Orientation in Nanostructured Thin Films

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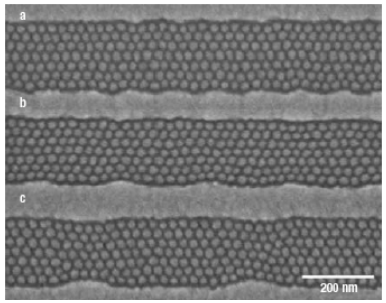
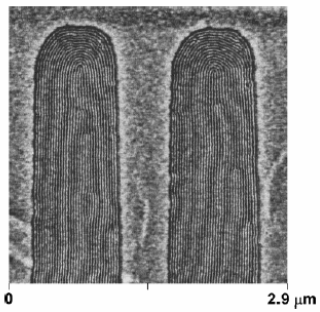
Controlling BCP Orientation

Physical Confinement

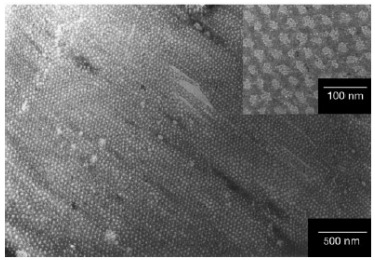


Cheng et al.,
Nature Materials 2004, **3**, 823



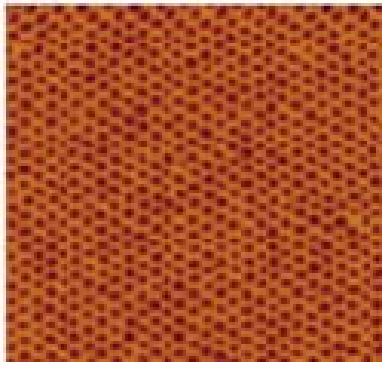
Sundrani et al.,
Langmuir 2004, **20**, 5091

Directional Solidification



De Rosa et al.,
Nature 2000, **405**, 433

Selective Solvent Casting

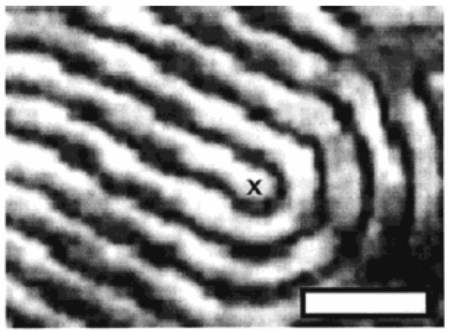


Kim et al.,
Adv. Mat. 2004, **16**, 226

Chemical Patterns

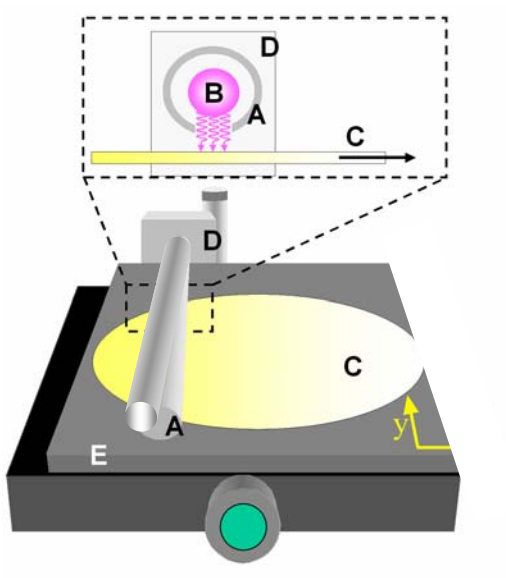
M. Stoykovich et al.,
Science 2005, **308**, 1442

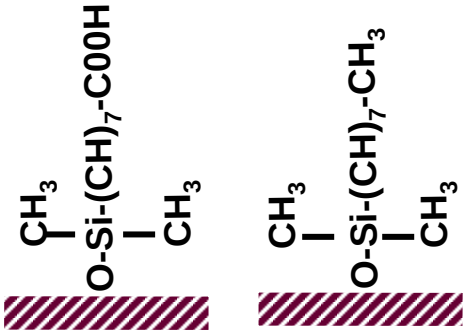
Average Surface Energy



E. Huang et al.,
Macromolecules 2000, **33**, 80

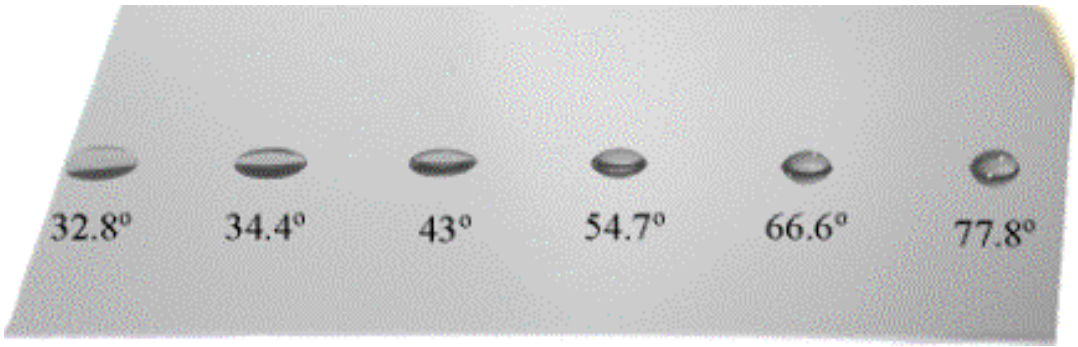
Continuous Surface Energy Gradient





Surface Energy Range:

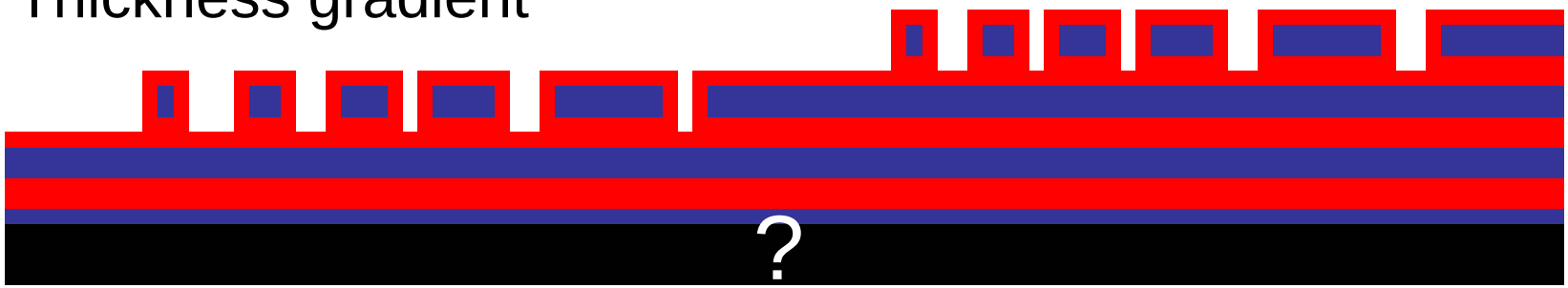
20 mJ/m^2 to 76 mJ/m^2



Continuous Film Thickness Gradient

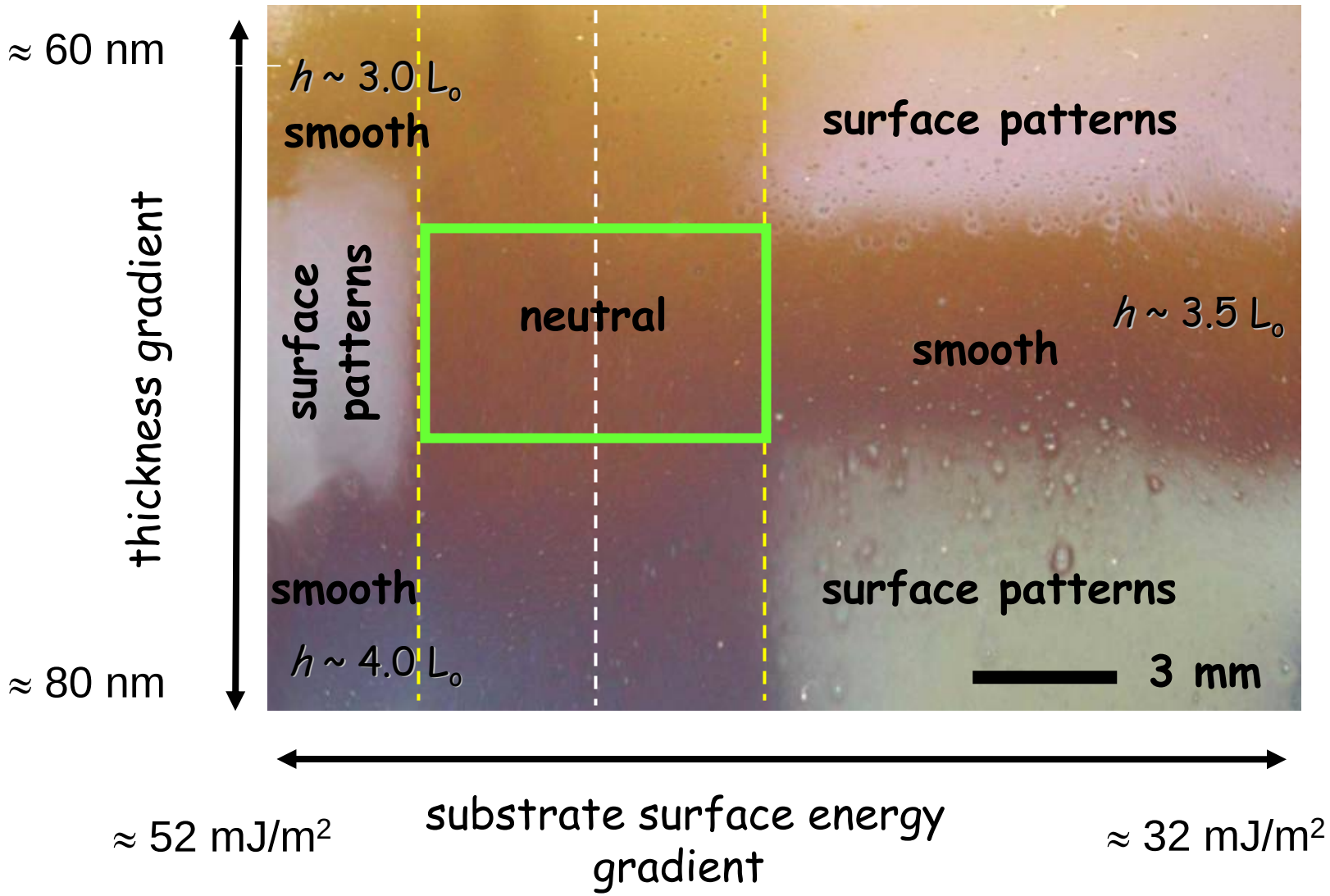
Surface energy gradient

Thickness gradient



Need 2-D thickness/surface energy block map

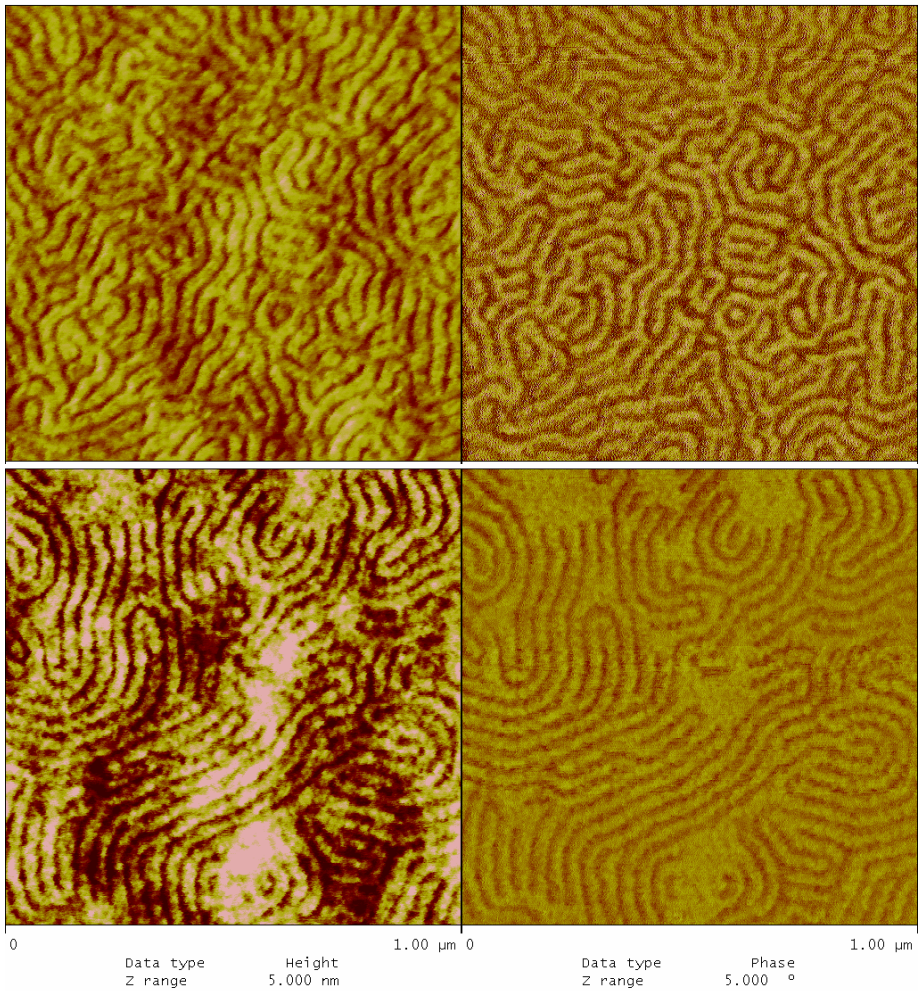
Morphology vs. Surface Energy



Evolution of Mixed Morphology

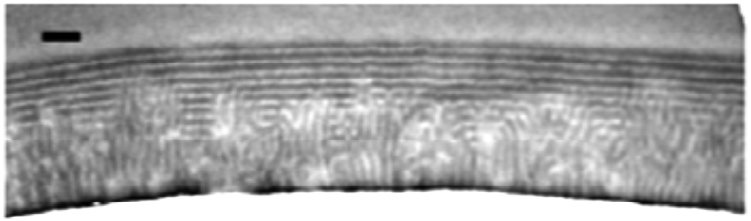
2h @ 180 C

10h @ 180 C



Probing Internal or Buried Morphologies

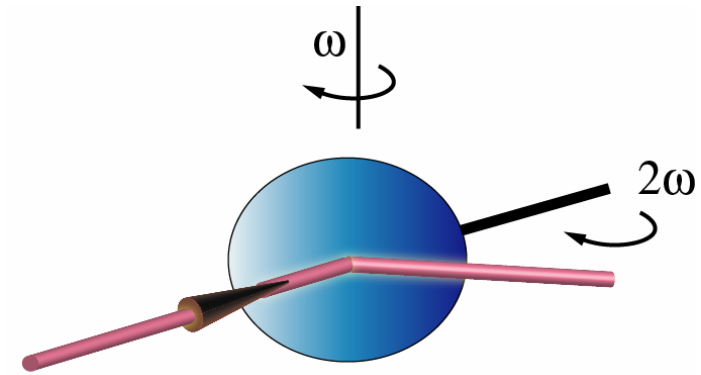
Xu et al., *Macromolecules* 2005, **38**, 2802



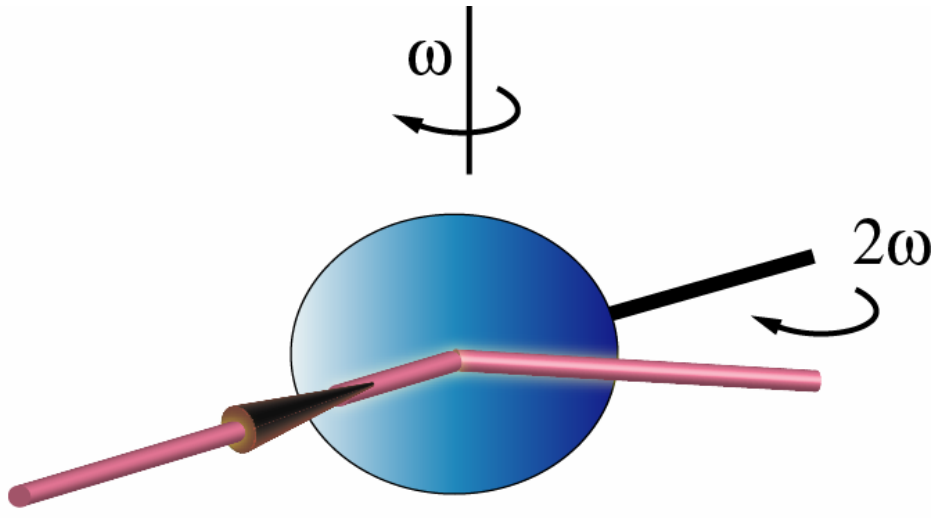
1. Cross Section Scanning Electron Microscopy (SEM)
2. Cross Section Transmission Electron Microscopy (TEM)

3. X-ray Reflectivity (XRR)
4. Neutron Reflectivity (NR)

5. Small Angle X-ray Scattering (CD-SAXS)
6. Small Angle Neutron Scattering (CD-SANS)



Neutron and X-ray Reflectivity



Scattering vector perpendicular to substrate

Neutrons can probe differences between D- and H- labels

X-rays probe differences in atomic number (polymer vs. air)

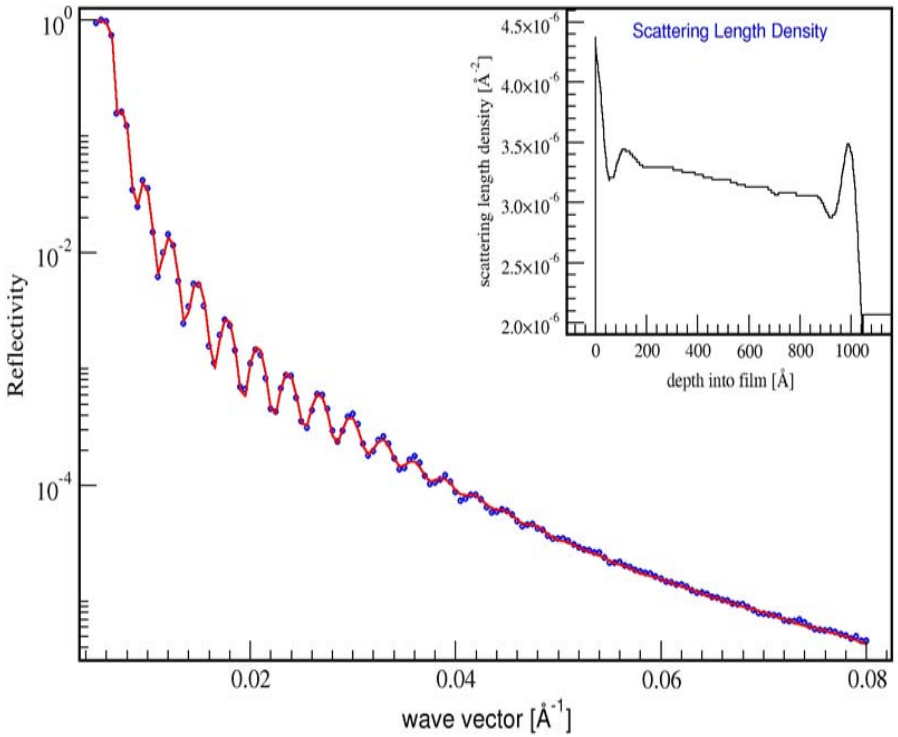
Sub-Angstrom resolution possible

Models can be complex

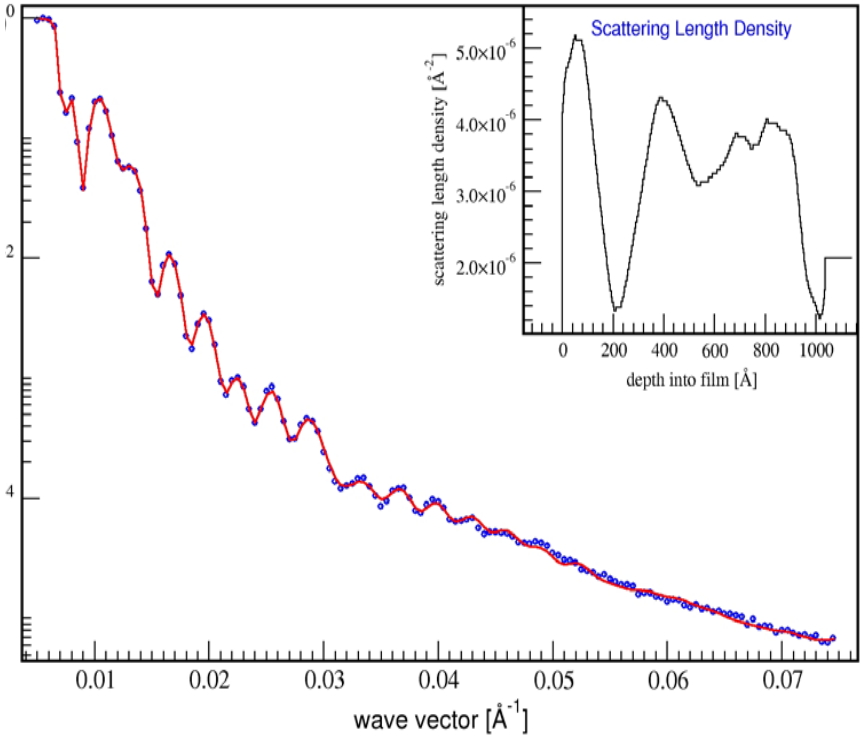
Q-space map limited to vertical information

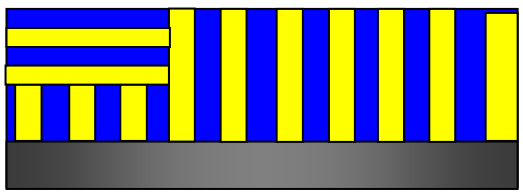
Evolution of Mixed Morphology

As-Cast



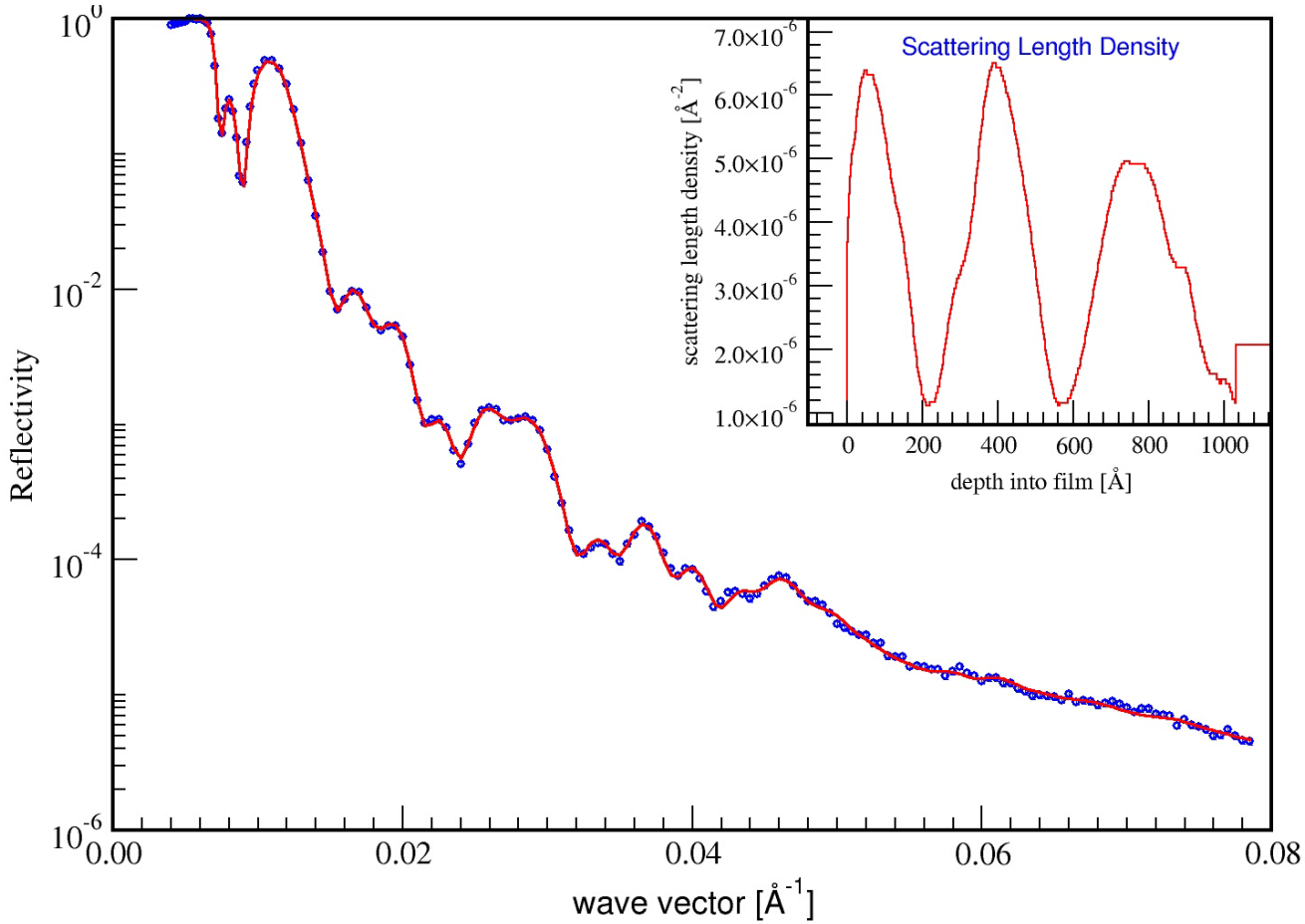
2h @180 C

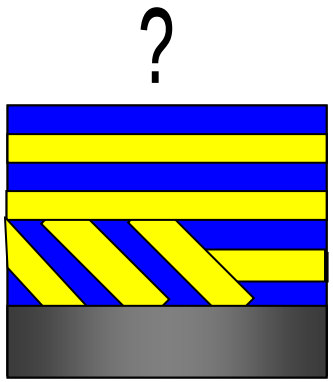




Long Term Annealed Internal Structure

10 h @ 180 C





Mixed Morphology

Probing Internal or Buried Morphologies

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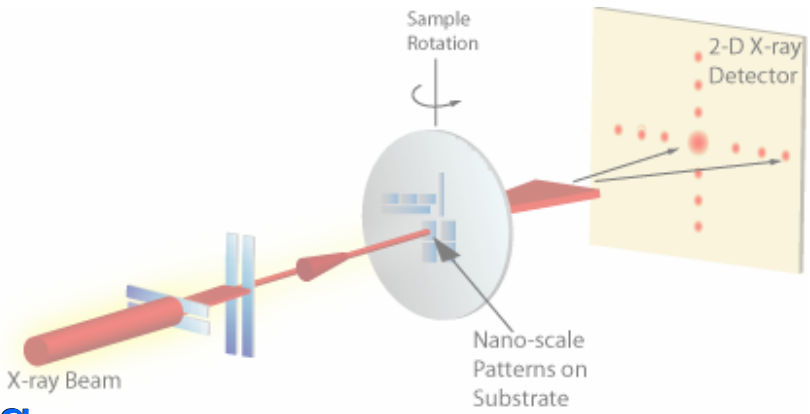
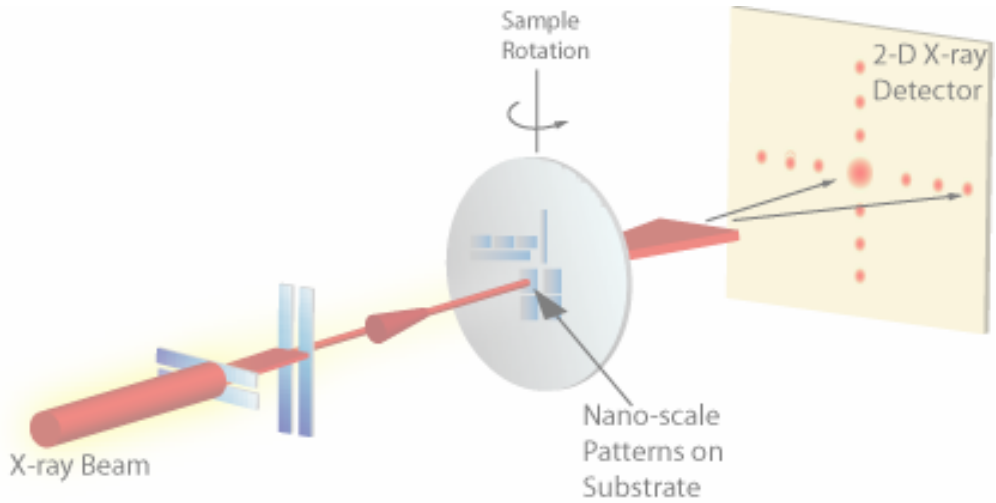


Critical Dimension SAXS



Transmission SAXS

- **Silicon transparent for E > 13 keV**
- **Non-destructive / No sample prep**
- **Beam spot size (40x40) micron**
- **Model fits simpler than GISAXS**

High Precision Dimensions (5-500 nm)

- **Sub-nm precision**
- **Sidewall angle**
- **Pattern Cross Section**

Development Team:

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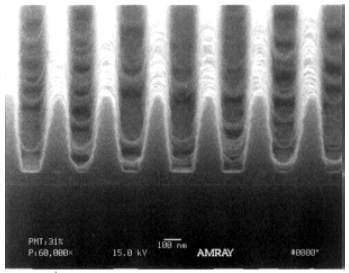
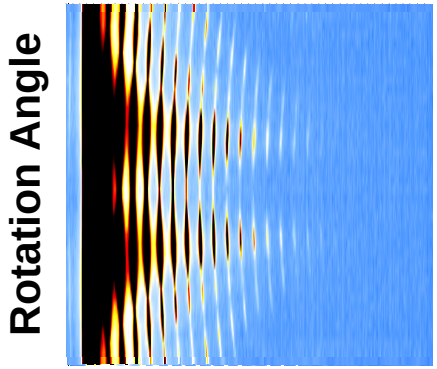
Tengjiao Hu (NIST)
Eric K. Lin
Wen-li Wu

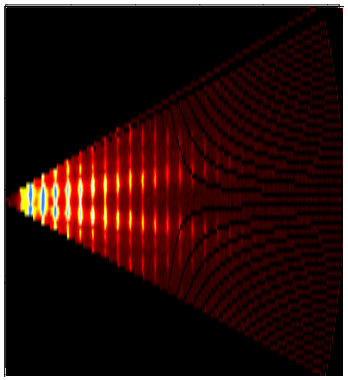
Argonne:
Diego M. Casa
Steven J. Weigand
Denis T. Keane

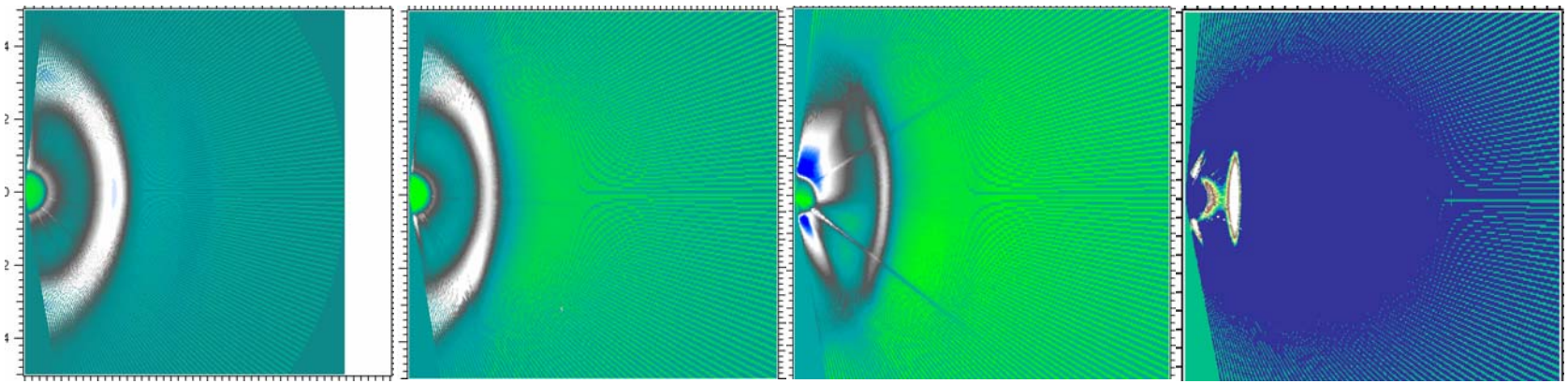
Orientation: Random → Ordered



(w. Q. Lin, IBM Yorktown Hgts)







Random Spheres → Random Cylinders → Semi-Oriented Cylinders → Very Oriented Lamellae

Ron Jones (NIST), Ho-Cheol Kim (IBM Almaden), Sangcheol Kim (NIST), and Robert Briber (U. Md)

Probing Internal or Buried Morphologies

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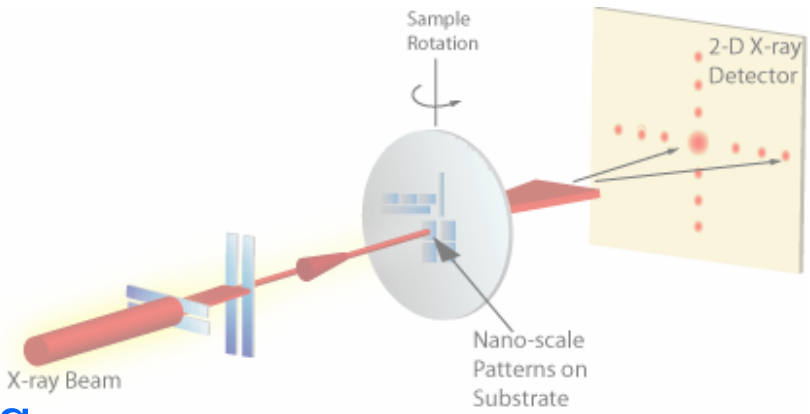
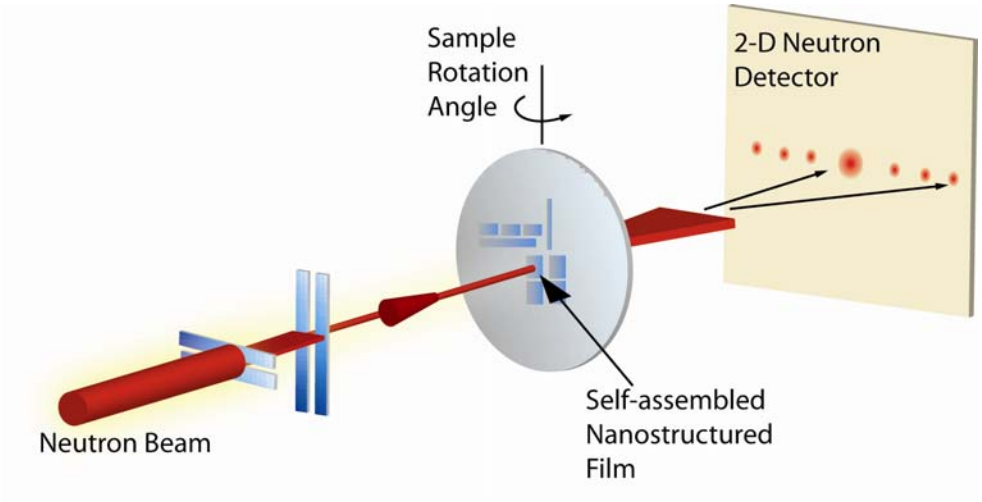


Nanostructure Morphology with CD-SANS

Critical Dimension Small Angle Neutron Scattering (CD-SANS)



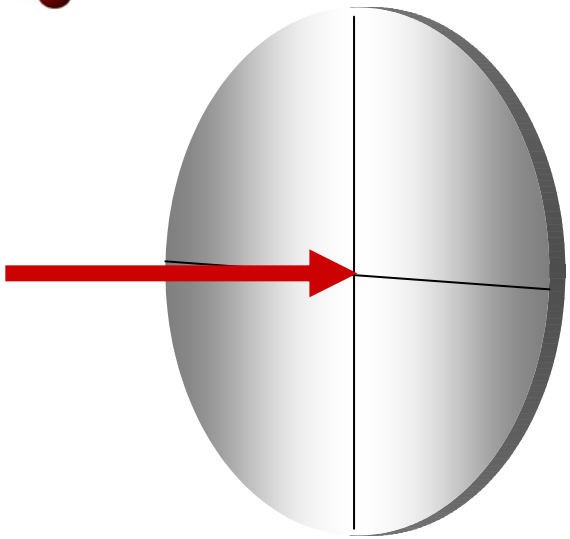
Transmission SANS

- **Deuteration provides contrast**
- **Silicon transparent for all energies**
- **Patterned media can be made transparent, only internal morphology visible**
- **High flux cold neutron source (NCNR)**

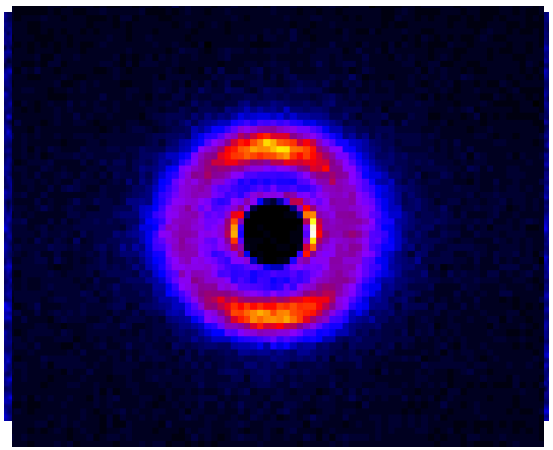
Probing Buried 3-D Morphologies

- **Protocol based on CD-SAXS**
- **Probes deep and dense structures**
- **Details of complex morphologies**
- **Non-destructive**
- **In-situ measurements possible**

CD-SANS of BCP films



Rotation Angle = -80



- Si/dPS-b-PMMA
- Contact Angle = 55 deg
- Annealed 1 hr @ T = 160 deg

- ***Symmetric ring at 0° only illustrates that lamellar morphology is NOT laying down***

- ***Asymmetry of ring at -80° confirms the orientation of morphology: lamellae are normal to substrate***

Summary

1. Versatile tunable SE strategy for controlling block-copolymers orientation with gradient polymer-substrate interactions
2. Self-assembly within films can produce complicated, depth dependent morphologies
3. Internal morphologies can be characterized in 3-D using a suite of measurement platforms including CD-SAXS, CD-SANS, and Neutron Reflectivity.