NEXAFS Microscopy and Soft X-Ray Resonant Scattering

Workshop: *"Unique Opportunities in Soft Materials and Nanoscience with an ERL"*

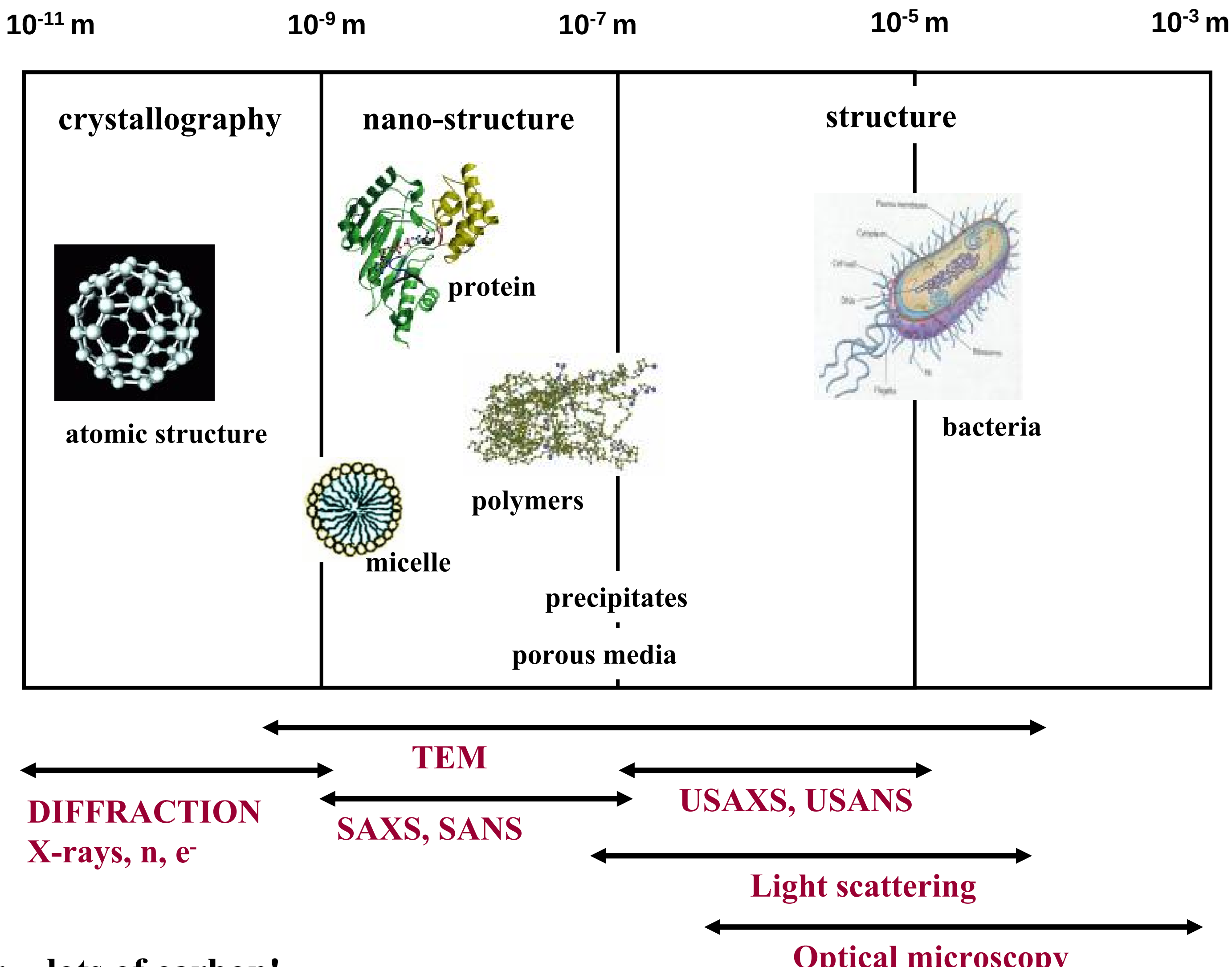
Cornell, June 19, 2006

H. Ade
Department of Physics
North Carolina State University
http://www.physics.ncsu.edu/stxm/

Thanks to J. Stoehr, G. Mitchell for their viewgraphs/data and many other colleagues, collaborators, and users

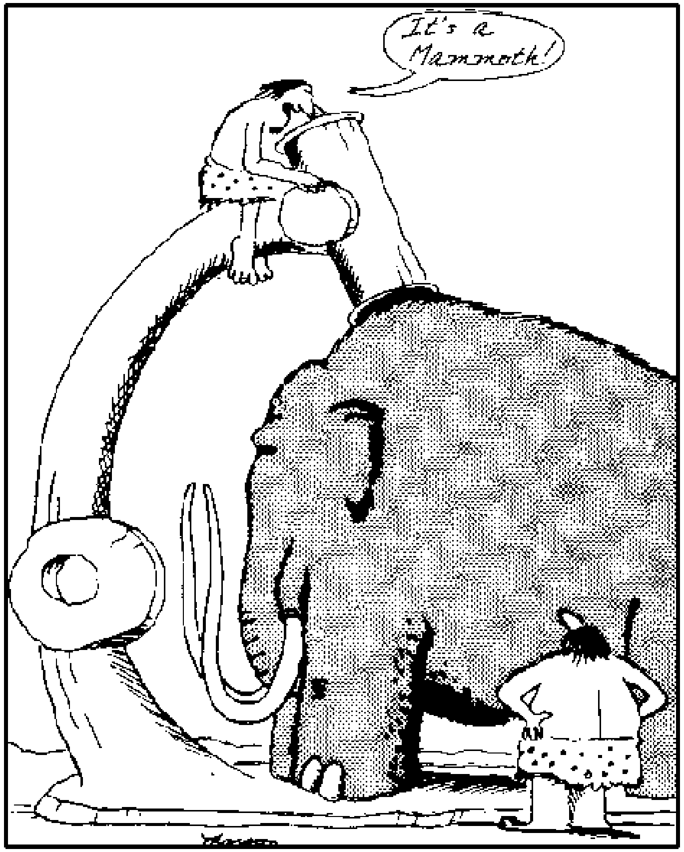
Thanks to organizers for the invitation and support and NSF, DOE, Dow Chemical for financial support over the years

Motivation and needs

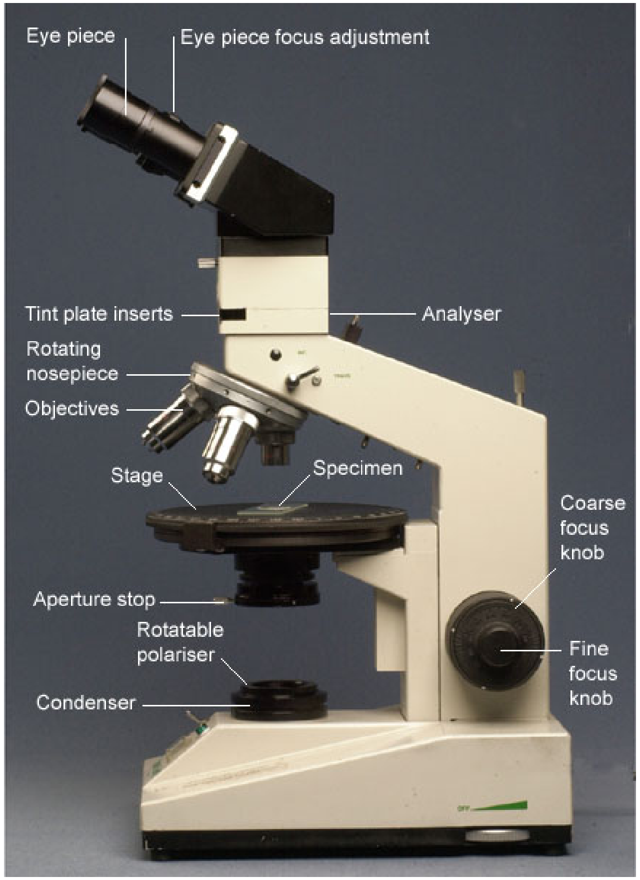


Soft matter = lots of carbon!

Microscopy:
Structure characterization in real space



Early Microscope

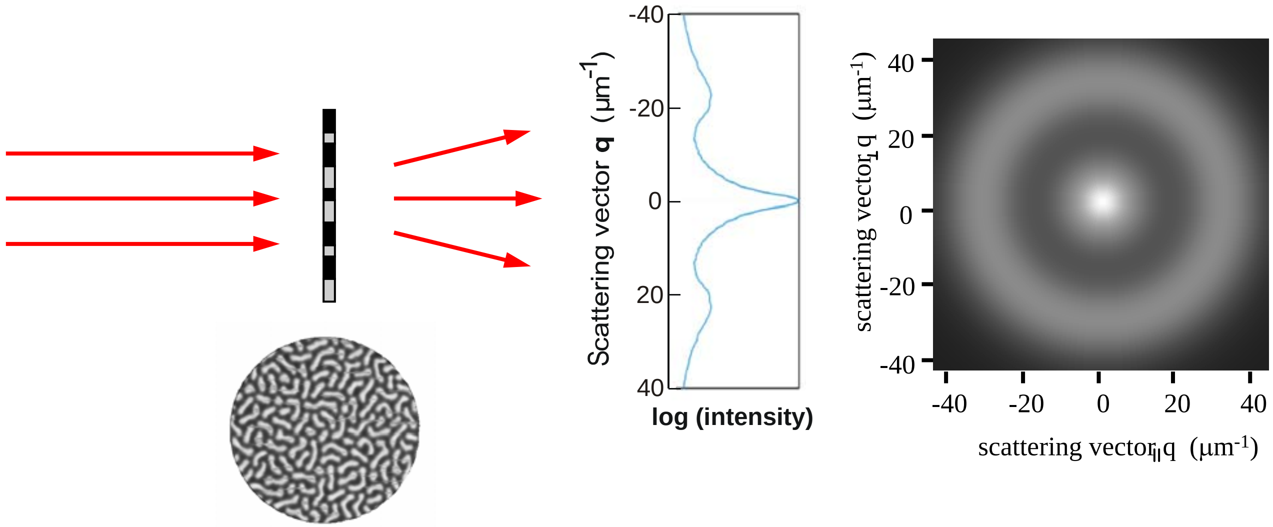


Scattering/diffraction: Structure characterization in reciprocal space

Small Angle Scattering

Coherence length larger than domains, but smaller than illuminated area

Spallation Neutron Source: total cost of $1.4 billion, http://www.sns.gov/



Structure function: information about domain statistics.

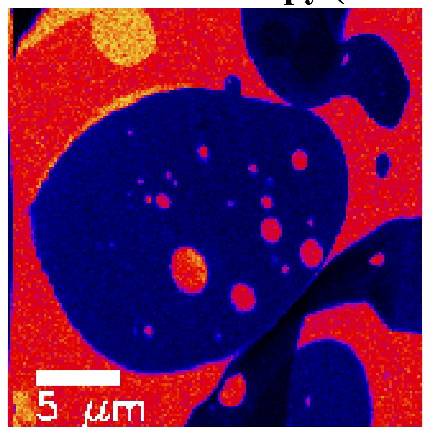
X-ray Microscopy has come a long way!

(Examples "biased" towards spectromicroscopy/polymers/magnetic materials. – No bio or cryo)

1895

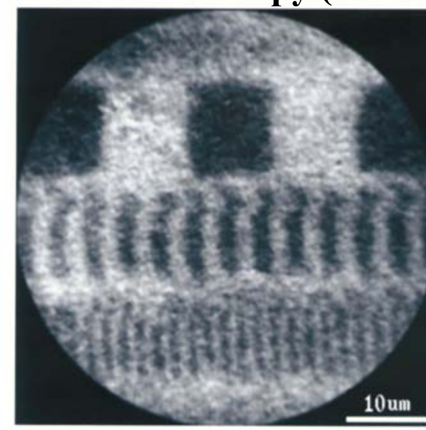
NEXAFS microscopy (STXM)

1992



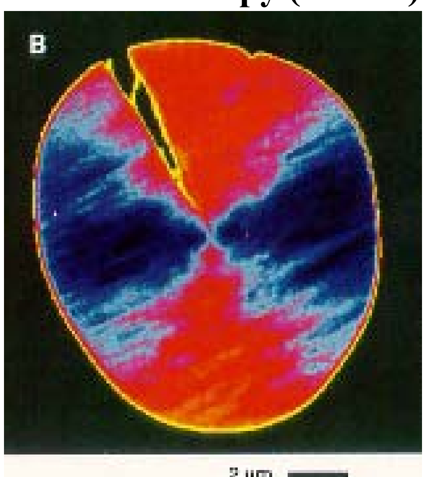
XMCD microscopy (PEEM)

1993



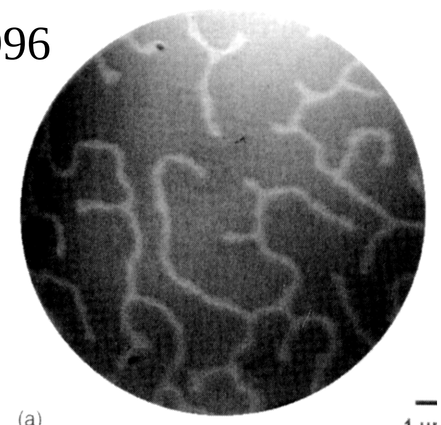
XLD microscopy (STXM)

1993

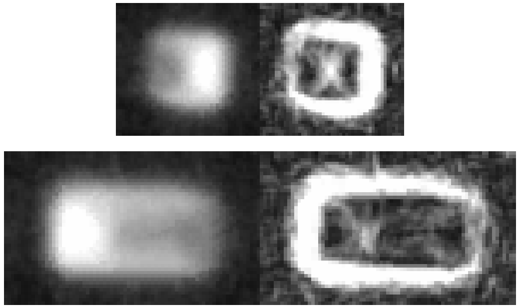


XMCD microscopy (TXM)

1996



Dynamics (PEEM)



2003

Still a long way to go before we hit fundamental limit!!!

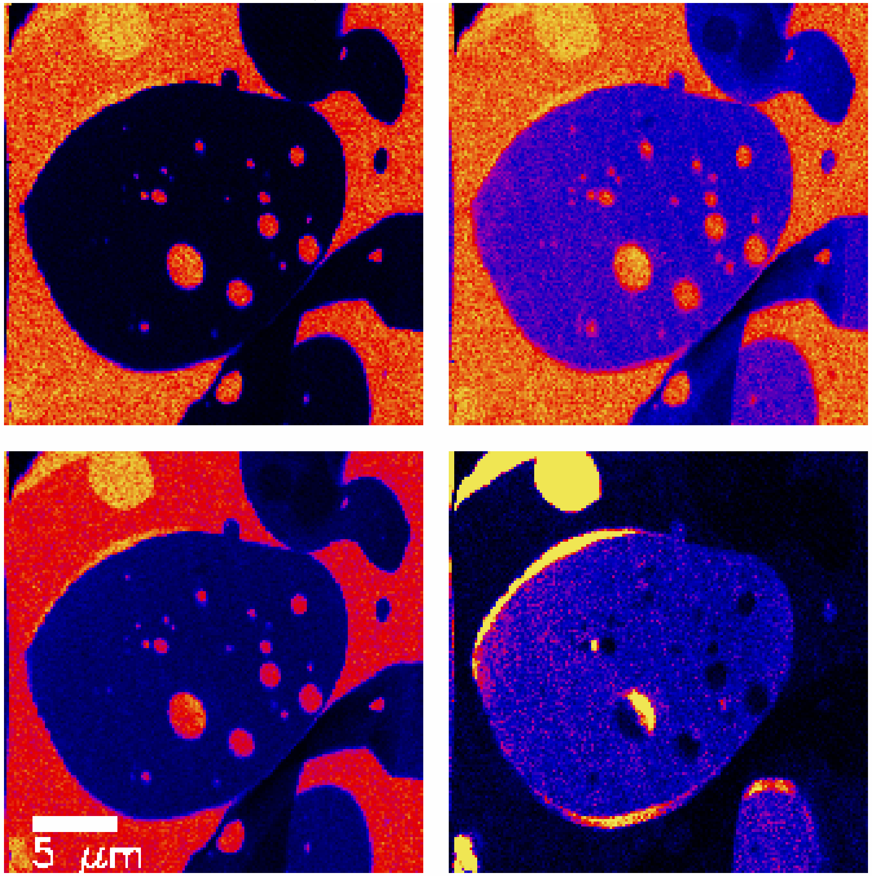
First NEXAFS imaging in transmission (1992)

polypropylene/styrene-acrylonitrile

- 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).
- Stony Brook-STXM not explicitly built to perform spectroscopy, but proved flexible enough to perform carbon NEXAFS.
  - Polymer Science was "enabled"

π^* of styrene (C=C, 285.5 eV)

(286.2 eV)



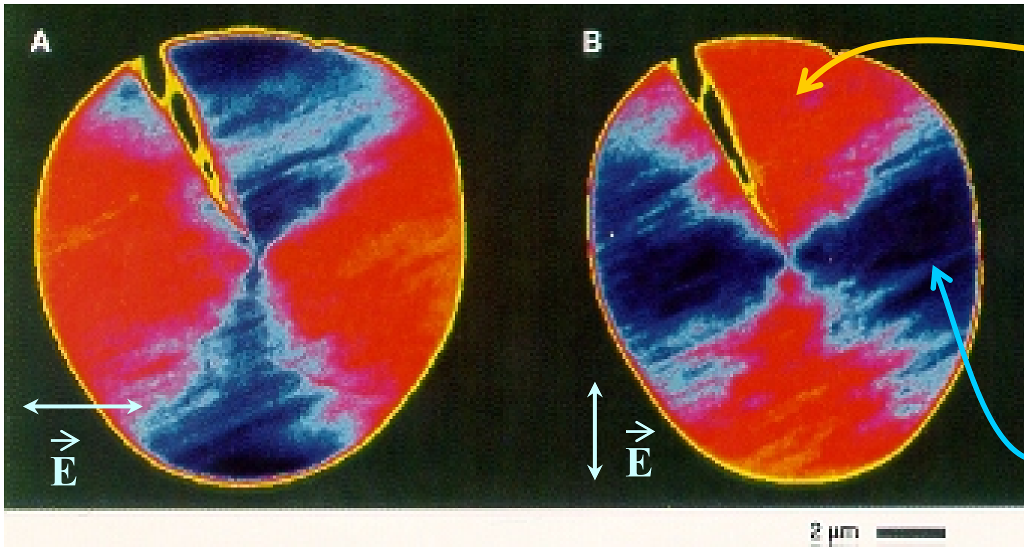
π^* of acrylonitrile (286.8 eV)

σ^* C-H (287.9 eV)

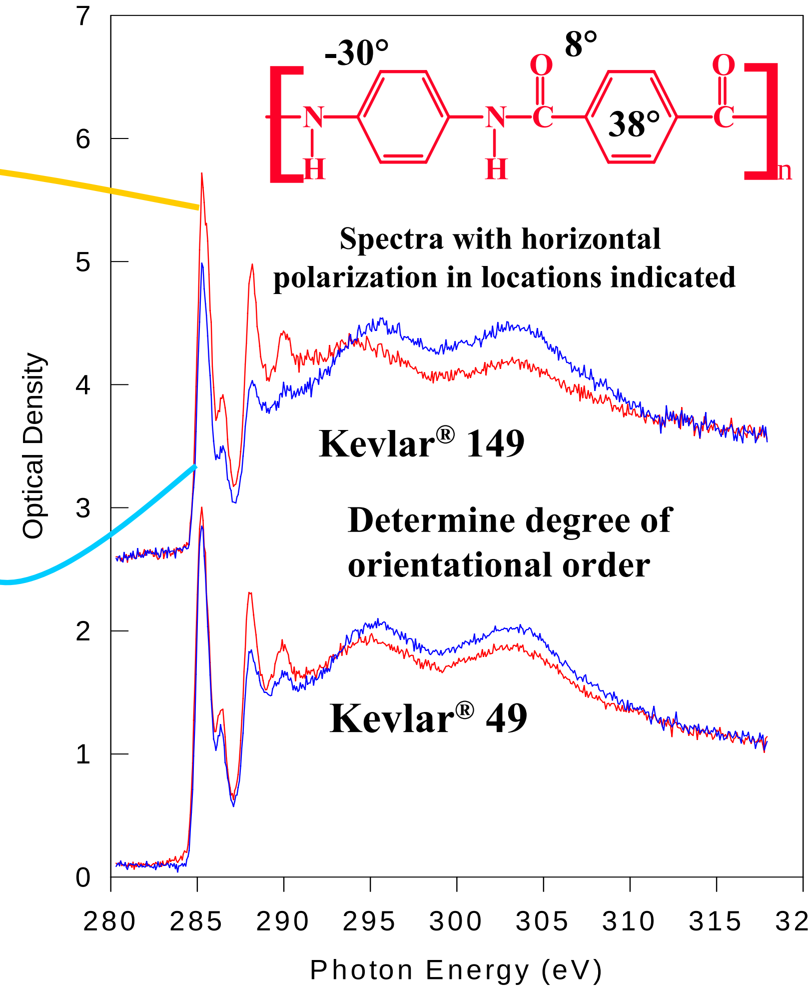
Data: Stony Brook STXM at NSLS

X-Linear Dichroism Microscopy

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



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



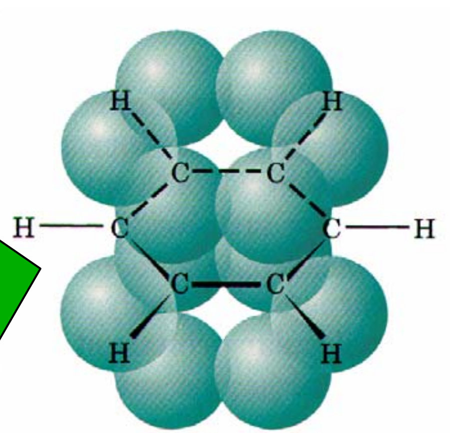
A. P. Smith and H. Ade.
Appl. Phys. Lett. 69, 3833 (1996)

- **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**
- **Degree of orientation of various fiber grades can be quantitified**

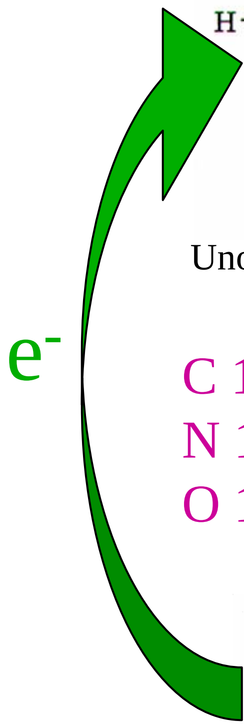
Data: Stony Brook STXM

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

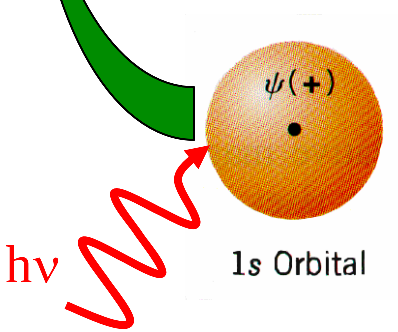
Example: “”Richness” of Polymer NEXAFS Spectra



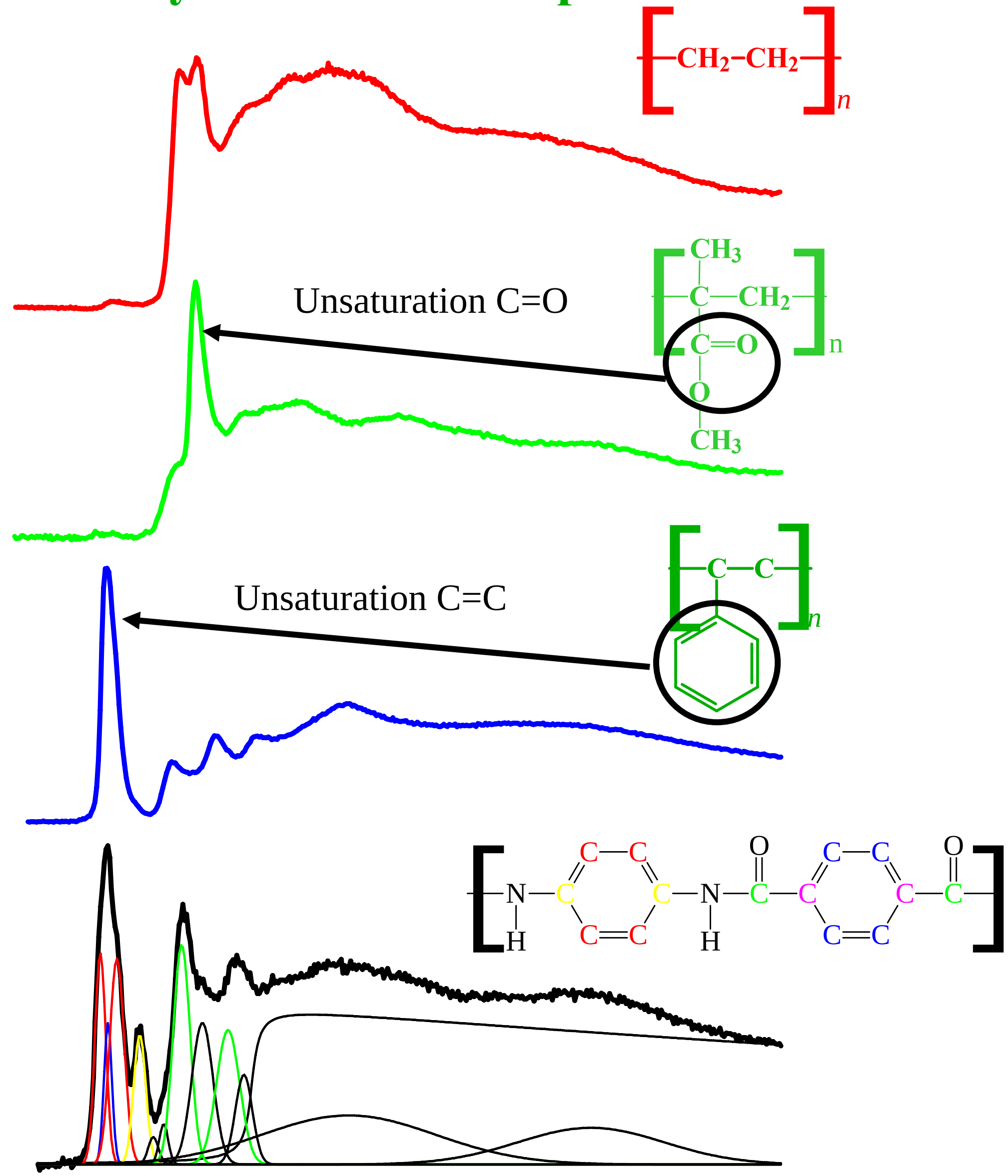
Unoccupied Molecular Orbital



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

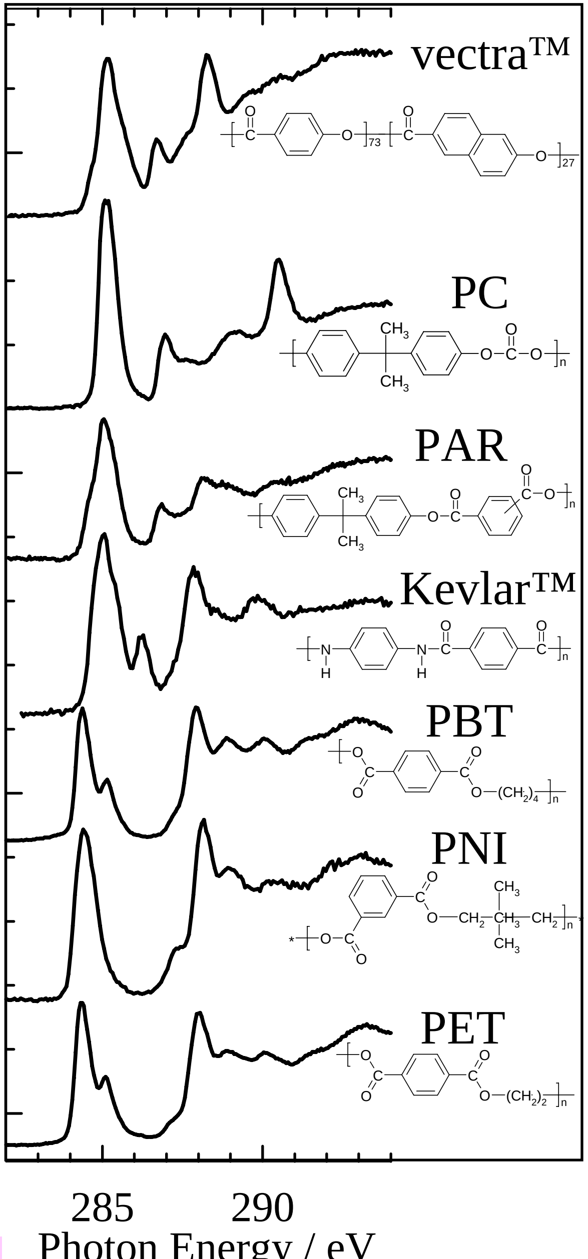


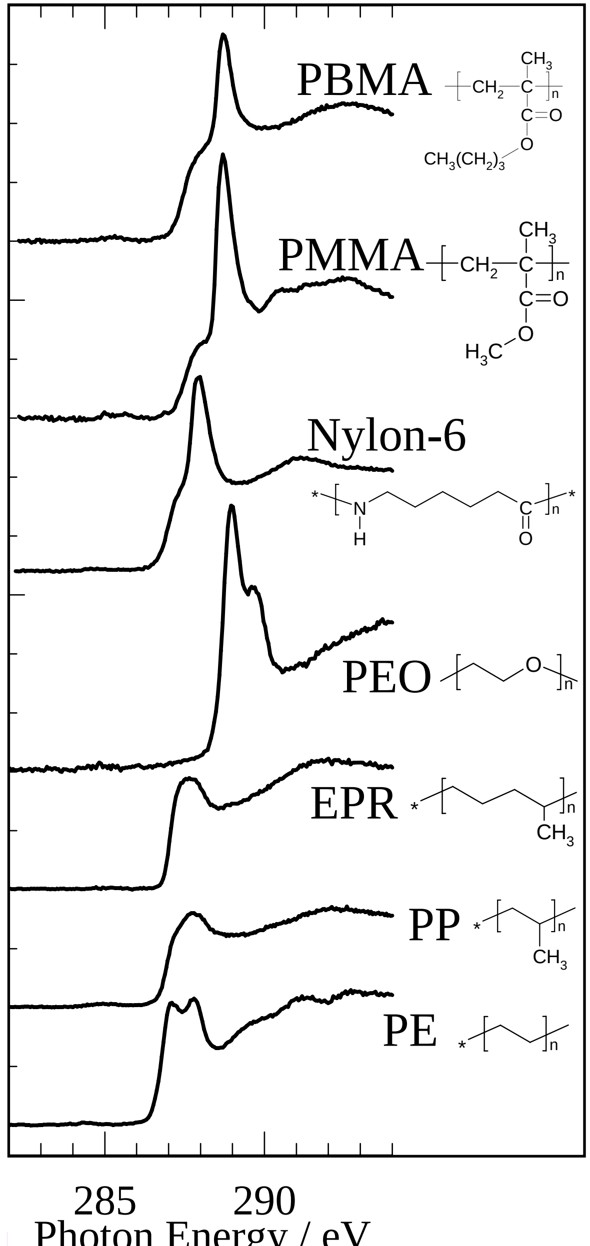
1s Orbital

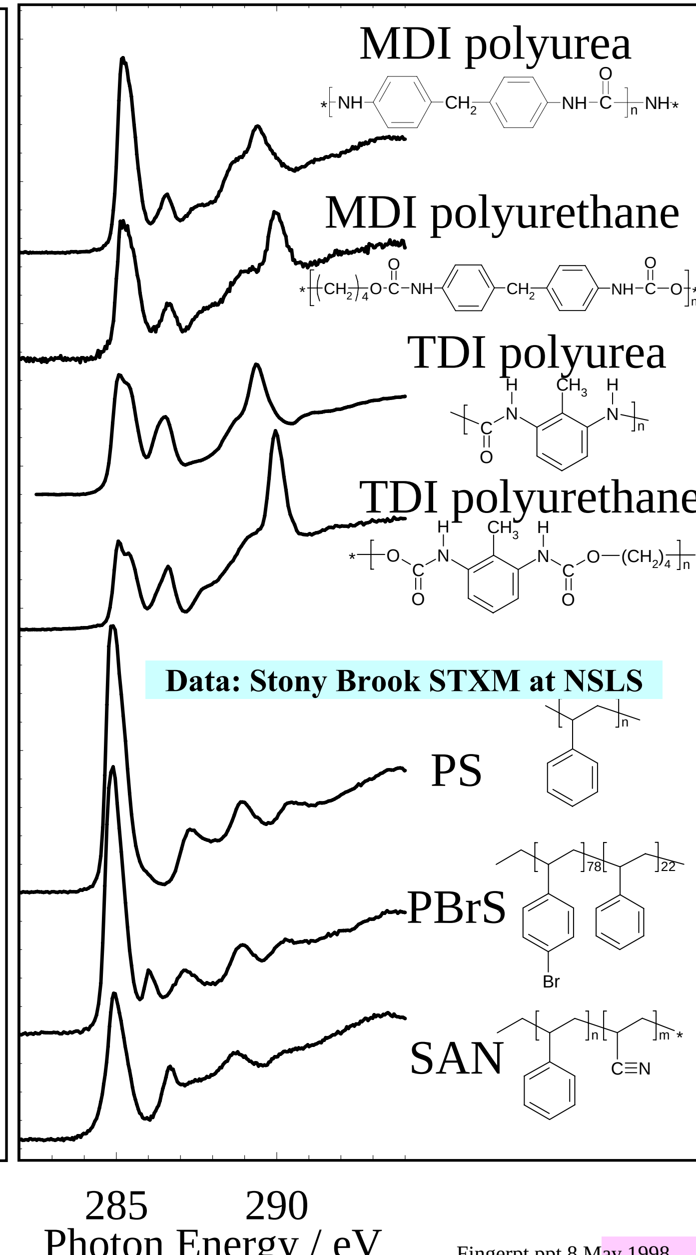


Some Polymer NEXAFS Spectra

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



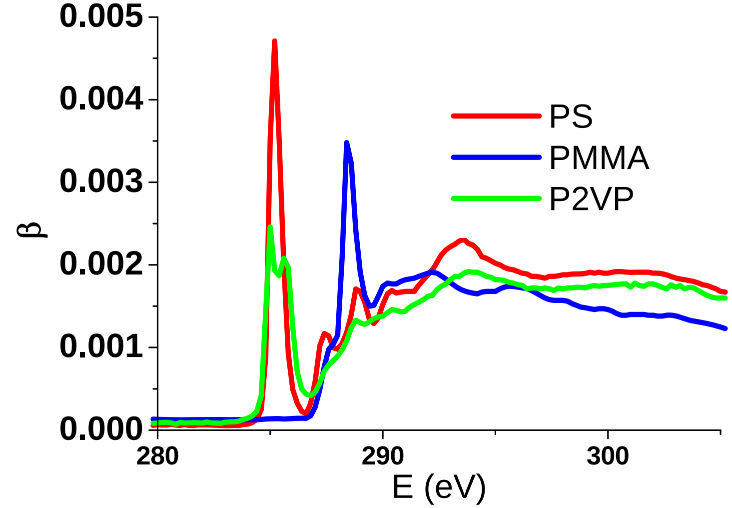




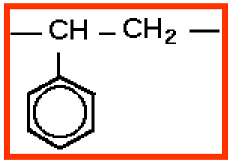
Basis for Resonant Scattering Contrast: Carbon edge examples

Scattering factors f' and f" (optical const. δ and β, respectively) show strong energy dependence

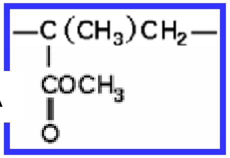
Absorption (NEXAFS)



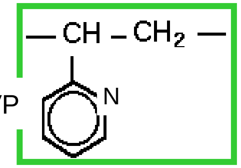
PS



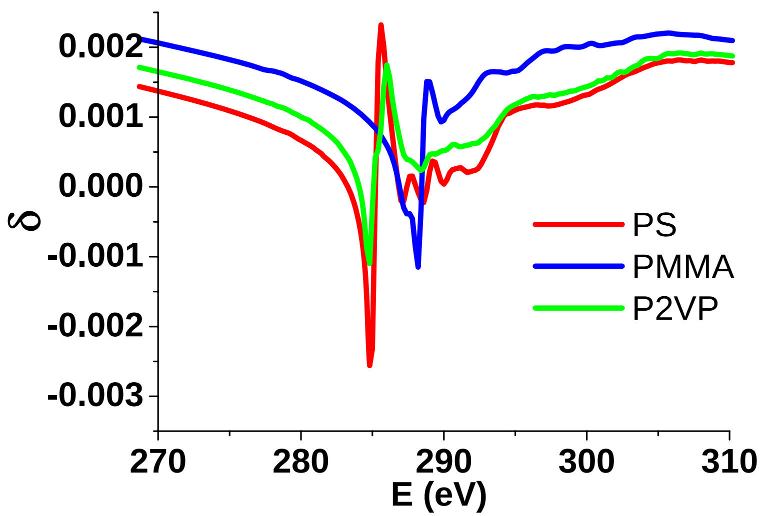
PMMA



P2VP



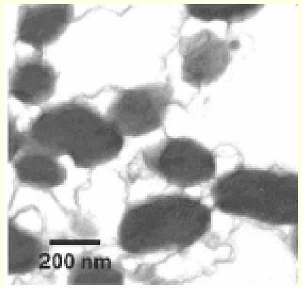
Dispersion



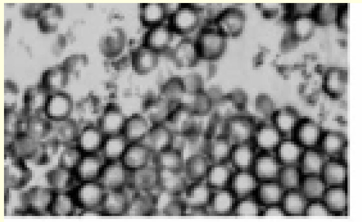
$$I \propto \Delta\delta^2 + \Delta\beta^2$$

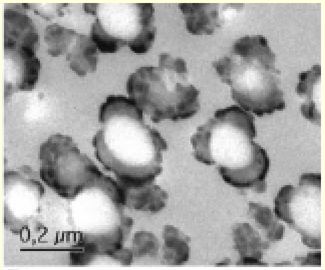
- **"Bond specific" scattering!**
- **Substantial potential as complementary tool!**

PMMA/P(BA-co-S)

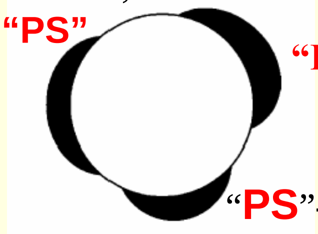


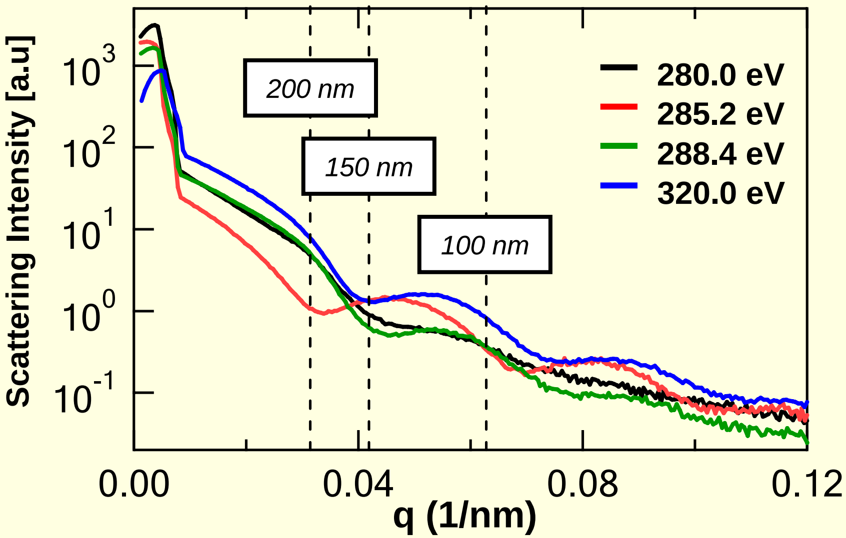
J.M. Stubbs,
D.C. Sundberg Polymer 46 (2005) 1125





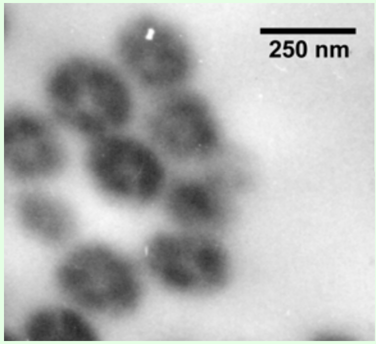
Idealized, "consensus" particle





- "PS" effective radius larger than PMMA "radius"

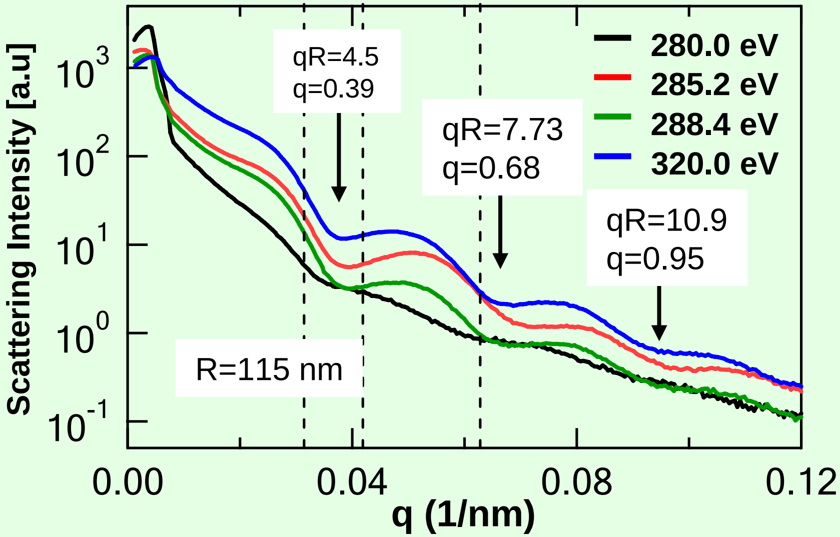
P(MA-b-MMA) / PS



(Figure courtesy J. Stubbs UNH)

Different process and composition

- Fuzzy TEM
- modified core/shell structure?
- Phase less separated?
- Where really is the PS?

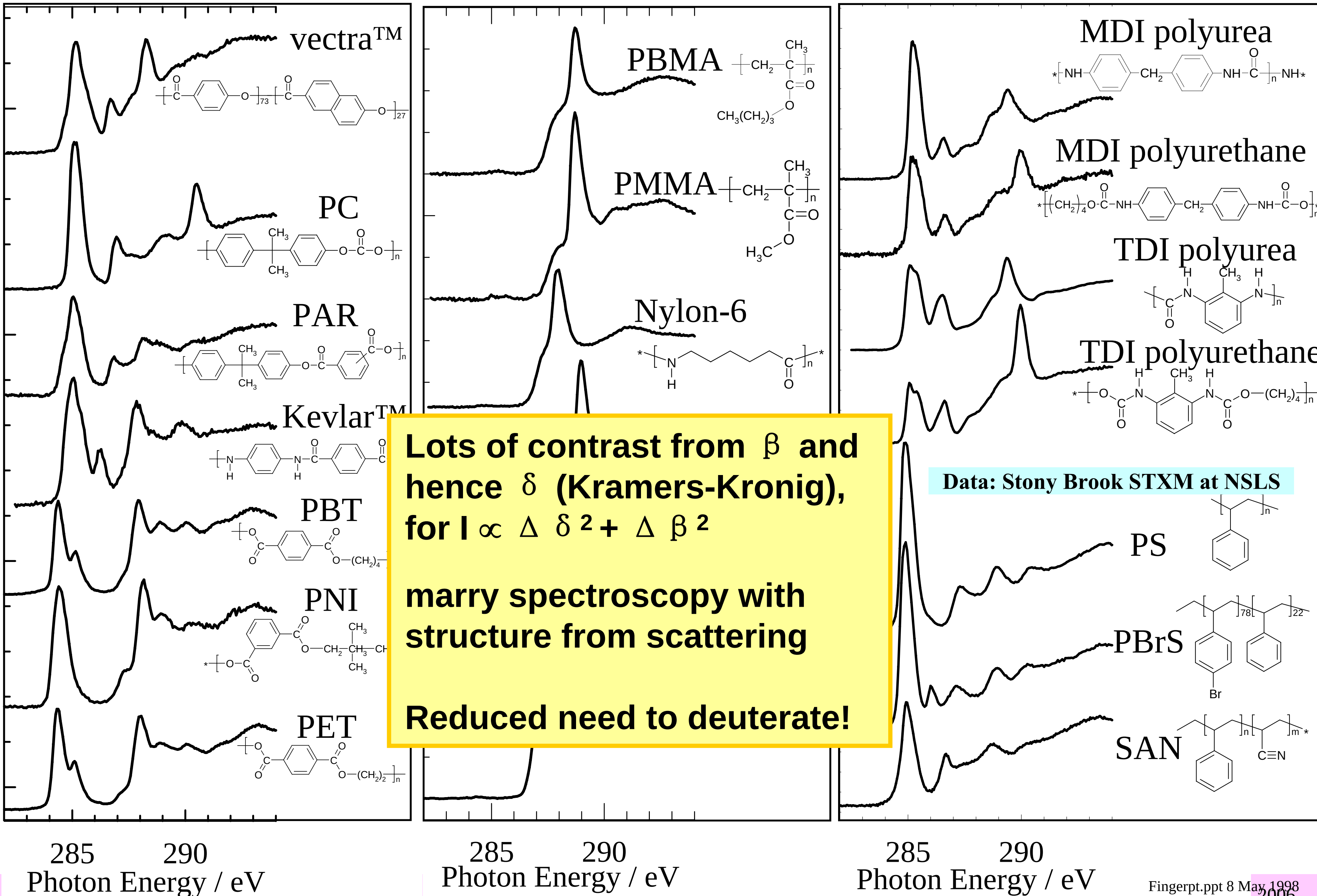


- "PS" about same size than PMMA/acrylate!
- Scattering indicates PS is slightly more in center of nanoparticle relative to PMMA/P(BA-co-S)

First results from structured polymer samples

Some Polymer NEXAFS Spectra

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



Lots of contrast from β and hence δ (Kramers-Kronig), for $I \propto \Delta\delta^2 + \Delta\beta^2$

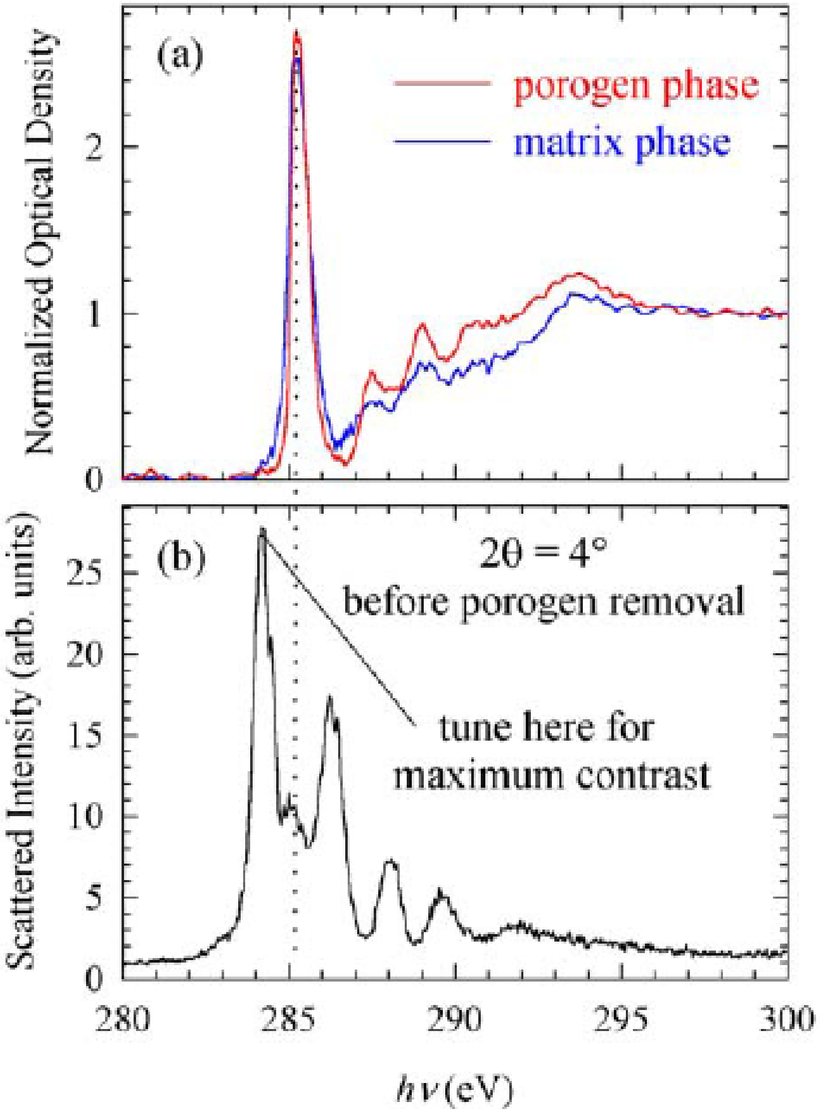
marry spectroscopy with structure from scattering

Reduced need to deuterate!

Low Contrast Example: Developmental Porous SiLK* Resins

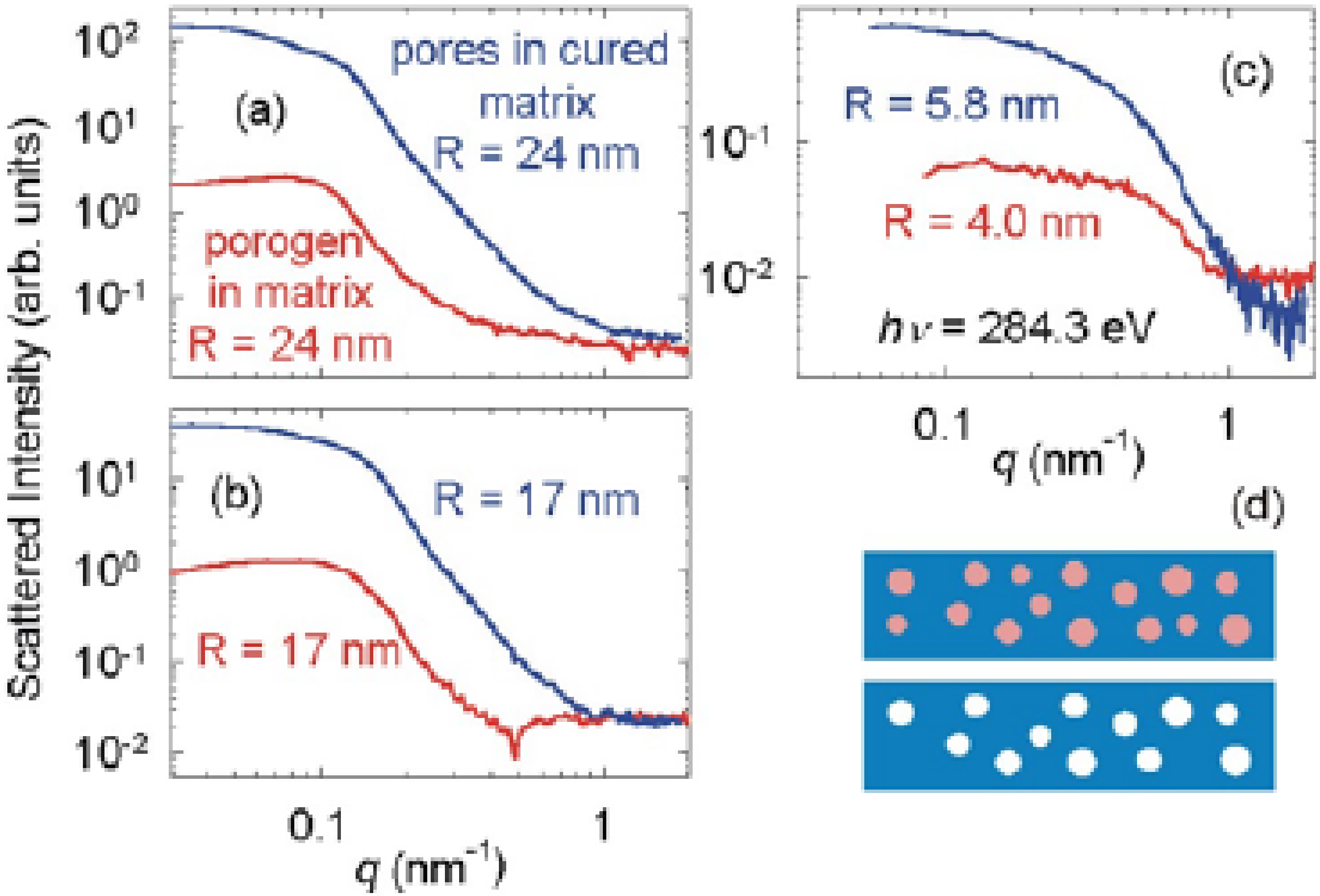
G. Mitchell, Dow Chemical

- Decreasing feature size in integrated circuits require lower dielectric constants for insulating layers to:
  - increase circuit speed, decrease power consumption, decrease crosstalk
- Adding pores to SiLK dielectric resin is used to decrease dielectric constant from 2.65 to 2.1 and less
- Future materials require more and smaller pores



G. E. Mitchell, I. Koprinarov, B. G. Landes, J. Lyons, B. J. Kern, M. J. Devon, E. M. Gullikson, and J. B. Kortright, Appl. Phys. Lett. (in press)

Systematic variation in porogen size

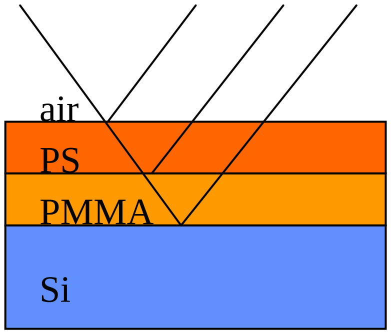


Smallest pores collapse

Wouldn't be able to do the experiment with STXM, TEM, or SAXS. - Deuteration and SANS would work.

Soft X-ray Resonant Reflectivity

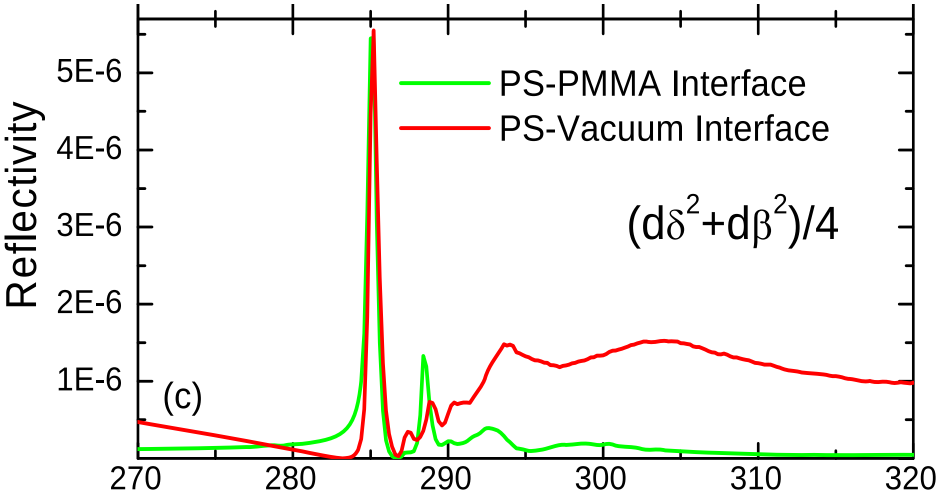
PS/PMMA bilayer

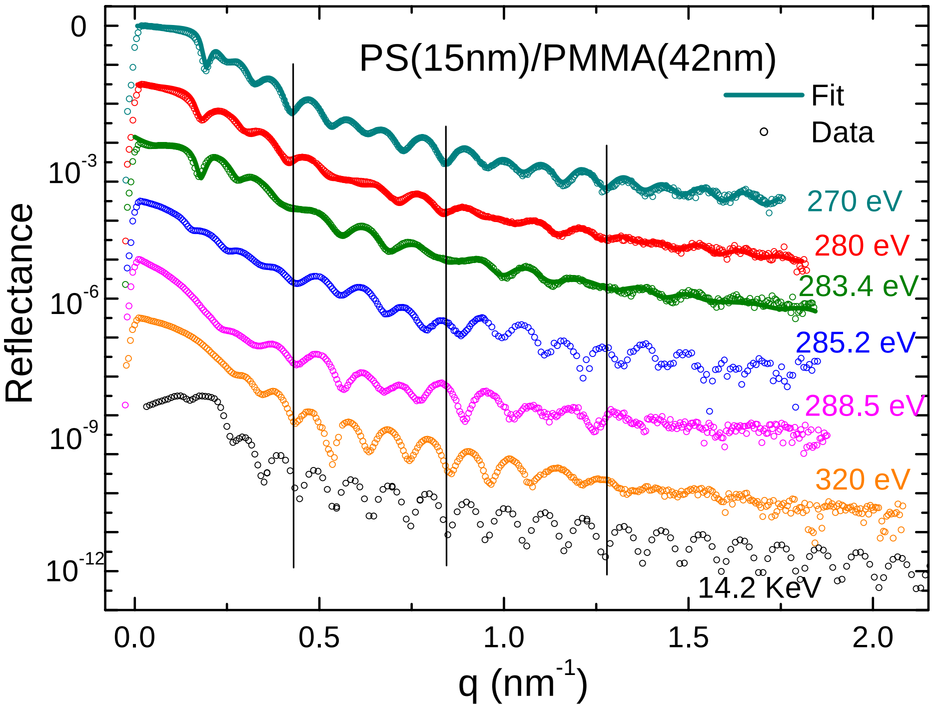


C. Wang, T. Araki, H. Ade
Appl. Phys. Lett. **87**, 214109 (2005)

Complementary Tool to Neutrons and hard X-rays

- Observed strong photon energy dependence
- Need to reduce uncertainty for δ and β





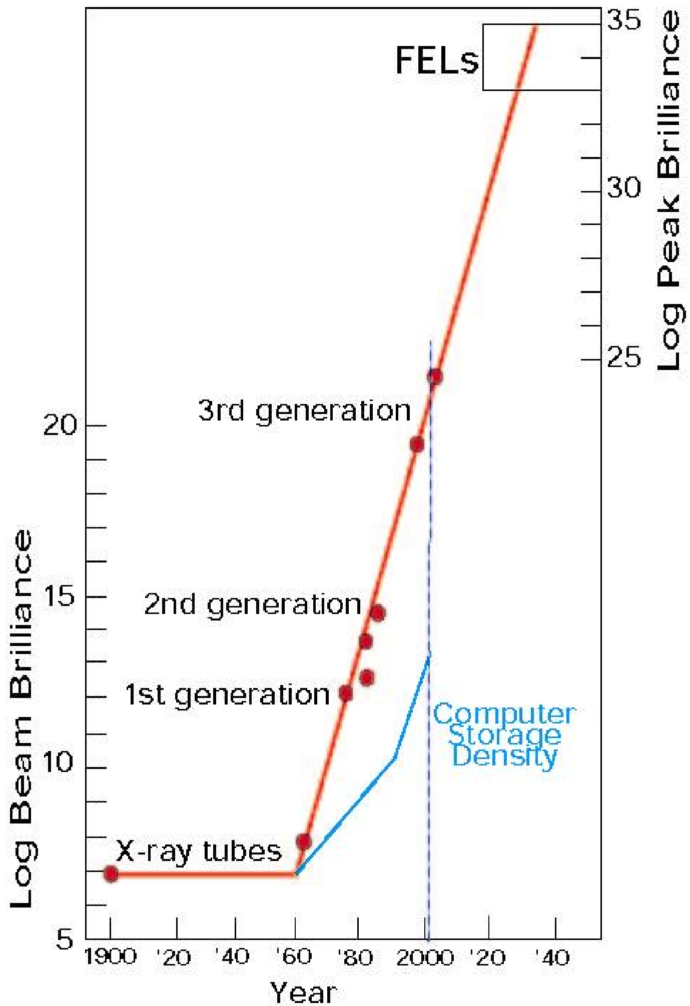
Potential: Diffuse scattering from interfaces

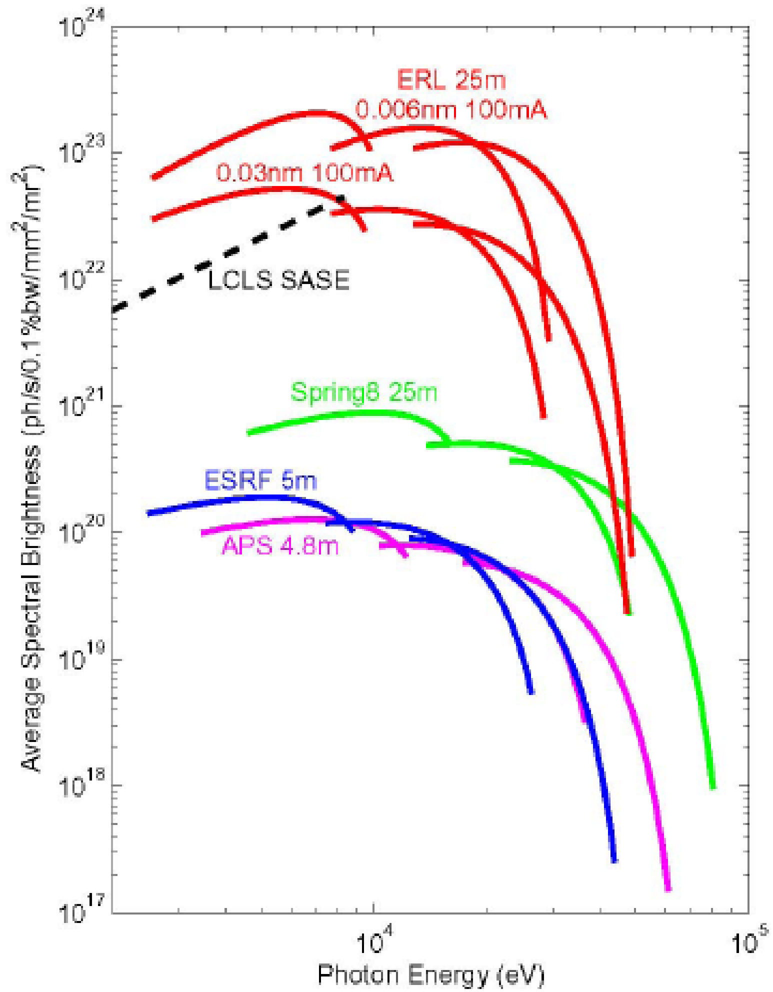
NEXAFS microscopy and Resonant Scattering

- **Unique tools for soft condensed (carbonaceous) matter**

Brighter Sources!

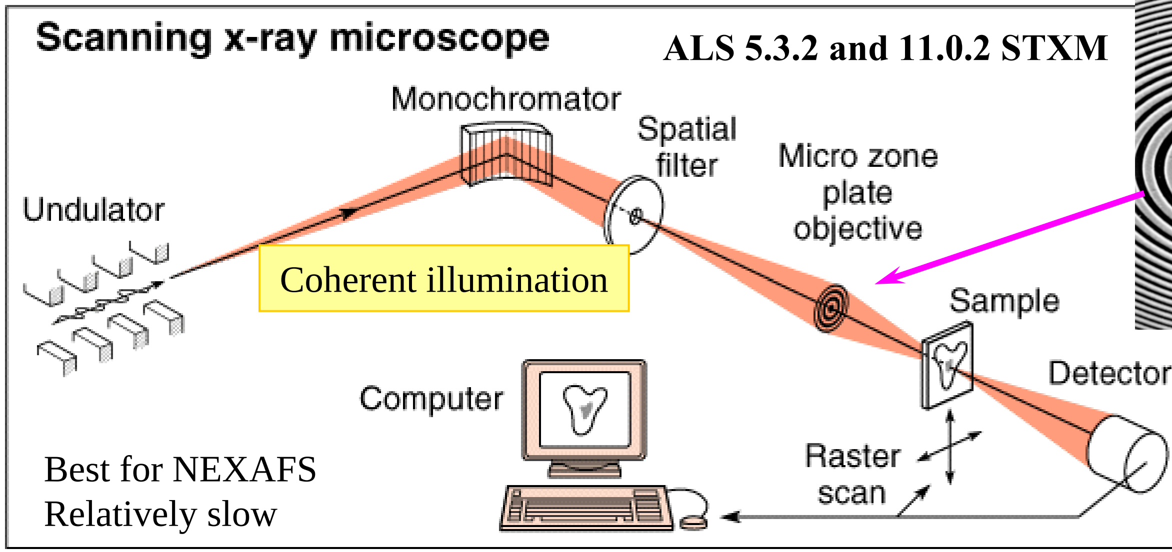
How do we take advantage of them? Space, time, energy?

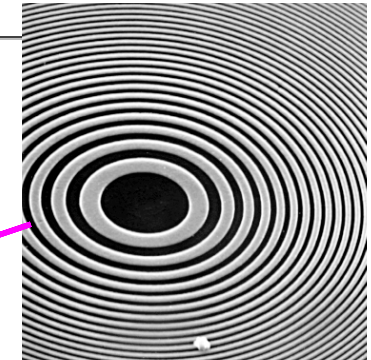


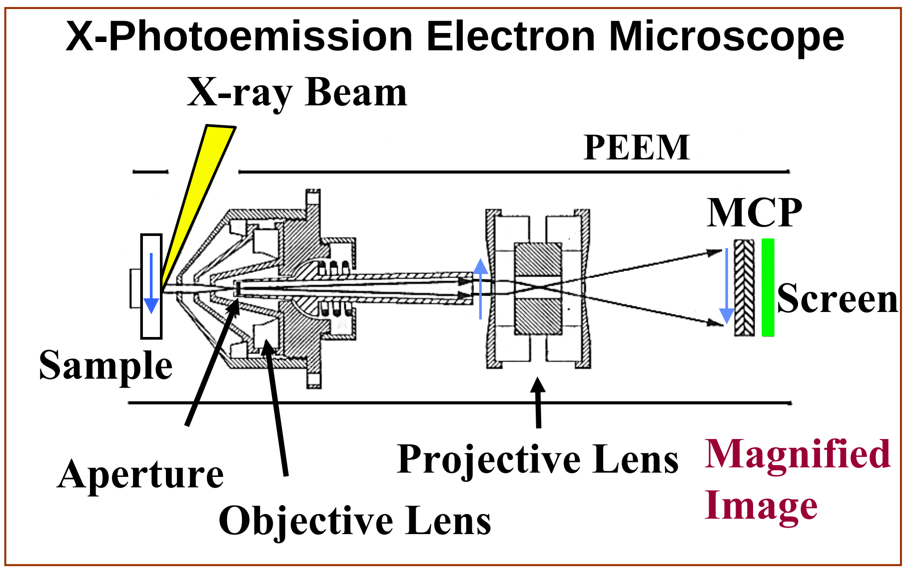


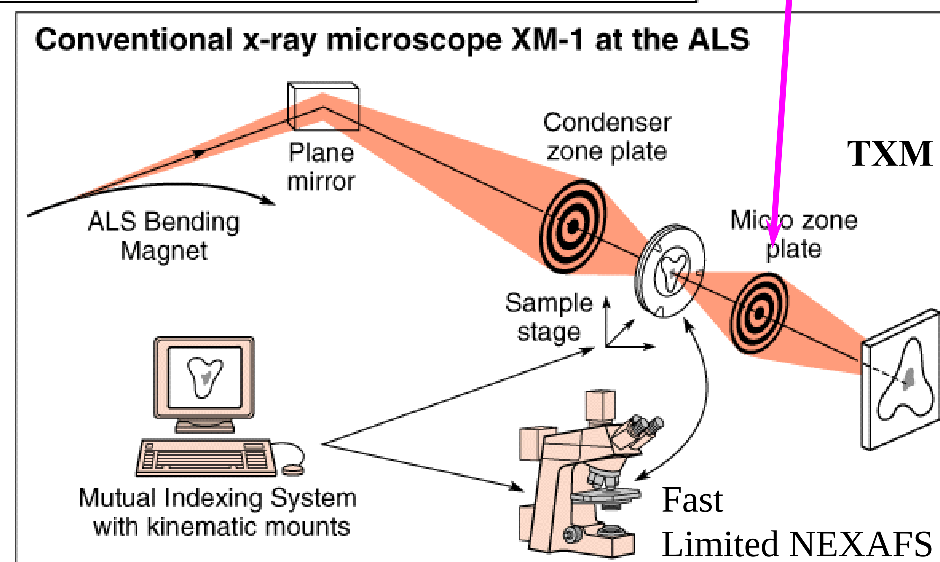
How about my favorite absorption edge?? Carbon, 300 eV?

Types of X-ray Microscopes









Also: Scanning Photoemission X-ray Microscope (SPEM) Ade et al. *Appl. Phys. Lett.* 56, 1841 (1990)
See talk by Maya Kiskinova for details

Zone Plates: Diffractive Optics for X-rays

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

- **1975: Modern 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**
  - **120 nm resolution**

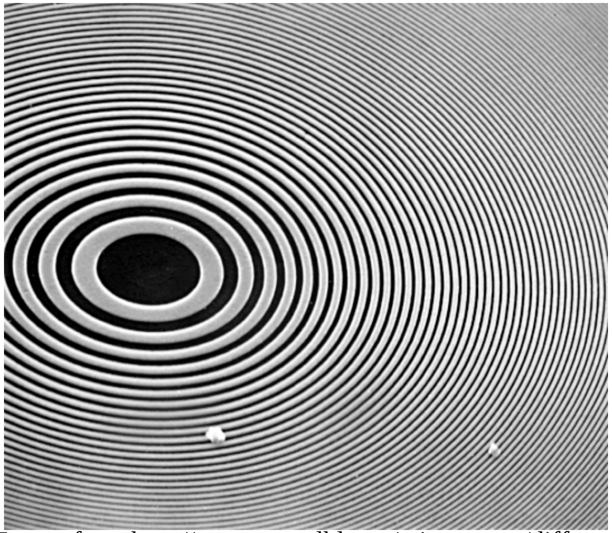
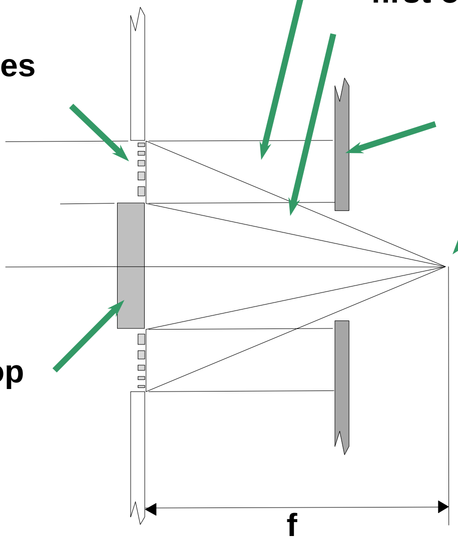


Image from http://www-cxro.lbl.gov/microscopy/diffractive.html

- **Circular Au, Ni, or Ge structures**
- **Nanofabrication with E-beam lithography**
- **Spatial resolution equal approx. outermost zone width**
- **Focal length is proportional to energy**

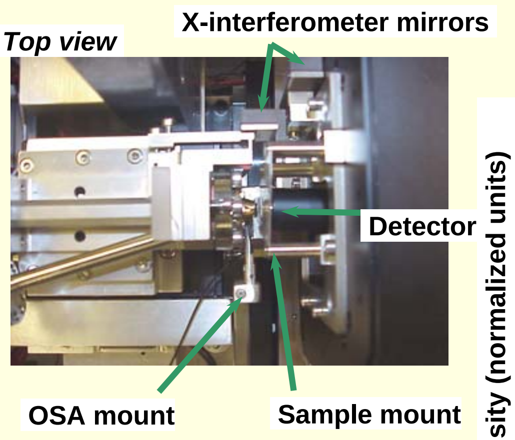
Arrangement in a Scanning Transmission X-ray Microscope (STXM)

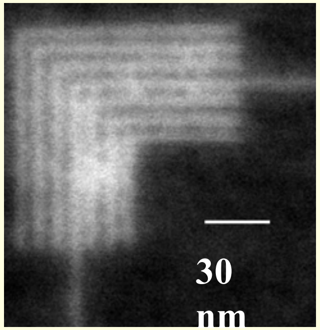


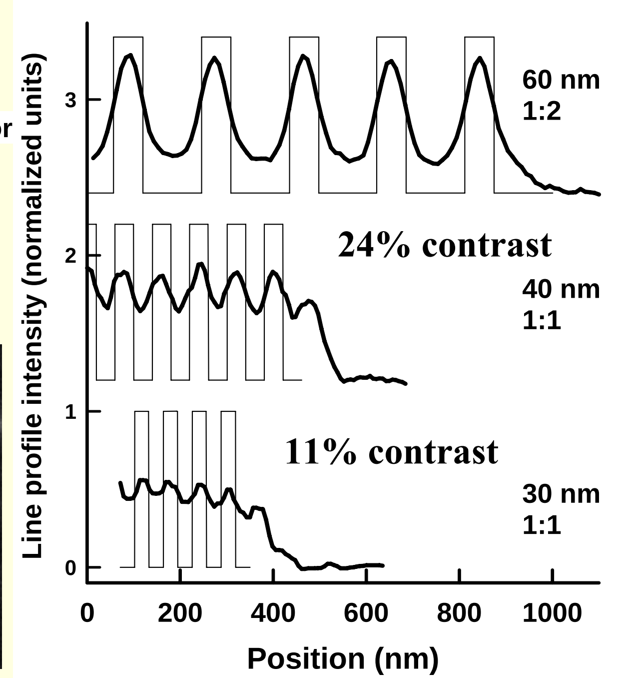
- **Diameter: 150-250 µm**
- **Zone widths presently as small as 15 nm**
- **Working distance: ~150 µm**

Recent STXM Technology Innovations:
1) Interferometer, 2) polarization control

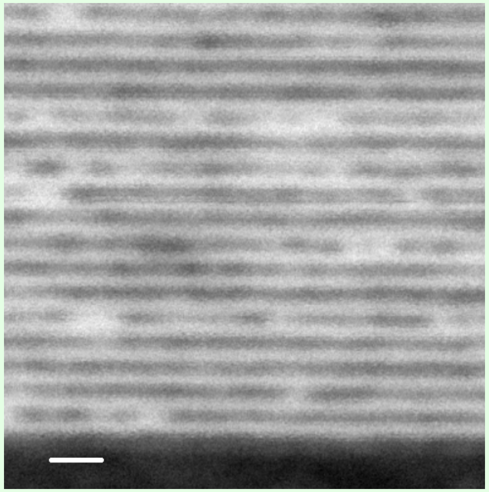
5.3.2 Polymer STXM , Fall 2001, “35 nm zone plate”
Soon to install “25 nm zone plate”







BL11.0.2.2 STXM
Spring 2004, “25 nm zone plate”

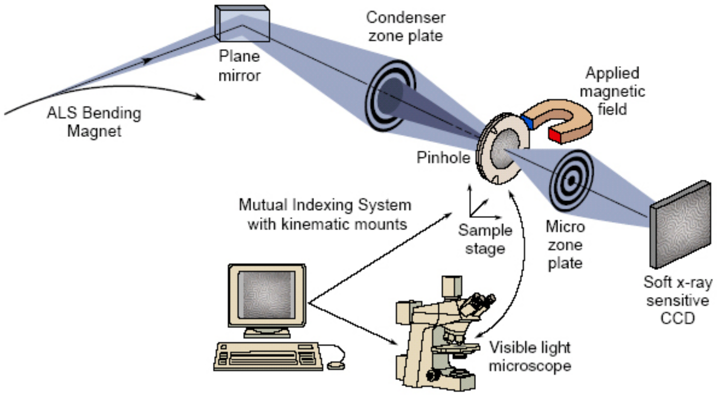


New 25 nm CXRO zone plate test:
25 nm lines of a test pattern obtained at 395 eV.
*** Polarization control**

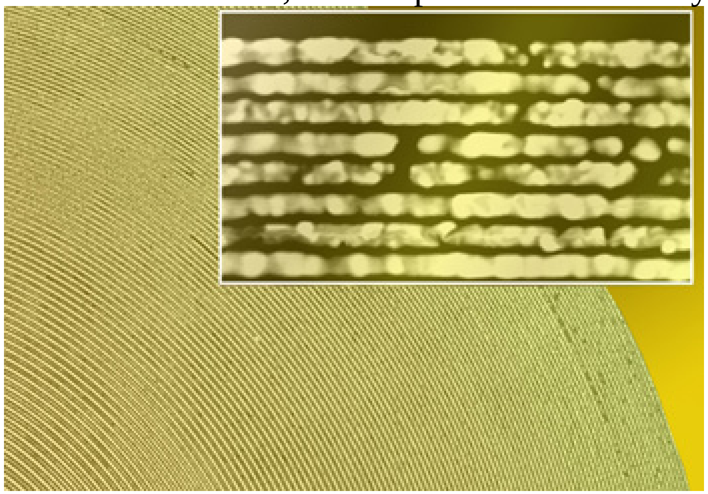
Impact: 1) Zone plate are now the spatial resolution limiting factor, 2) enables magnetism, 3) quantification, wider range of samples

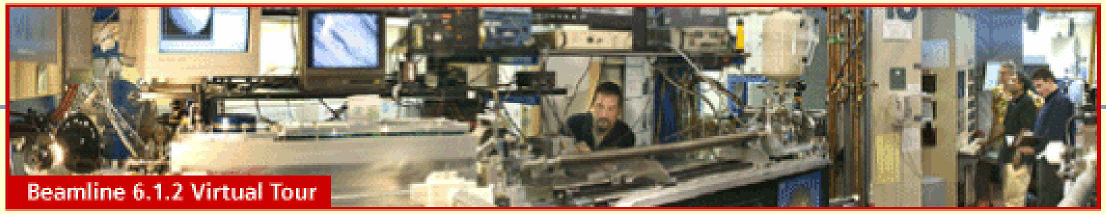
TXM: ALS Beamline 6.1.2 XM-1

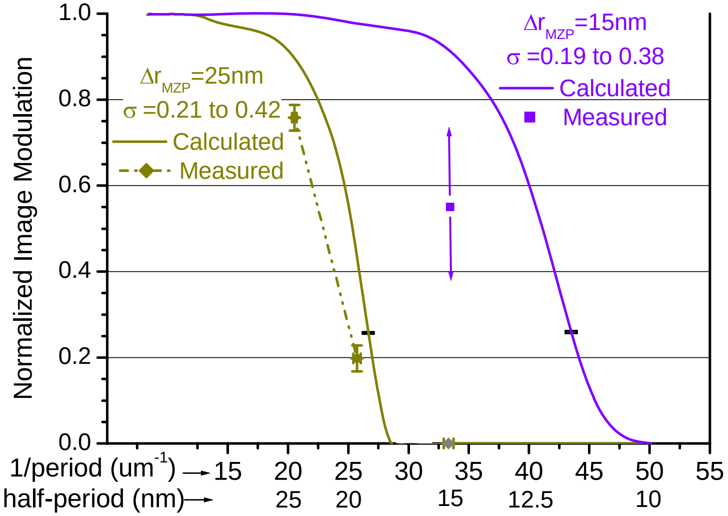
Spatial resolution record

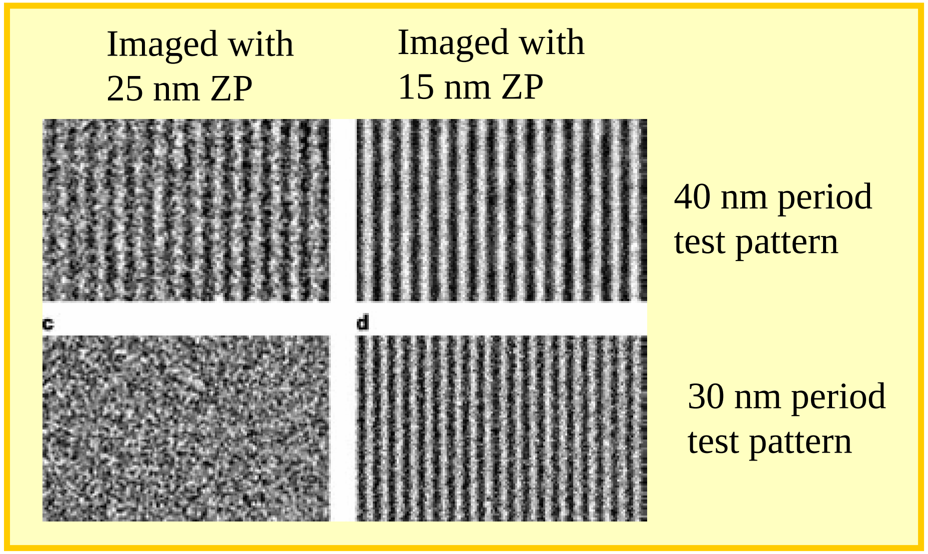


15 nm zone width, 1.7 nm placement accuracy





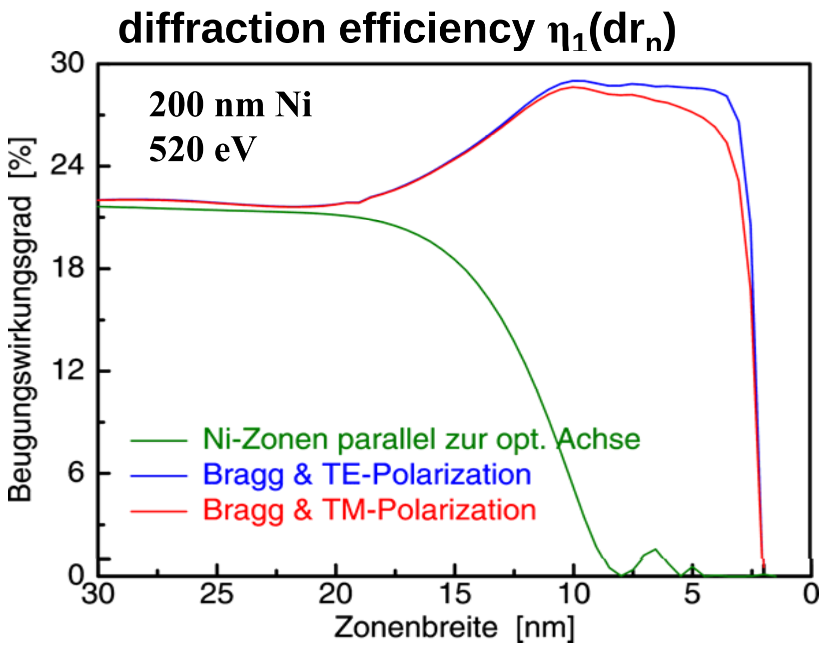




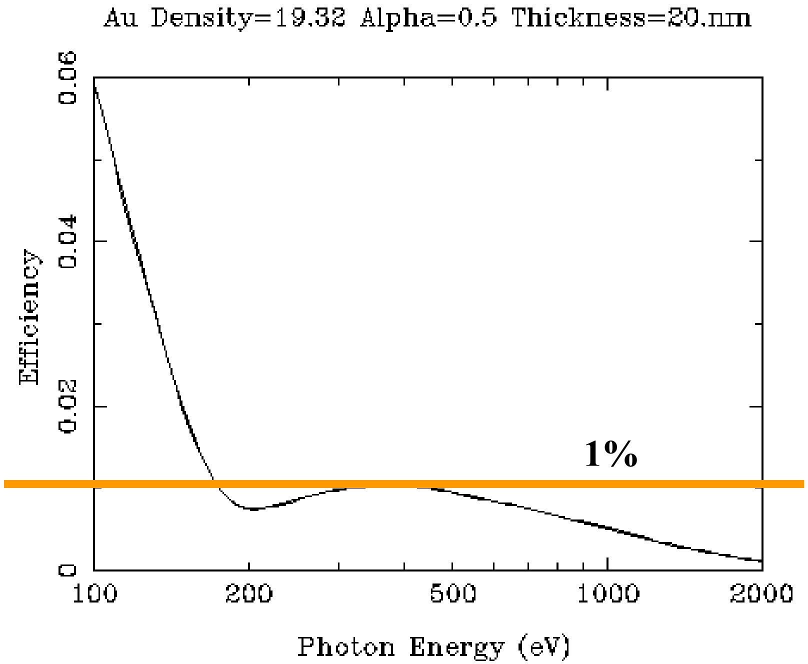
Weilun Chao, B. D. Harteneck, J.A. Liddle, E. H. Anderson, and D. T. Attwood, Nature **435**, 1210 (2005)

How do we get to <10 nm resolution?

Volume zone plates with tilted structures
Gerd Schneider, BESSY, Berlin



Thin ZP plates



http://www-cxro.lbl.gov/optical_constants/tgrat2.html

- **Volume zone plate very difficult to make**
- **Aspect ratio for low efficiency zone plates is easier to achieve**
- **ERL eliminates need for high efficiency zone plates**
  - **Low efficiency is compensated for by increased brightness**
- **Alternative: Use third order: 1/9th the efficiency, 3x better spatial resolution**

Instrument challenges for STXM

Relative ZP/sample vibrations (5.3.2 STXM)

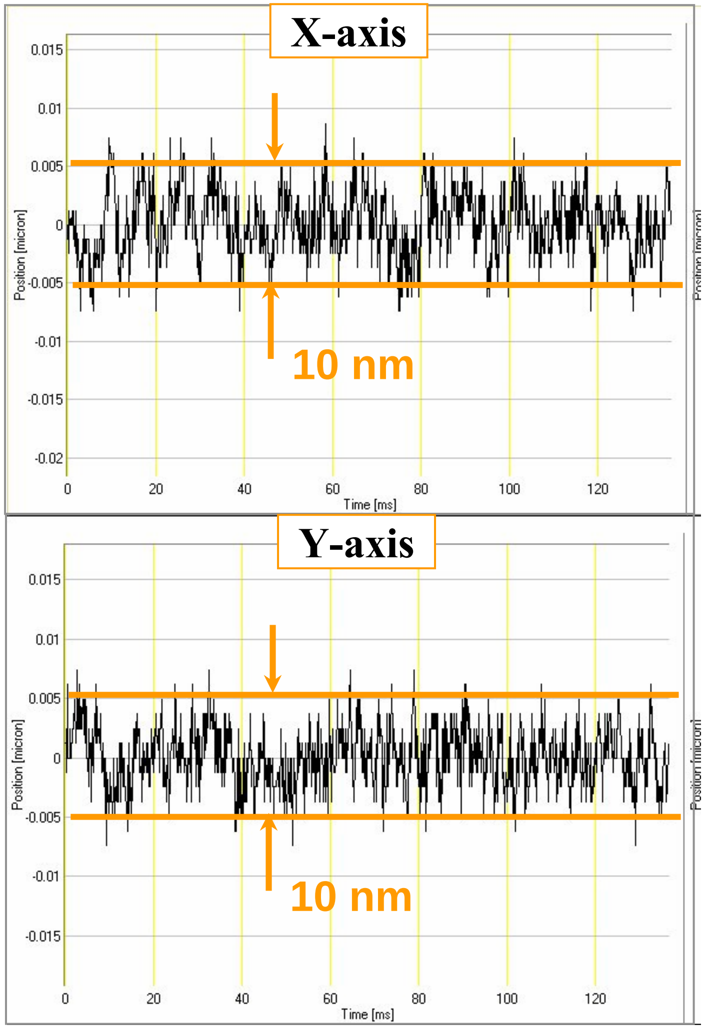
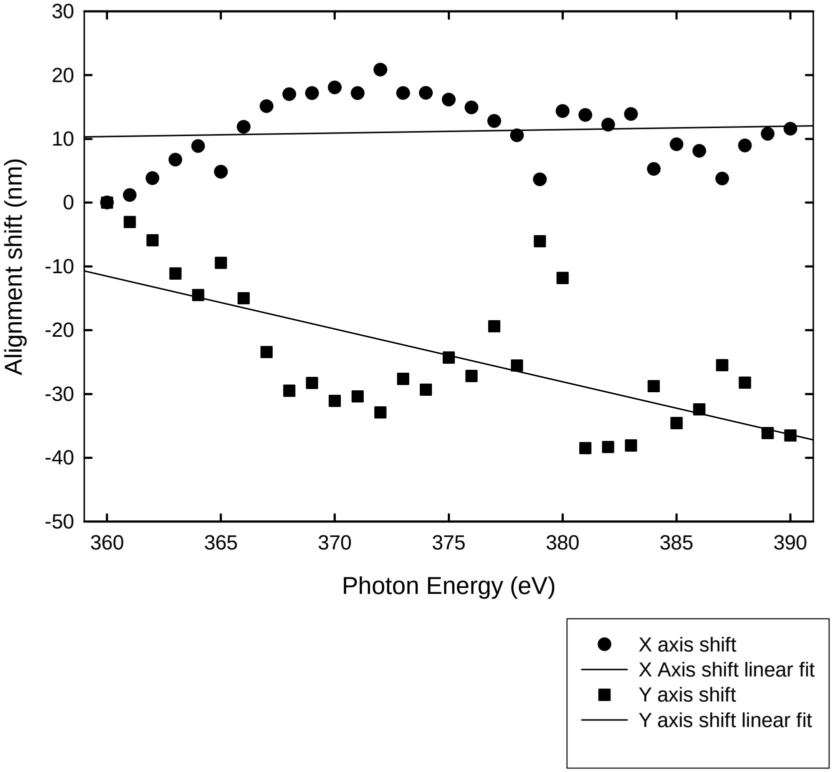


Image-sequence alignment

- **Auto-correlate images to detect shifts**
  - **Random shits less than 30 nm**
  - **some residual misalignment in y**



Time resolution real space: STXM

- **Recall: Mechanical scan of sample or optics**
- **“Scan speeds” presently as low as 100 μs/20 nm pixel**
- **1000x1000 pixel image in 2 minutes**

- **Difficult to imagine technology that can really take advantage of ERL for imaging speed alone**
  - **Pump probe on radiation hard materials (e.g. magnetic materials) in STXM and PEEM**

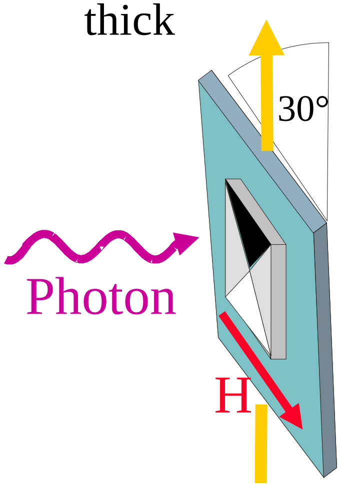
Sine excitation @ STXM

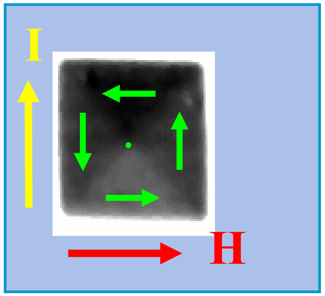
H. Stoll et al. MPI, Stuttgart

(sample prep.: I. Neudecker, D. Weiss, C.H. Back, Regensburg Univ.)

Permalloy sample A

(1.5 x1.5) µm², 50 nm thick

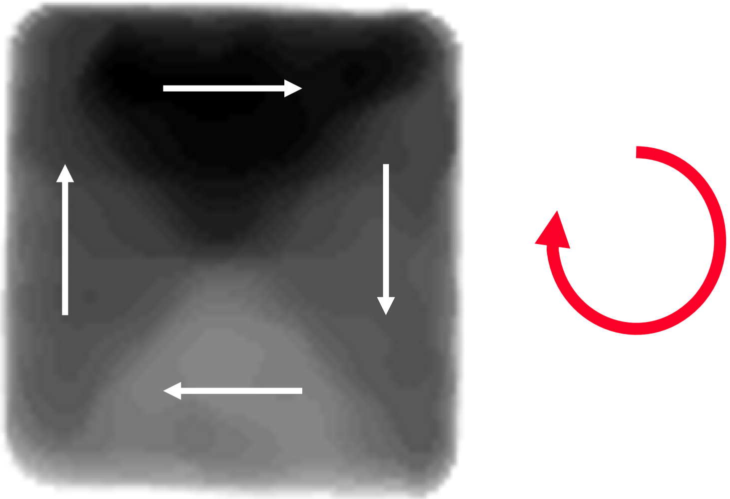




$B = B_0 \sin(2\pi f t)$

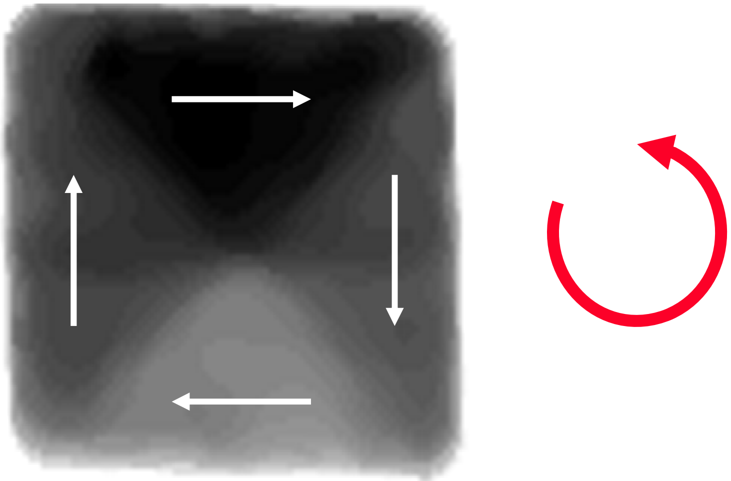
$B_0 \approx 16$ mT

f = 250 MHz



$B_0 \approx 10$ mT

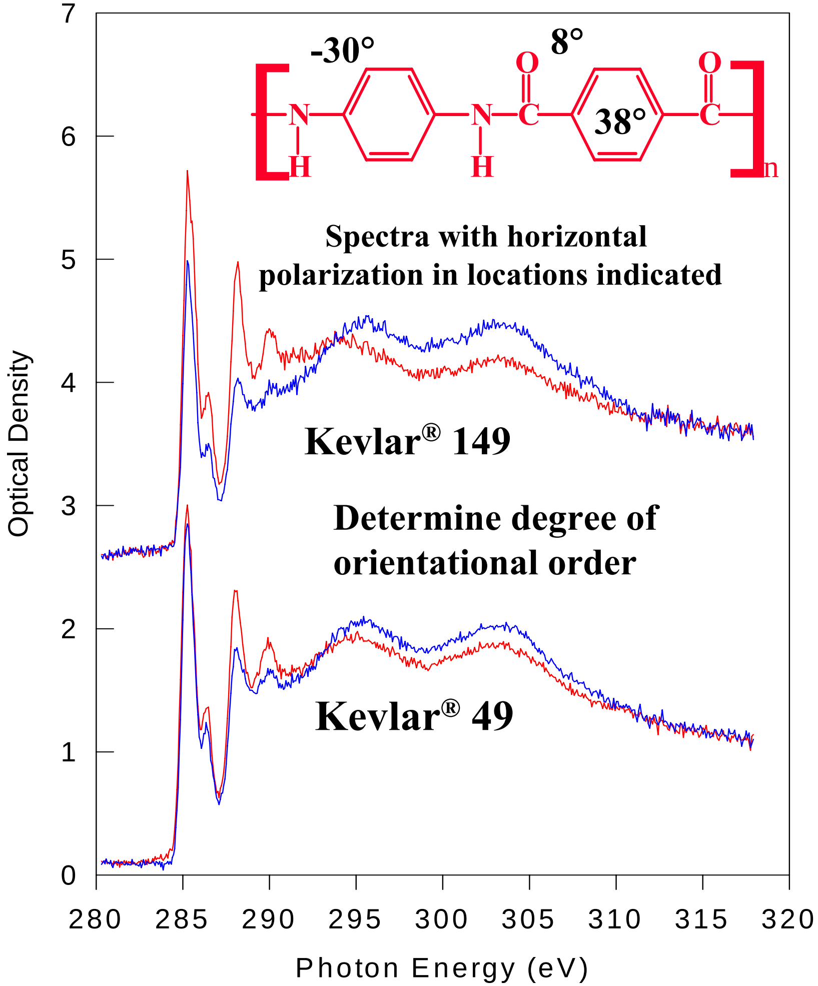
f = 250 MHz



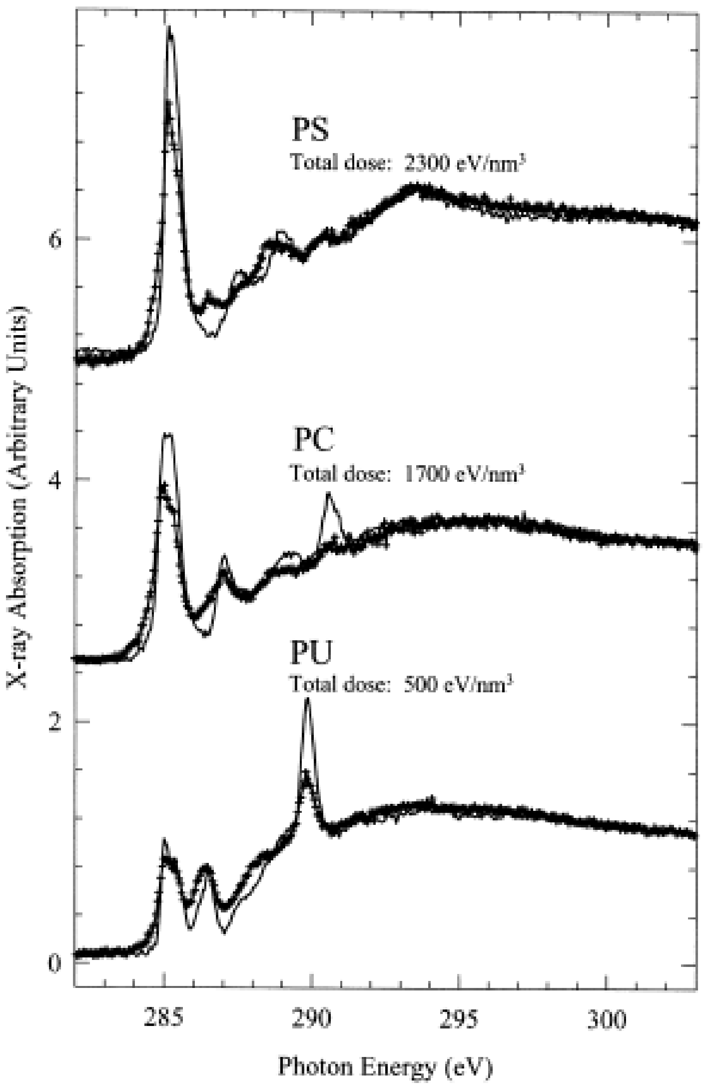
Change of vortex core chirality (handedness)

Use ERL for improved energy resolution?

- **NEXAFS already limited by core-hole lifetime**
- **Resonant Inelastic X-ray Scattering for improved spectroscopy**
  - **But, damage!**
  - **Need to back off on spatial resolution**



Radiation Damage



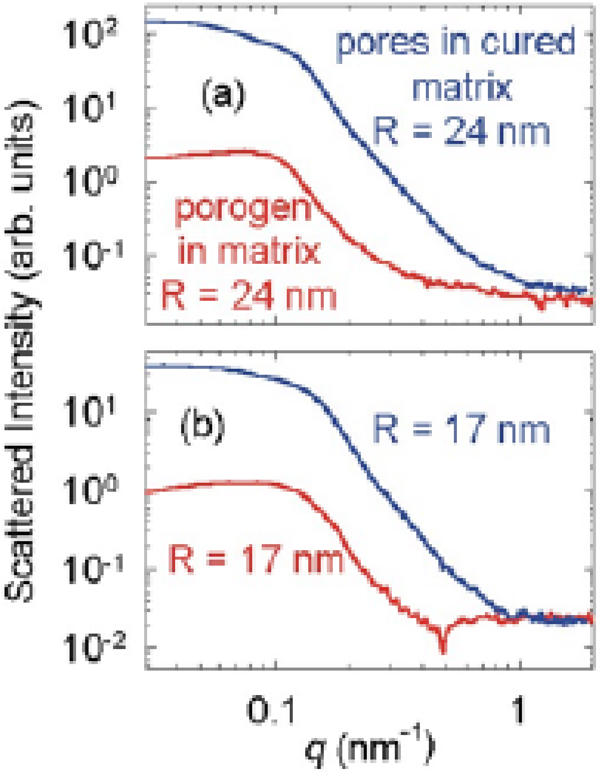
T. Coffey et al. J. Electron Spectroscopy 122 (2002) 65 –78

- **Typical critical dose ~ 1000 eV/nm^3**
- **Rose criterion for detection: S/N=5**
- **Transmission, S=-ln(I/I$_0$)**
- **(10 nm)^3 PS feature has S/N of 5 for 650 incident photons, and 115 absorbed photons in pi* peak at 285 eV**
  - **Dose= ~32 eV/nm^3**
- **Quantitation/spectra/tomography typically require 100x dose**
  - **Near critical at 10 nm for PS**
  - **Dose $\propto$ 1/($\Delta\alpha$)**
- **Imaging using phase contrast**
- **Scattering using phase and absorption contrast**

What about scattering?

- $I \propto \Delta\delta 2 + \Delta\beta 2$
  - Works with low contrast
- Q-range ~ 3 nm^{-1} (@300 eV)
- Dose is distributed!!
- Time resolution could be quite good
- "SAXS" not intrinsically a brightness driven experiment

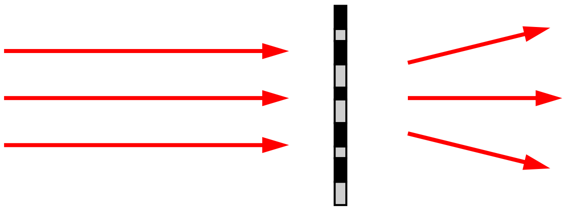
- Combine low resolution STXM and SAXS: Microbeam scattering
  - Damage?

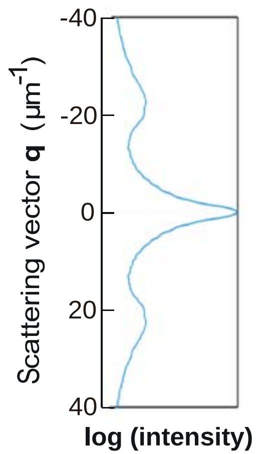


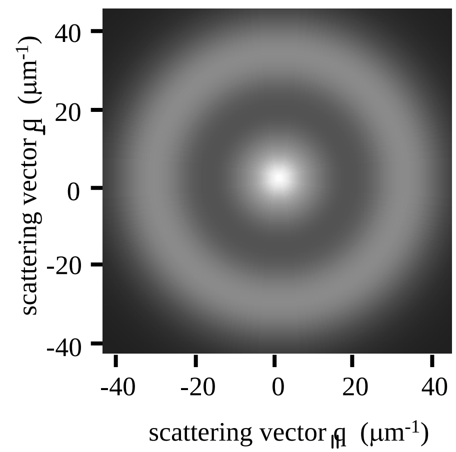
"Incoherent" vs. Coherent X-Ray Scattering

Small Angle Scattering

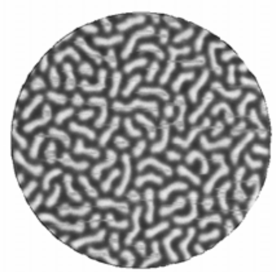
Coherence length larger than domains, but smaller than illuminated area





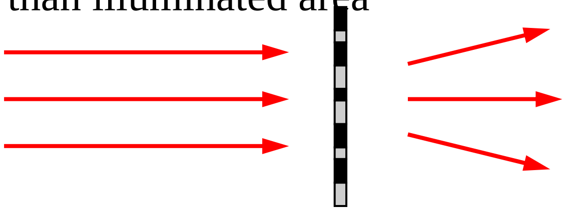


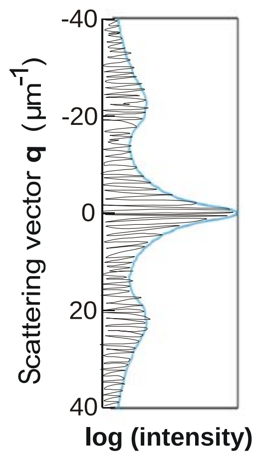
information about domain statistics

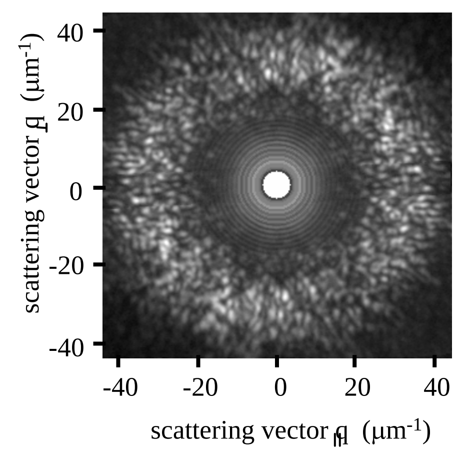


Speckle

Coherence length larger than illuminated area







true information about domain structure

Figure courtesy J. Stohr

Resonant scattering and resonant coherent speckle/imaging should be excellent tools for many materials !

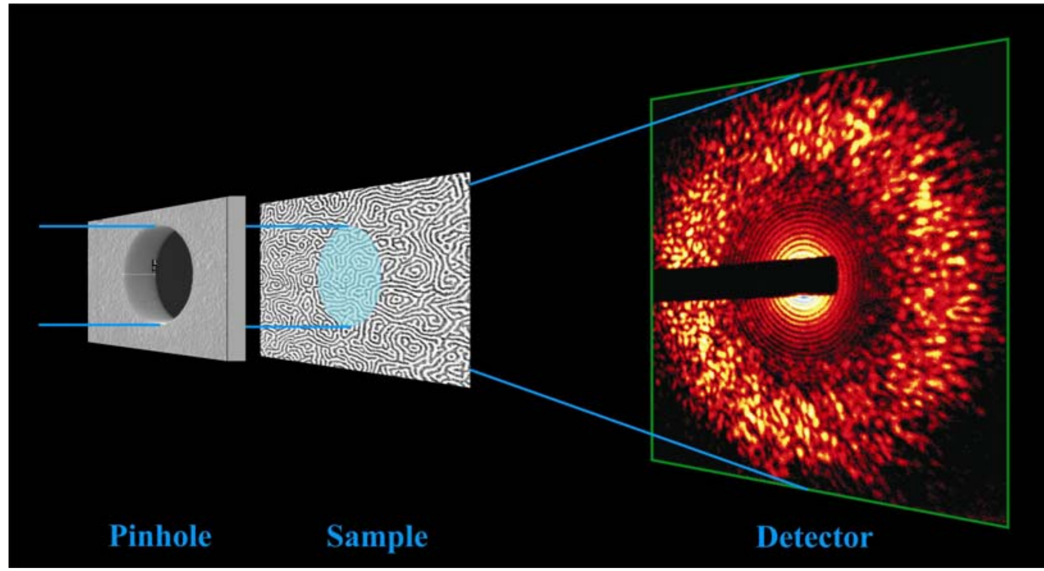
New tools

(Jan Luning's talk)

Coherent X-Ray Imaging

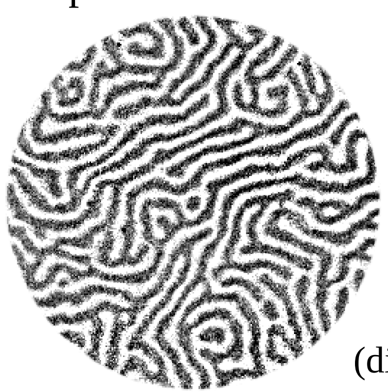
Technique of choice for use at ERLs

damage limit?

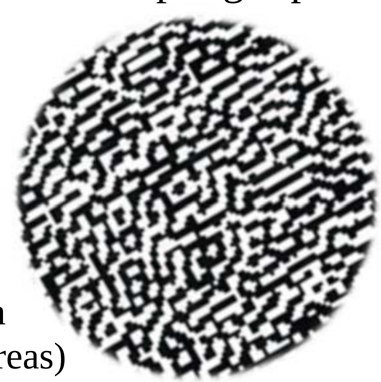


Phase problem can be solved by "oversampling" speckle image

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)

For more recent data see. Eisebitt et al. Nature 432, 885 (2004)

Conclusions

- **NEXAFS imaging, Resonant Scattering**
  - **High, tunable contrast: Compositional, i.e. "bond specific" sensitivity**
- **Technology: STXM, PEEM, SPEM, scattering, speckle**
  - **Good progress over the last 20 years**
  - **These techniques will benefit greatly from new sources, more capacity, more competition, better zone plates**
- **New zone plate optics strategy**
  - **STXM with spatial resolution < 10 nm possible, but challenging**
- **Higher energy offer relatively larger payoff (coherent volume $\propto \lambda^2$)**
- **Radiation damage a limitation in absorption mode**
- **Microbeam scattering**
- **Resonant coherent imaging in phase mode is good idea (Jan Luning's talk?)**
  - **Resonant photon correlation spectroscopy**
- **Pump probe experiments will have better time resolution**

Thank you for your attention!!!!

Post Doc hire by this fall

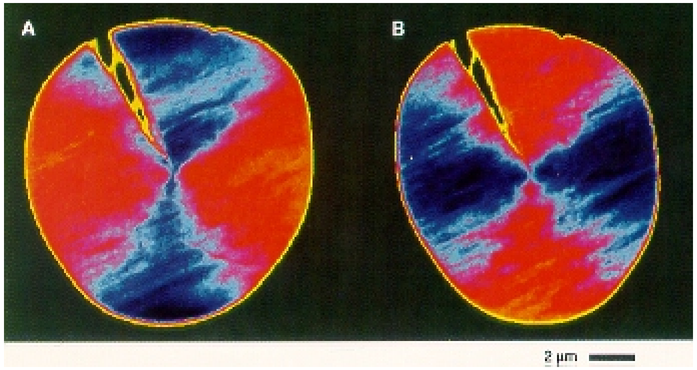
Resonant scattering/reflectivity: Conclusions

- **High, tunable contrast**
- **Compositional, i.e. bond specific, sensitivity**
- **Multiple modes: Scattering and reflectivity**

- **Soft X-ray should be good complement to neutrons and hard x-rays**
- **Good complement to TEM, SPM, STXM, SANS/SAXS**
  - **Reality check!???**

Future:

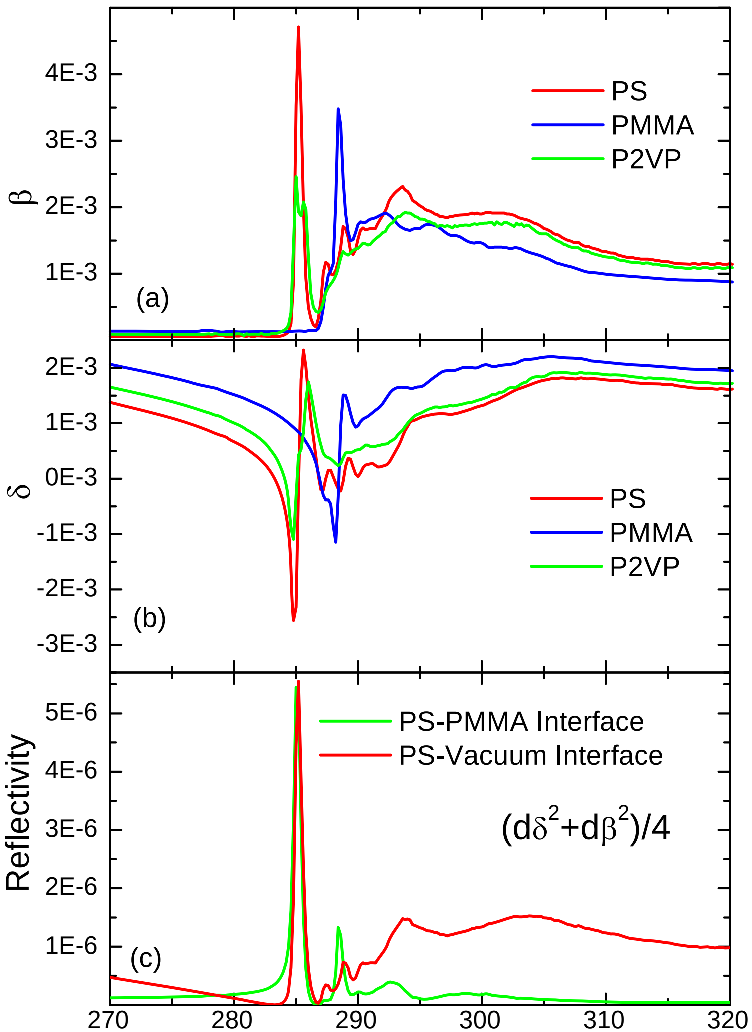
- **Contrast from orientation!**
- **Control of sample environment**
- **Resonant coherent imaging?**



NEXAFS microscopy sensitive to orientation

Soft X-ray Resonant Reflectivity

C. Wang, T. Araki, H. Ade



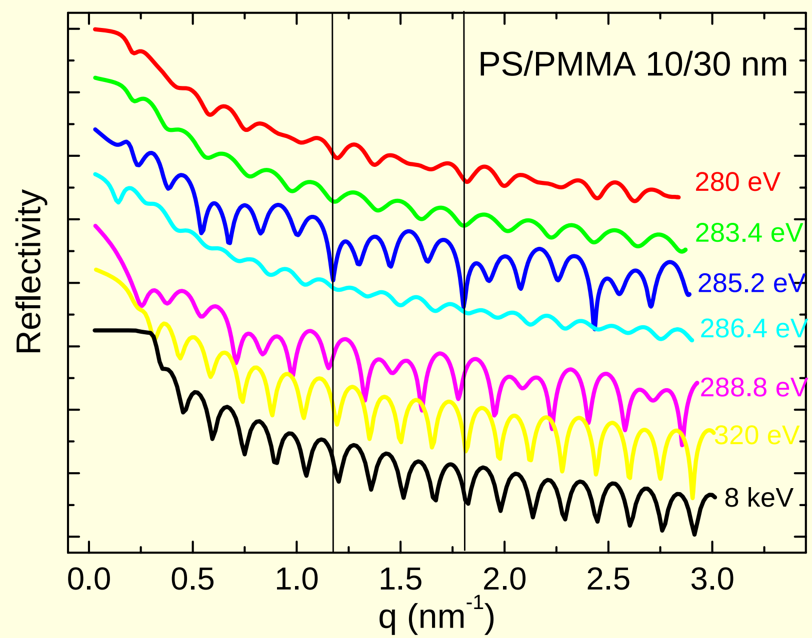
Can use large angles, hence, get good q-range

Reflectivity at the PS/PMMA interface is related to the contrast between PS and PMMA

$$R_{12} = r_{12}^2 \cong \left| \frac{(\delta_2 - \delta_1) + i(\beta_2 - \beta_1)}{(1 - \delta_1 - i\beta_1) + (1 - \delta_2 - i\beta_2)} \right|^2 \cong \frac{\Delta\delta^2 + \Delta\beta^2}{4}$$

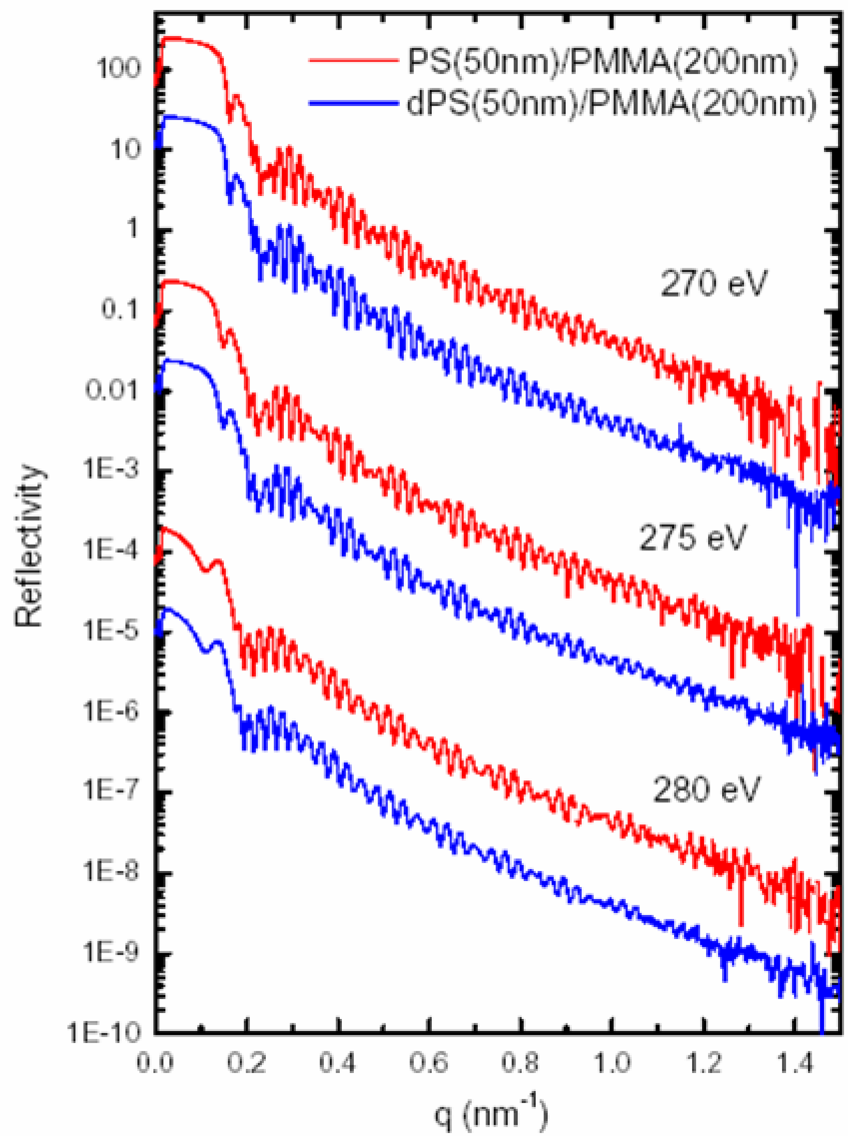
Rapid changes as the function of photon energy.

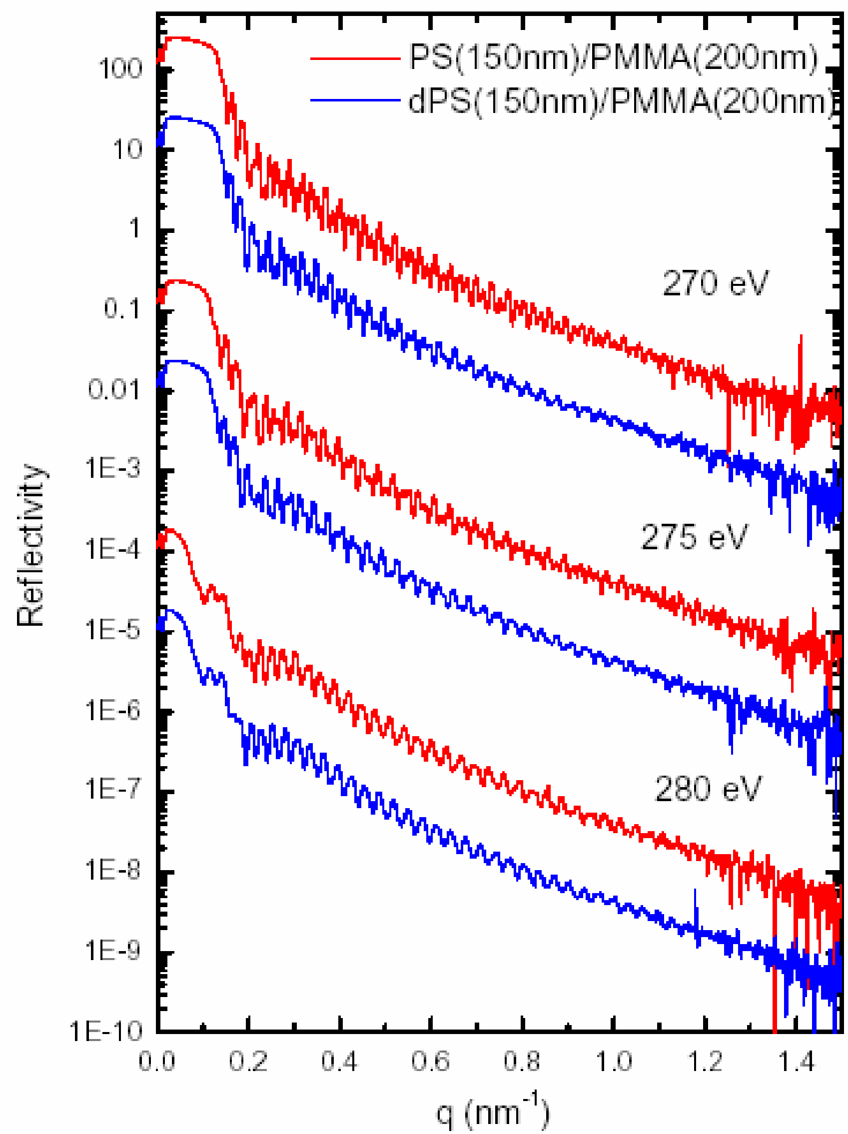
Simulations



- At 280, 285.2eV 288.8eV ----- bilayer signature
- 283.2eV --- only single PMMA layer
- 320 eV and 8 keV --- essentially only full layer signal

PS/PMMA interface: hPS and dPS



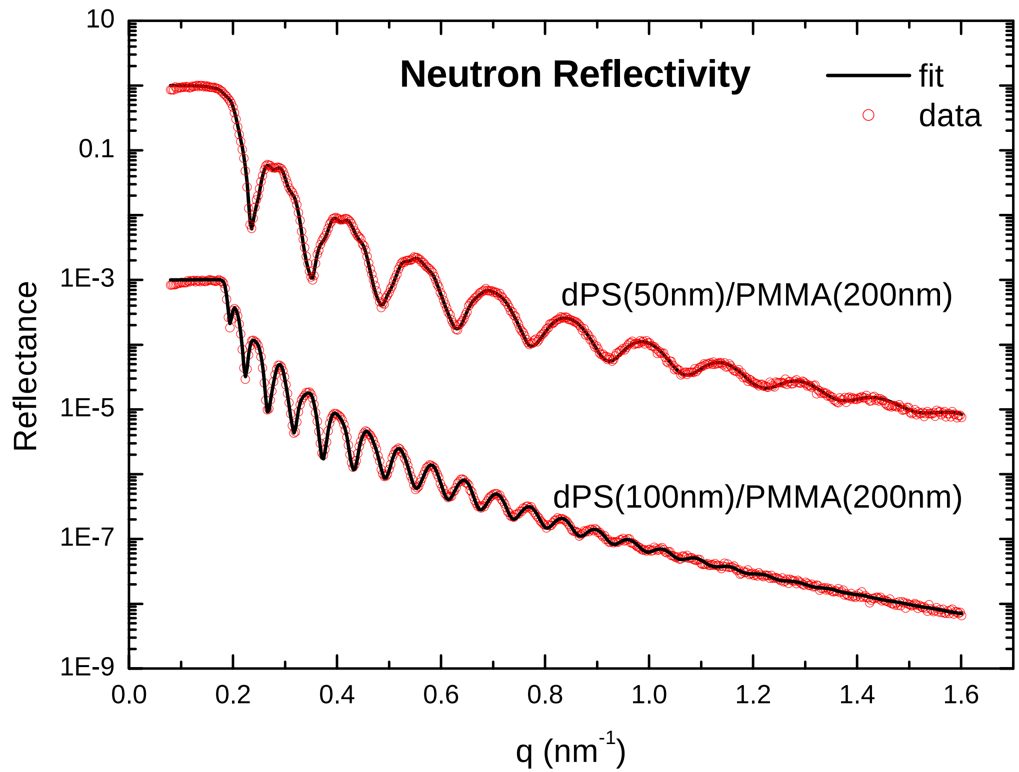


dPS/PMMA has larger interface than hPS/PMMA

- **Implications for neutron work, comparison to theory, capillary waves, etc.**

H. Ade et al.,ERL 2006

Direct comparison to Neutron Reflectivity



Method	Bilayers	D (nm) dPS	D (nm) PMMA	σ_{rms} (nm) dPS/Air	σ_{rms} (nm) dPS/PMMA
RXR	dPS(50nm)/ PMMA(200nm)	43.3	187.3	0.55	1.48
	dPS(100nm)/ PMMA(200nm)	98.5	189.3	0.77	1.48
Neutron Reflectivity	dPS(50nm)/ PMMA(200nm)	41.7	188.8	0.43	1.34
	dPS(100nm)/ PMMA(200nm)	96.5	190.3	0.49	1.46

σ_{rms} hPS/PMMA =1.16 nm

Conclusions
Opportunities

- **Technology: STXM, PEEM, SPEM, scattering, speckle**
  - **Tremendous progress over the last 20 years**
  - **Clearly all these techniques will benefit greatly from new sources, more capacity, more competition, better zone plates**

and most importantly new and exited users

- **Science**
  - **Polymers! - Yes, but radiation damage might set a limit**
    - **Polymer-inorganic bybrids**
    - **Templating**
  - **Magnetic materials**
  - **Nanoscience in general**
  - **Biology**