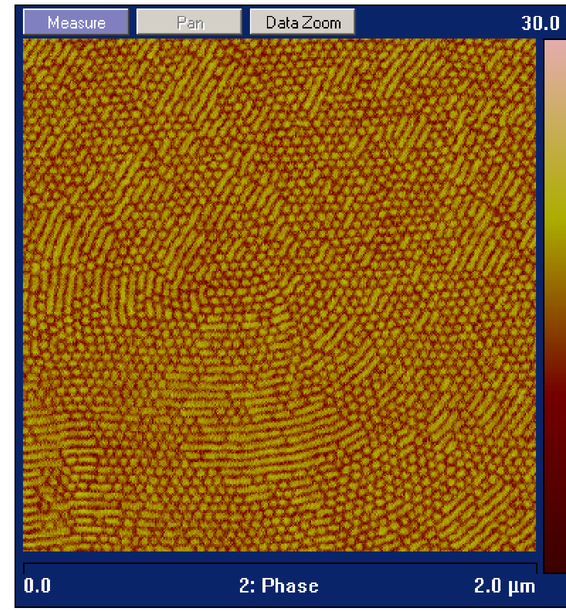



**n-hexane Exposure**

Swollen
parallel cylinders


**Reference Film**

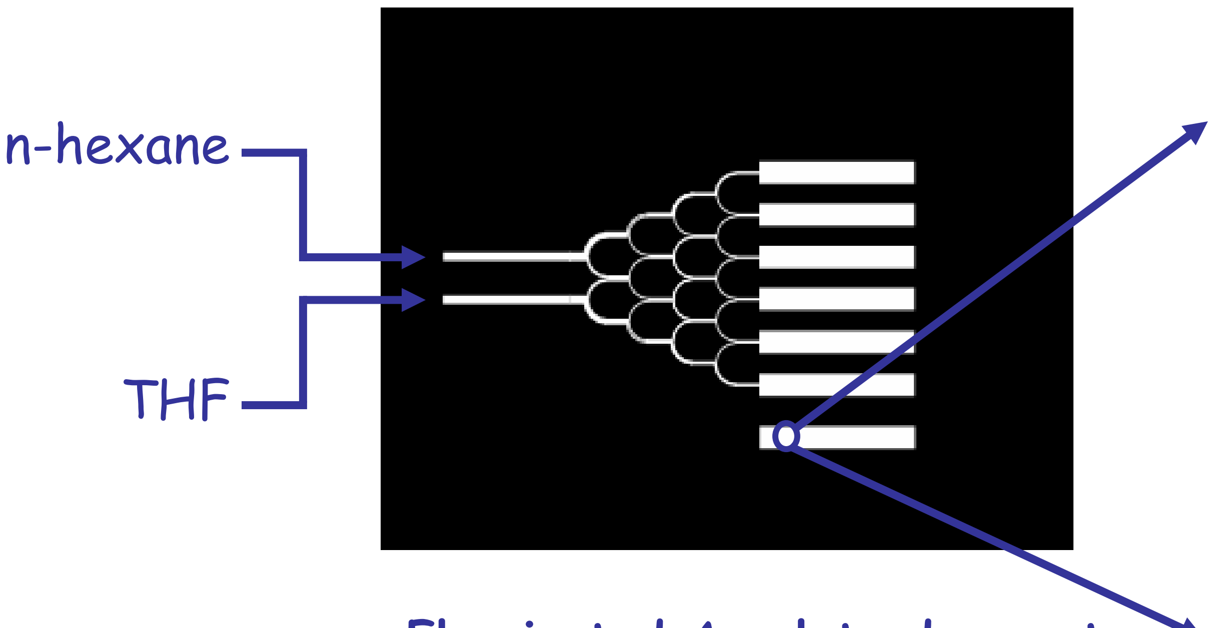
Parallel cylinders

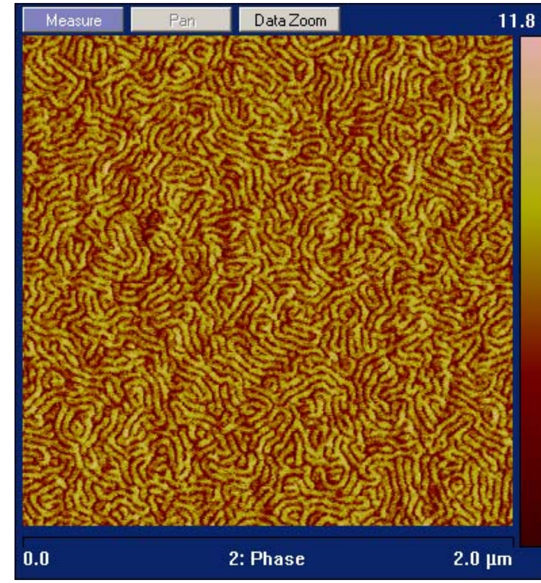


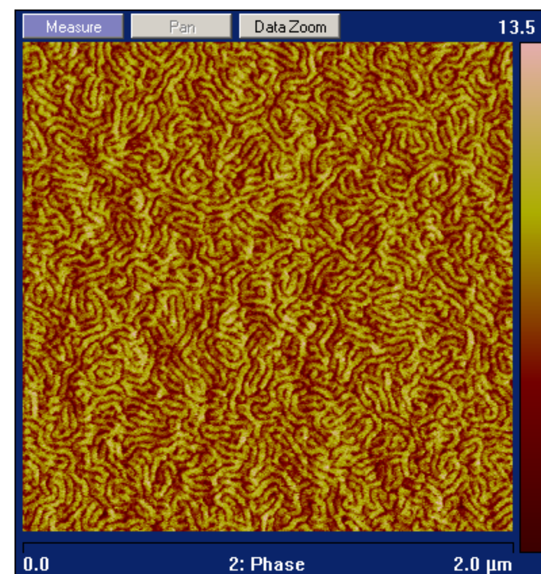

**THF Exposure**

Perpendicular cylinders
+
Dewetting

# Gradient Device Experiments (Reference Channel)

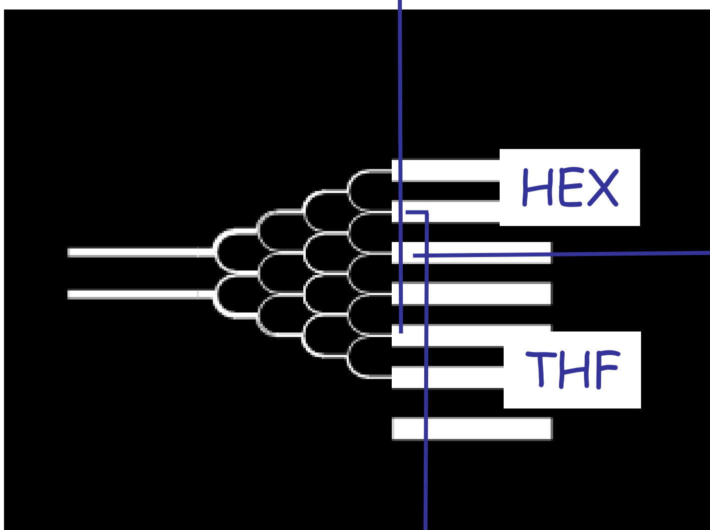


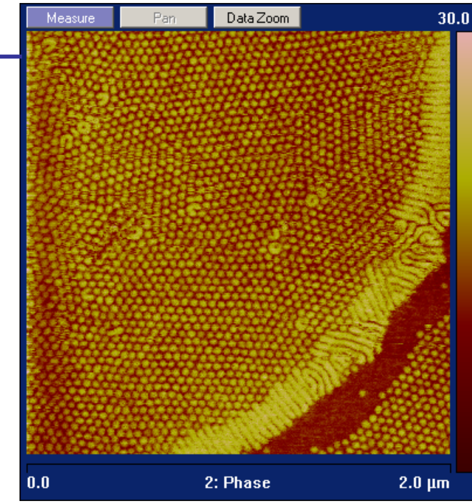



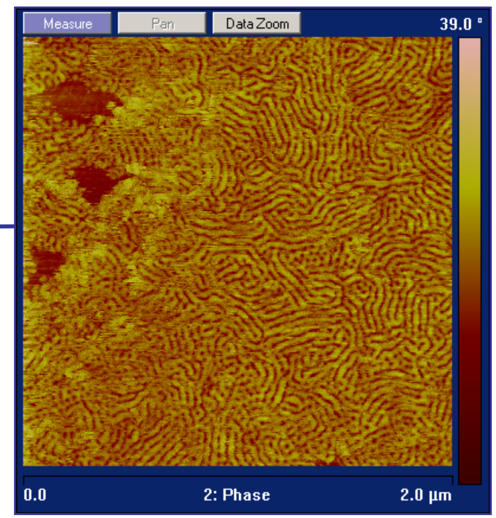

- Fluorinated Acrylate does not influence polymer morphology
- Solvent Vapors do not appreciably penetrate device walls

# Gradient Device Experiments

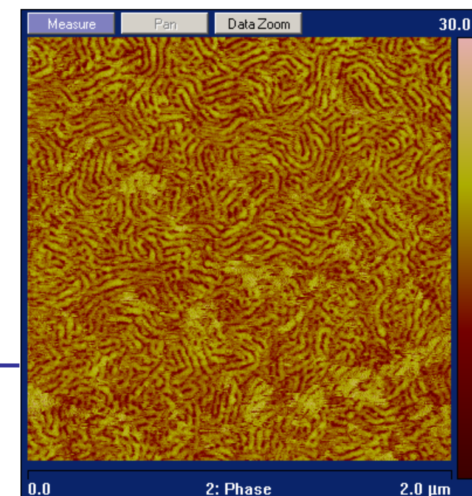



Channel 2 (98% THF)



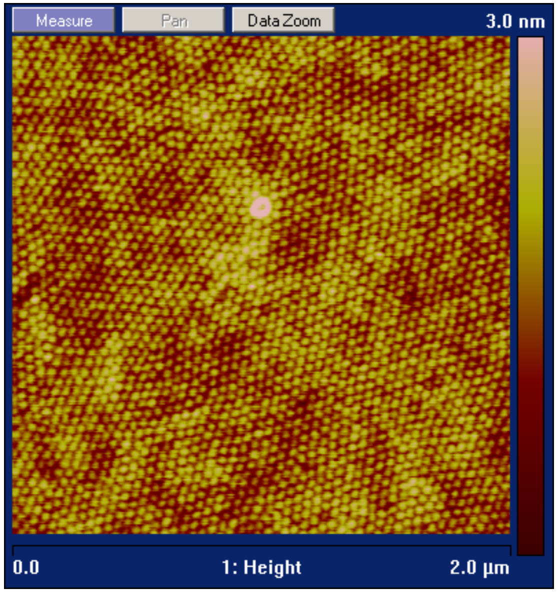

Channel 4 (81% THF)



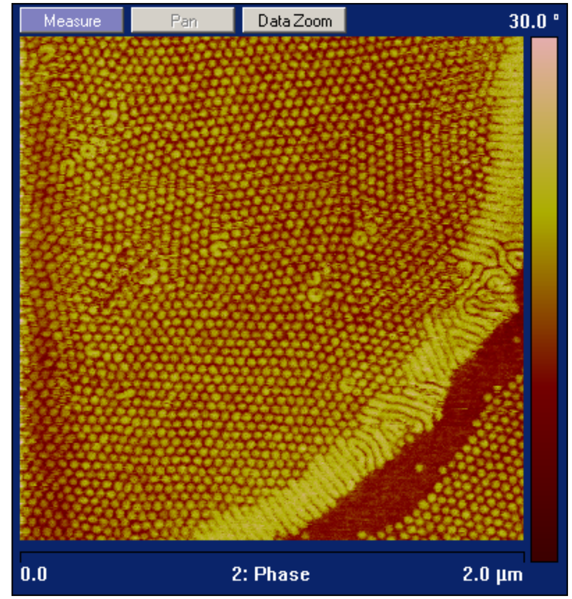

Channel 5 (46% THF)

# Gradient Device Experiments (Across Channels)

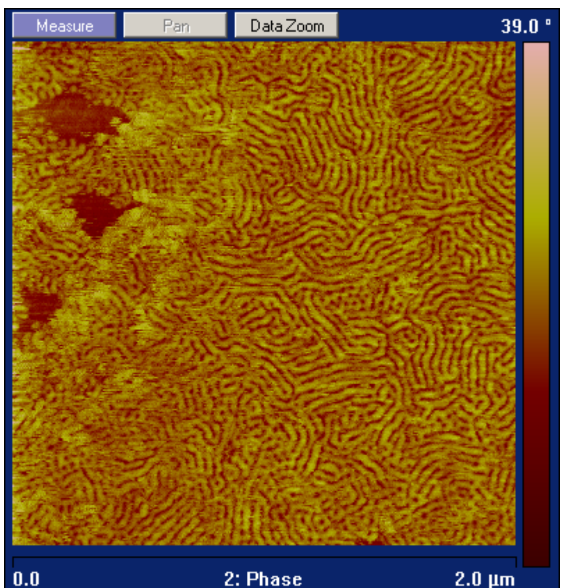
Channel 1 (100% THF)



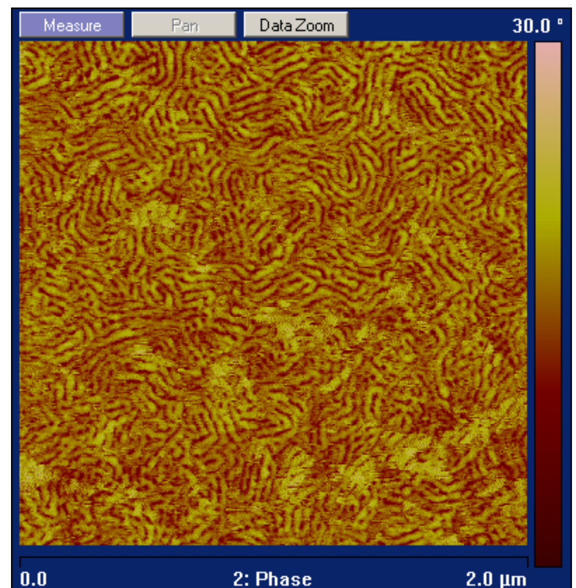

Channel 2 (98% THF)




Channel 4 (81% hexane)




Channel 5 (46% hexane)



# Gradient Device Experiments (Along Channels)

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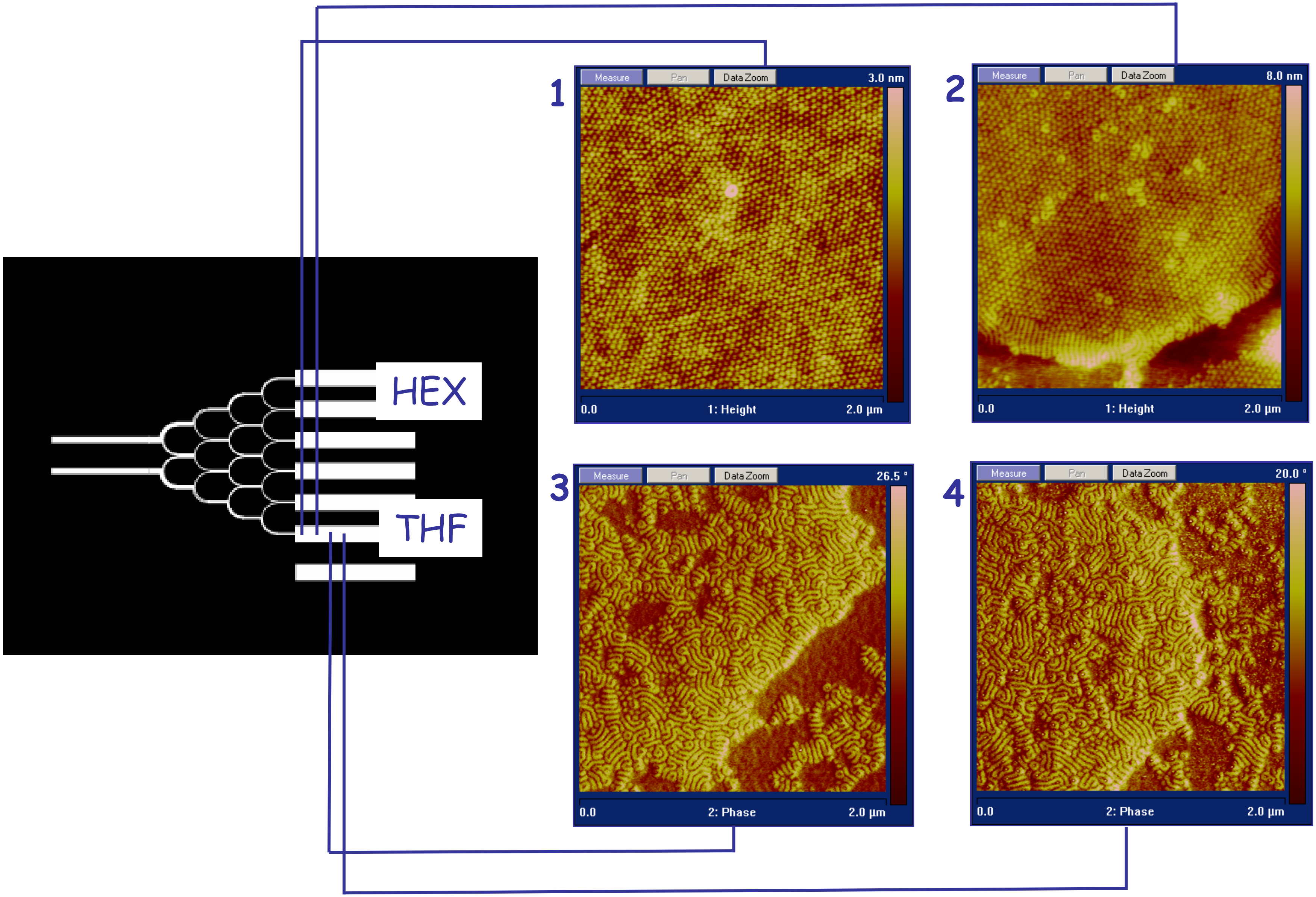
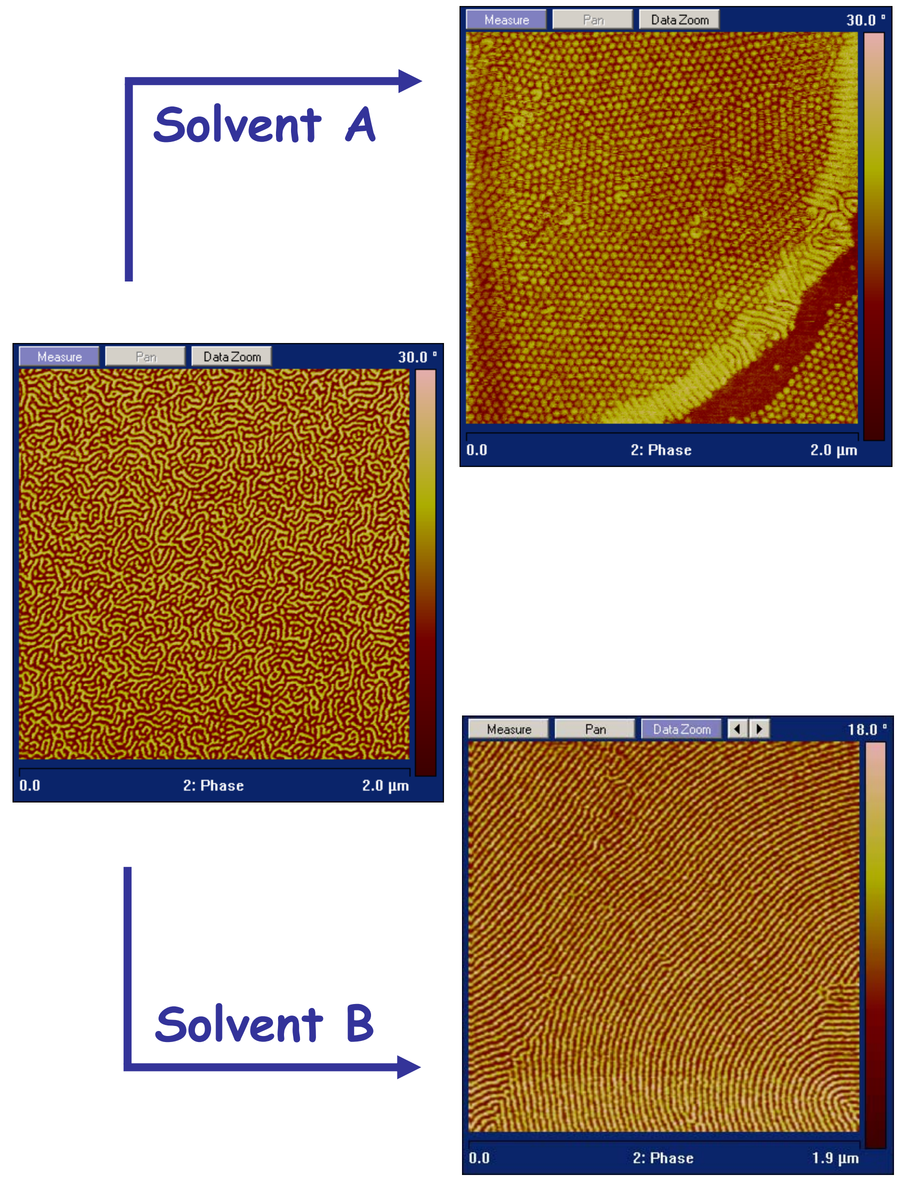


# Other Solvent Effects

- Thin films annealed in various solvents
- Parallel versus perpendicular orientations
- Possible uses include adjusted the transport direction of membrane materials



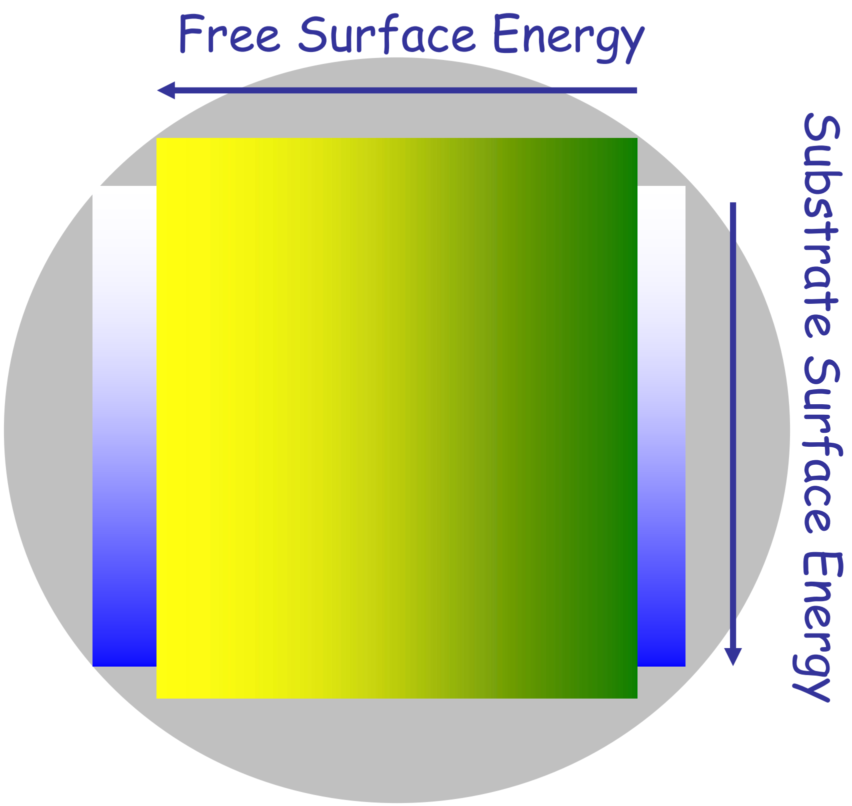
Polymers Division

# Summary Part II

- Fluorinated acrylate suitable for solvent vapor experimentation (minimal vapor penetration)
- Discrete solvent vapor gradients created using acrylate device
- Gradients behavior mimics control (bell jar) experiments using both pure and mixed solvent vapor streams
- Variations both across channels and along single channel

# Next Step -
# 2D Combinatorial Gradient






Example of two-dimensional gradient for characterizing block copolymer response to surface fields

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