Chemical Imaging of Polymers in Real- and Reciprocal Space

NSLS-II Workshop
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Thanks to J. Stoehr, G. Mitchell, J. Genzer, G. Cody for their viewgraphs/data and many other colleagues, collaborators, and users

Thanks to NSLS-II organizers for invitation and NSF, DOE, Dow Chemical for financial support over the years

X-ray Microscopy:

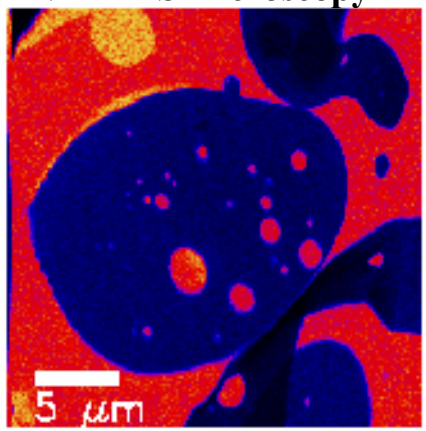
X-rays have come a long way!

(Examples "biased" towards polymers/magnetic materials)

1895

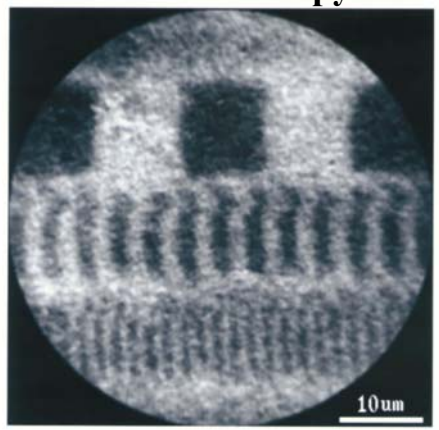
NEXAFS microscopy

1992



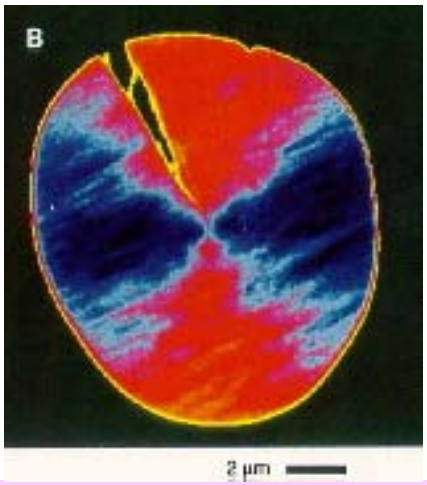
XMCD microscopy

1993



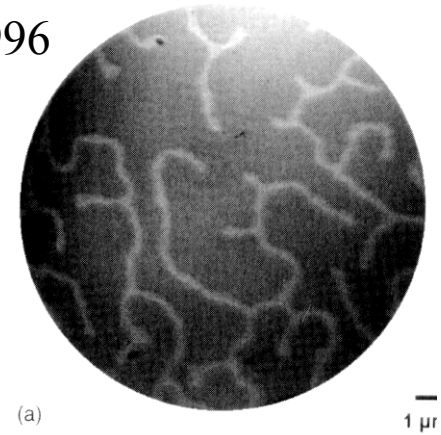
XLD microscopy

1993

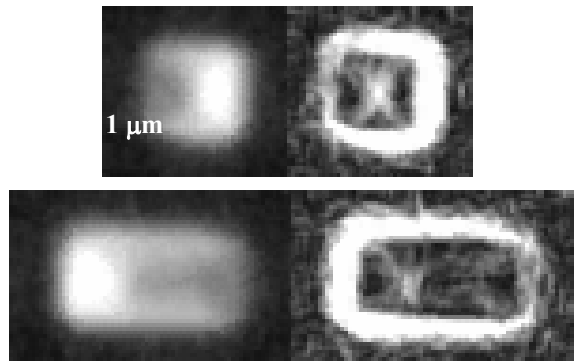


XMLD microscopy

1996



Dynamics



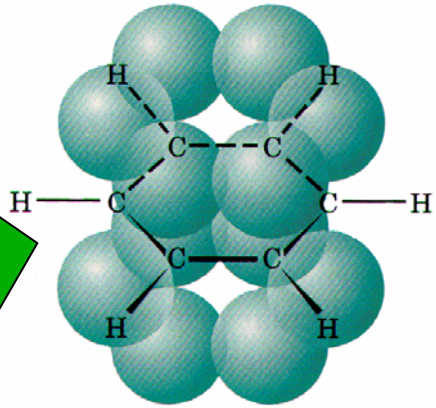
2003

Outline

- **Chemical Imaging = Spectromicroscopy**
  - **Beamson and Turner (early 1980's) coined the (unwieldy) term "spectromicroscopy"**
- **Near Edge X-ray Absorption Fine Structure (NEXAFS): The Basics**
  - **Organic materials as examples. Magnetic materials also important class of materials**
- **Microscopy: Basics**
- **NEXAFS Microscopy of Polymers**
  - **Some examples that exemplify applications.**
- **Resonant Scattering. NEXAFS "microscopy" in reciprocal space**
- **Future Perspective**

Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

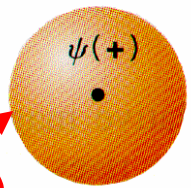
Example: “”Richness” of Polymer NEXAFS Spectra



Unoccupied Molecular Orbital

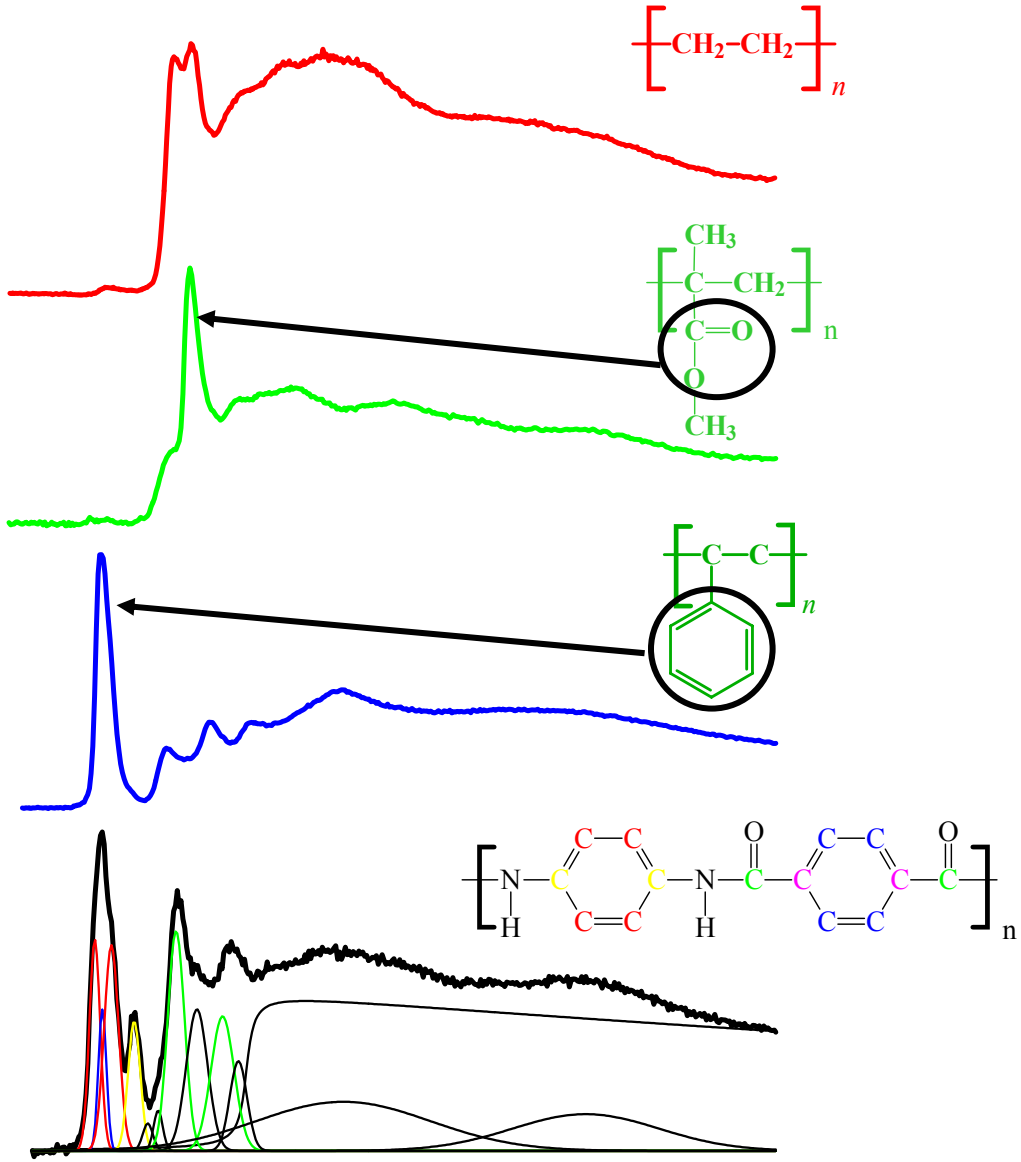
e-

C 1s edge ~ 290 eV
N 1s edge ~ 405 eV
O 1s edge ~ 540 eV



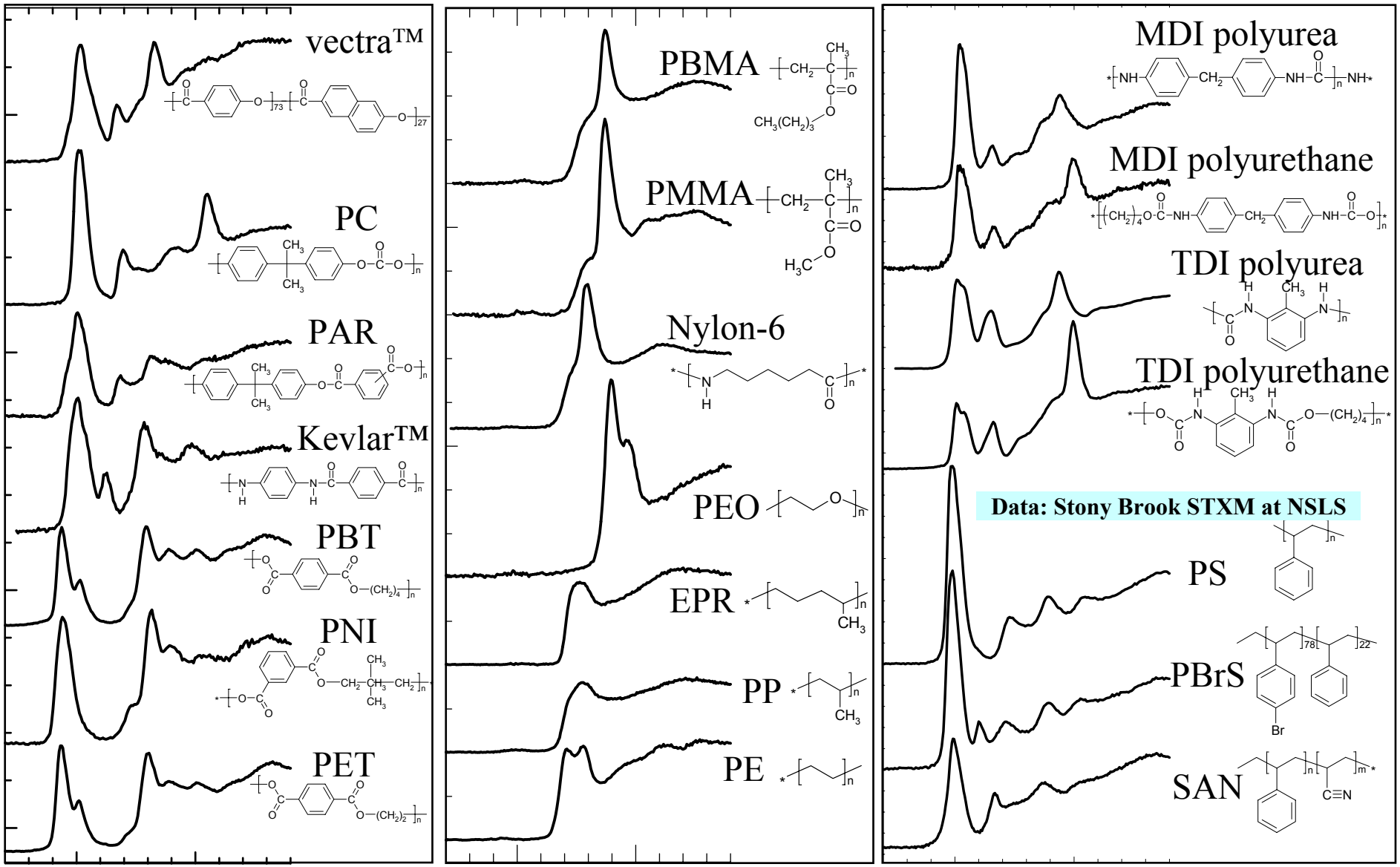
hν

1s Orbital

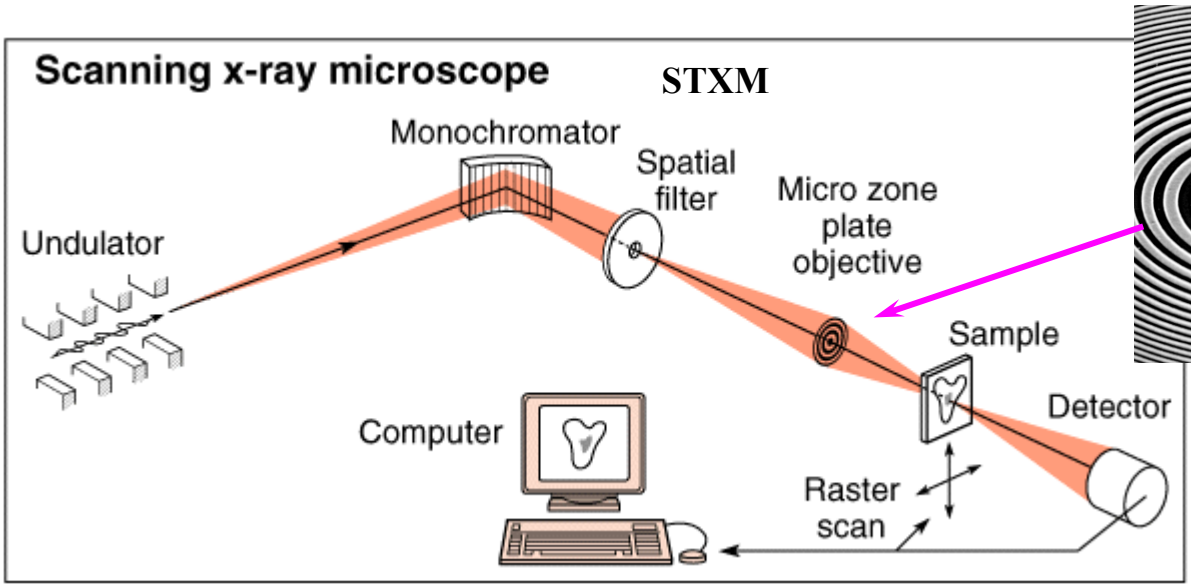


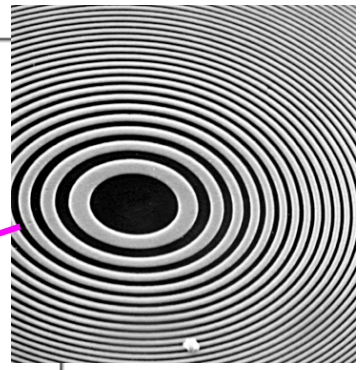
Some Polymer NEXAFS Spectra

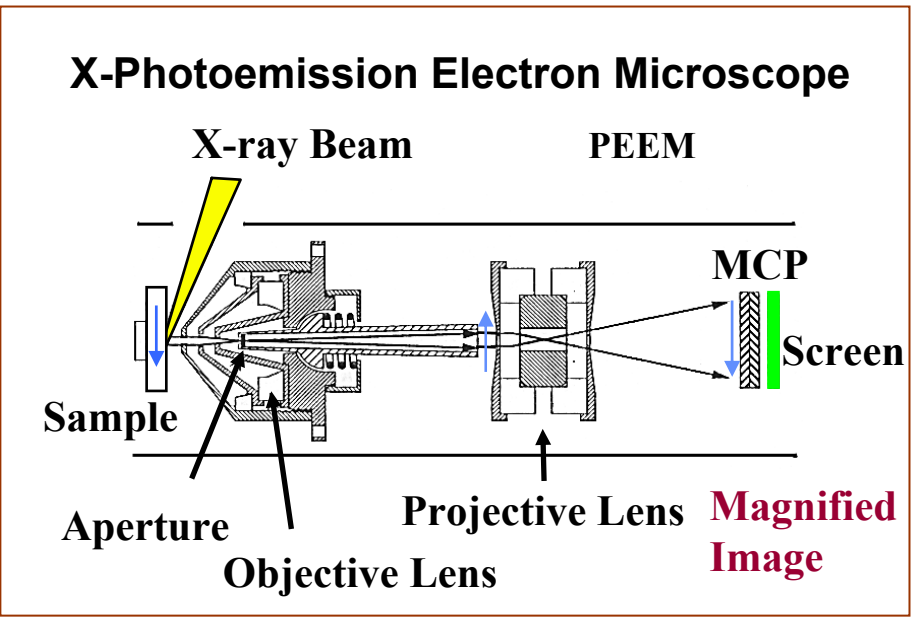
Dhez, Ade, and Urquhart
J. Electron Spectrosc. 128, 85 (2003)

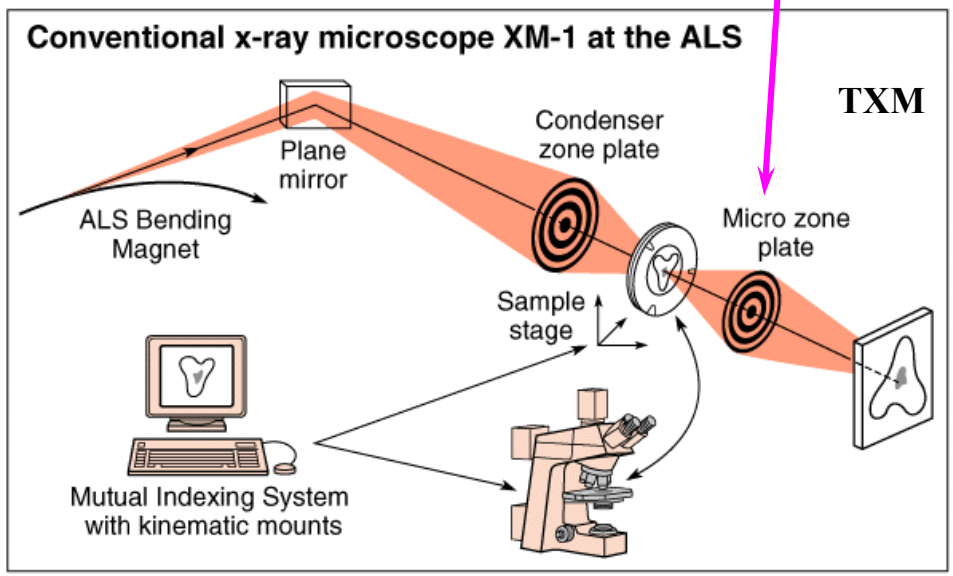


Types of X-ray Microscopes





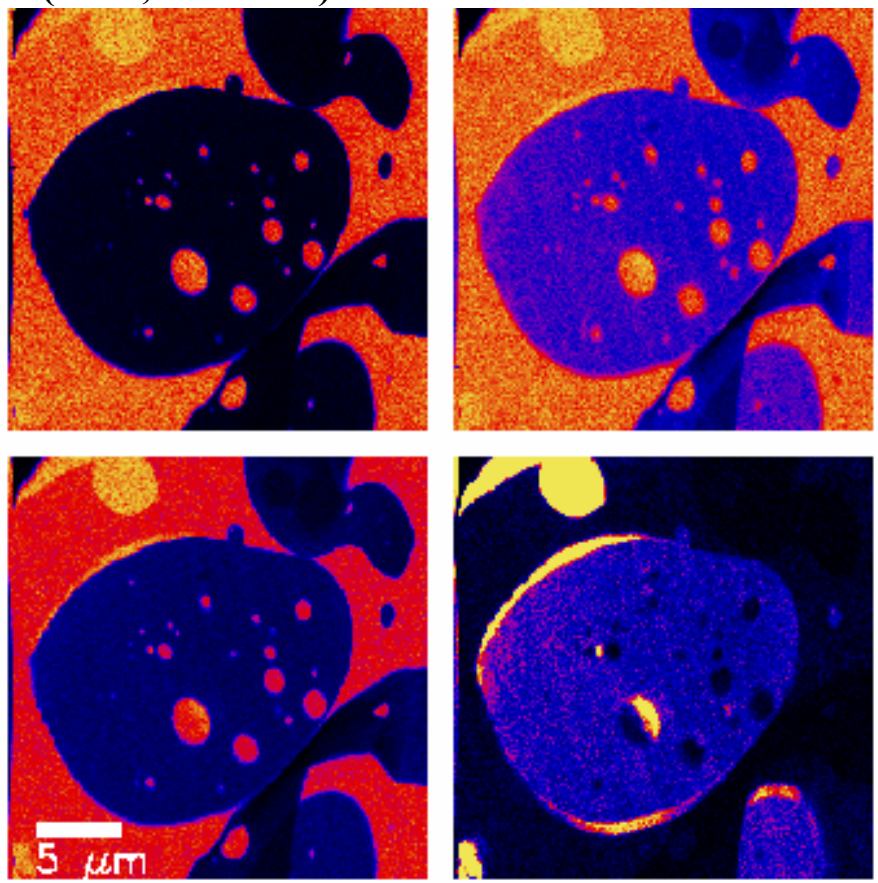




Also Scanning Photoemission X-ray Microscope (SPEM) Ade et al. 1992

X-ray imaging of polypropylene/styrene-acrylonitrile
First NEXAFS imaging in transmission (1992)

- Based on the Stony Brook X1A-STXM (1989-present)
  - J. Kirz, H. Ade, et al., Rev. Sci. Instrum. 63 (1) (1992).
  - C. Jacobsen, S. Williams, et al., Opt. Commun. 86, 351 (1991).
- X1A-STXM not explicitly built to perform spectroscopy, but proved flexible enough to perform carbon NEXAFS.
  - Polymer Science was "enabled"

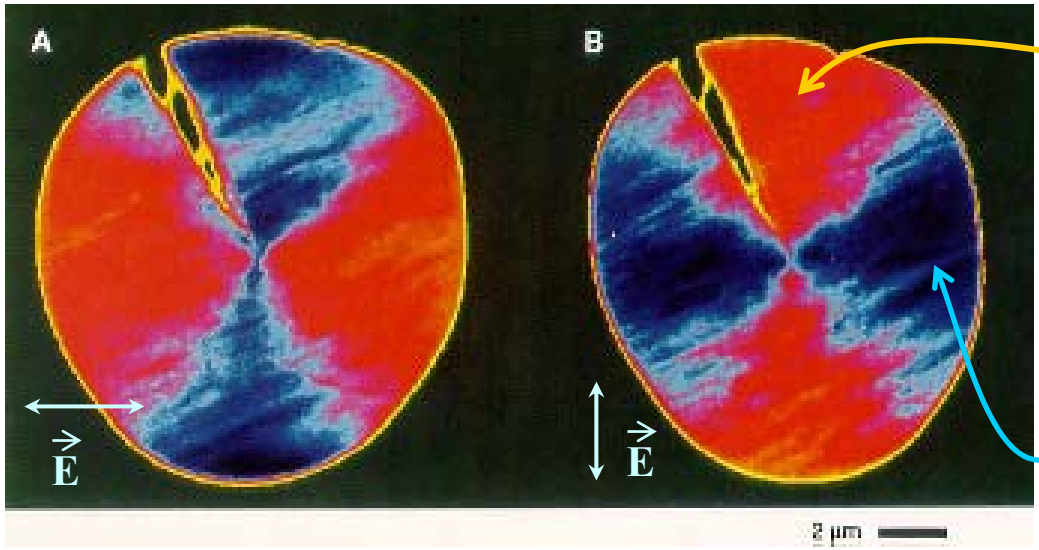


Data: Stony Brook STXM at NSLS

H. Ade, X. Zhang, S. Cameron et al., Science 258, 972 (1992)

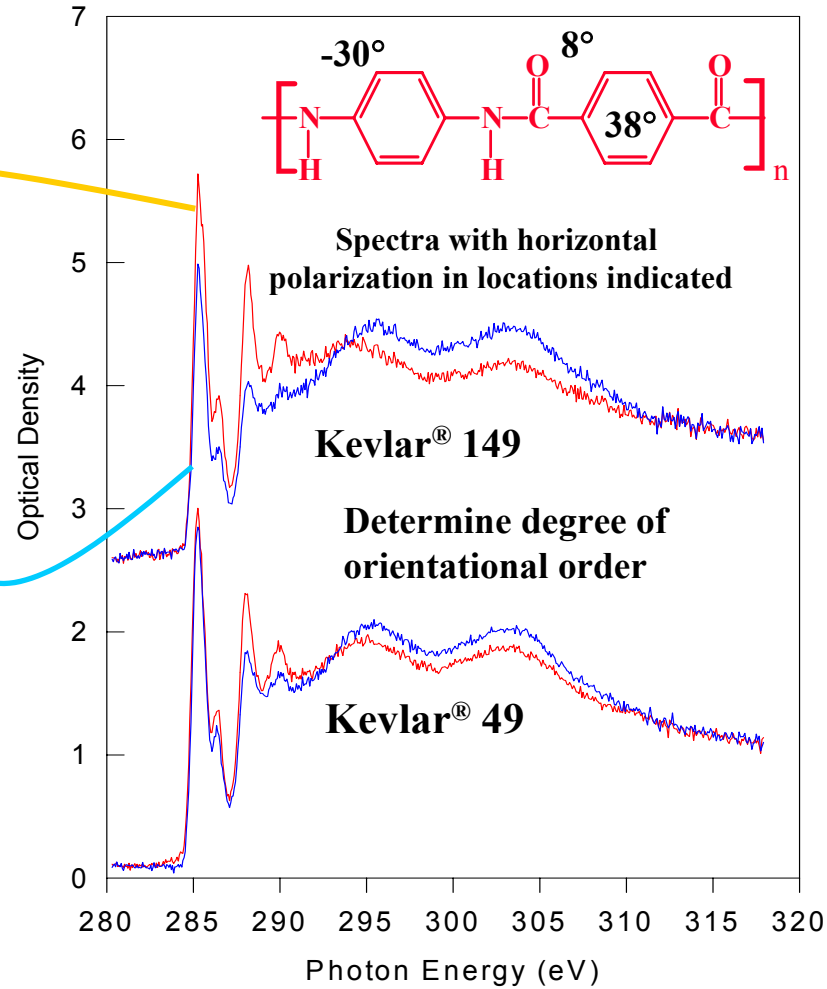
X-Linear Dichroism Microscopy

Kevlar 149 fibers, 200 nm thick, imaged at 285.5 eV



H. Ade and B. Hsiao, Science 262, 1427 (1993)

- Pattern rotates with rotation of polarization due to radial orientation of phenyl groups
- Phenyl and carbonyl groups point (on average) radially outward
- π* and σ* resonances show complementary dichroism



A. P. Smith and H. Ade.
Appl. Phys. Lett. 69, 3833 (1996)

NEXAFS Microscopy:
A number of examples for organic materials

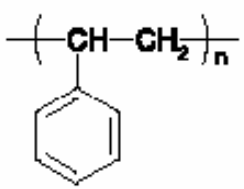
- **Bilayers of thin polymer films. Can mixing be induced by physical means, i.e confinement?** - e.g. Zhu *et al*., Nature 40, 49 (1999)
- **Super-absorbent polymers, gels** G. Mitchell et al. Macromol 35, 1336 (2002)
- **Organic geological materials**
- **Polymer surfaces**

- **Composition of macrophases in polyurethanes**
- **Polymer compatibilization with clays** (ongoing)
- **Semi-crystalline polymers**
- **Meteorites**
- **Diamond like carbon films**
- **Biofilms**
- **Biology**
- **……..**

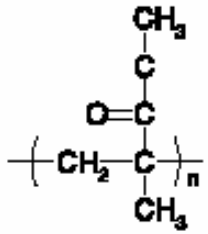
PS/PMMA/clay nano-composites

A universal and less expensive method of polymer compatibilization?

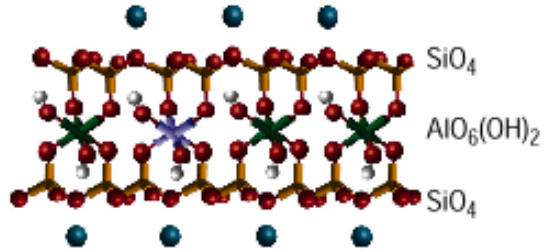
Sample Preparation



Polystyrene (PS)



Poly(methyl methacrylate) (PMMA)



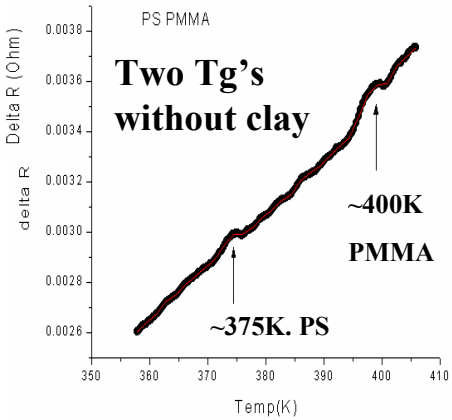
Montmorillonite
Cloisite® 6A - Southern Clay Products
Exfoliated clay
Platelet of 3000Å x 3000Å and thickness of 20Å.

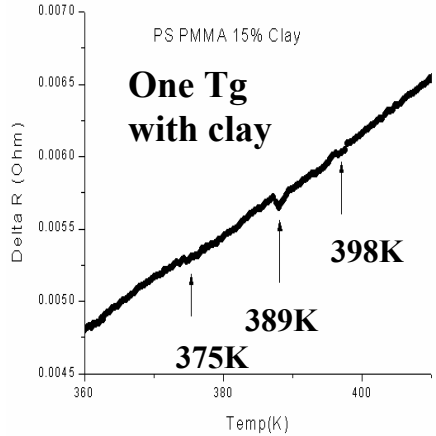
1. Polystyrene (PS), Poly(methyl methacrylate) (PMMA) polymer blends and Clay are codissolved in toluene.
2. Solution are dispersed under ultra sound for 20 mins.
3. Films are spun-cast from solution onto Si_3N_4 with thickness between 800Å to 2000Å.
4. Films were annealed in 10^{-3} Torr, oil free vacuum environment.

H. Ade, A.L.D. Kilcoyne, A. Winesett, O. Dhez, W. Zhang, X. Hu, M. Lin, M. Rubinstein, M. Rafailovich, J. Sokolov

Polymer Clay Composites:
PS/PMMA

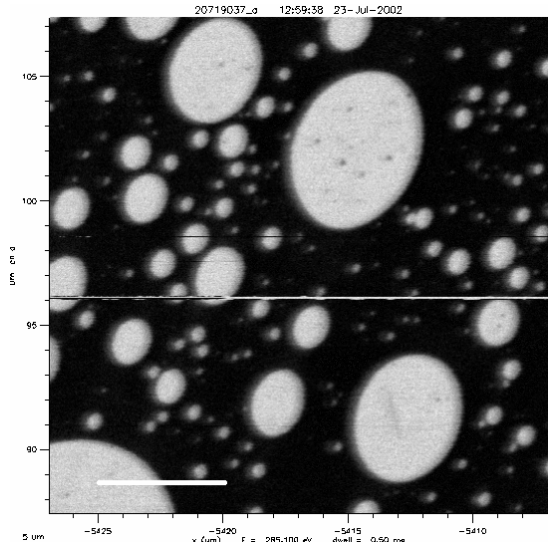
- Clay works better than use of block copolymer to "compatibilize" the blend
- Observe the same in bi-layer geometry



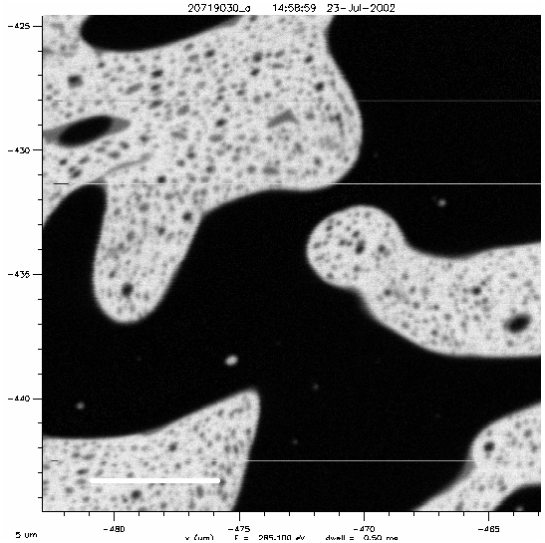


DSC suggest formation of "single" phase in the presence of clay

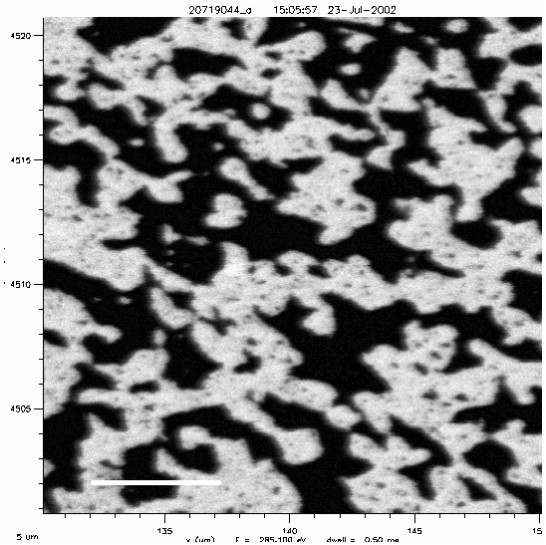
PS/PMMA 70/30



PS/PMMA/P(S-b-MMA) 45/45/10



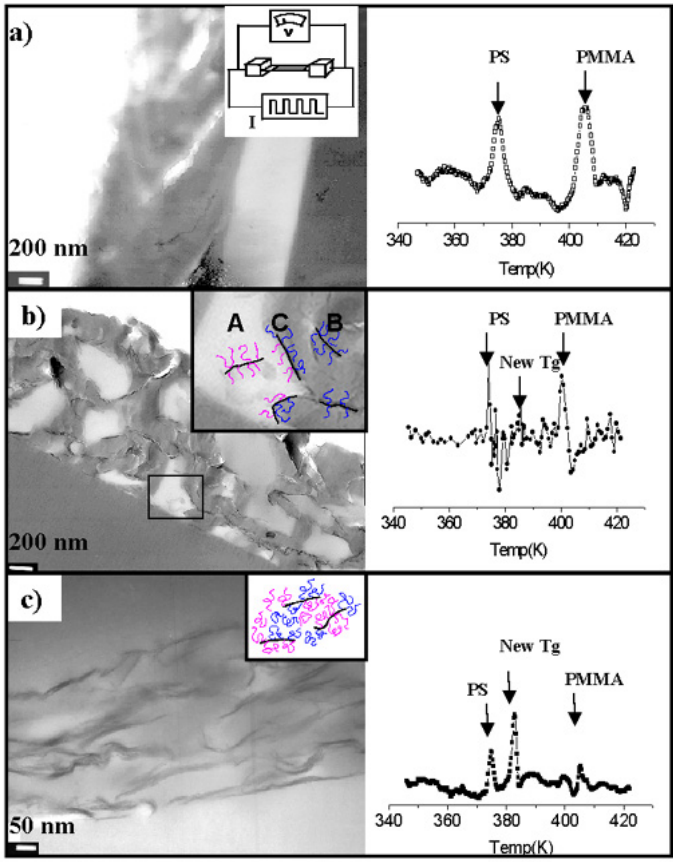
PS/PMMA/Clay 45/45/10



H. Ade, A.L.D. Kilcoyne, A. Winesett, O. Dhez, W. Zhang, X. Hu, M. Lin, M. Rubinstein, M. Rafailovich, J. Sokolov

Compatibilization mechanism?

TEM DSC



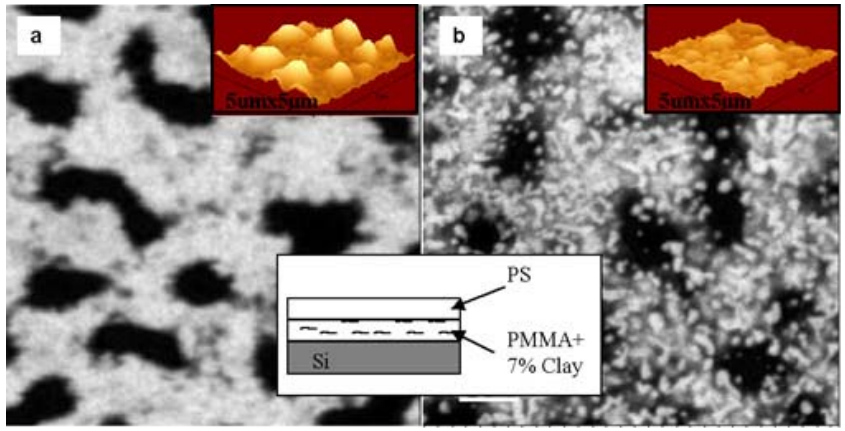
5% Cloisite 6a

10% Cloisite 6a

STXM

PMMA preannealed at 170° for 24 hrs

No preannealing



annealed after bilayer was created for 72 hrs at 170°

Data: Polymer STXM at ALS

Formation of polymer-clay grafts.
Process is not diffusion controlled, but absorption controlled

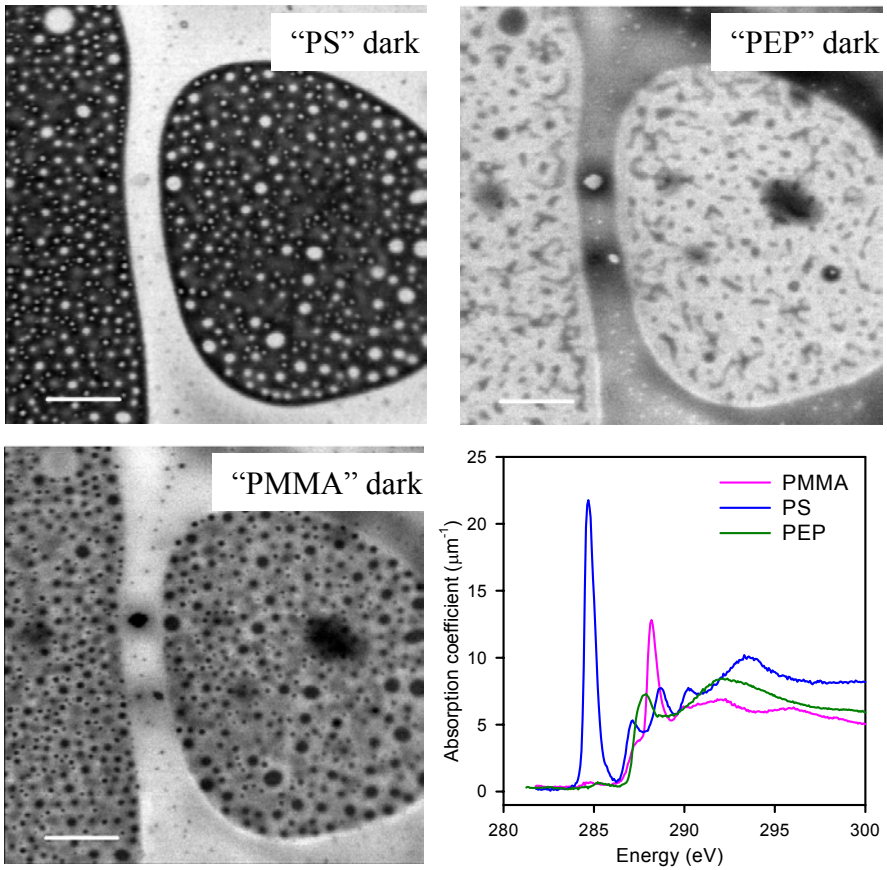
Why NEXAFS microscopy?

- Lots of characterization for than tertiary and more complicated blends
- Quantitative analysis of domains

PS/PMMA/PEP and PS/PMMA/PVC ternary blends

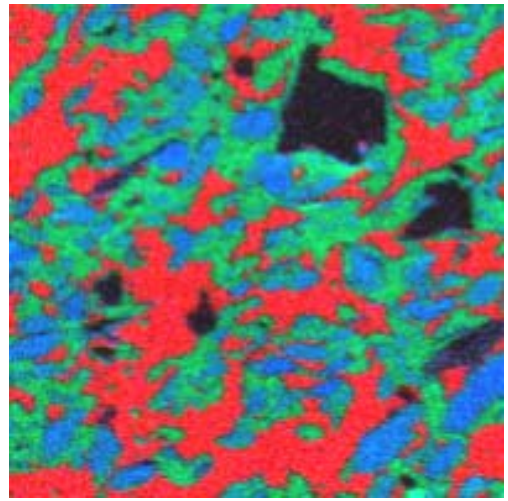
Where are all the components? – Ongoing projects!

PS/PMMA/PEP



Mixtures of PS/PMMA/PEP w/ clay would benefit from better spatial resolution

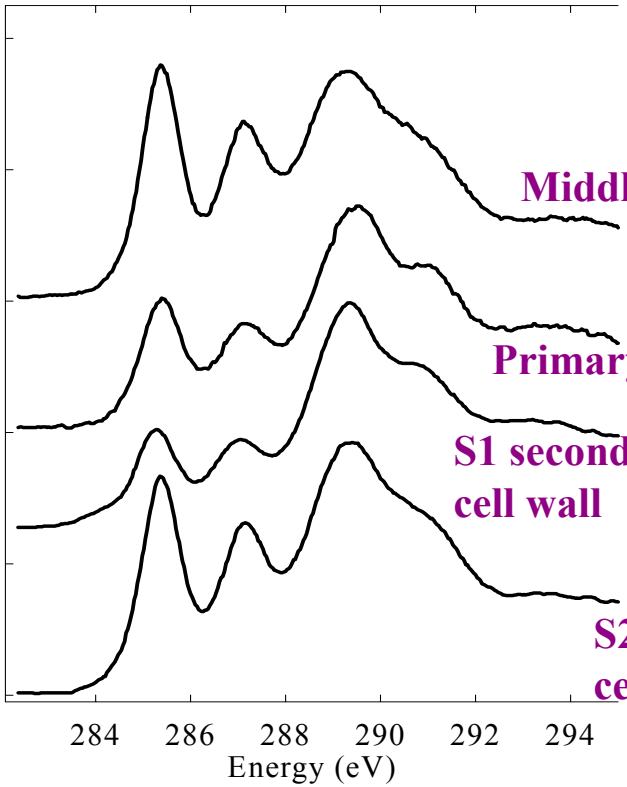
PS/PMMA/PVC



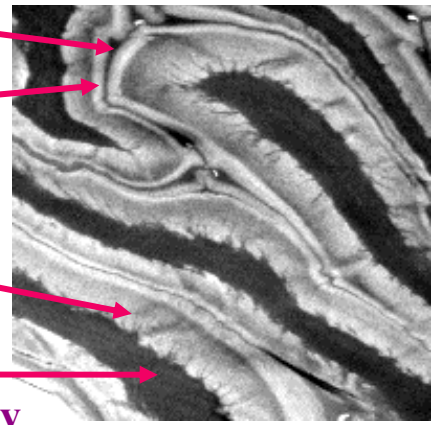
RGB color composite image PS (red), PMMA (green) and PVC (blue) clearly delineating each component. Black areas are holes.

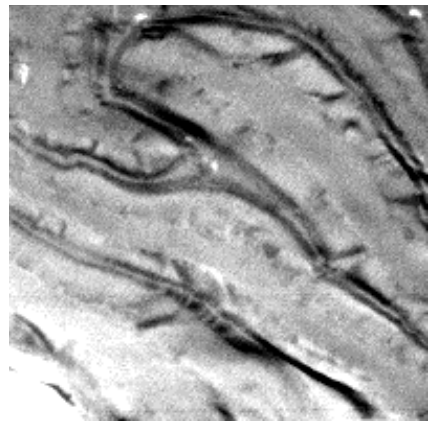
Organic geochemistry, solid phase biomaterials

(G. Cody et al. Geophysical Laboratory, Carnegie Inst.)



Eocene Wood
40 million year old





Map lignin and carbohydrate distribution and characterize their thermal/time evolution

- **Also, spectacular data on evolution of coke → metallurgical coke, steel production**
- **Followed evolution of sporopollenin in coal → may address mechanism/timing of oil generation**
- **More recent wood: Some fungus rot attacks lignin selectively**
- **Organic sediments**

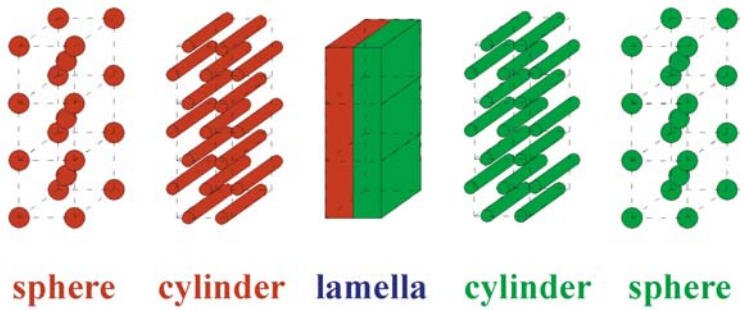
Data: Stony Brook STXM

Why are copolymers so "cool"?

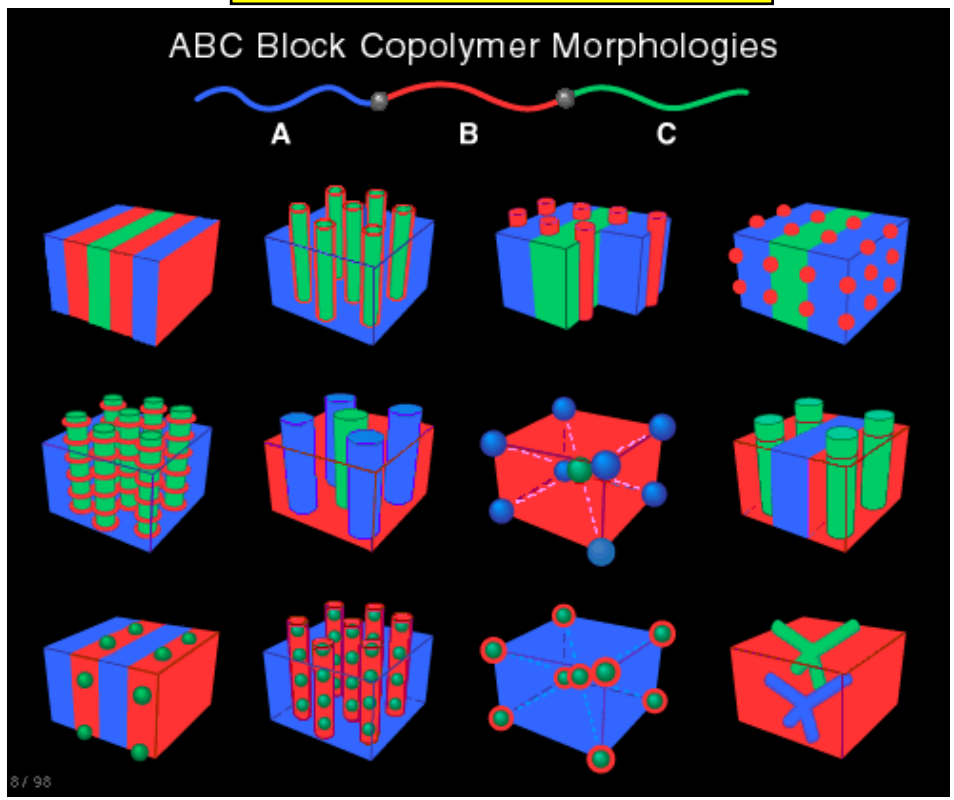
Patterning, selfassembly

Webster's dictionary:

co · pol · y · mer (kō-pŏl'∂-mer) n.
"A polymer of two or more different monomers."

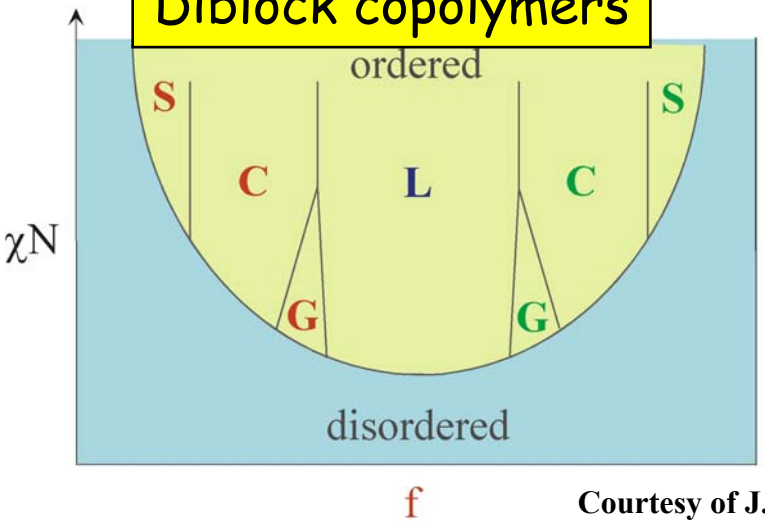


Triblock copolymers



Courtesy of G. H. Fredrickson (UCSB)

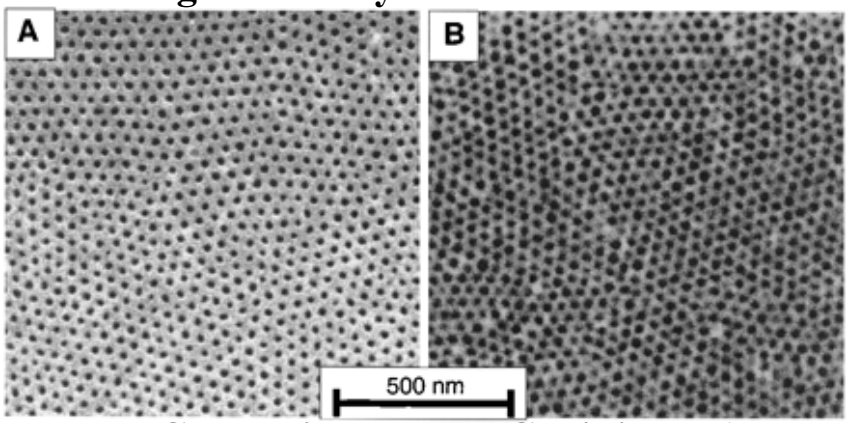
Diblock copolymers



Courtesy of J. Genzer, Chem. E, NCSU

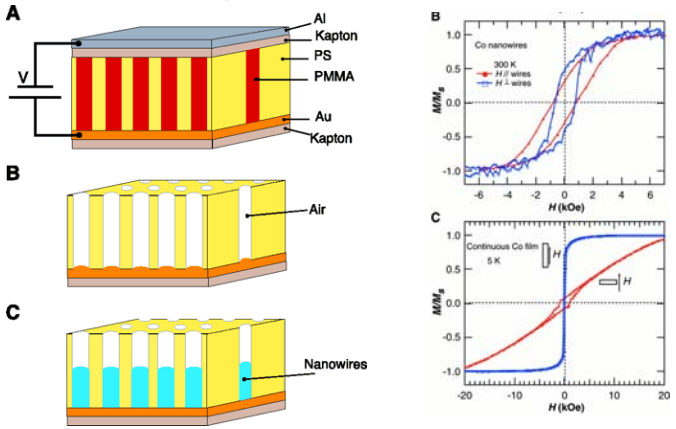
Nanolithography for quantum dots, magnetic storage

Semi-regular Arrays of ~10^{11} holes in 1 cm^2



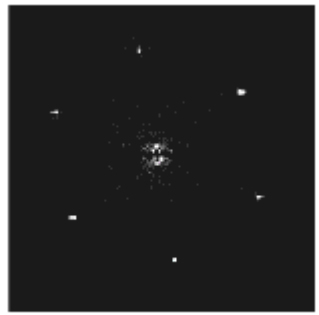
M. Park, C. Harrison, P. M. Chaikin, R.A. Register, D. H. Adamson, Science 276, 1401(1997)

Ultrahigh-Density Nanowire Arrays Grown in Self-Assembled Diblock Copolymer Templates , T. Thurn-Albrecht, et al. Science 290: 2126 (2000)

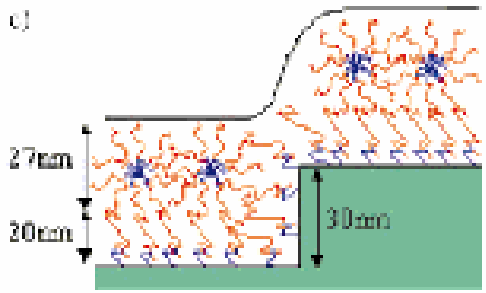


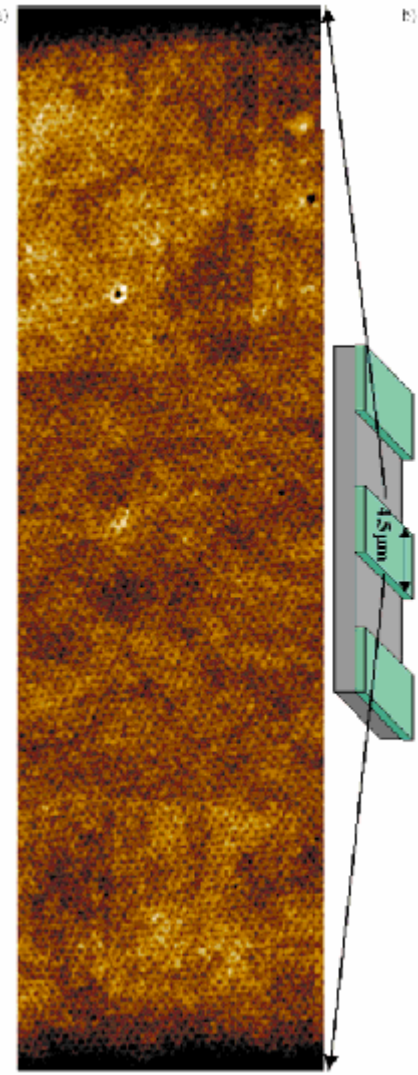
Markedly enhanced coercivity

4.5 μm



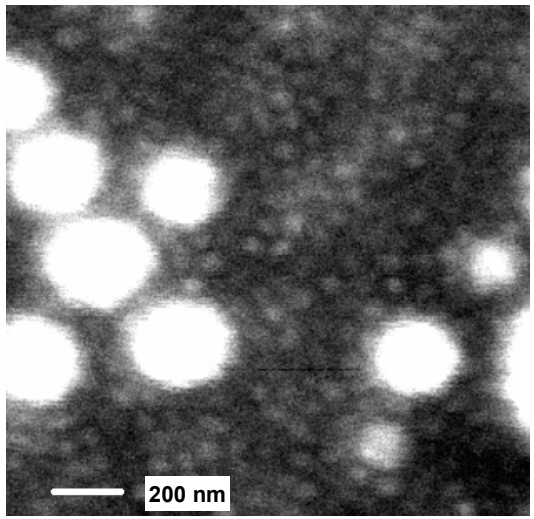
Graphoepitaxy of Spherical Domain Block Copolymer Films
R A. Segalman, H. Yokoyama, E. J. Kramer, Adv. Mater.13, 1154 (2001)



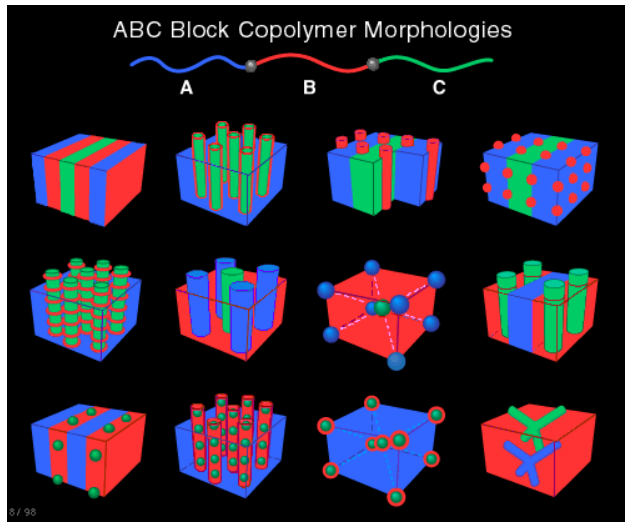


Blockcopolymers:
First attempts with ALS 5.3.2 Polymer STXM

- STXM images at 285.1 eV of 90k-PS-*b*-PEO.
- Hexagonally arranged PEO cylindrical microdomains are about 50 nm in size.
- Larger features are thickness variations.



Blockcopolymer/homopolymer mixtures:
Important class of materials, templating



- Morphologies could be highly complex
- Where does the homopolymer go?

- Higher resolution, higher intensity needed!!!

NEXAFS microscopy of organic materials

- **NEXAFS microscopy is a powerful characterization tool for any organic nanomaterial**
  - **Quantitative compositional analysis (surfaces and transmission)**
  - **Orientational analysis (surfaces and transmission)**
  - **Wet (solvated) samples (special cell in transmission)**
  - **Relatively low radiation dose/damage**
- **Oxygen and nitrogen K edge NEXAFS can provide additional information if O and N present**
- **Still a lot of room for instrument/methodology/source improvements**
- **STXM**
  - **50-250 nm thick samples ideal for best S/N**
  - **few minutes for images or good spectra**
  - **lower damage than TXM**

RESONANT X-RAY SCATTERING

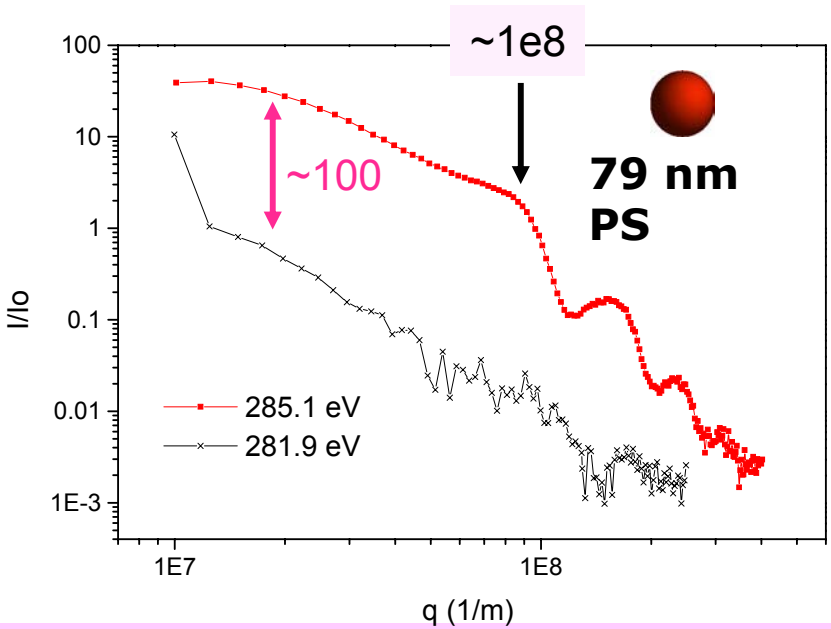
Ensemble-average "NEXAFS Microscopy": Size, shape, distribution

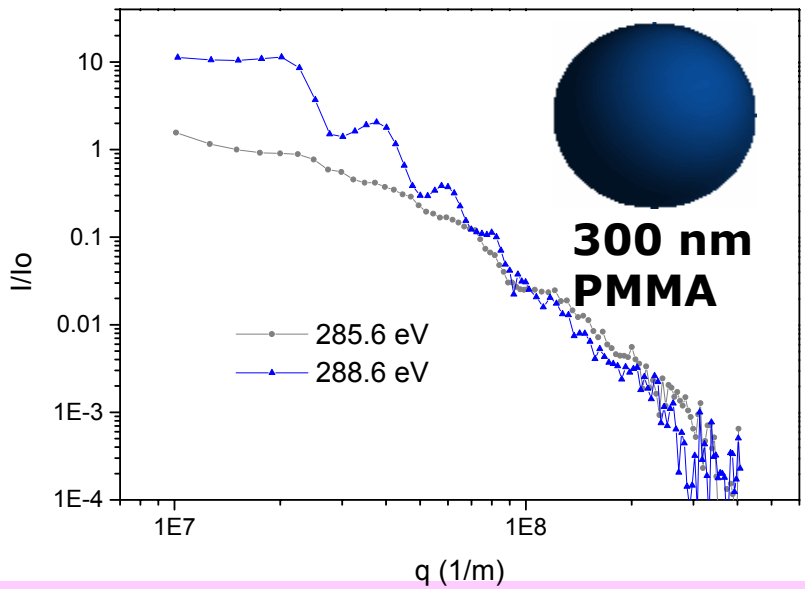
Gary Mitchell,B. Landes, J. Lyons, B. Kern, M. Devon, I. Koprinarov, J. Kortright

Complex atomic scattering factors for carbon in the forward scattering direction

$$f_1 = Z + \frac{1}{\pi r_e hc}\int_0^\infty \frac{\varepsilon^2 \sigma_a(\varepsilon)}{E^2 - \varepsilon^2} d\varepsilon \qquad f_2 = \frac{\sigma_a}{2 r_e \lambda}$$

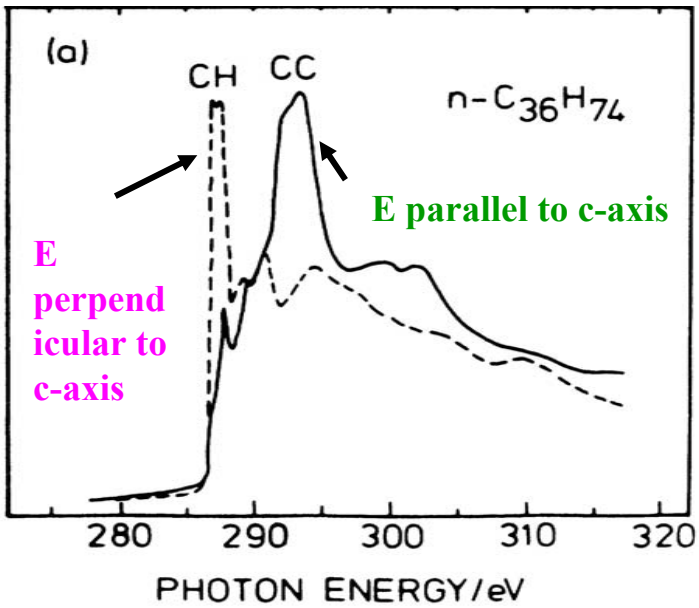
Tuning to the certain energies will switch on/off the scattering.



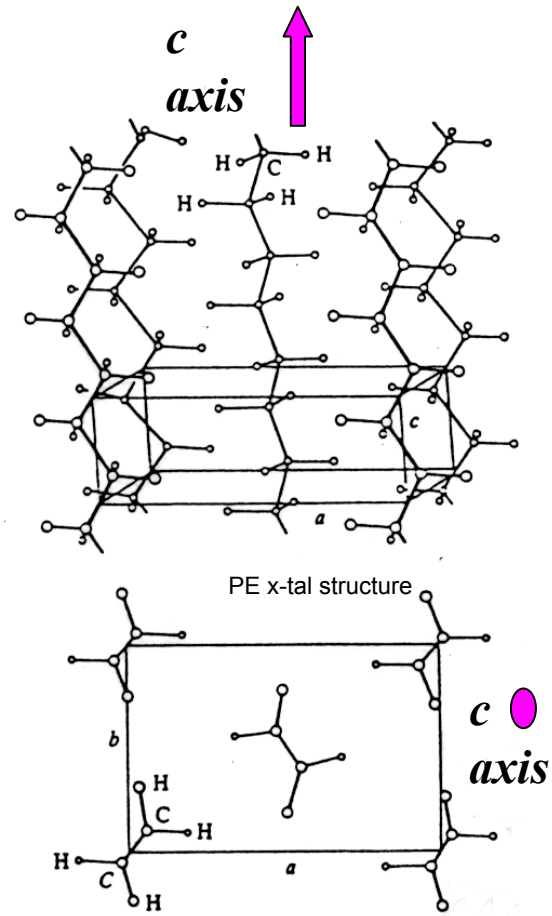


The Future:

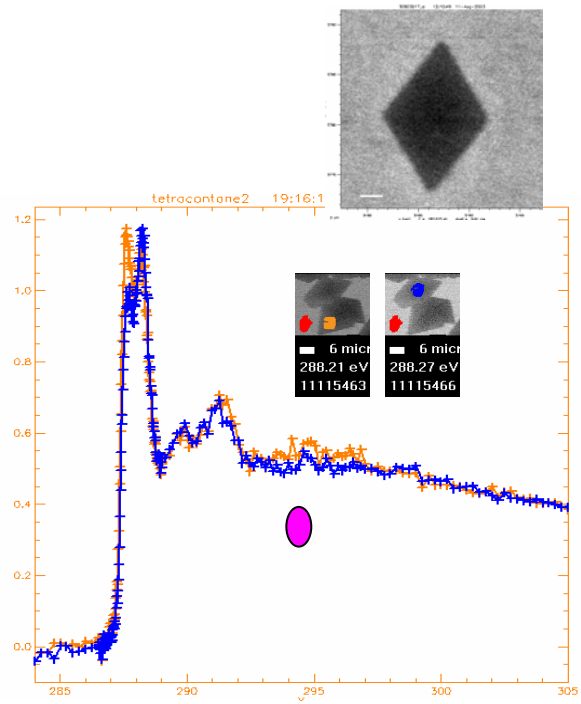
Ingredient #1: Better spectroscopy/understanding



Sign of Dichroism: Molecule is "standing" up on surface, i.e. c-axis of orthorombic cell is normal to surface



Sample: tetracontane

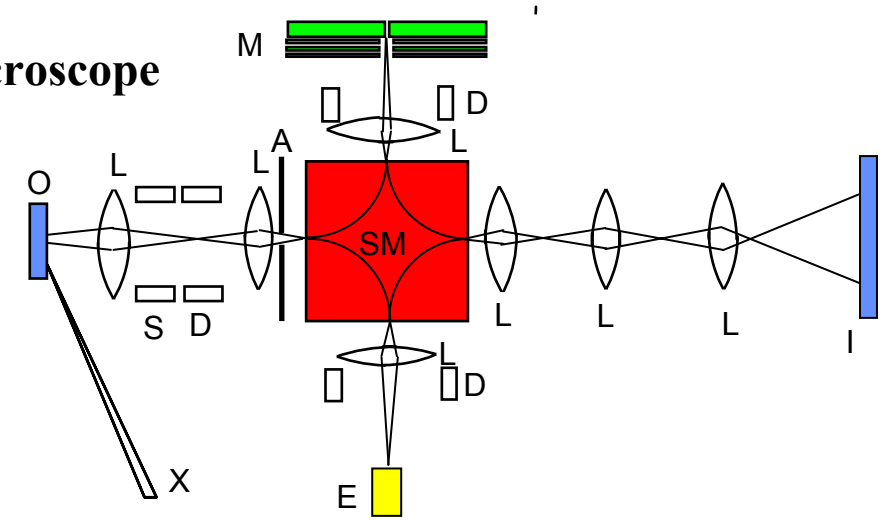


(Appel, Koprinarov, Ade, unpublished. ALS 7.0 STXM)

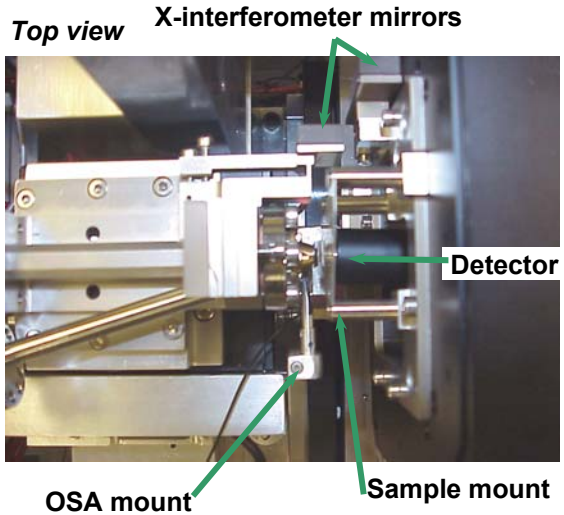
The Future:

Ingredient #2: Better instruments

Aberration corrected Photoemission Microscope
Anticipated 2 nm spatial resolution



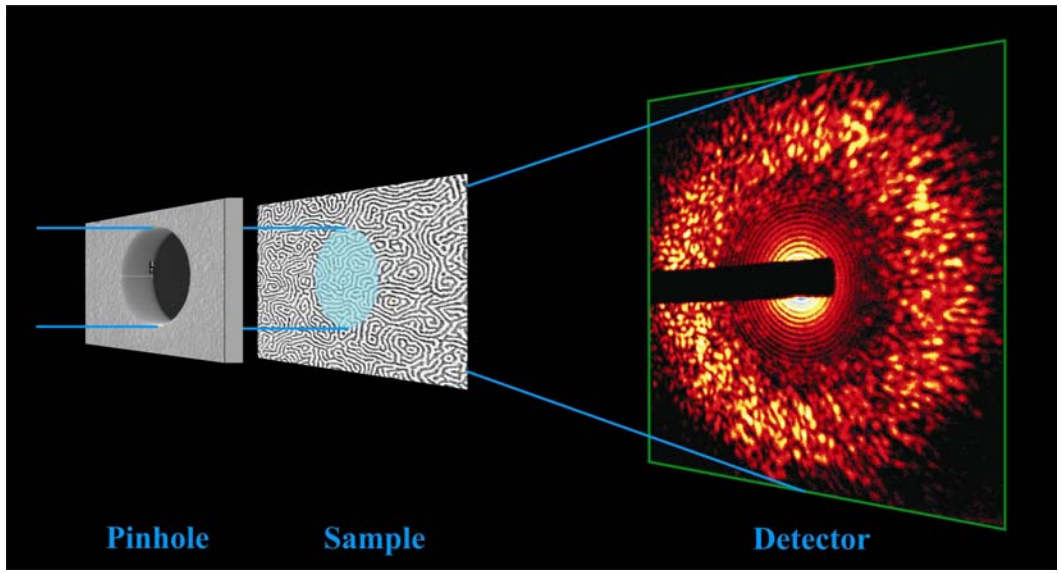
Interferometer based STXM's ready for 10 nm zone plates



The future:
Ingredient #3:
New tools

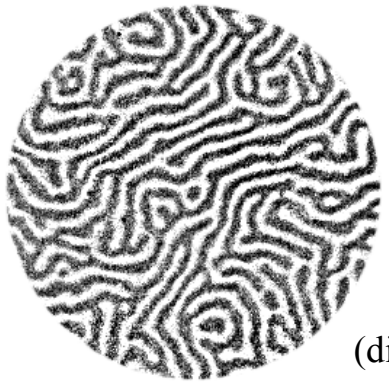
Technique of choice for dynamics

Imaging by Coherent X-Ray Scattering

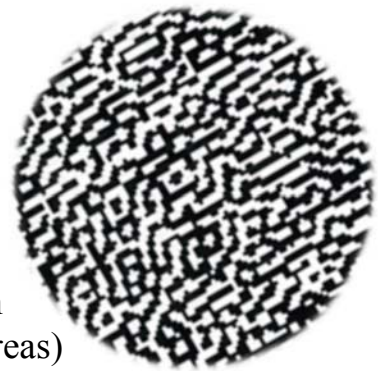


Phase problem can be solved by "oversampling" speckle image

Transmission X-ray Microscope



∅ 5 μm (different areas)



Reconstruction from Speckle Intensities

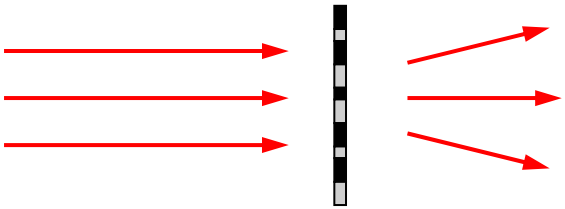
Figure courtesy J. Stohr

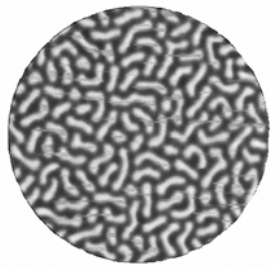
S. Eisebitt, M. Lörgen, J. Lüning, J. Stöhr, W. Eberhardt, E. Fullerton (unpublished)

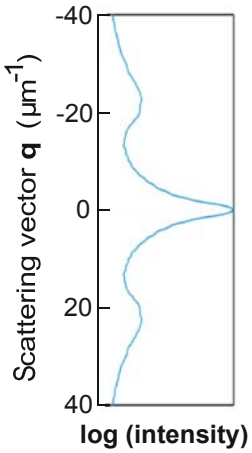
Incoherent vs. Coherent X-Ray Scattering

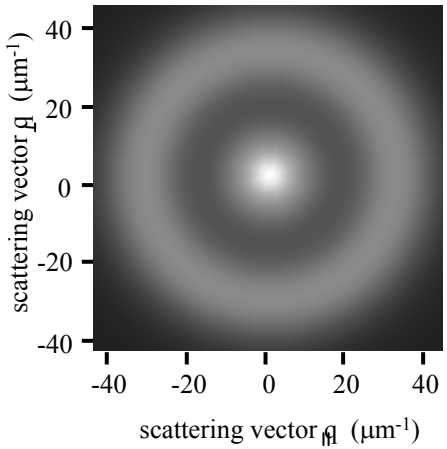
Small Angle Scattering

Coherence length larger than domains, but smaller than illuminated area





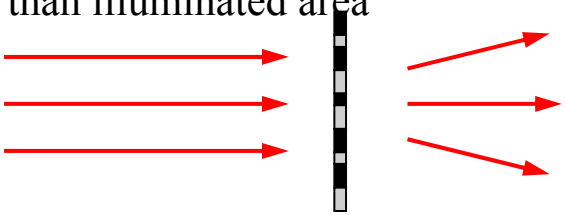


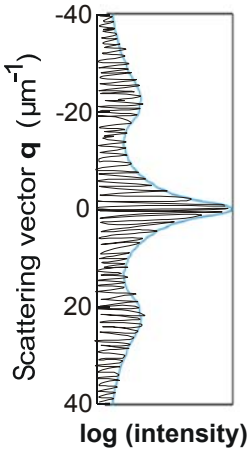


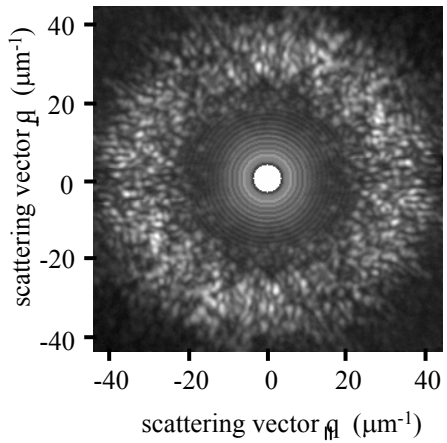
information about domain statistics

Speckle

Coherence length larger than illuminated area







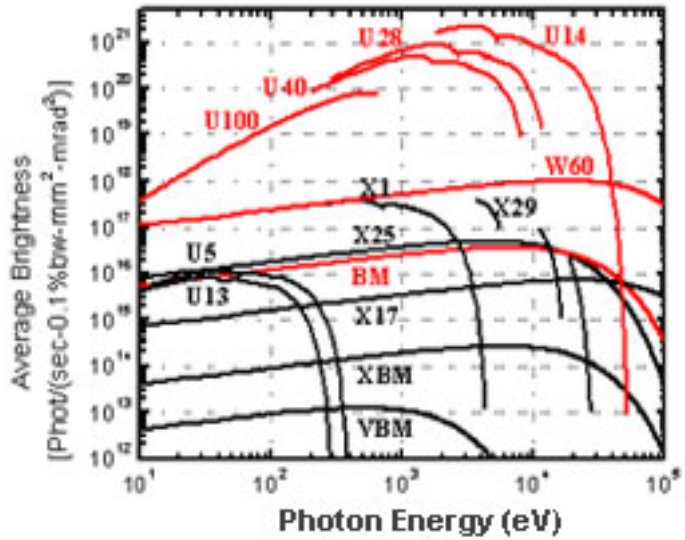
true information about domain structure

Figure courtesy J. Stohr

Resonant scattering and resonant speckle should be excellent tools for organic materials !!!!

The future:
Ingredient #4: New sources; NSLS-II main characteristics

- **Bending magnet STXM as work-horse.**
  - **If optimized, >10x performance of Stony Brook STXM at X1A. (ALS 5.3.2 "Polymer" STXM is benchmark.)**
- **Undulator STXM, correlative microscopy**
  - **polarization control**
  - **150-2000 eV, many elements**
  - **Fluorescence detection, low concentrations**
- **SPEM**
  - **Work on surfaces benefit most from increased brightness**



The future:
Opportunities

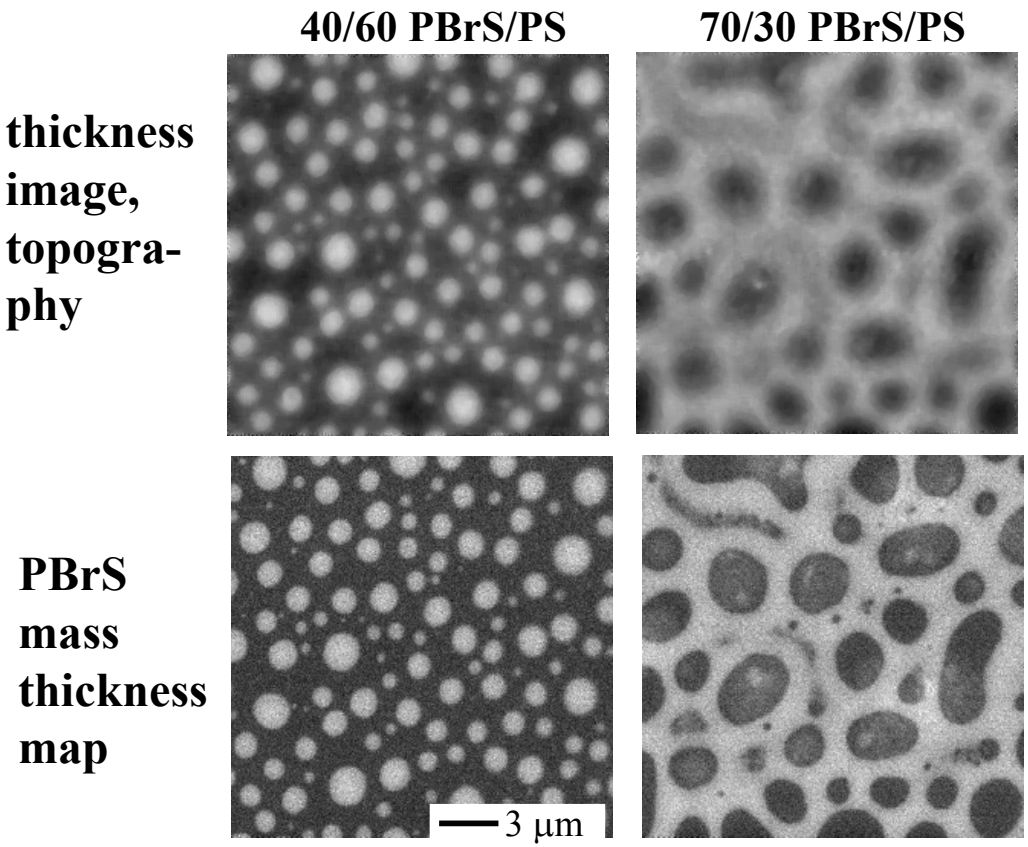
- **Technology: STXM, PEEM, SPEM, dynamic speckle**
  - **Clearly all these techniques will benefit tremendously**

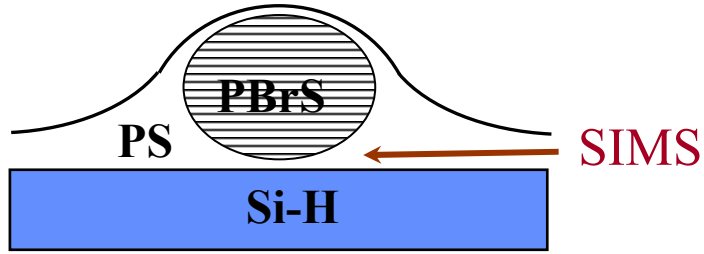
- **Science**
  - **Polymers! Yes, but radiation damage might set a limit**
  - **Polymer-inorganic bybrids**
    - **Templating**
  - **Electronic structure of single carbon nanotube (sorry, no cartoon)**
    - **Robust and important material**
    - **Back of the envelop calculations show this should be doable in transmission and/or in TEY-mode**
    - **Due to significantly increased S/N requirements, source stability requirements are very high**

Thank you for your attention!!!!

PBrS/PS blends in thin films

1000A thick films spun on Si (HF stripped oxide), annealed at 170°C for 12 hrs.





$\gamma_{PS/vac}$ = 30.5 dyn/cm and $\gamma_{PBrS/vac}$ = 33.7 dyn/cm

dispersive contribution of PBrS surface found to be $\gamma_{PBrS/Si\text{-}H}^{d}$ < 20 dyn/cm

Surface tension of PBrS is about 39% polar

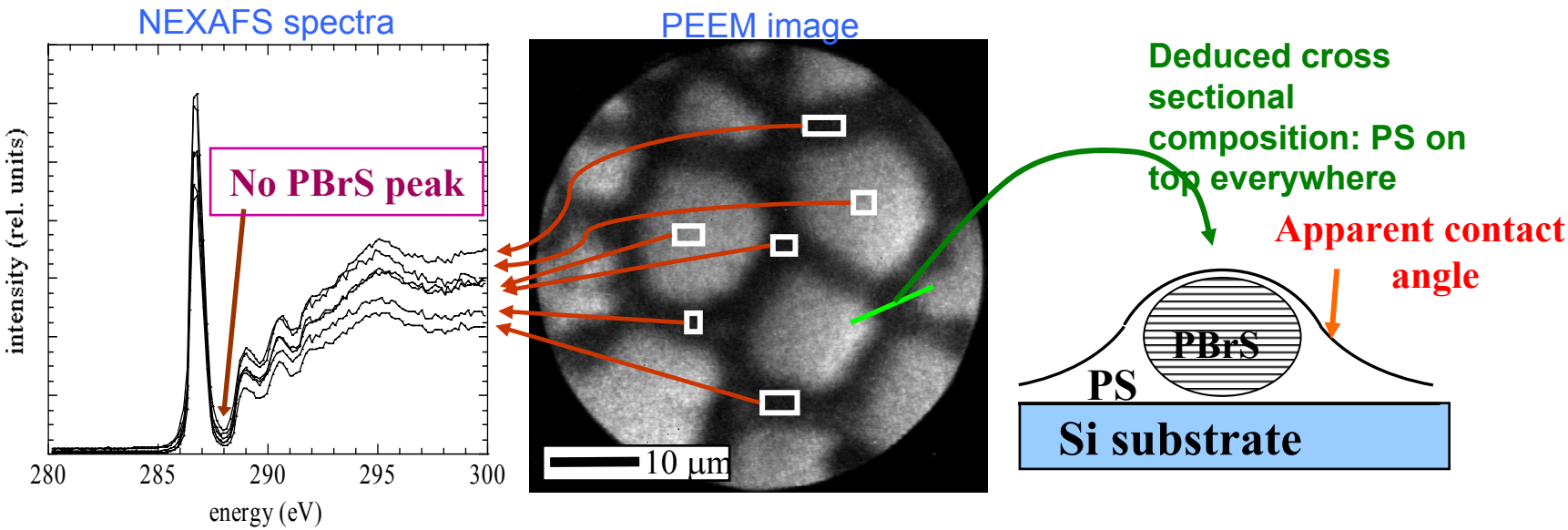
D. Slep, J. Asselta, M. H. Rafailovich *et al.*, Langmuir 14, 4860 (1998)

Dewetting of polymer bilayers

30 nm of PBrS on top of 50 nm PS

H. Ade et al.
Appl. Phys. Lett. 73, 3775 (1998)

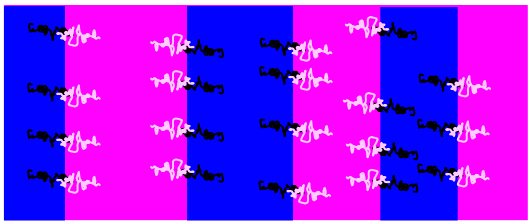
- STXM (or other technique) can not tell for sure which polymer is on surface
- Surface NEXAFS spectra via X-PEEM
  - 2-10 nm surface sensitivity, here about 200 nm spatial resolution
  - 1 week at 180° C, spectra show only PS peak, no PBrS signature



- Could monitor dynamics and deduce pathways
  - PBrS gets encapsulated via plug flow, not PS diffusion through PBrS

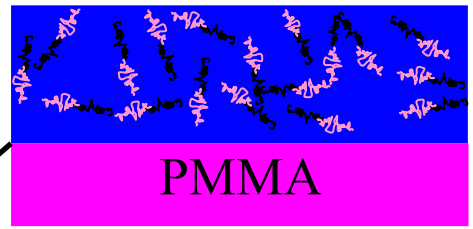
Compatibilization of PS/PMMA thin film bilayers/blends

Preferred/ideal case

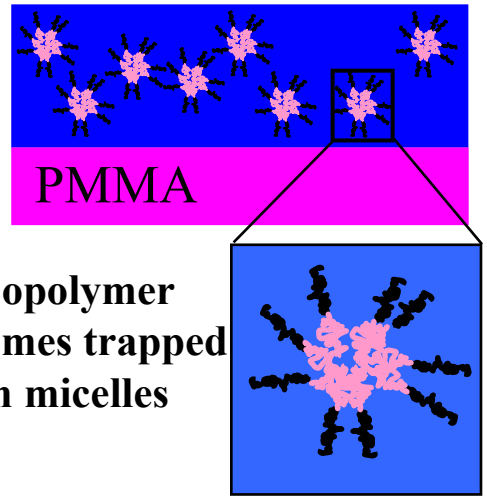


Copolymer locates to the interface to reduce interfacial energy.

Addition of PA/PMMA diblock copolymer



Reality in many cases



Copolymer becomes trapped in micelles

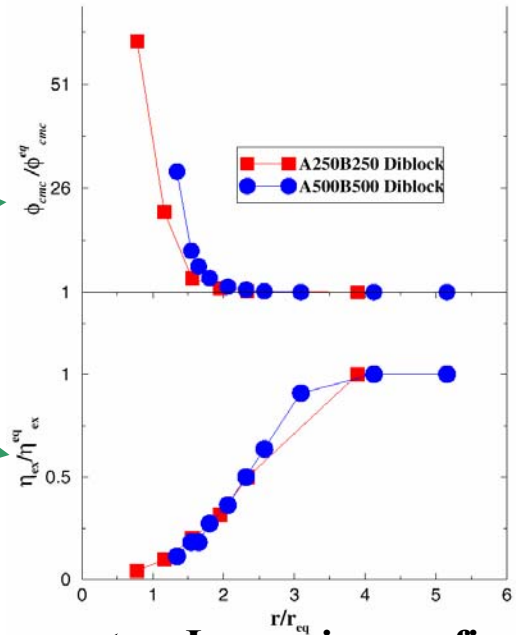
Effects of Confinement

Theory by D. Gersappe, et al

Confinement (small r) increases the critical micelle concentration, ϕ_{cmc}

Consequently, micelle size (η) is reduced which significantly increases the chemical potential of micelle formation

With high degree of confinement, ($r < \eta_{bulk}$), the creation of micelles becomes energetically unfavorable



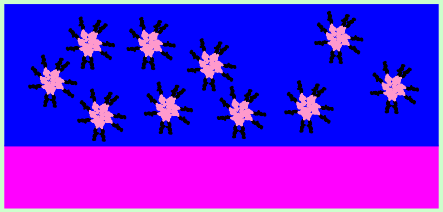
← Increasing confinement

S. Zhu, Y. Liu, M. H. Rafailovich *et al.*, Nature 40, 49 (1999)

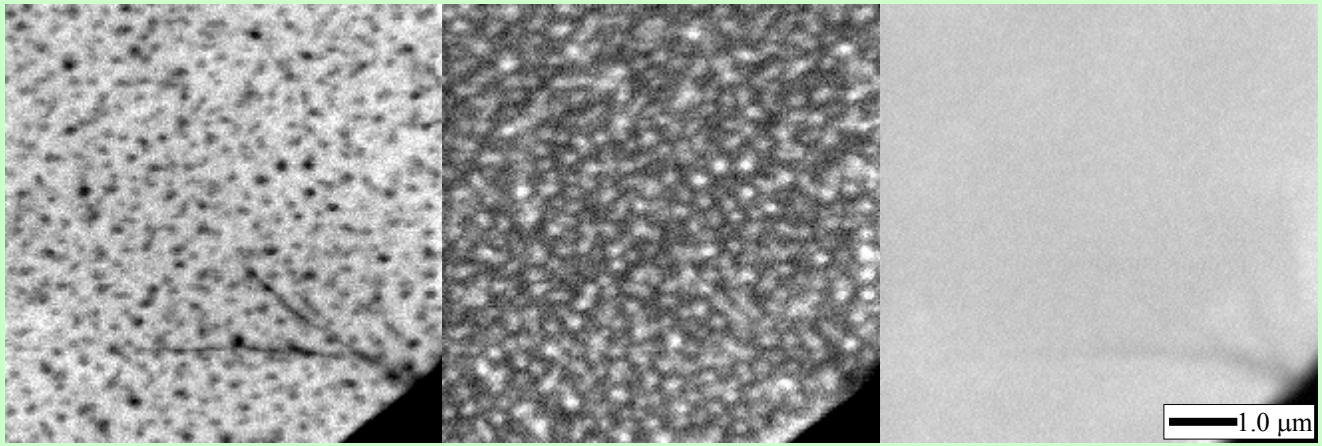
Results

Compositional mapping.
Samples annealed 4 days at 170° C.

78 nm Top Diblock layer

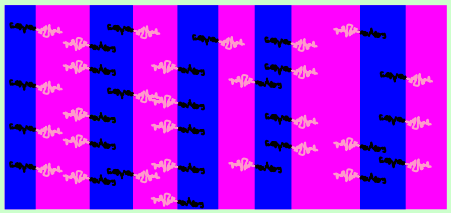


Micelle formation

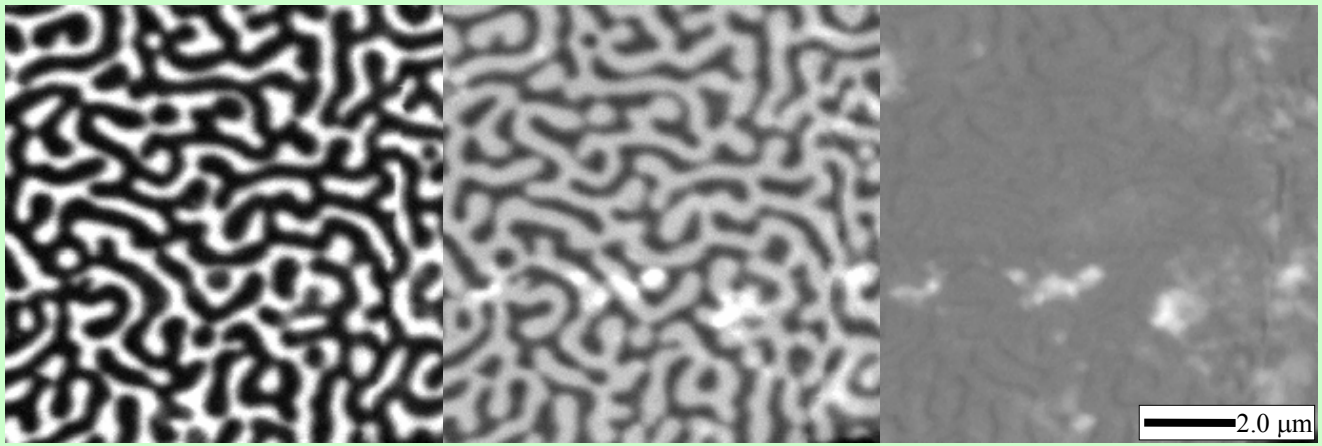


PS PMMA PS + PMMA

30 nm Top Diblock layer

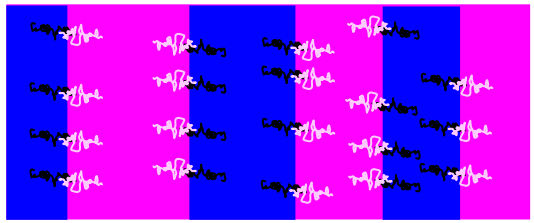


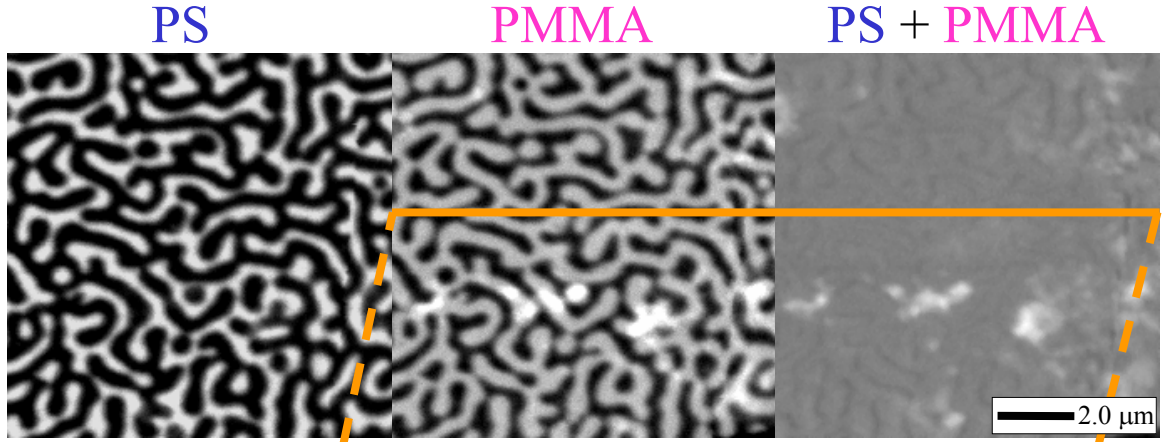
Micro-emulsion



30 nm Top PS/Diblock layer, 80 nm lower layer

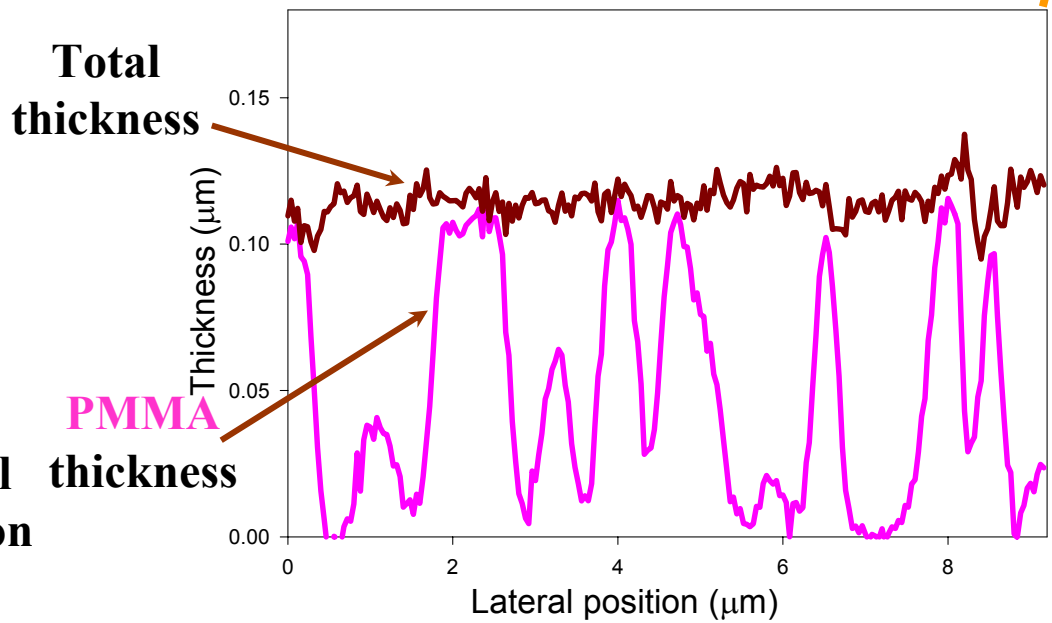
Annealed for 4 days





Quantitative compositional mapping with NEXAFS microscopy reveals:

- **PS and PMMA phases extend through entire film**
  - **Micro-emulsion phase is two dimensional**
- **Our approach, based on a physical phenomenon, removes limitation on the kind of polymers that can be used for thin film blends**



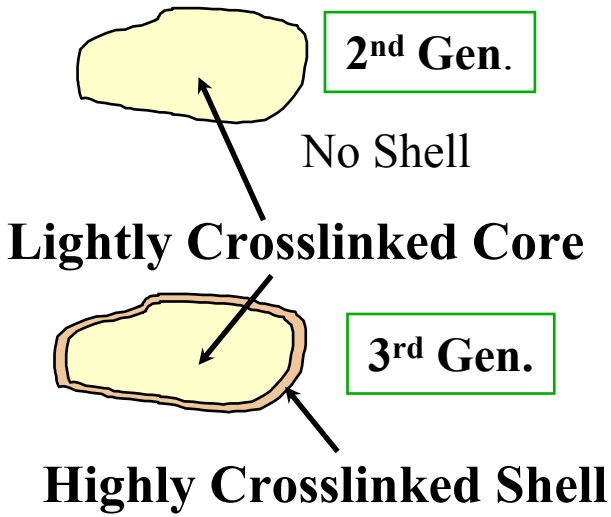
Data: Stony Brook STXM, NSLS S. Zhu, Y. Liu, M. H. Rafailovich *et al.*, Nature 40, 49 (1999)

X-ray Microscopy of Superabsorbent Polymers (SAP)

G. Mitchell, E. Rightor, et. al (Dow), S. Urquhart, H. Ade (NCSU), A. Hitchcock (McMaster) et al.

- Superabsorbent polymers absorb up to 60x their weight in water (~30x in salt water). Primarily medical and cosmetic applications
- 3rd generation SAP technology provides enhanced properties using structured crosslinking
- No conventional tool to measure surface crosslink density

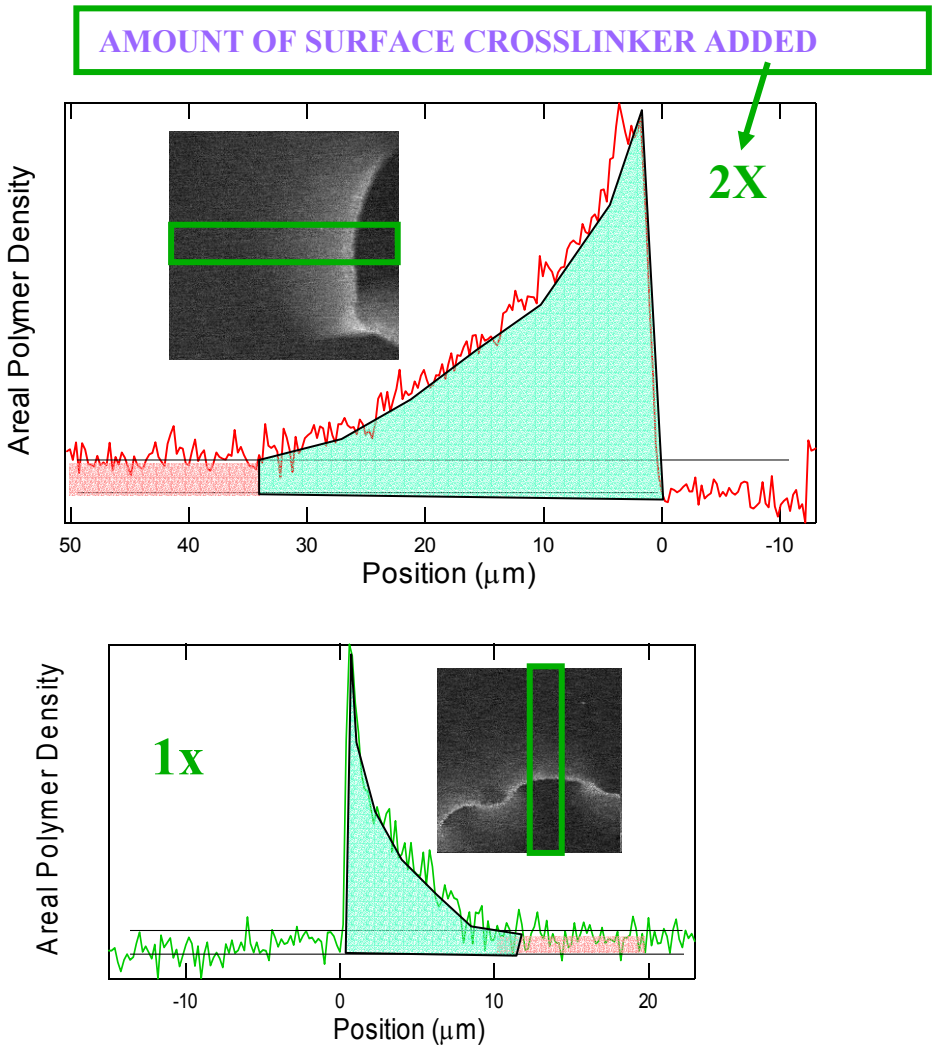
- STXM has visualized crosslink density in 3rd generation superabsorbent polymers
- Understanding the actual crosslink density will help to design improved SAPs and to tailor them to particular applications
- These experiments will also provide insight into competitive processes and economics



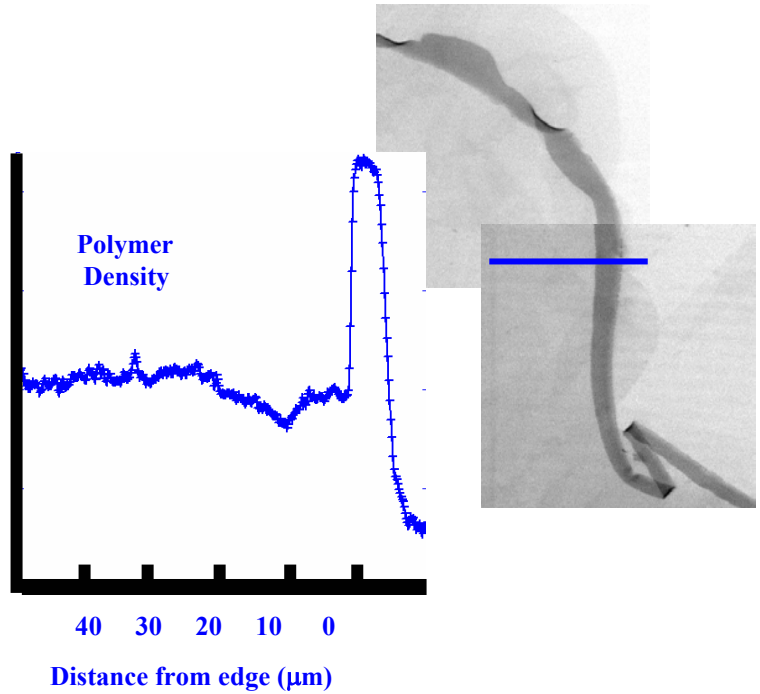
This is actually High-Tech !

Characterize and Compare Different Surface Crosslink Processes

Process I: "Diffusion Controlled"



Process II: "Reaction controlled"



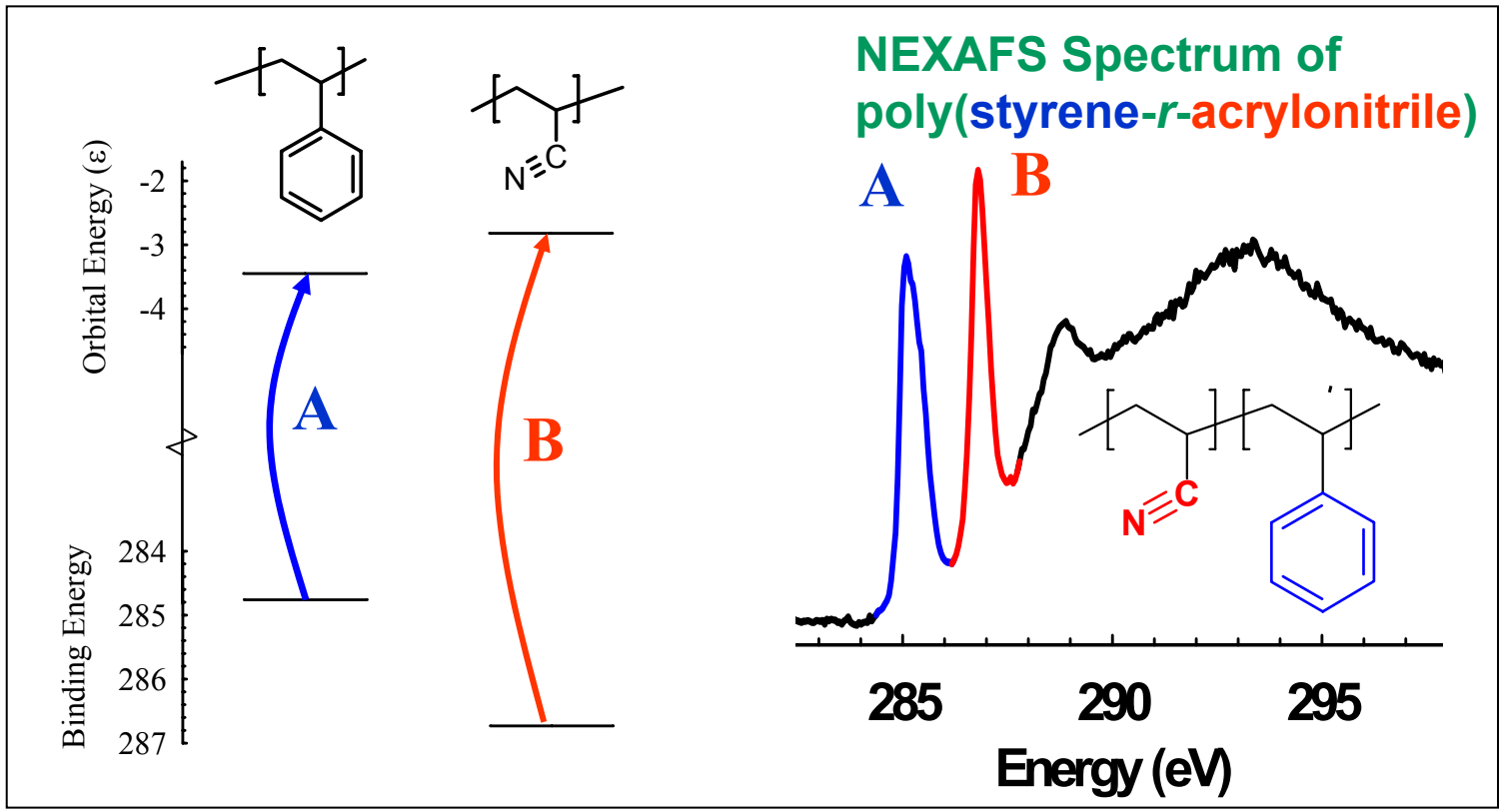
Very different crosslink density profile

G. Mitchell and E. Rightor received ALS Shirely Science Award in 2001

Data: BL7.0 STXM

G. Mitchell et al. Macromol 35, 1336-1341 (2002).

NEXAFS Quantitation: Additivity



- **Spectral features are "additive" if there is no change in the electronic structure due to chemical, i.e. bonding, or matrix interactions**
- **Generally, there are no matrix effects between molecules or polymer chains**
  - **Exceptions in PE and maybe all semi-crystalline polymers**

Polymer STXM "community" in North America

- NCSU: A. P. Smith, D. A. Winesett (now EXXON), O. Dhez, G. Appel, A. Garcia, R. Spontak, R. Fornes, R. Gilbert, D. Kilcoyne, ...
- McMaster: A. P. Hitchcock, Ivo Koprinarov, Tolek Tyliszczak (now ALS), et al.
- Univ. of Saskatchewan at Saskatoon: S. Urquhart et al.
- SUNY@Stony Brook: M. Rafailovich, J. Sokolov, et al. ..
- Geophysical Laboratory, Carnegie Institution: G. Cody
- Dow Chemical: G. Mitchell, E. Rightor, ...
- EXXON: J. Das, D. A. Winesett, P. Stevens, S. Cameron, ...
- DuPont, GE, AlliedSignal, IBM
- Photons Unlimited: C. Zimba
- UMASS: T. Russel et al.

- Instruments: S. Anders, T. Warwick, C. Jacobsen, J. Kirz, S. Wirick, etc.

Funding at NCSU (Research and 5.3.2 Polymer STXM)):

- NSF-NYI (DMR-9458060), NSF (DMR-9975694, DMR-0071743)
- DOE (DE-FG-02-98ER45737), Dow Chemical, DuPont, NCSU.

Zone Plates: Diffractive Optics for X-rays

Developed by groups in Goettingen, LBNL, Stony Brook/Lucent, a few others

- 1975: Modern Area X-ray Microscopy starts: First TXM at DESSY. B. Niemann, D. Rudolph and G. Schmahl
  - 1978: Move to ACO
  - 1982: Move to BESSY-I
- 1982: First STXM at NSLS: Rarback and Kirz

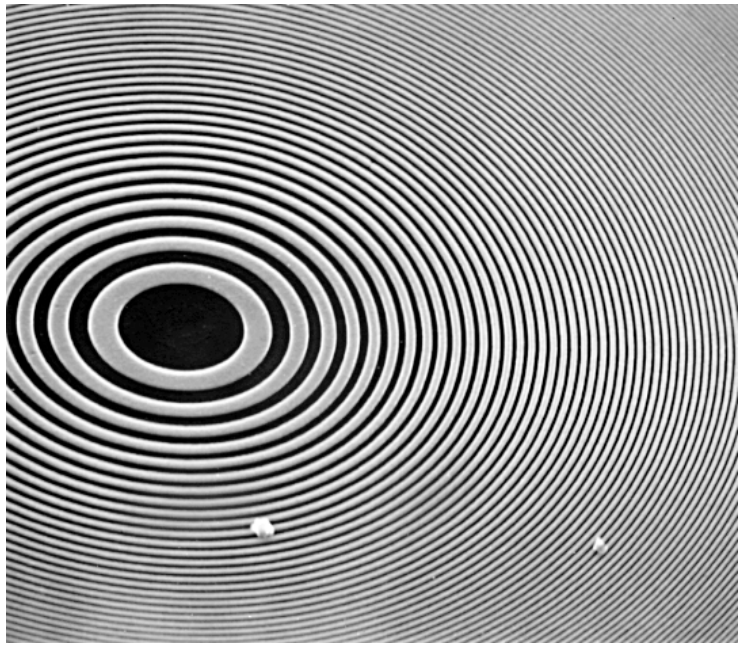


Image from http://www-cxro.lbl.gov/microscopy/diffractive.html

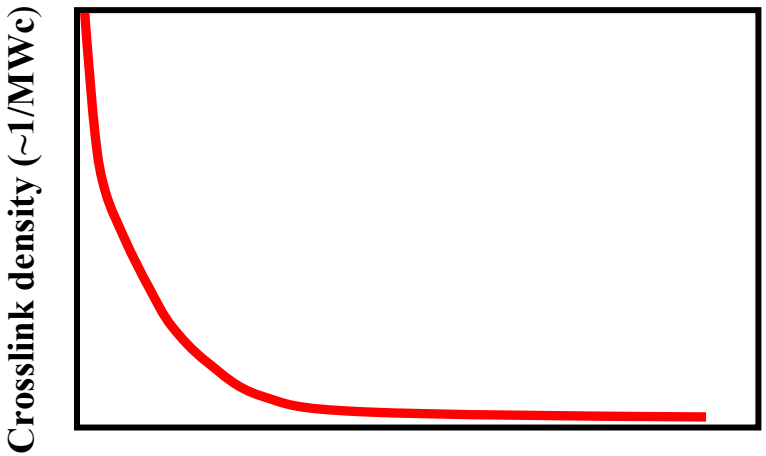
- Circular Au, Ni, or Ge structures
- Nanofabrication with E-beam lithography (early on it was holography)
- Spatial resolution approx. outermost zone width
- Focal length is proportional to energy

- Diameter: 50-200 microns
- Zone widths presently as small as 20 nm

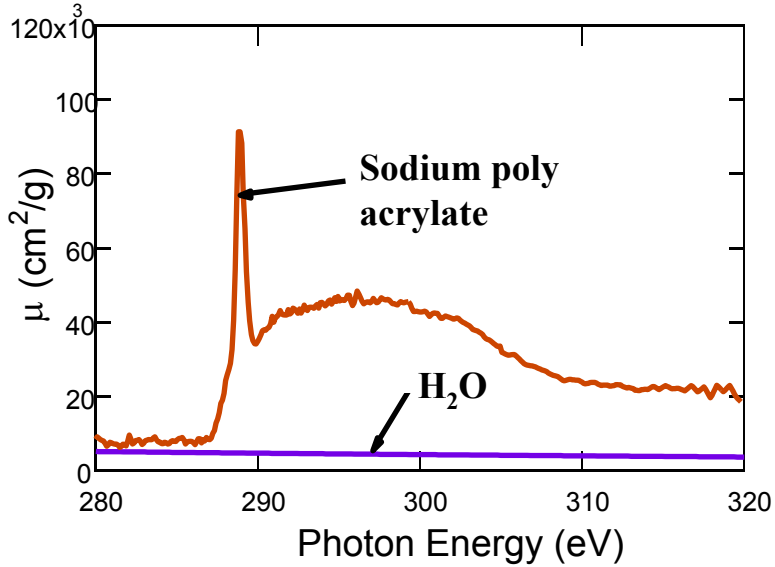
- Crosslink density about 0.1%
- hard to detect spectroscopically

Flory-Rehner equation relates swelling and crosslink density:

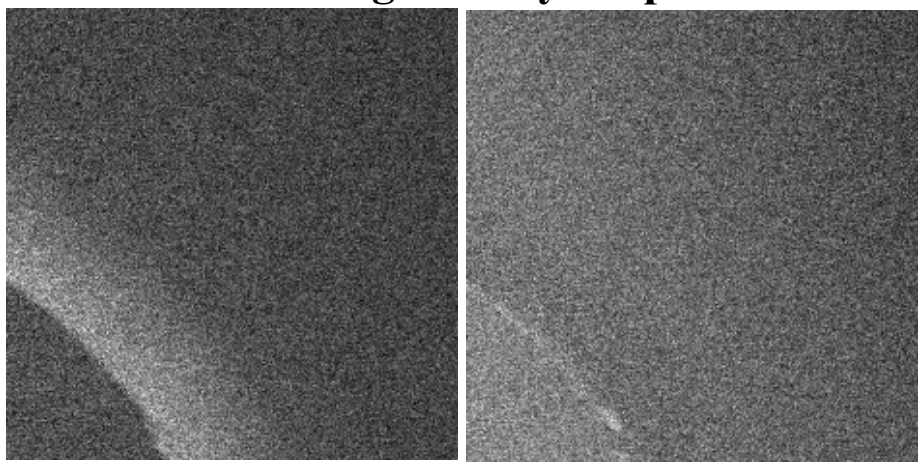
$$MW_c = \frac{V_s d_p (\Phi_p^{1/3} - \Phi_p)}{(Ln(1 - \Phi_p) + \Phi_p + \chi\Phi_p)}$$



P. Flory, and J. Rehner, Journal of Physical Chemistry, 11(1943) 512



Resulting Density Maps:

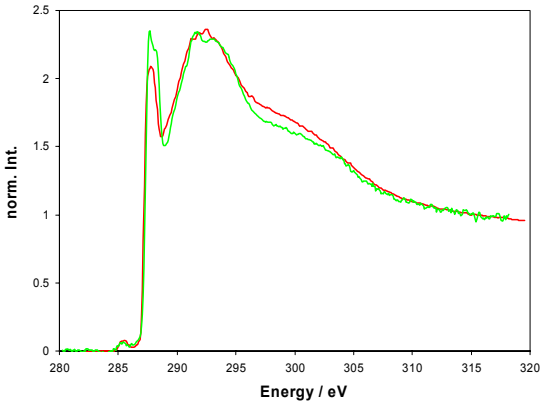


Polymer **water**

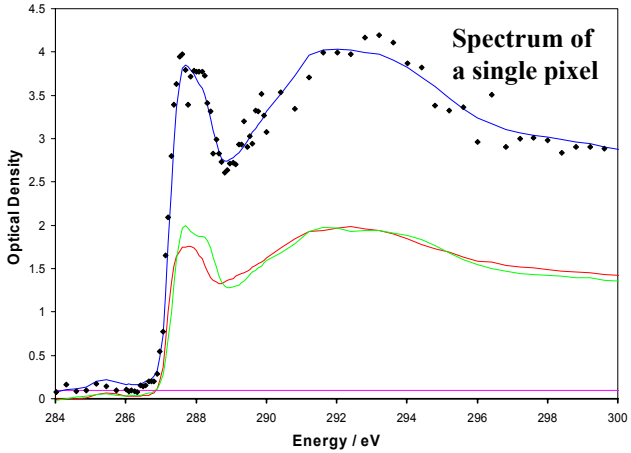
Images: Quantitative Analysis

We assume "ideal" behavior: The spectra of mixed phases are fitted by a linear-combination of the reference spectra and a constant:

Reference Spectra

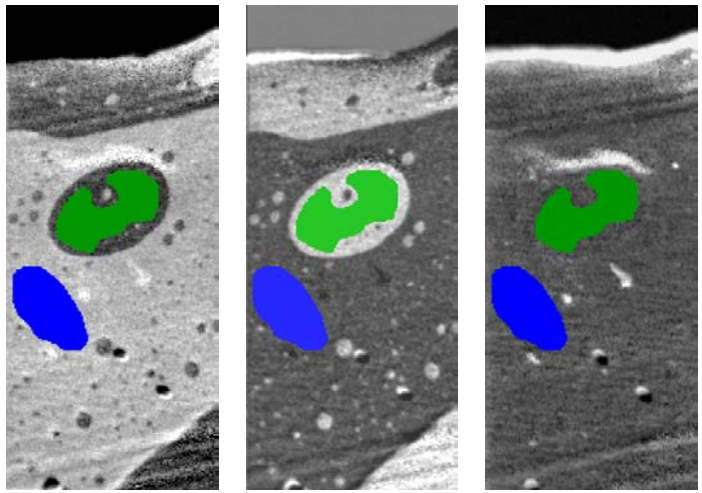


"Stack" Fit*)



Component Maps

EO BO constant



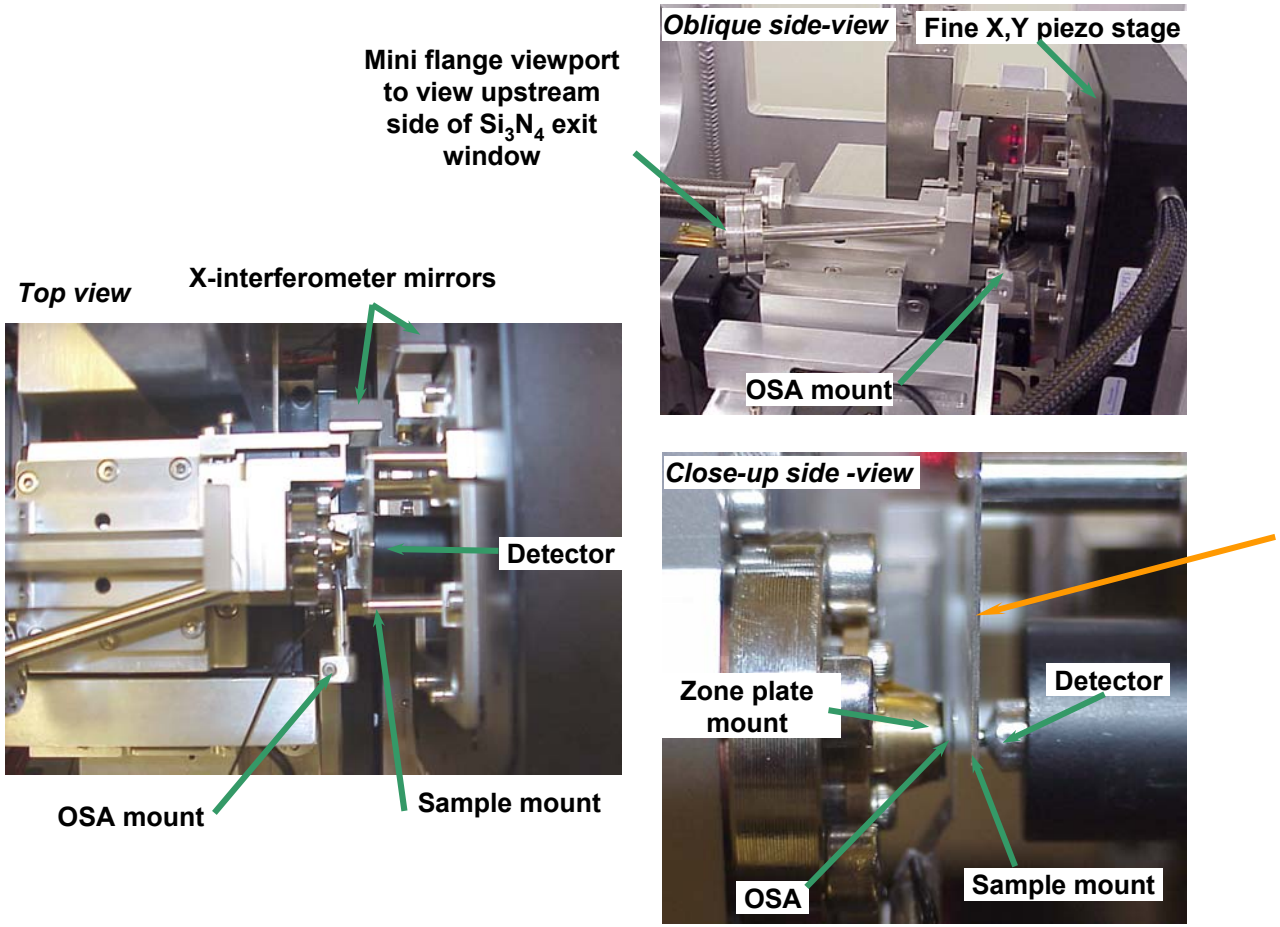
- Average over undisturbed regions of the **matrix** and the **minority phase**.
- Normalize to get the composition of these phases:

$$\Phi_{oct} = \frac{t_{oct}}{t_{oct} + t_{but}}$$

$$OD(E, x, y) = t_{oct}(x,y)*R_{oct}(E) + t_{but}(x,y)*R_{but}(E) + constant(x,y)$$

*) Hitchcock A.P., AXIS 2000 (Analysis of X-ray microscopy Images and Spectra, Version 2.0).

Some close-up views of 5.3.2 hardware



10-20 micron reproducible mounting. - VLM pre-indexing in the future with absolute coordinate system

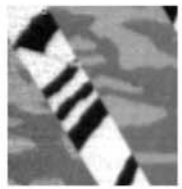
Space

The Microworld

10^{-3} m — 1 mm

100 μm

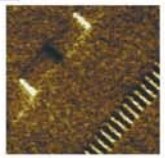
AFM & FM domains



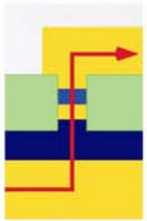
10 μm

10^{-6} m — 1 μm

Recorded "bits"



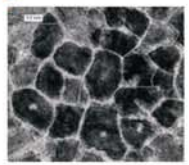
Spin injection



The Nanoworld

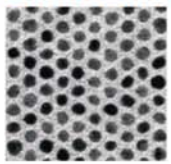
100 nm

Media grains



10 nm

Nano-particles

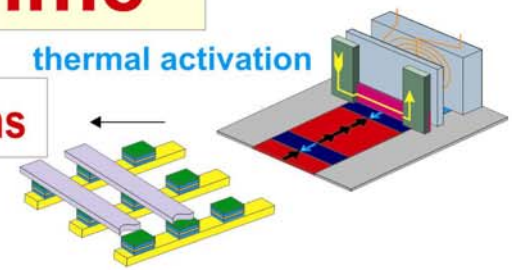


10^{-9} m — 1 nm

Time

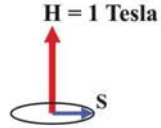
10^{-9} s — 1 ns

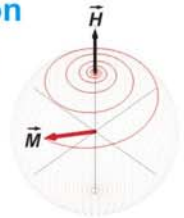
thermal activation



100 ps

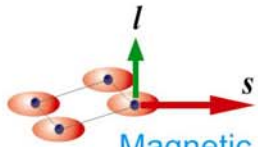
spin precession and damping





10 ps

10^{-12} s — 1 ps



Spin-orbit coupling

Magnetic anisotropy

100 fs

10 fs

Exchange interaction

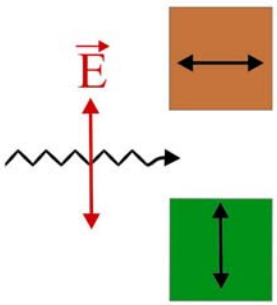
10^{-15} s — 1 fs

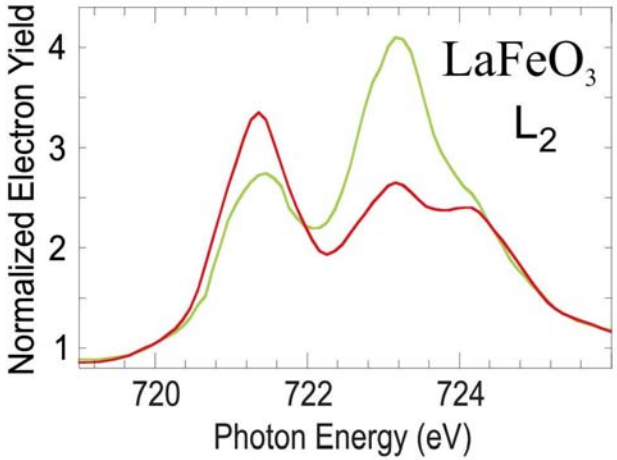
Note: Δt (fs) = 4 / ΔE (eV)

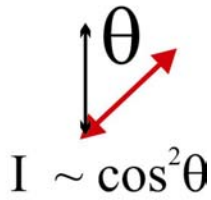
H. Ade et al., NSLS-II_ade_march2004.ppt

Magnetic Spectroscopy and Microscopy

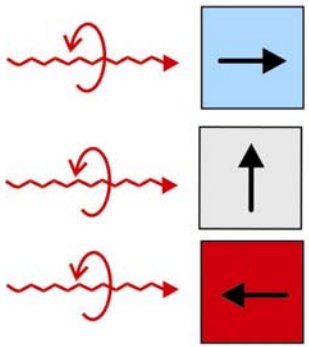
X-ray Magnetic Linear Dichroism: Antiferromagnets

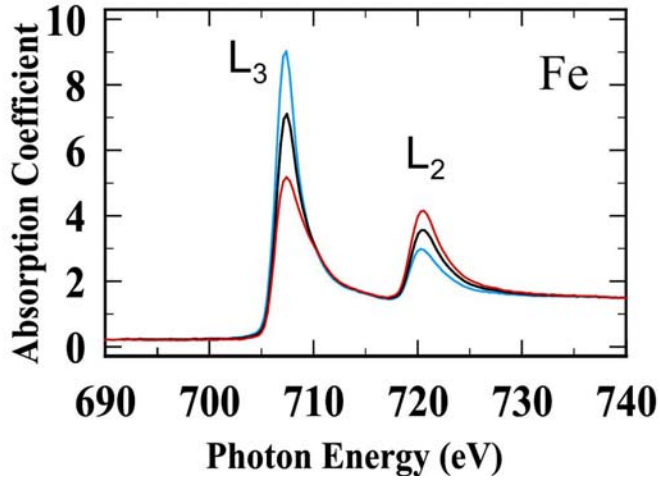


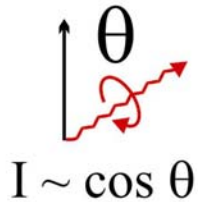




X-ray Magnetic Circular Dichroism: Ferromagnets







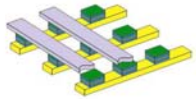
(courtesy J. Stohr)

Time

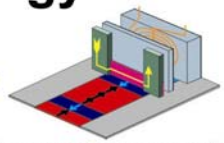
Science

Technology

10^{-9} s — 1 ns

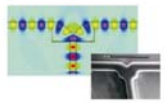


Computing time per bit

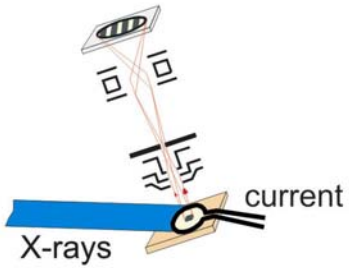


Magnetic recording time per bit

100 ps

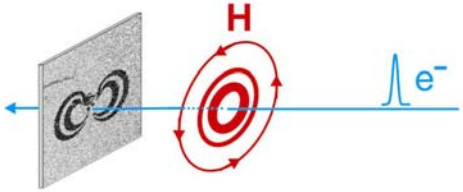


Optical network switching time per bit



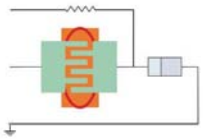
3rd gen. synchrotron

10 ps



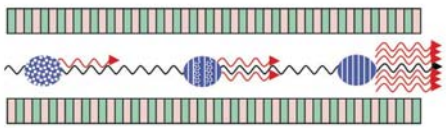
SLAC electron pulse

10^{-12} s — 1 ps



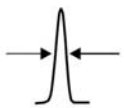
Laser pulsed current switch

100 fs



X-Ray Lasers

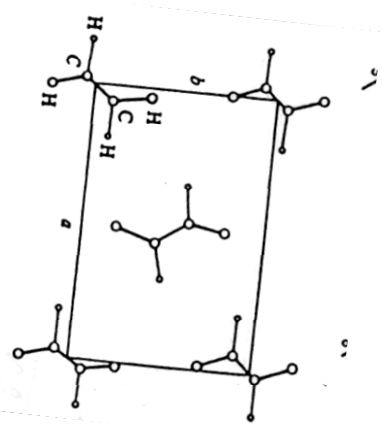
10 f s

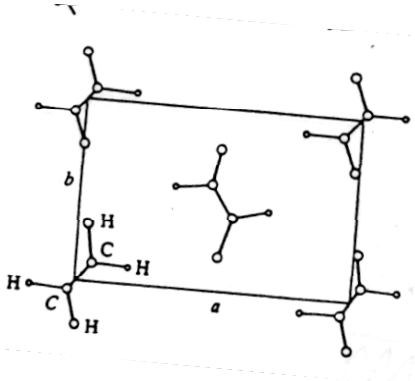


Shortest laser pulse

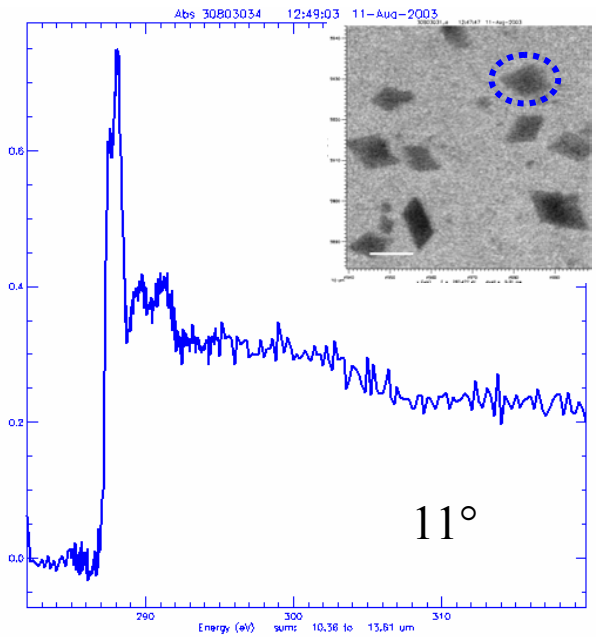
10^{-15} s — 1 fs

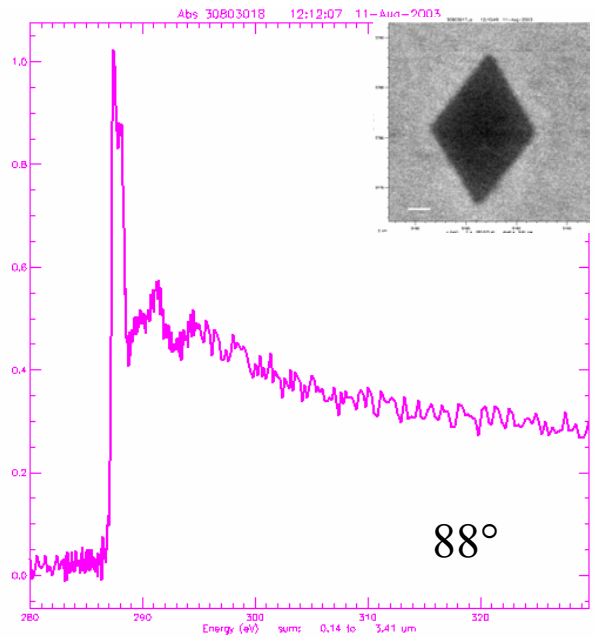
Dichroism in tetracontane:
transverse to C-C backbone





Angles of crystals correspond to unit cell if crystal terminates as (1,1,0), etc.





Solution cast single crystals randomly oriented on Si3N4 membrane