Spatial resolution and spectroscopy:
The ultimate "cross-over" tool in real and reciprocal space?

NSLS-II Workshop
February 11, 2008

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

Goal: Frame afternoon discussion

workshop is tasked with "what kind of beamlines"
and
science case

- **Revolutionary of evolutionary?**
- **Extrapolation of techniques?**
  - **What will be new?**
- **Totally new techniques?**

- **Are we going to just move "stuff/beamlines"?**
  - **We should prevent that!**

How much better?

NSLS-II is not an FEL, ERL

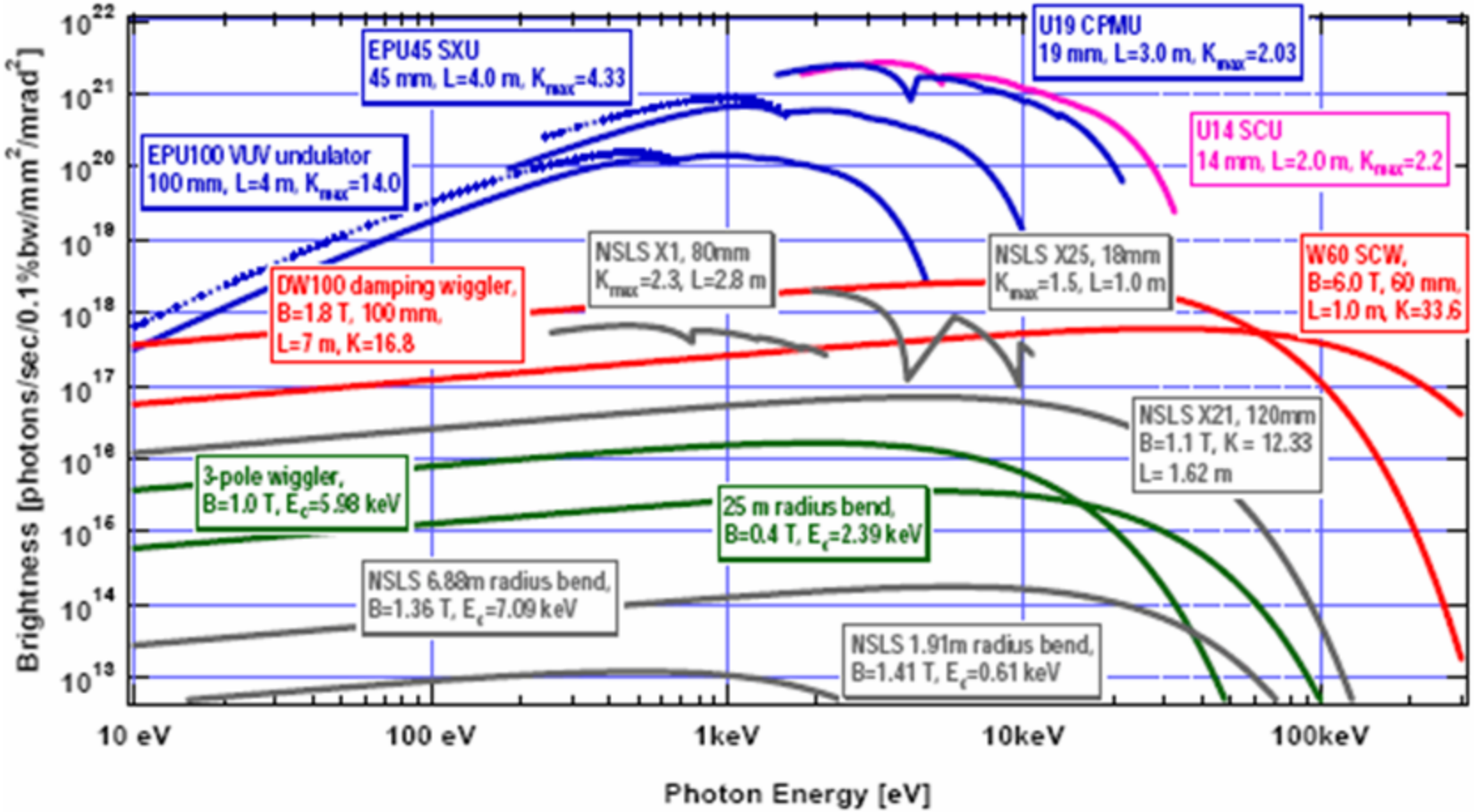


Figure 3. Brightness comparison for NSLS-II and NSLS sources.

Soft matter

- Consists mostly of C, N, and O
- 250-600 eV covers C, N, and O edge

- > 2 orders of magnitude improvement in brightness
  - > 1 order of magnitude improvement in S/N
    - Low signal experiments
  - > 2 order of magnitude in acquisition speed

Opportunities: Parameter Space

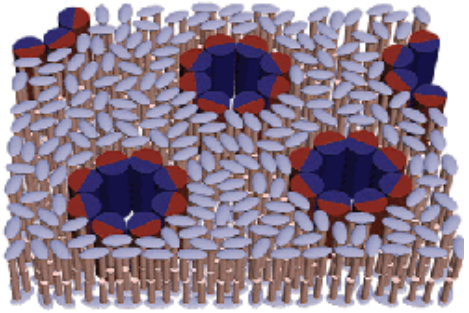
- **Spatial resolution**
  - **Small, with large dynamic range generally best**
- **Spectral resolution, specific interactions**
  - **Composition, labeling**
- **Time resolution**
  - **Dynamic phenomena**
- **Sample environment**
  - **X-ray cross sections?**
- **Polarization control**

Combination of the above!

Opportunities: Science

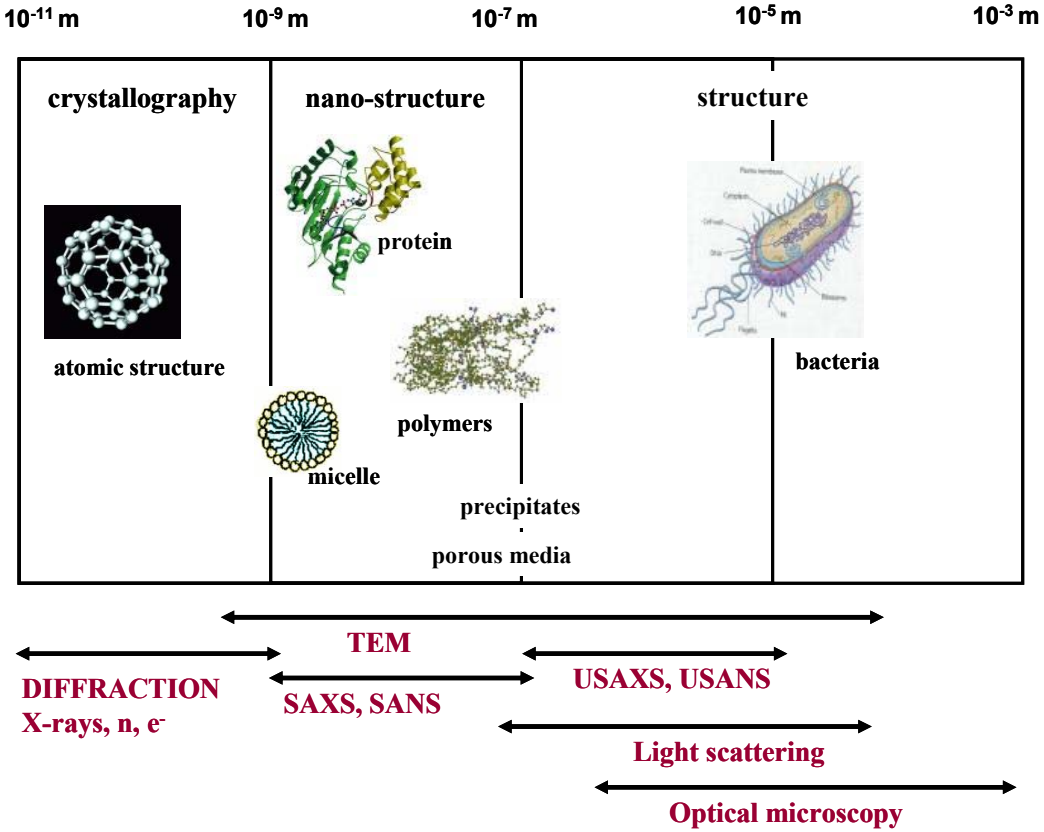
- **Membranes**
  - **Water purification**
  - **Fuel cell**
  - **Biology: rafts**
- **“Shampoo” and other complex matter (Helmut Frey)**
- **Organic devices**
  - **OLEDs**
  - **PVs**

Length scales probed by some "conventional" tools



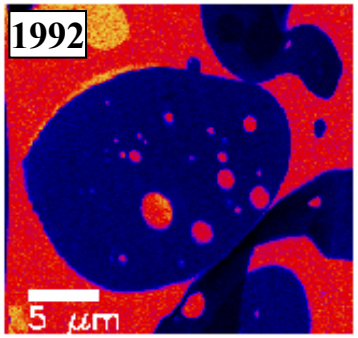
Example: Neutron-scattering at IPNS, ANL…peptides (cylinders) inserting themselves in holes they form in a cell membrane.

But:…, the best way to see part of a biomolecule is by replacing hydrogens with deuterium.
http://www.sns.gov/aboutsns/importance.htm



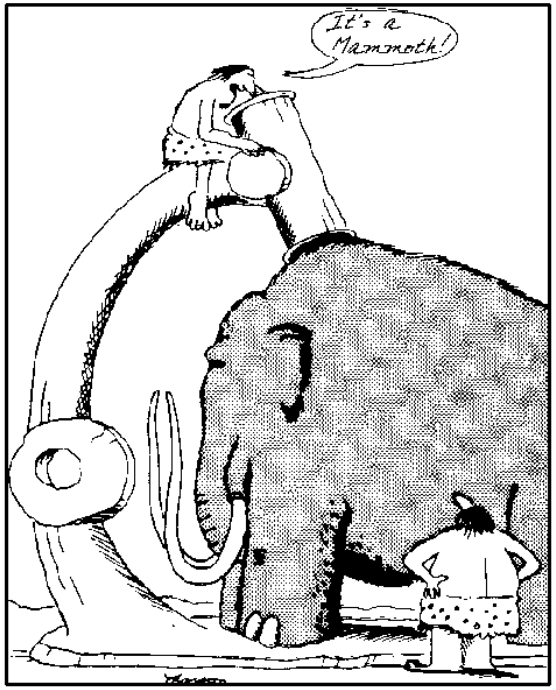
- RSoXS - complement to SANS, conventional SAXS
- Real space info would be best, but
  - Contrast? Spatial resolution? Damage limits?
    - TEM needs staining
    - NEXAFS in STXM and PEEM limited to ~40 nm spatial resolution
    - In-situ environments?

NEXAFS microscopy

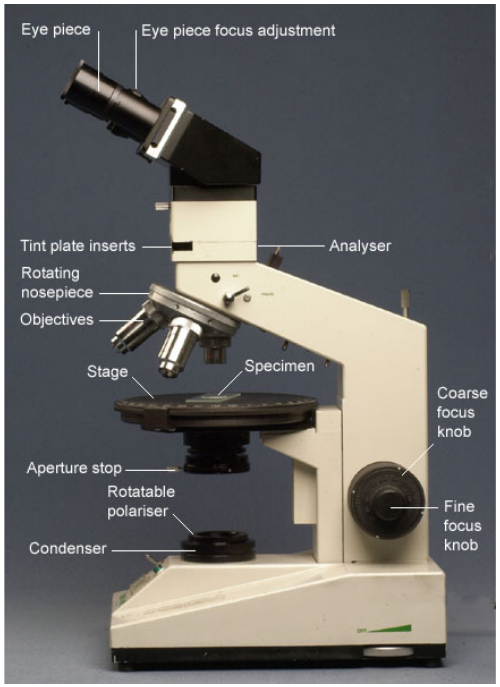


H. Ade et al., Science 258, 972 (1992)

Microscopy:
Morphology characterization in real space



Early Microscope



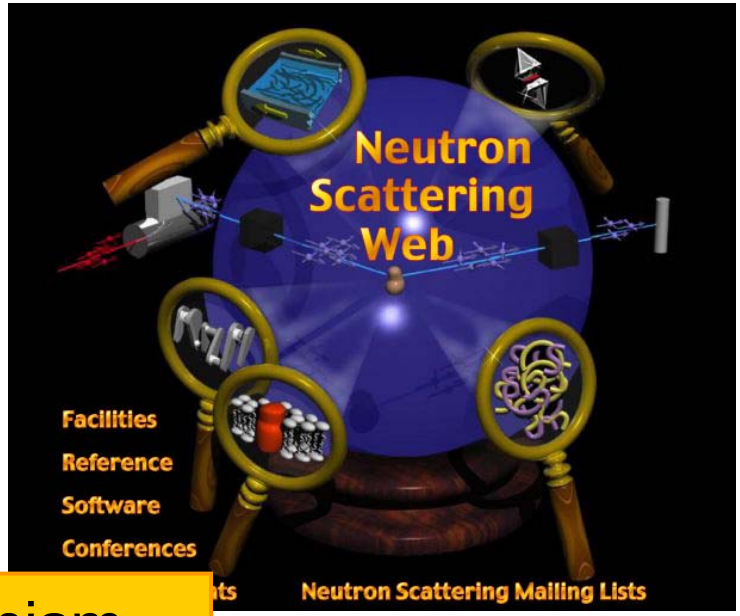
- Visible light microscopy
- Electron microscopy
- Scanning probe micros.
- Infra Red
- Raman microscopy
- NMR microscopy

- X-ray Microscopy???

- Contrast Mechanism
- Effective “resolution”?
- Quantitation?

Scattering/diffraction: Structure/morphology characterization in reciprocal space

X-rays alternative to neutrons



Small Angle Scattering

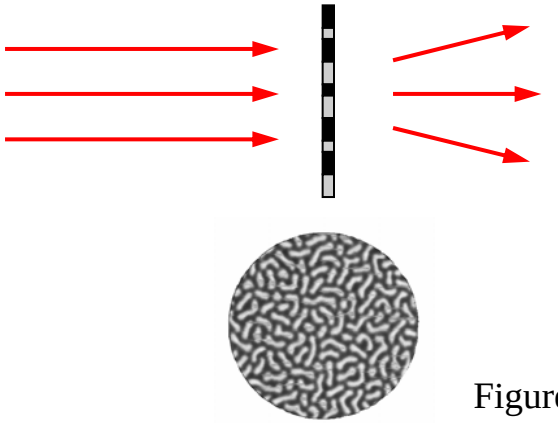
Coherence length larger tha

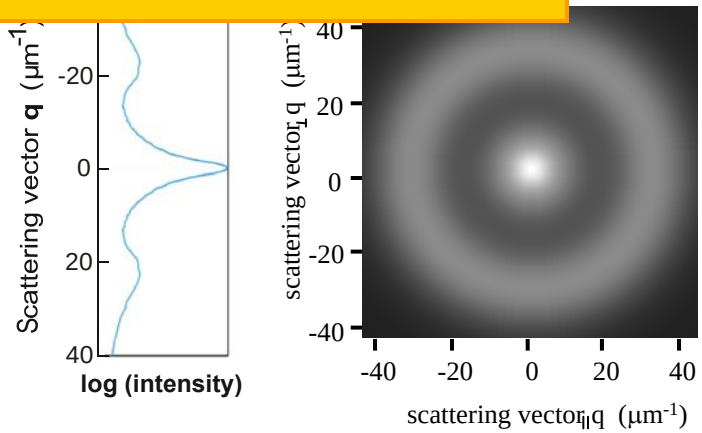
but smaller than illuminated

on Source: total cost of $1.4 billion,

gov/

- Contrast Mechanism
- Effective "resolution"?
- Quantitation?





Structure function: information about domain statistics.

Figure courtesy of J. Stohr

X-ray Microscopy:

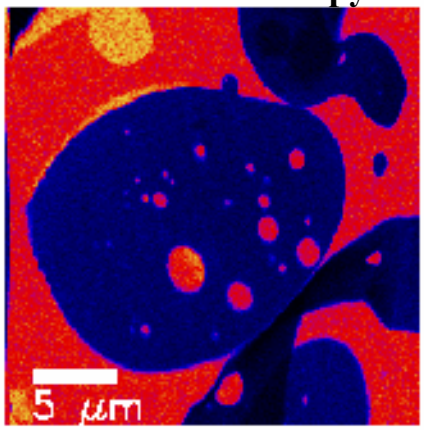
X-rays have come a long way!

(Examples "biased" towards polymers/magnetic materials)

1895

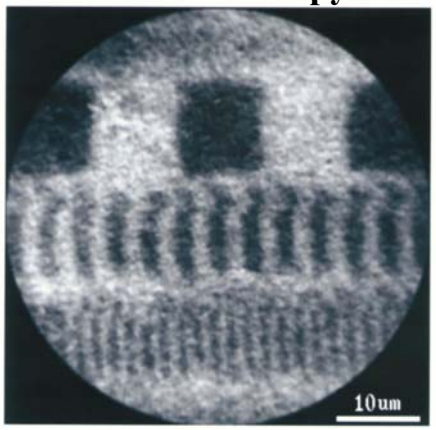
NEXAFS microscopy

1992



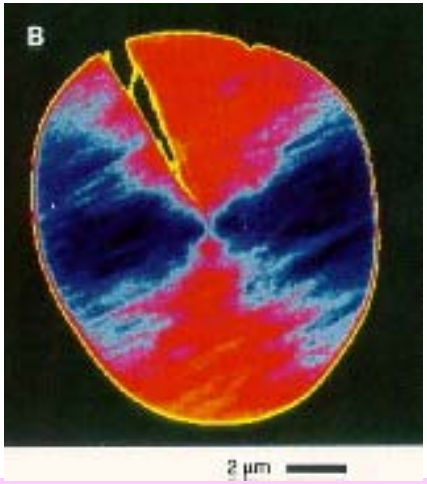
XMCD microscopy

1993



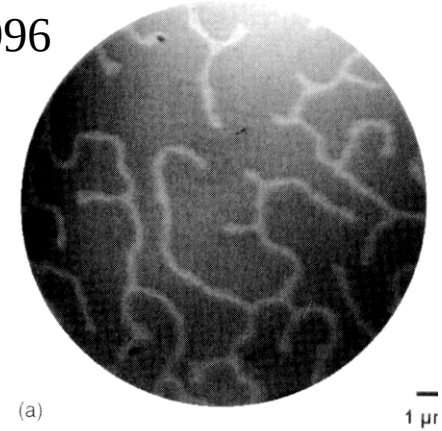
XLD microscopy

1993

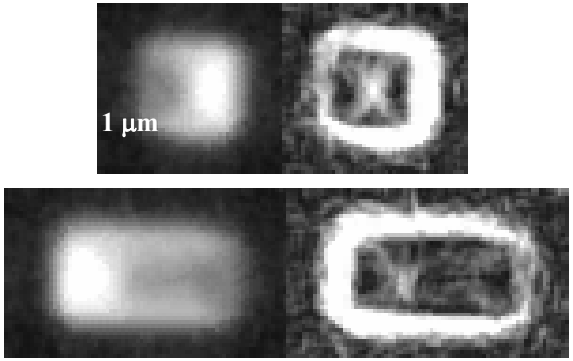


XMLD microscopy

1996



Dynamics



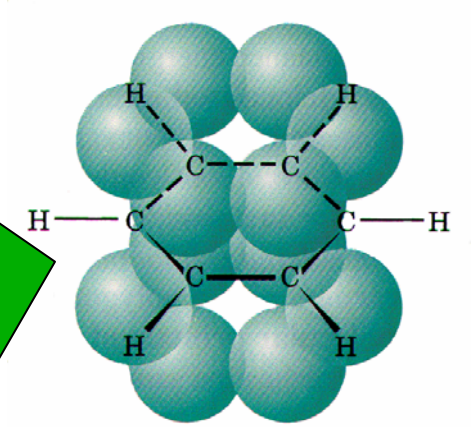
2003

Soft X-rays

Unique interaction with matter
yields unique contrast
and
unique characterization capabilities

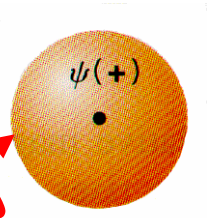
Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Example: “”Richness” of Polymer NEXAFS Spectra

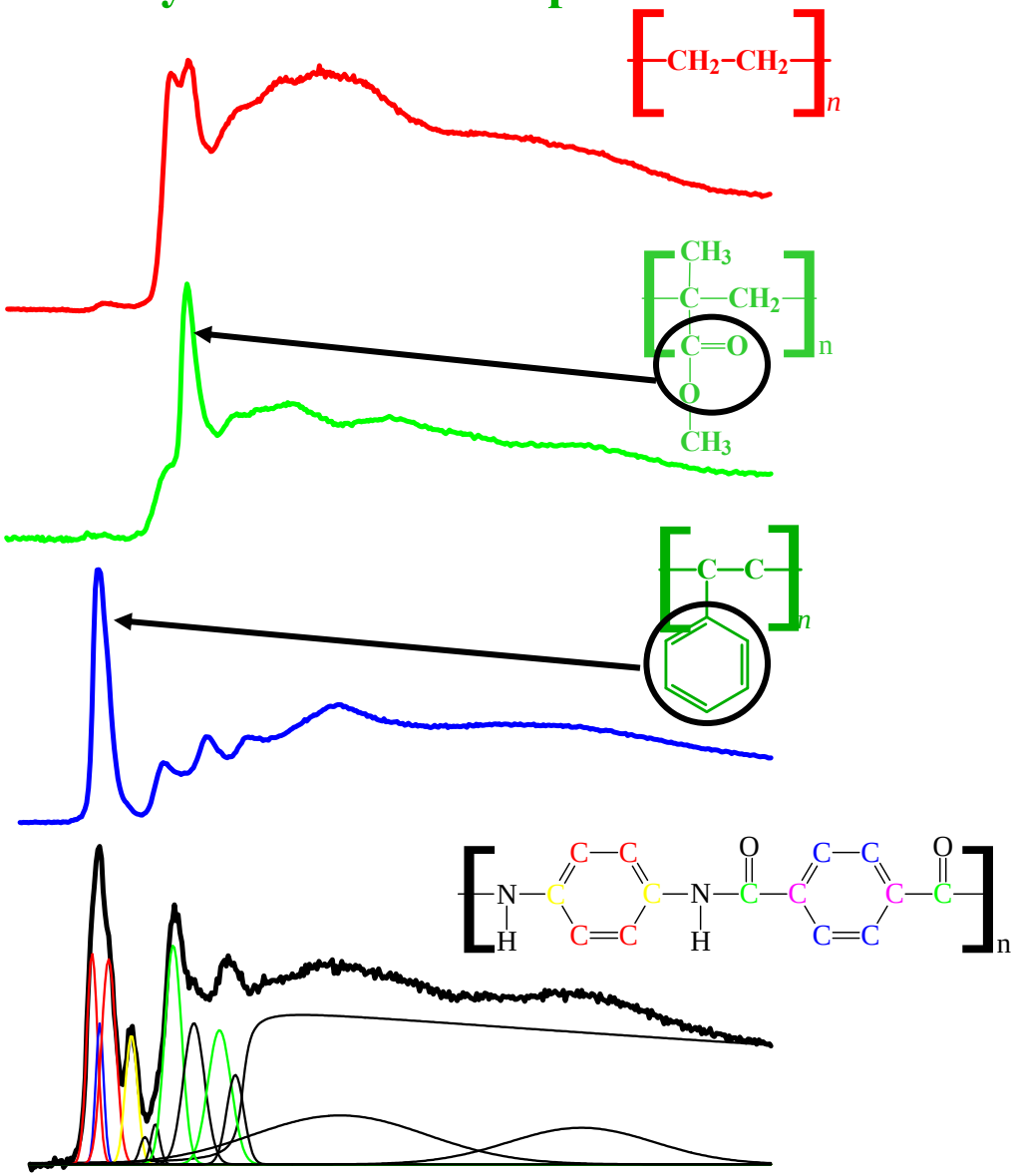


e-

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

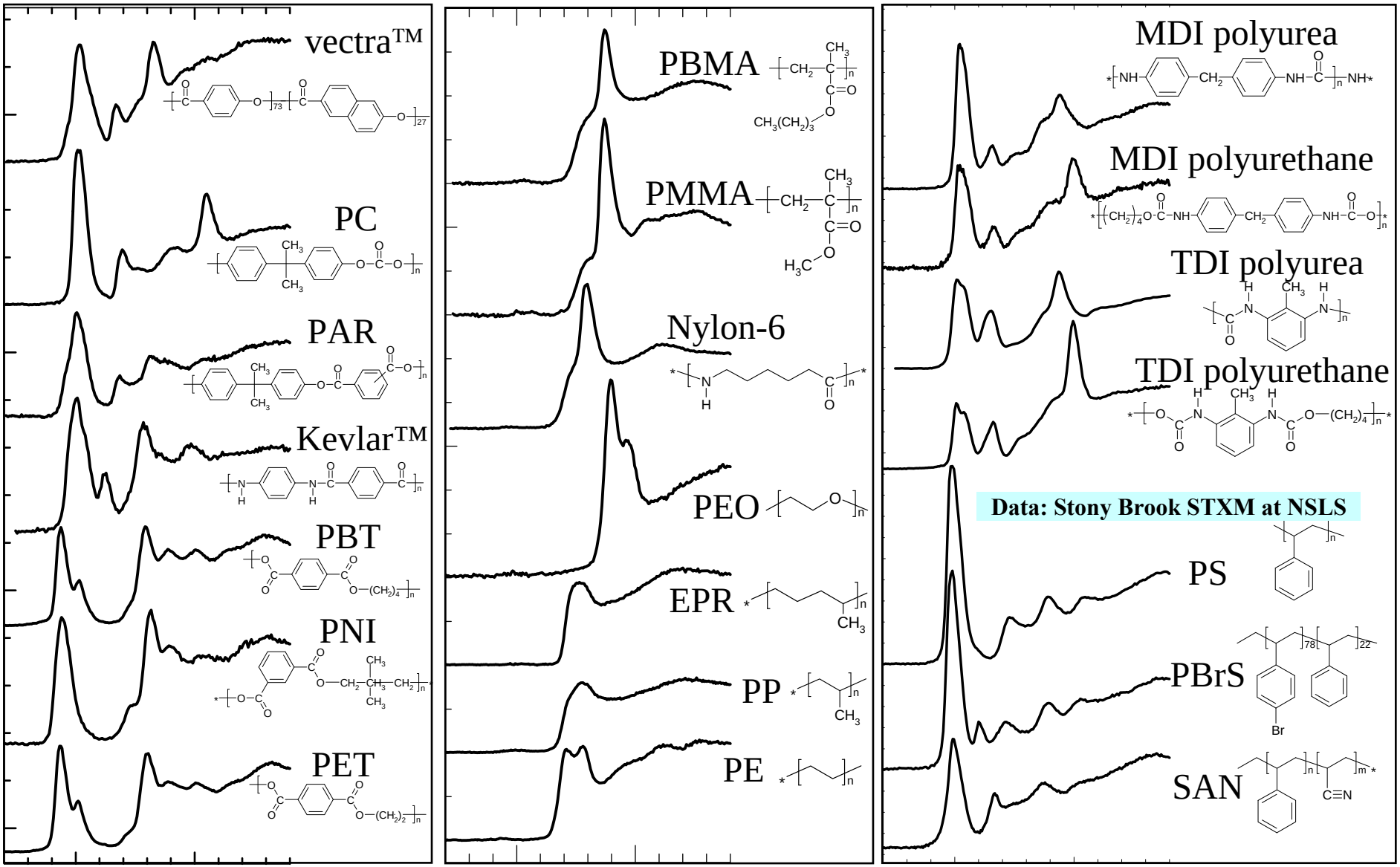


hν

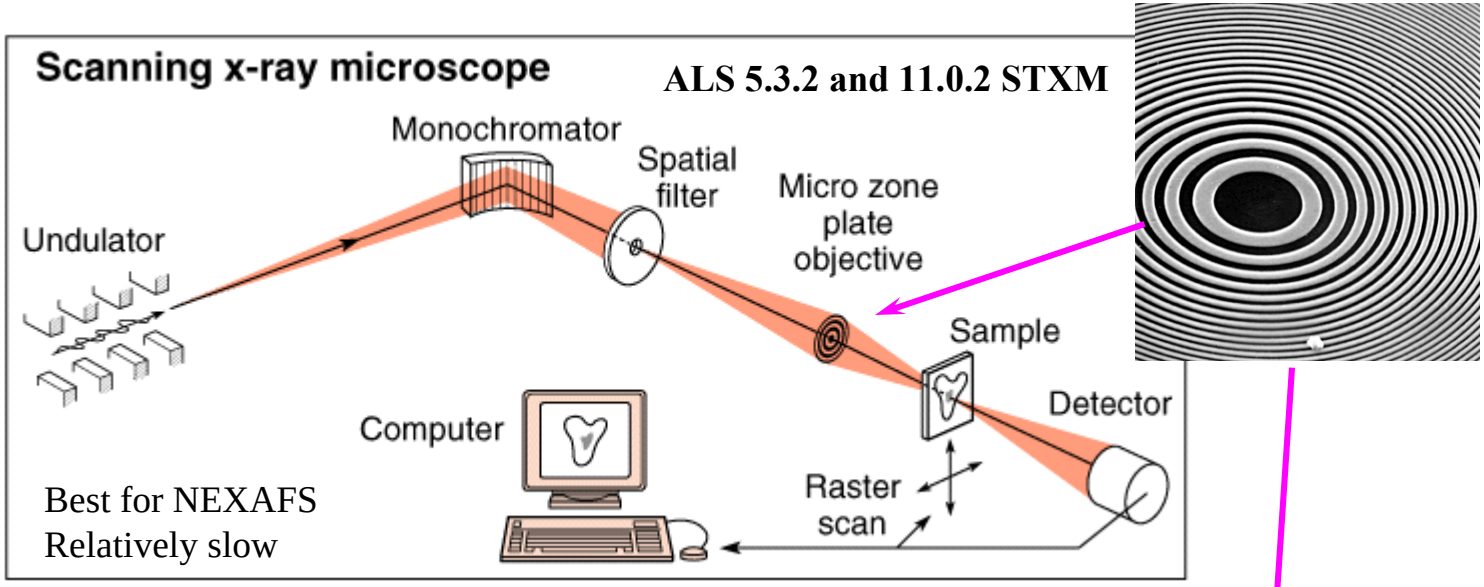


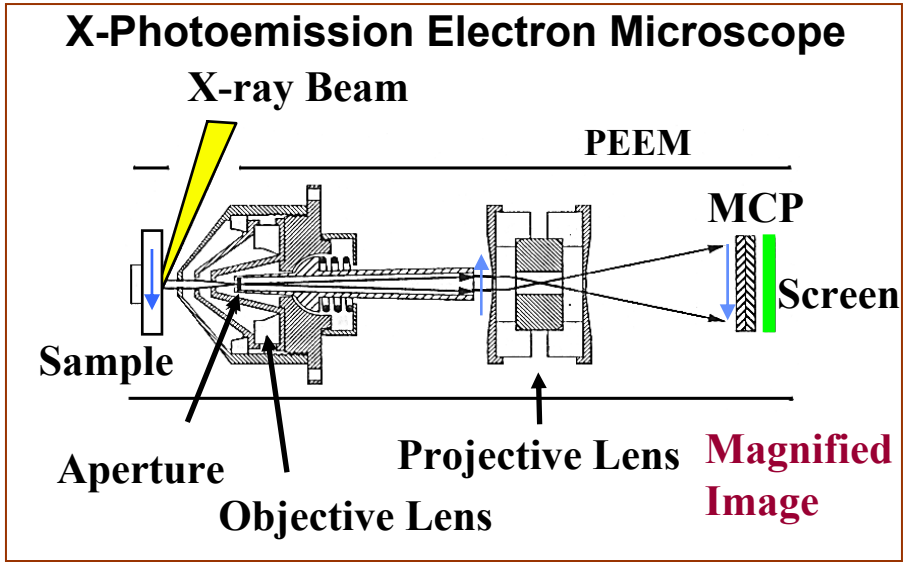
Spectroscopy = high resolution

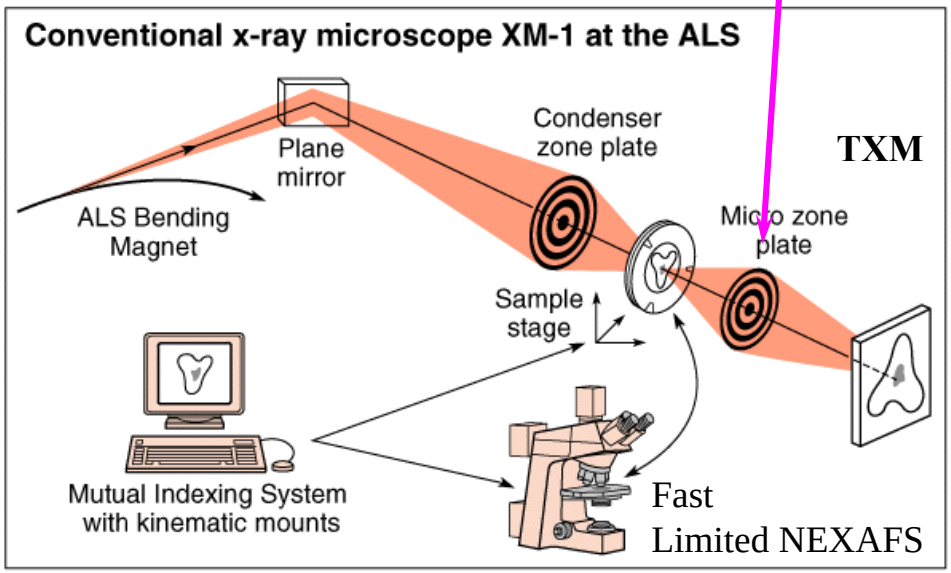
Dhez, Ade, and Urquhart
J. Electron Spectrosc. 128, 85 (2003)



Types of X-ray Microscopes

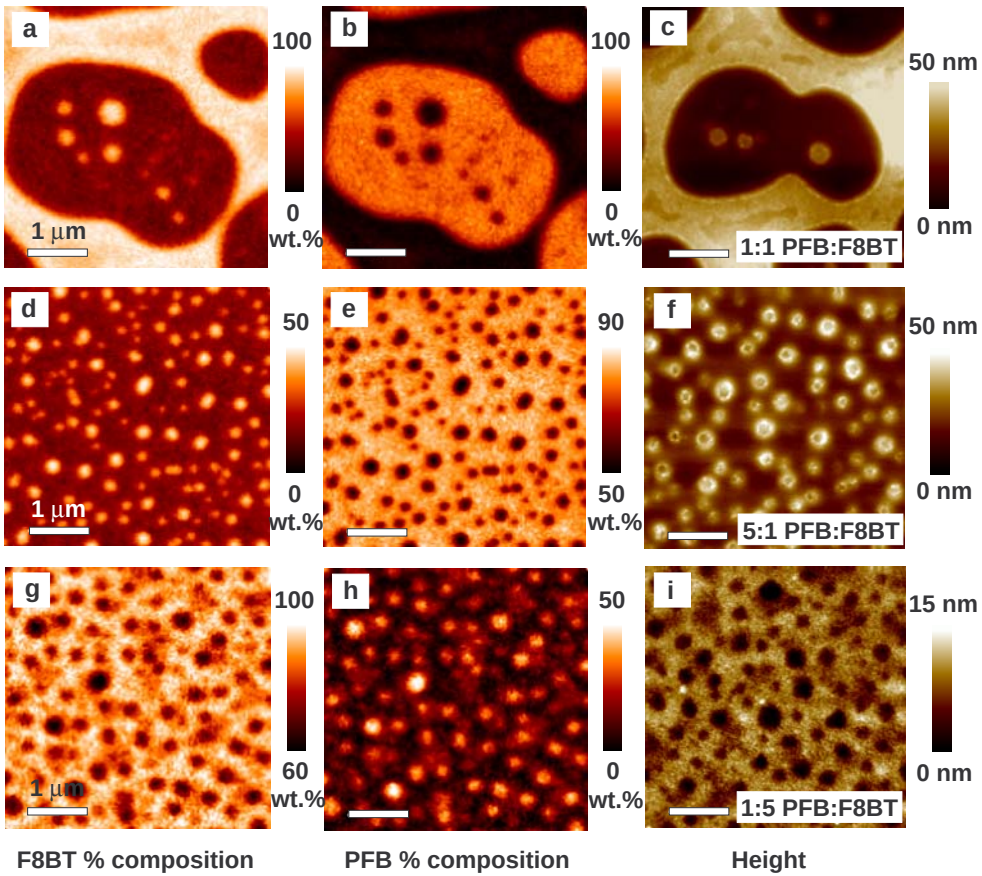


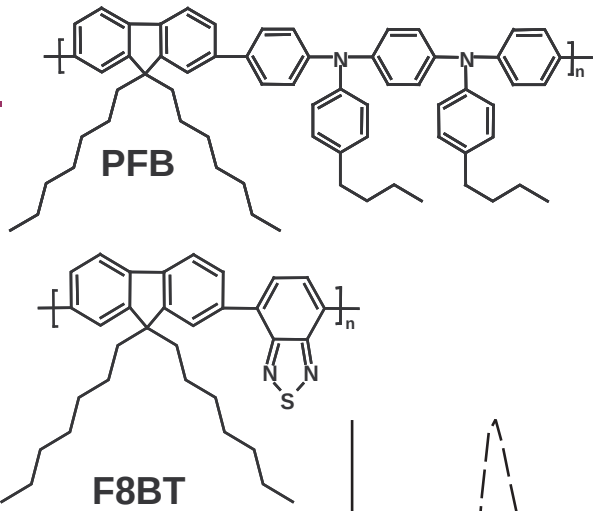




Also: Scanning Photoemission X-ray Microscope (SPEM) Ade et al. *Appl. Phys. Lett.* 56, 1841 (1990)

poly(9,9′-dioctylfluorene-*co*-bis-*N*,*N*′-(4,butylphenyl)-bis-*N*,*N*′-phenyl-1,4-phenylene-diamine) (PFB) and poly(9,9′-dioctylfluorene-*co*-benzothiadiazole) (F8BT) solar cells





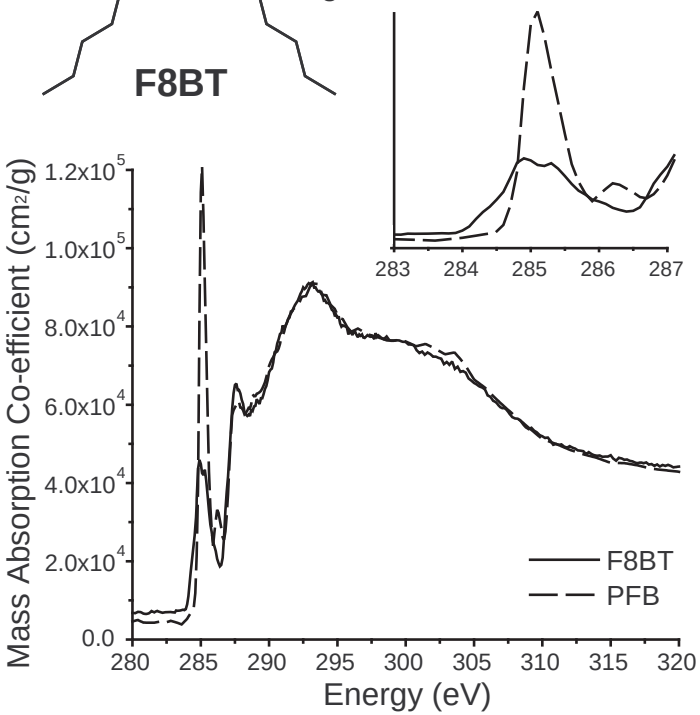


Figure courtesy C. McNeill

C. R. McNeill et al. Macromolecues **40**, 3263 (2007)

Soft X-ray Beam Induced Current (SoXBIC) Microscopy

First results on OPVs – Correlation of efficiency to composition

B. Watts, H. Ade (NCSU)
D. Queen. F. Hellman (UCB)
A.L.D. Kilcoyne (ALS)

L·B·N·L

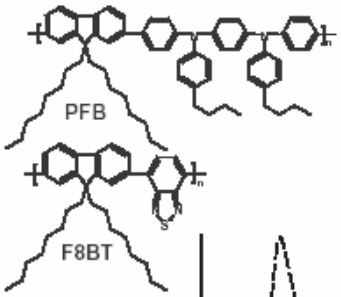
Advanced Light Source

NC STATE UNIVERSITY

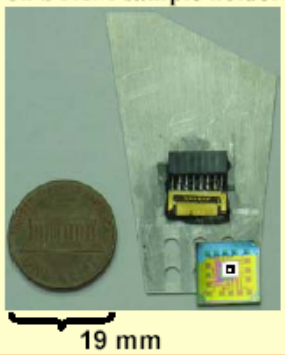
Experiments: B. Watts, D. Queen. May 12, 2007
5.3.2 Scanning Transmission X-ray Microscope (STXM) at ALS

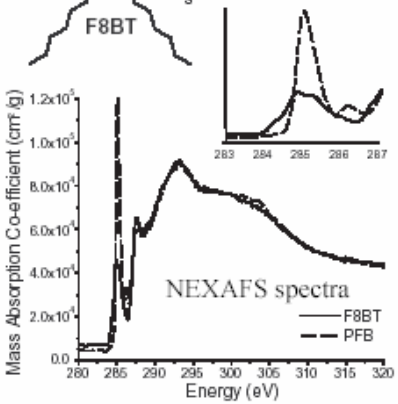
Supported by DOE grants DE-FG02-98ER45737 and DE-AC02-05CH11231

Sample prep.: Bulk heterojunction organic photovoltaic (OPV) device based on PFB and F8BT

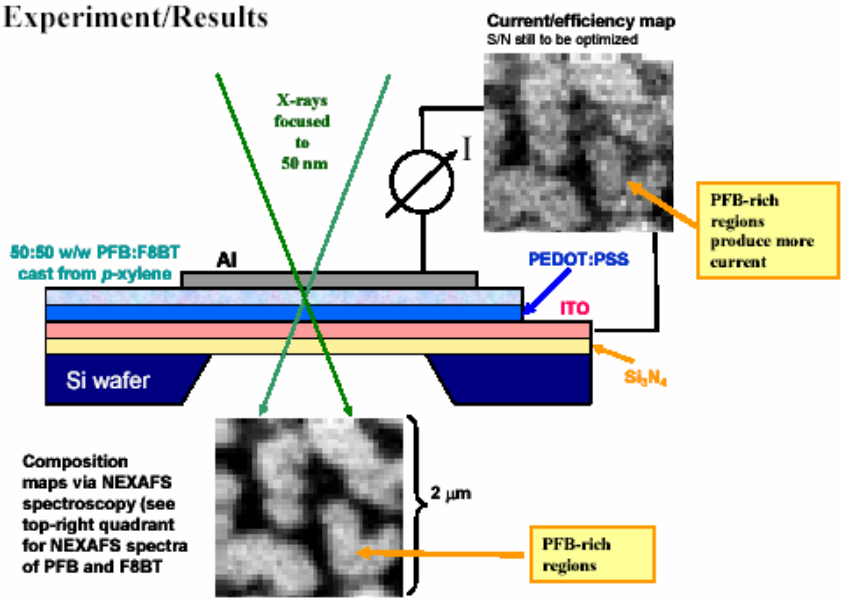


Fully functional OPV device on STXM sample holder





Experiment/Results



Payoffs/Advantages/Future

- OPV device process control and optimization
  - Process *feedback* greatly improved by this kind of characterization
- Quantitative, simultaneous ***composition and efficiency*** maps
  - Better understanding of ***device bottlenecks***
  - Aids ***device optimization***
  - No imaging artifacts such as coupling to topography
- S/N of SoXBIC can still be ***significantly improved***
  - these are the very first results
- Potential of ***10 nm*** spatial resolution in near future (now 50 nm)
  - 10 nm is matched to exciton diffusion length
- Potential to do ***3D tomography***
  - 3D morphology is critical device parameter
  - Determine wetting layers
- Characterization of multicomponent (n>2) systems possible

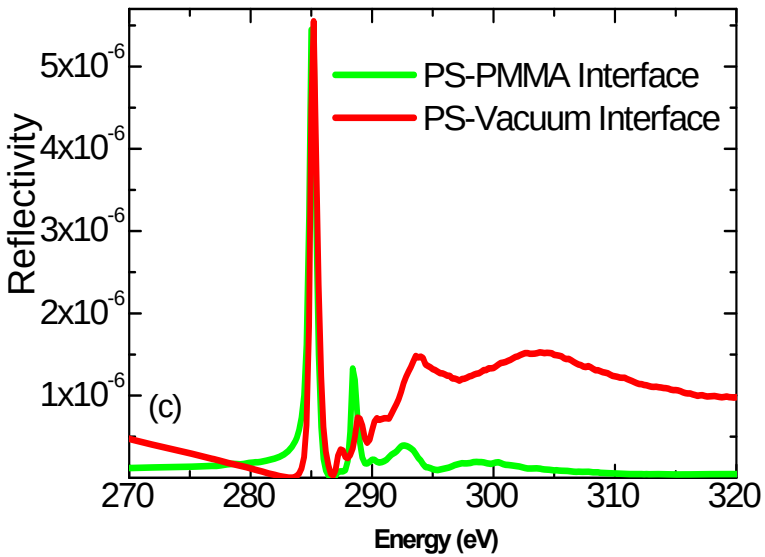
"Parameter space" for real space microscopy:
Higher brightness, more intensity

- **SoXBIC would clearly benefit**
  - **Damage threshold?**
- **Surface (SPEM, PEEM) microscopy would benefit**
  - **Damage threshold?**

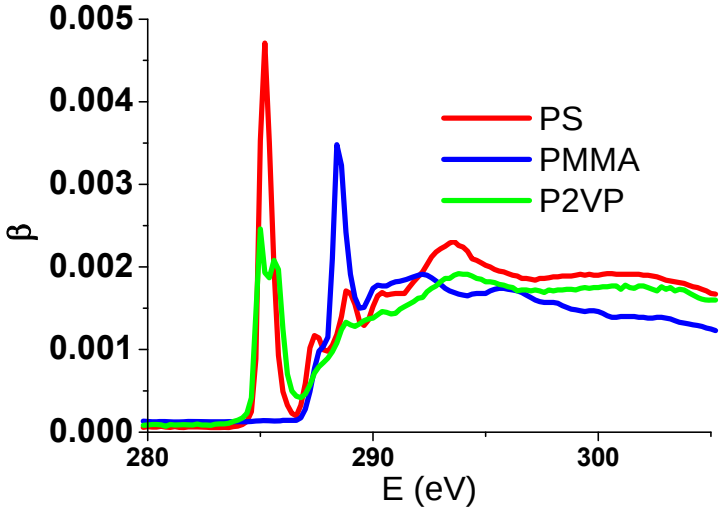
- **Traditional NEXAFS microscopy**
  - **Transmission: Relatively little benefit from NSLS-II undulator**
    - **Unless some form of time resolution is achieved**
    - **Would need better detectors and scanning stages**
    - **Great workhorse on bending magnet beamline**
  - **Secondary yield mode**
    - **Clear benefit, but technological hurdles**
    - **Damage threshold for soft matter?**

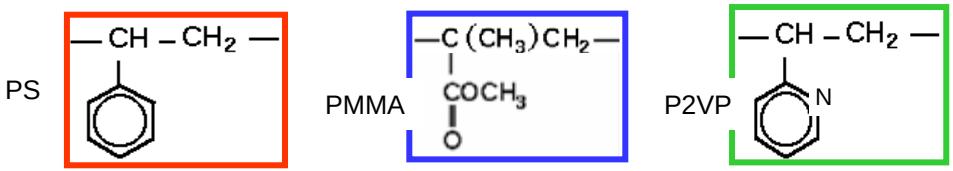
Resonant Scattering/Reflectivity Contrast: Carbon edge examples

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



Absorption (NEXAFS)





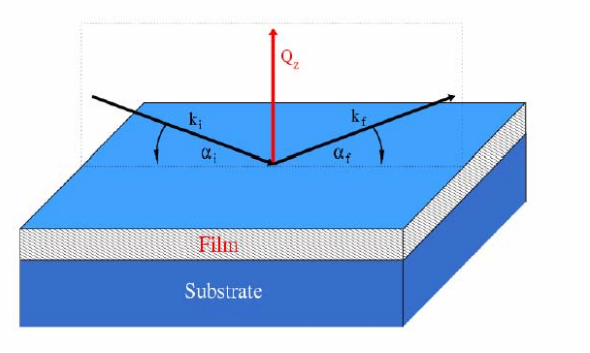
$$R \text{ or } I \propto (\Delta\delta^2 + \Delta\beta^2)$$

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

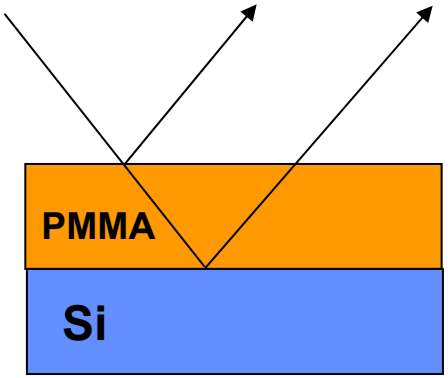
Reflectivity: Tuturial-1

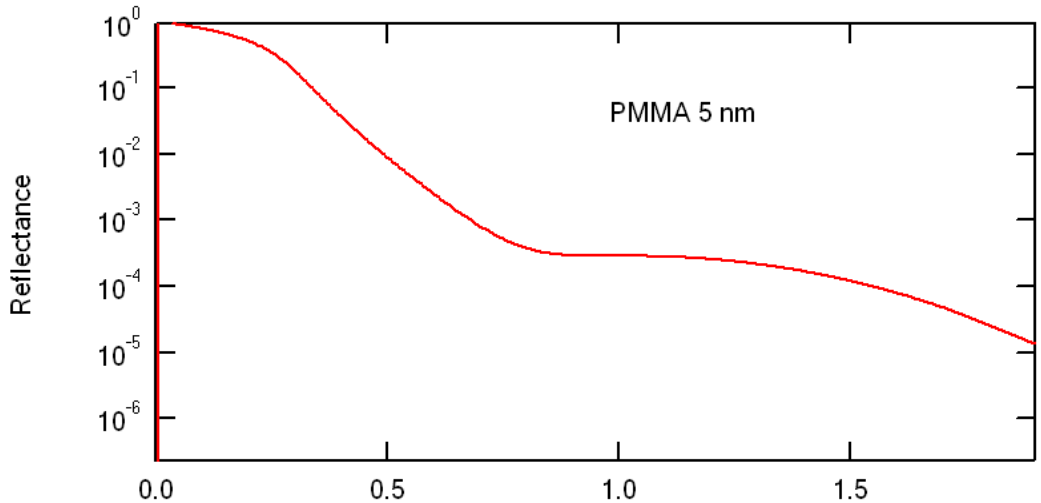
270 eV

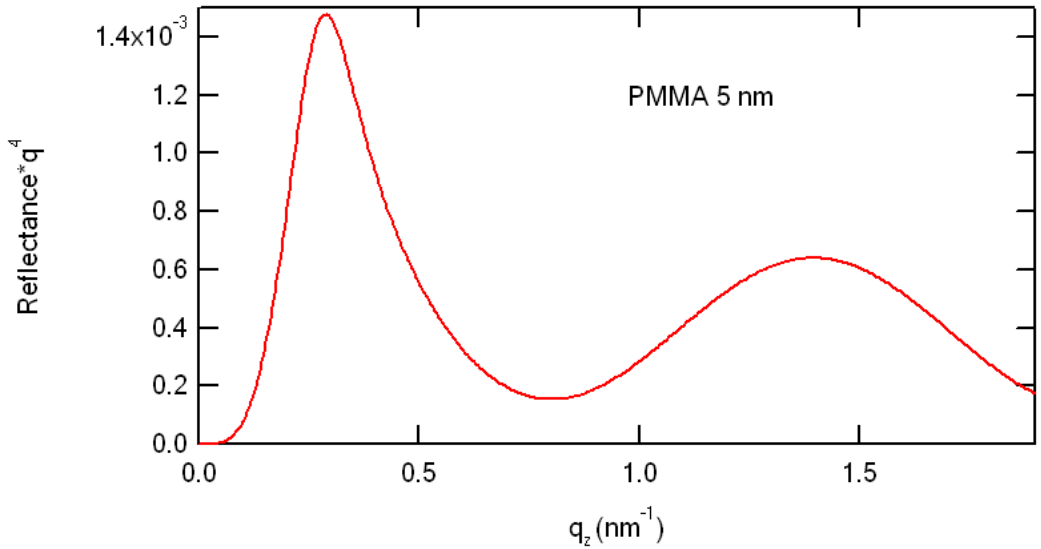
Momentum transfer:



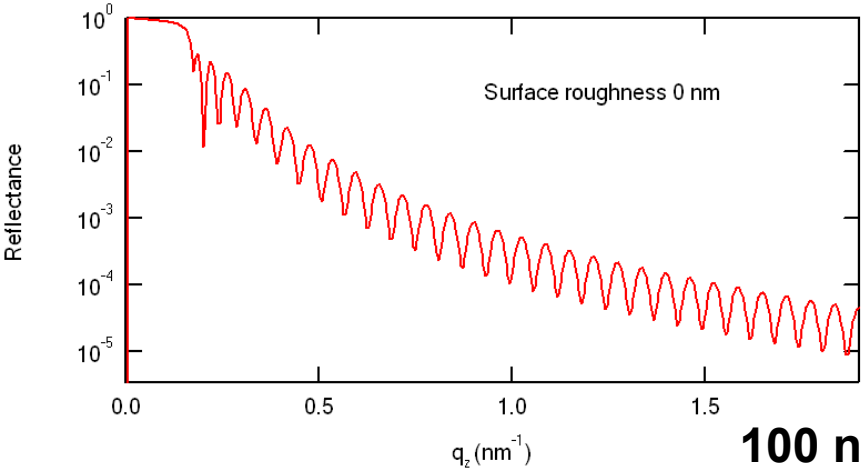
$$\vec{q} = \vec{k}_f - \vec{k}_i \qquad q_z = \frac{4\pi \sin\alpha_i}{\lambda}$$

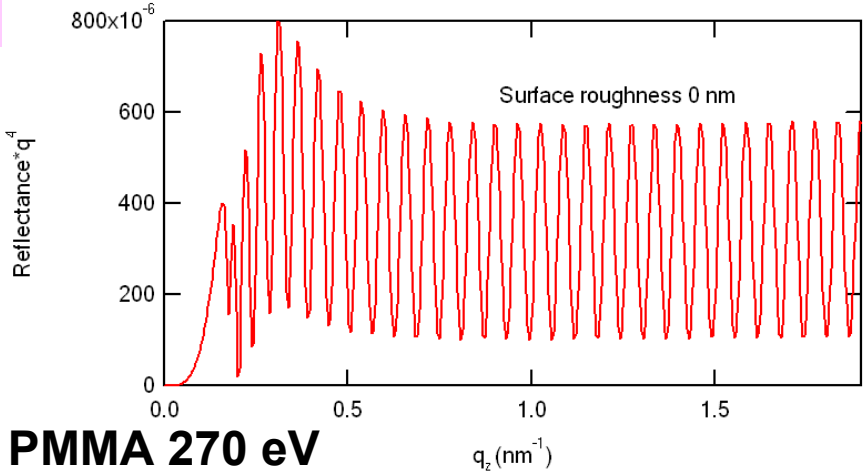


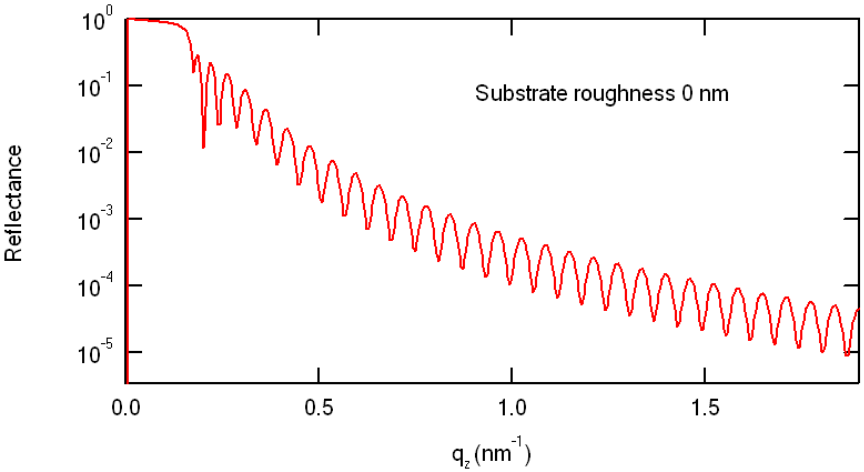


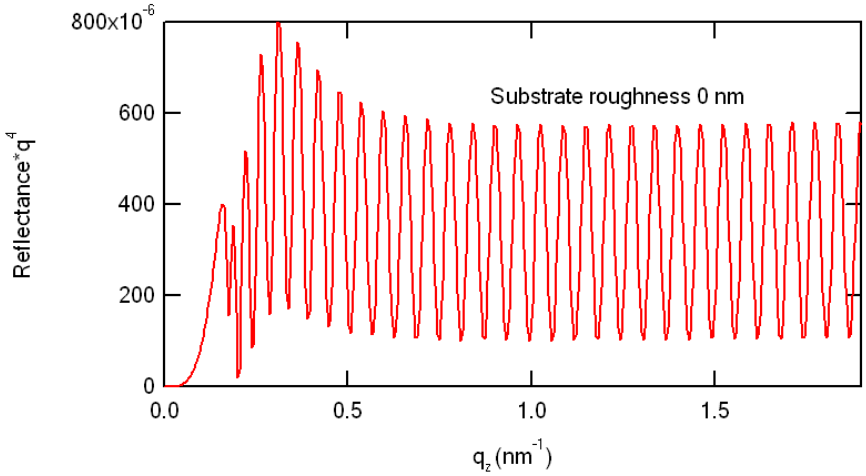


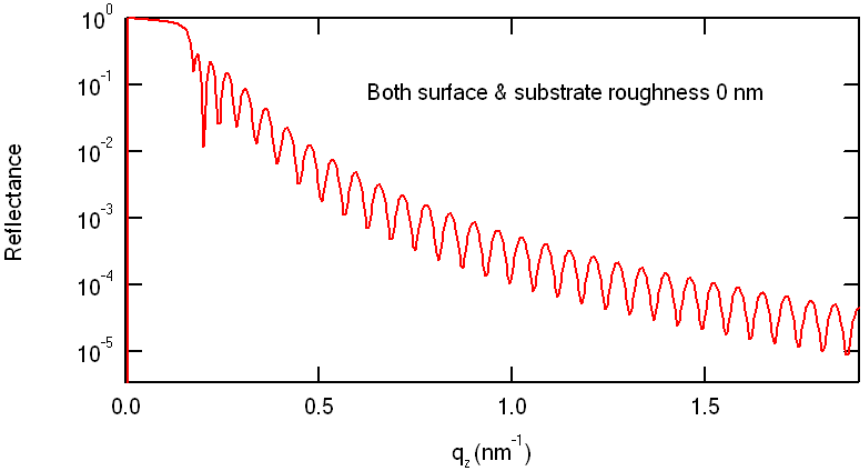
100 nm PMMA 270 eV

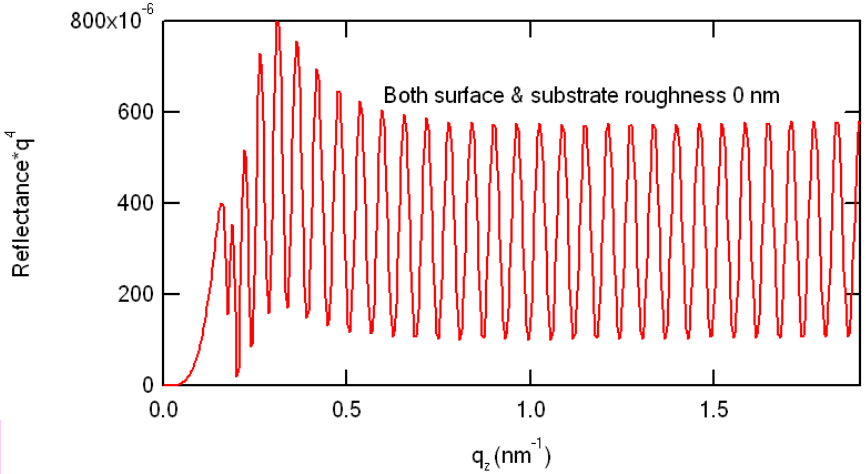










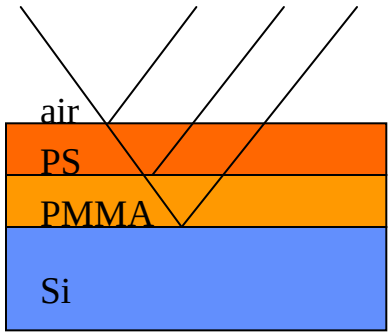


pt

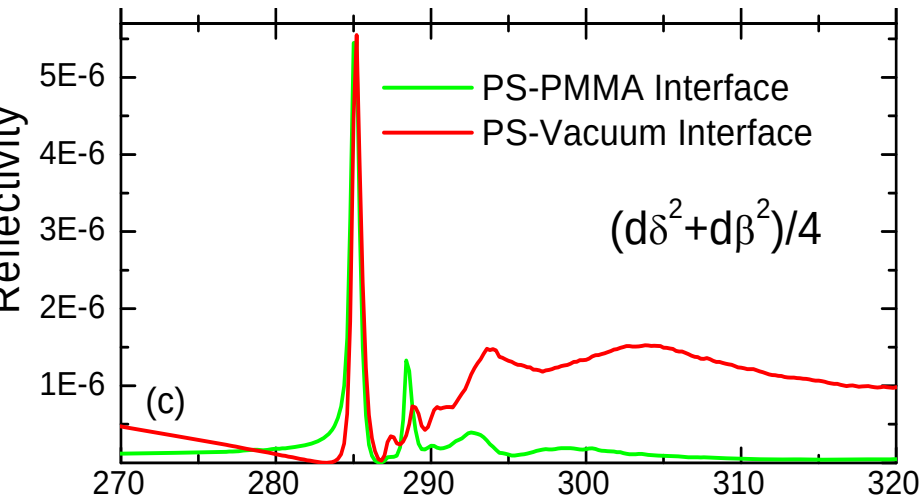
Soft X-ray Resonant Reflectivity

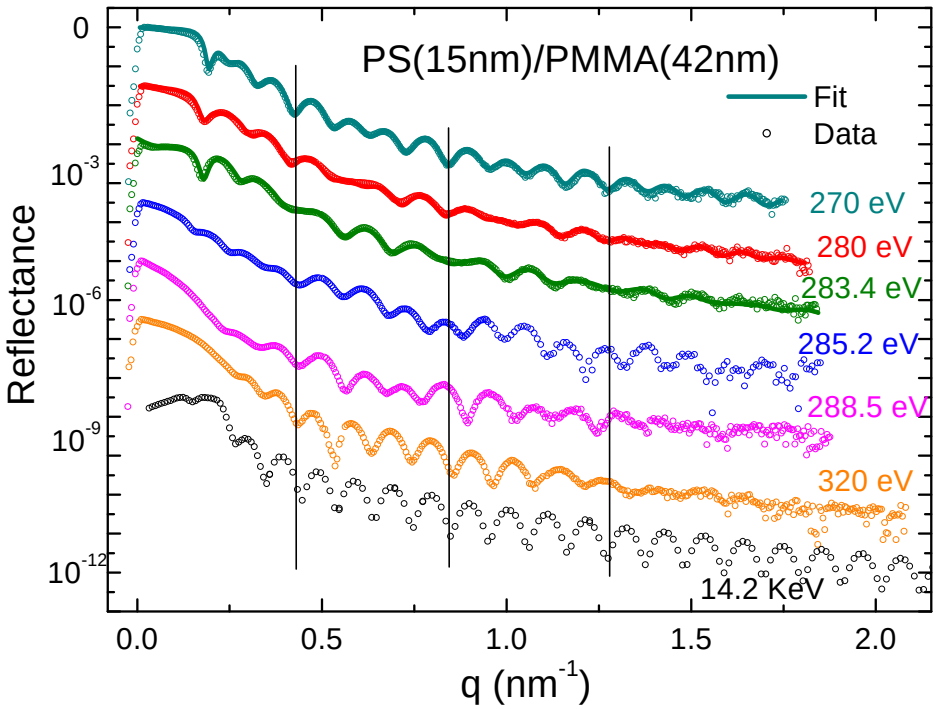
PS/PMMA bilayer

Complementary Tool to Neutrons and hard X-rays



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



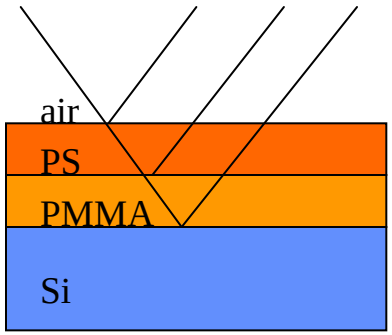


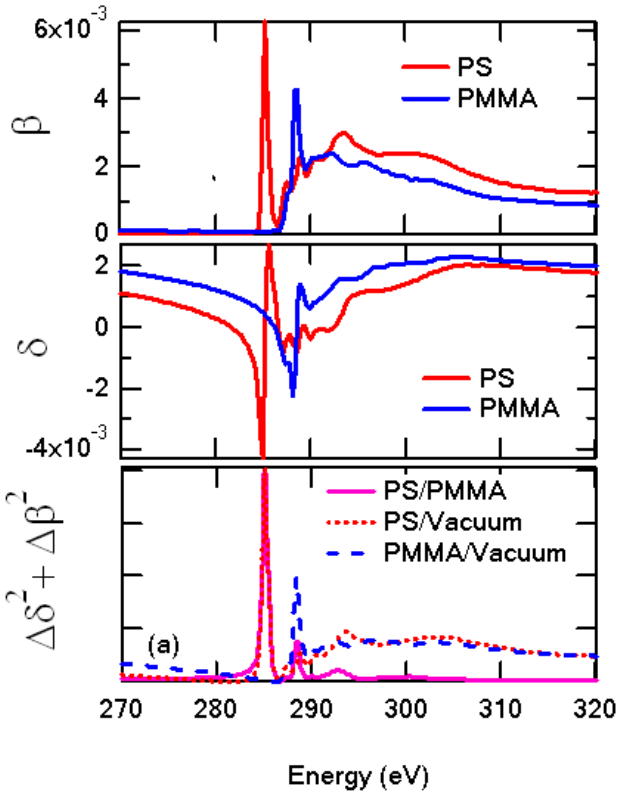
- **Observed strong photon energy dependence**

Potential: Diffuse scattering from interfaces

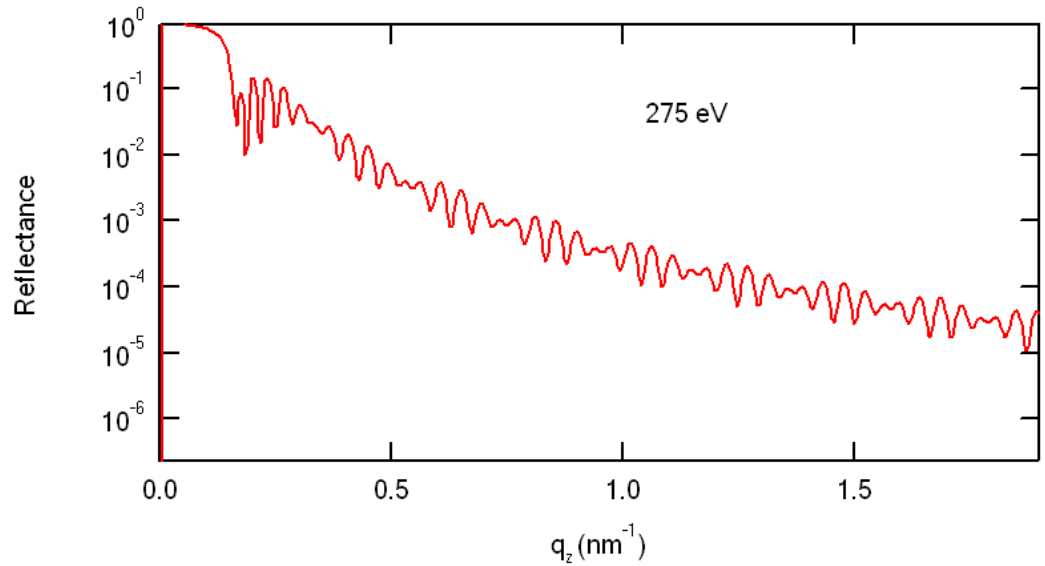
Data: Araki, BL6.3.2. ALS, Berkeley

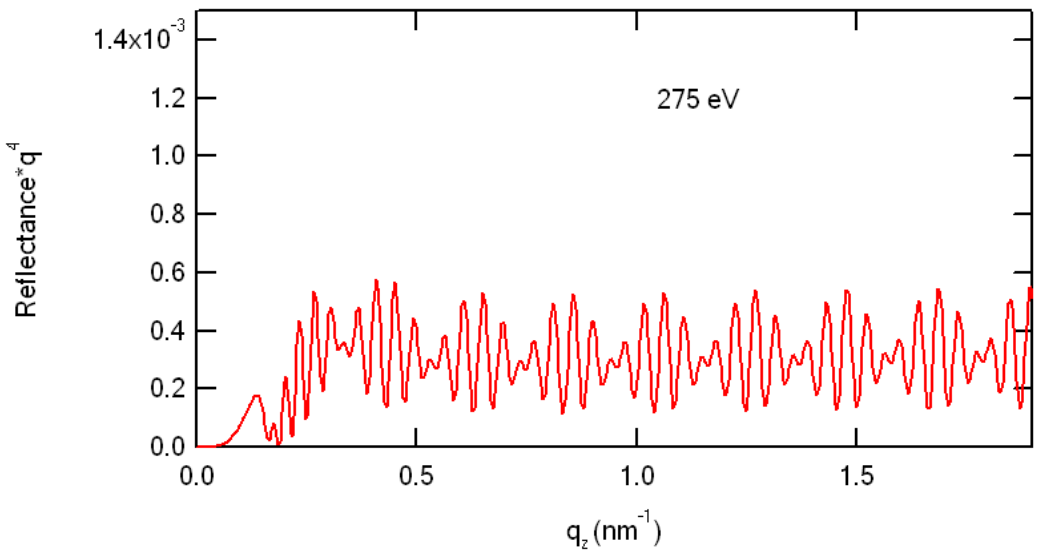
Reflectivity: Tuturial-2





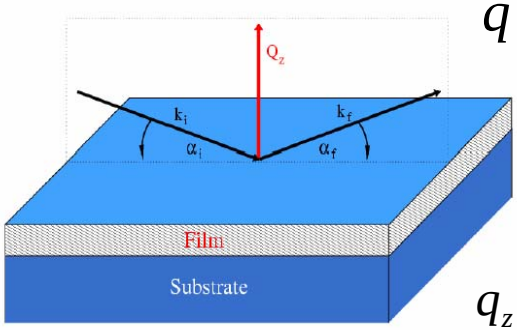
PS 50nm/PMMA 200nm



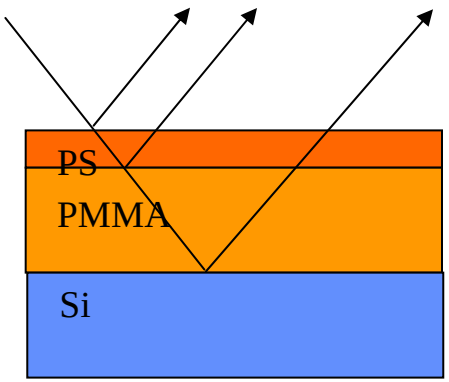


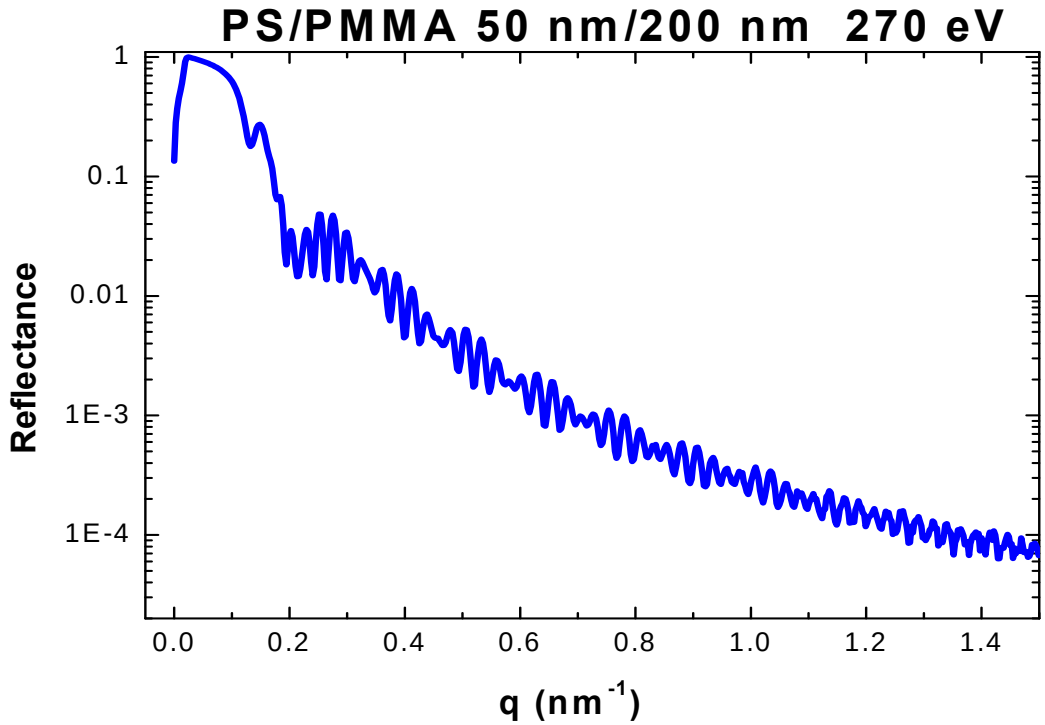
Interpretation of Reflectivity Data

Momentum transfer: $\vec{q} = \vec{k}_f - \vec{k}_i$



$$q_z = \frac{4\pi \sin\alpha_i}{\lambda}$$





Phenomenon	Physics behind it
High frequency fringes	Total film thickness, sensitivity to the surface
Damping of the amplitude	Surface roughness
Low frequency beating	Sensitivity to the interface
Damping of the beating	Interfacial roughness

Polymer LED interfaces

poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) and poly[9,9-bis(6'-N,N,N,-trimethylammoniumhexyl)fluorene-co-alt-1,4 phenylene bromide] (PFNBr)

- **MEH-PPV is a neutral conjugated polymer spun-cast from non-polar solvent**
- **PFNBr is a charged conjugated polymer (conjugated polyelectrolyte) spun-cast from polar solvent**
- **interface influence?**
  - **little is known about the interfacial structure and how it affects properties of such devices**

C.Wang, B. Watts, T. Araki, H. Ade (NCSU) A. Hexemer, A. Garcia, T.-Q. Nguyen, G. C. Bazan, K.E. Sohn, and E.J. Kramer (UCSB).

JACS COMMUNICATIONS

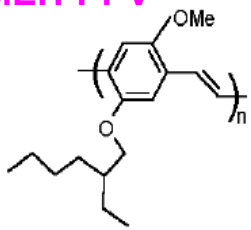
Published on Web 10/20/2006

Control of Cationic Conjugated Polymer Performance in Light Emitting Diodes by Choice of Counterion

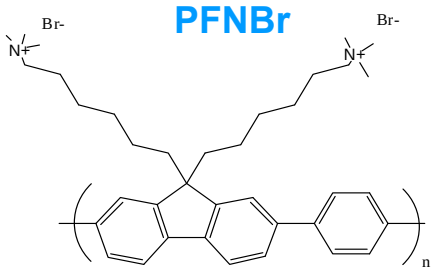
Renqiang Yang,† Hongbin Wu,†,‡ Yong Cao,‡ and Guillermo C. Bazan*,†

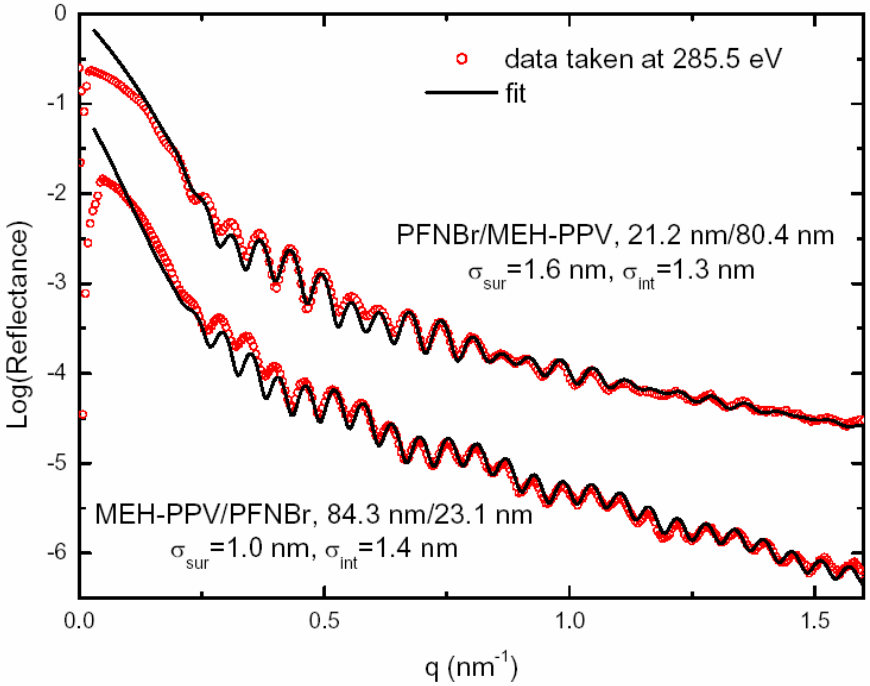
J. AM. CHEM. SOC. 2006, *128*, 14422−14423

MEH-PPV

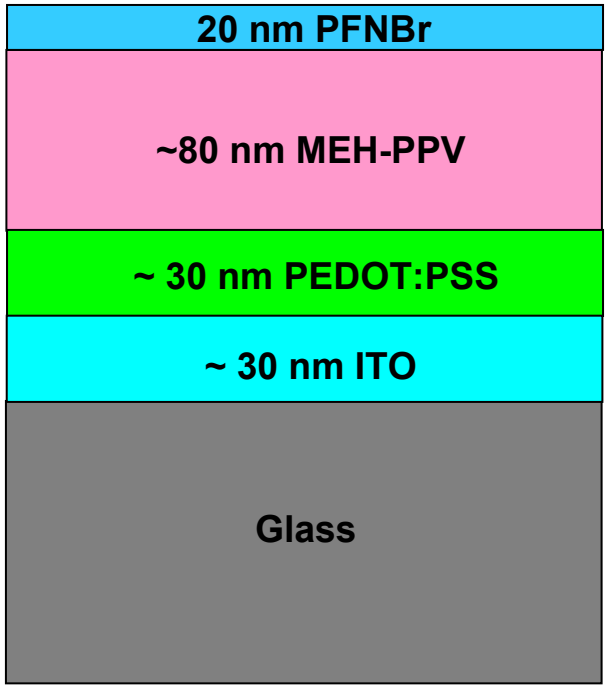


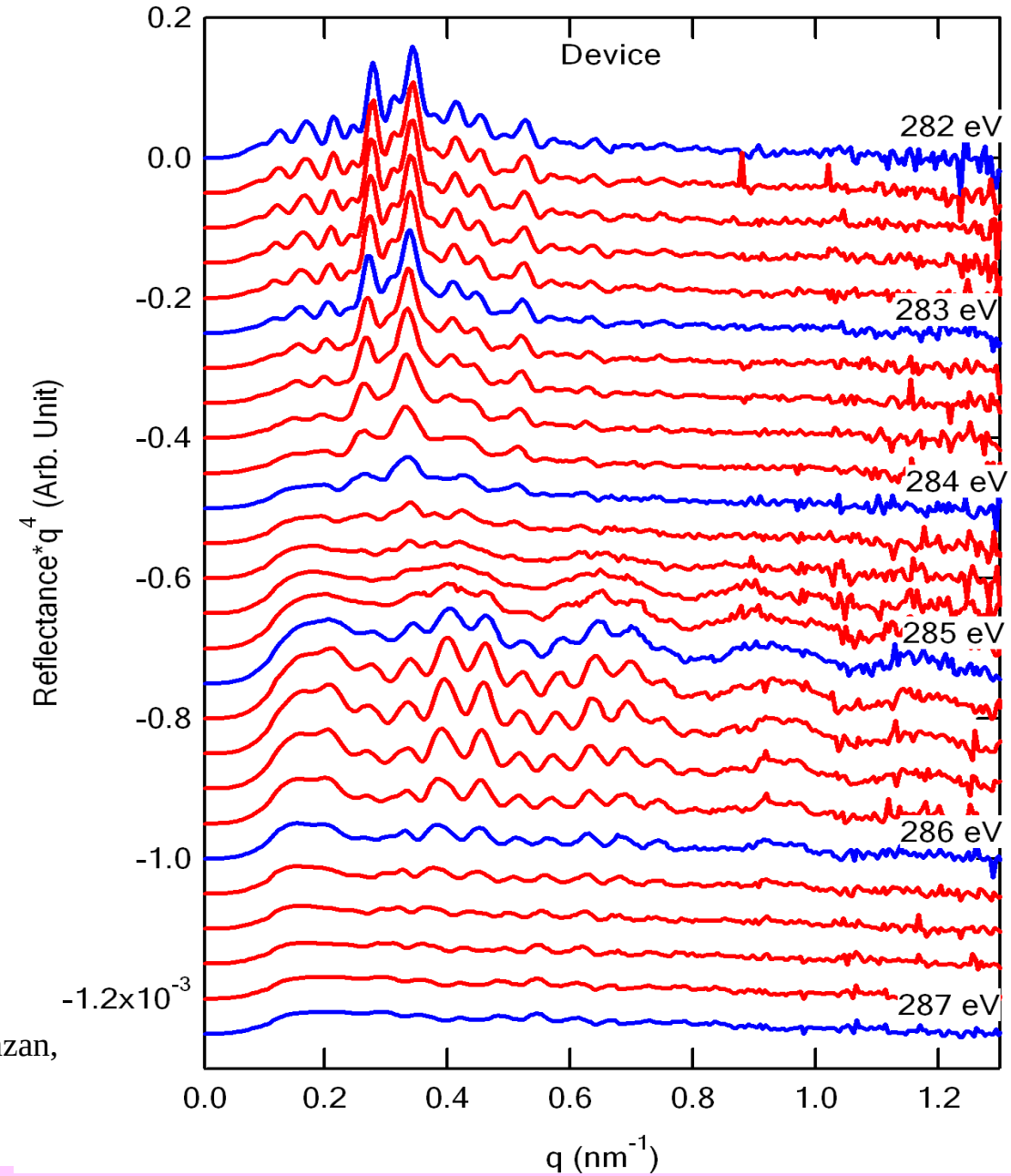
PFNBr





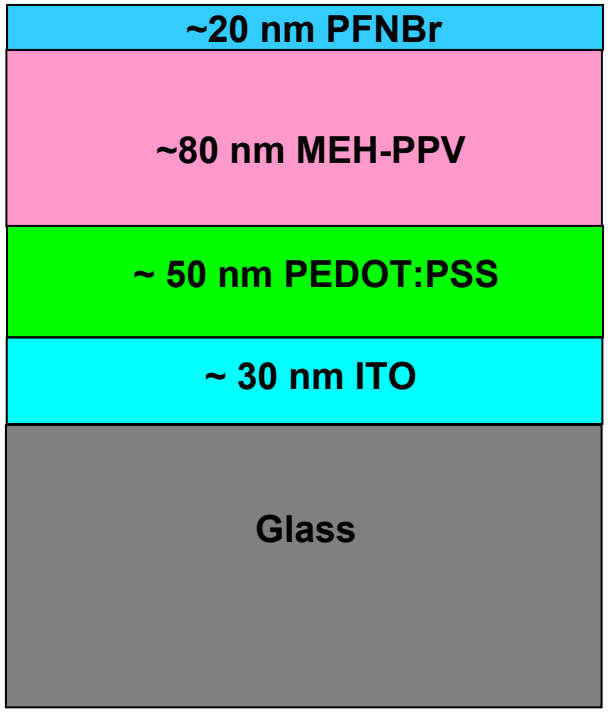
Multilayer Device

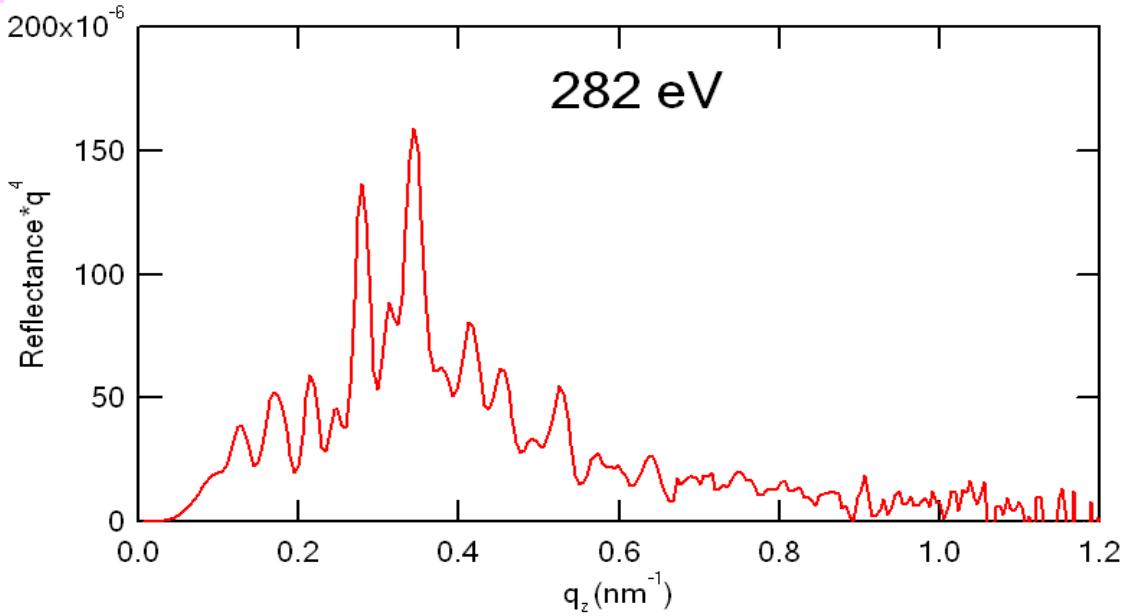


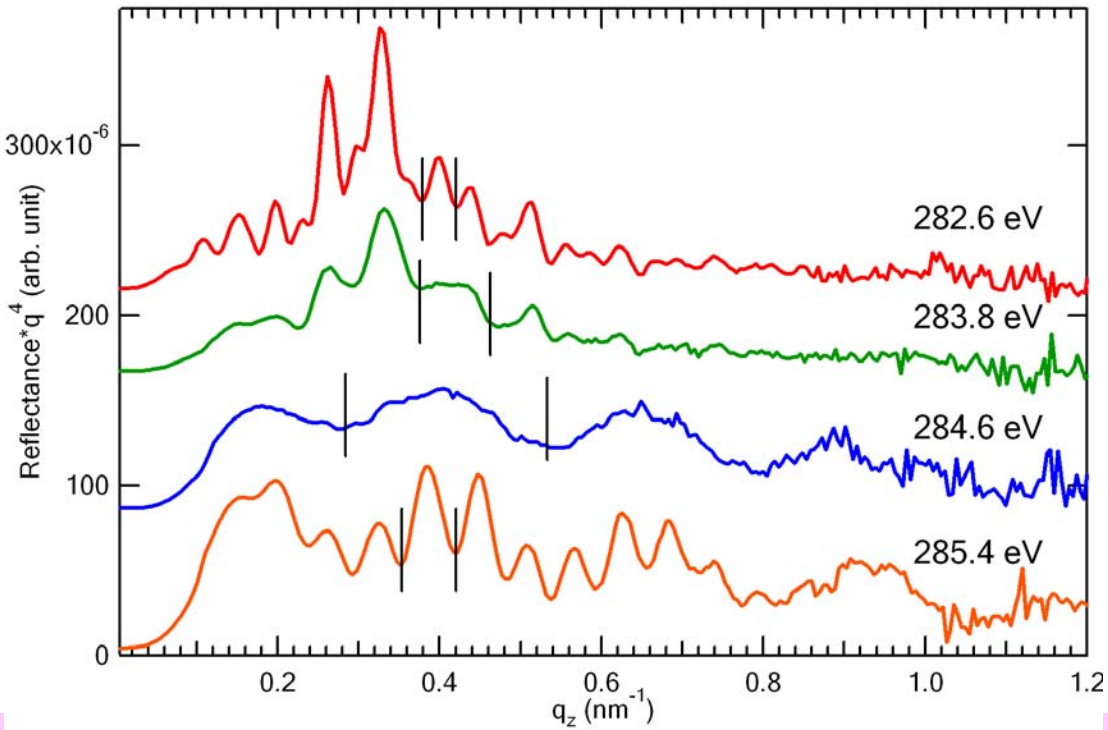


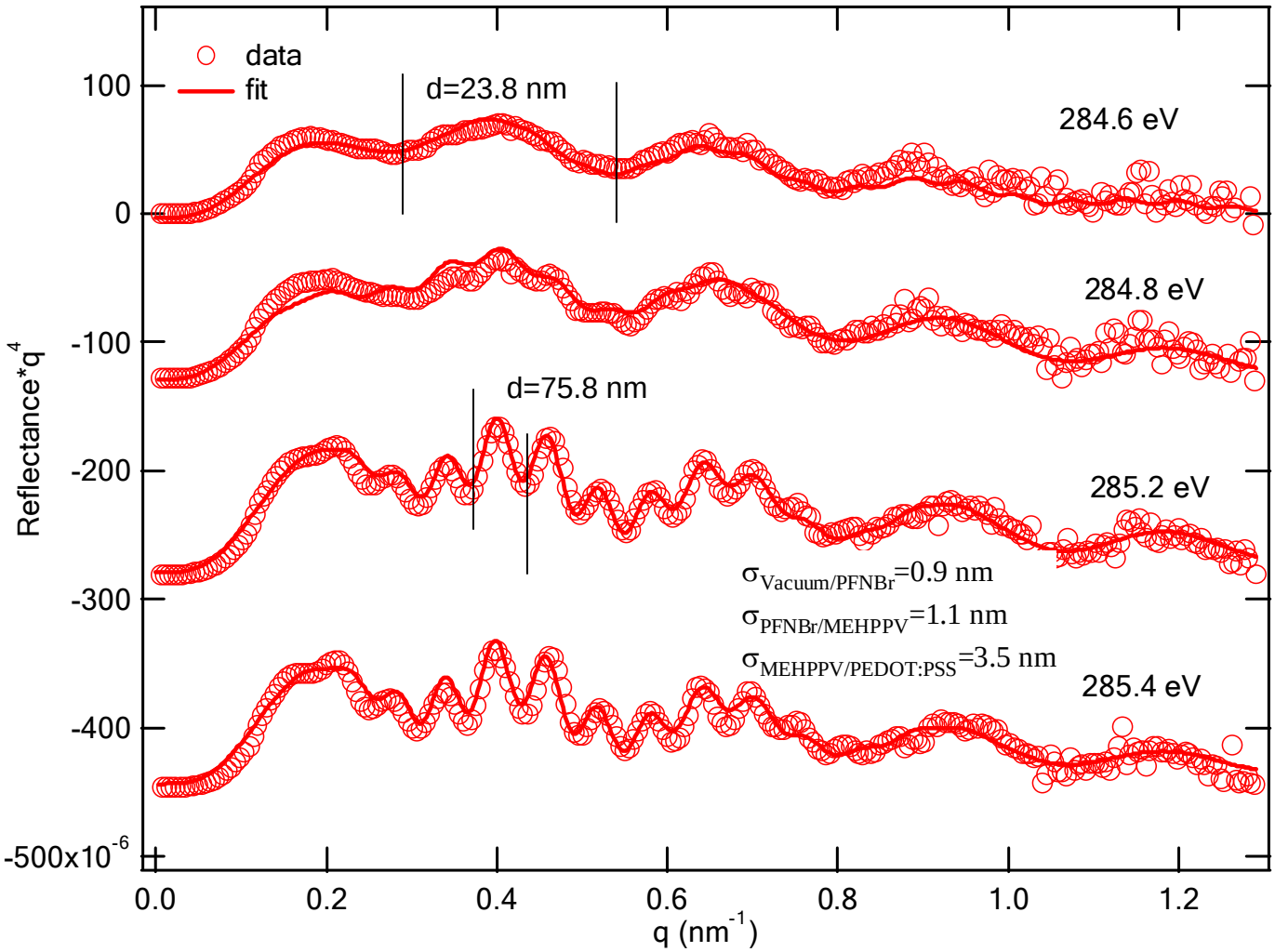
Sample A. Garcia, T.-Q. Nguyen, G. C. Bazan, K.E. Sohn, and E.J. Kramer (UCSB).

Multilayer Device



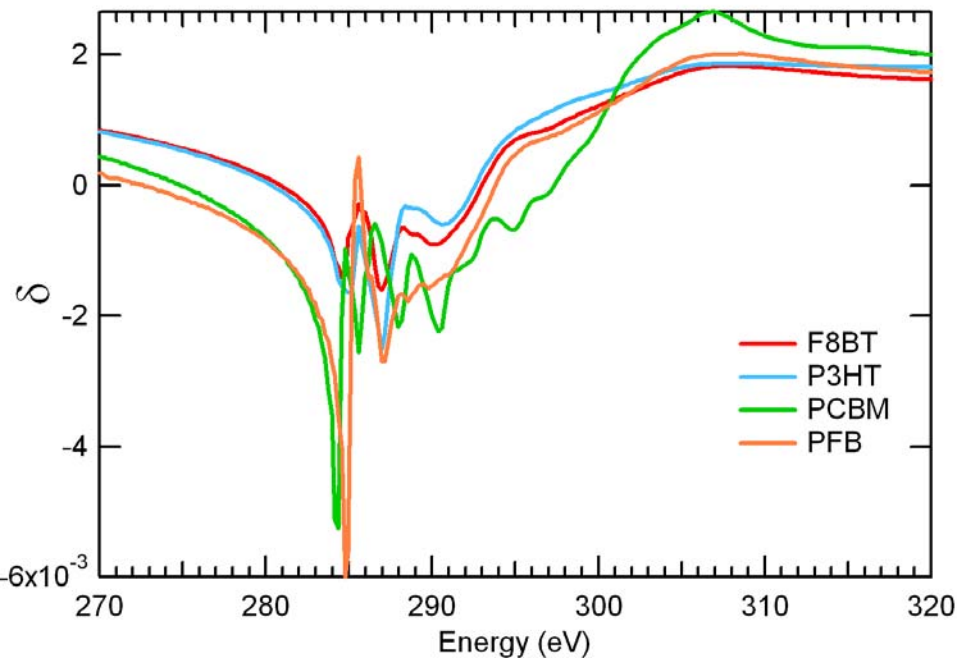


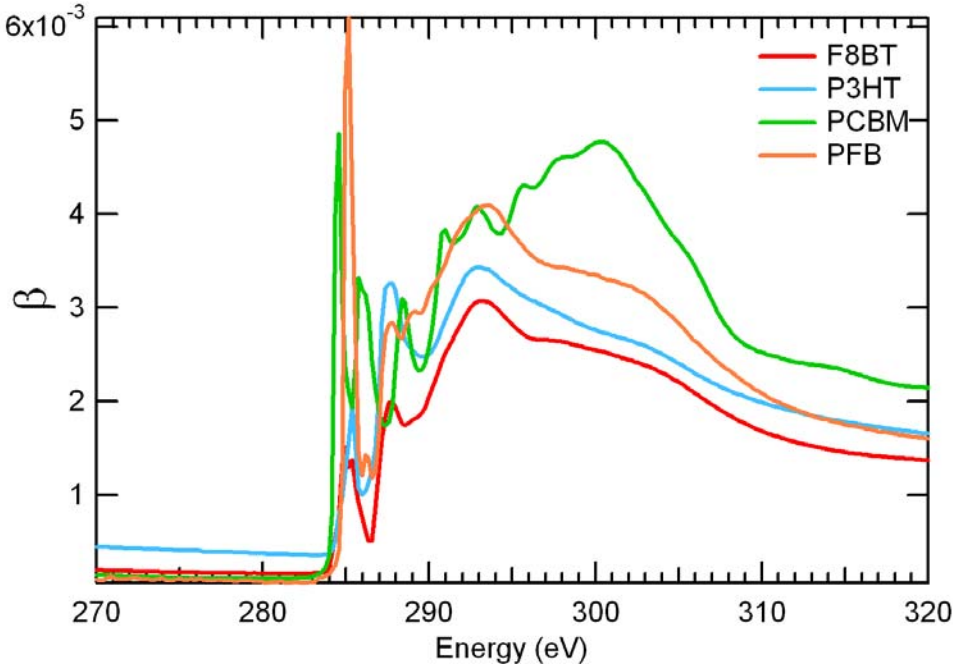




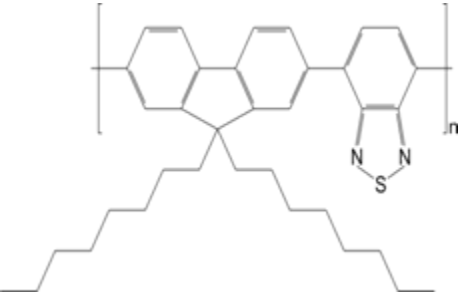
Sample A. Garcia, T.-Q. Nguyen, G. C. Bazan, K.E. Sohn, and E.J. Kramer (UCSB).

Other organic electronic materials

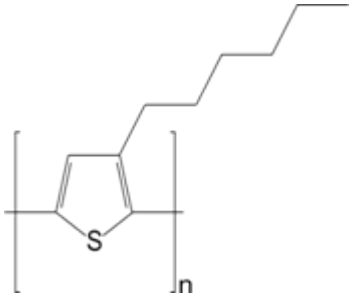




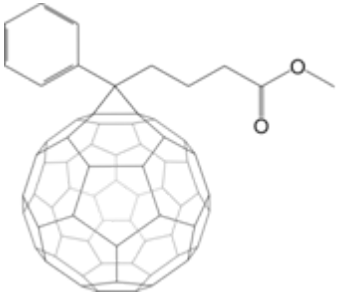
F8BT



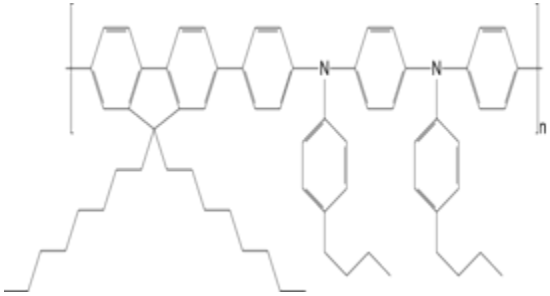
P3HT



PCBM



PFB

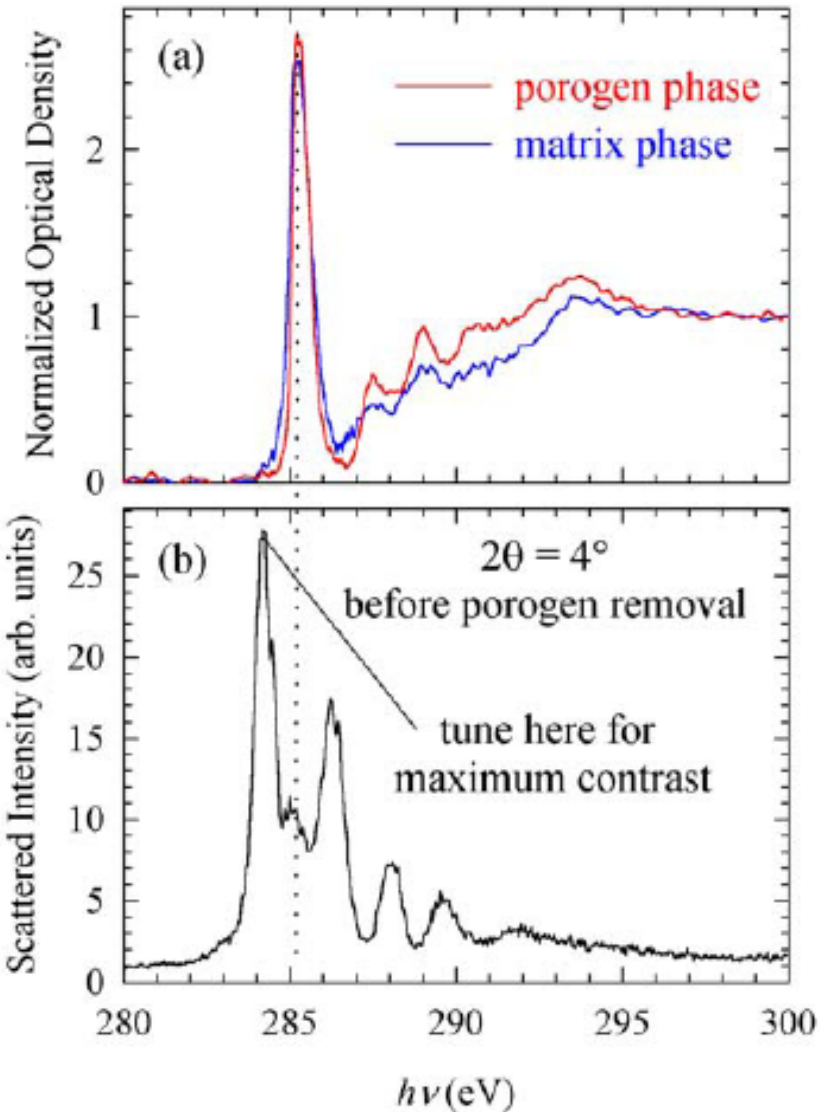


Resonant Soft X-ray Scattering
(hard x-rays terminology ASAXS)

Resonant Scattering: Low Contrast Example - Developmental Porous SiLK* Resins

G. Mitchell, Dow Chemical

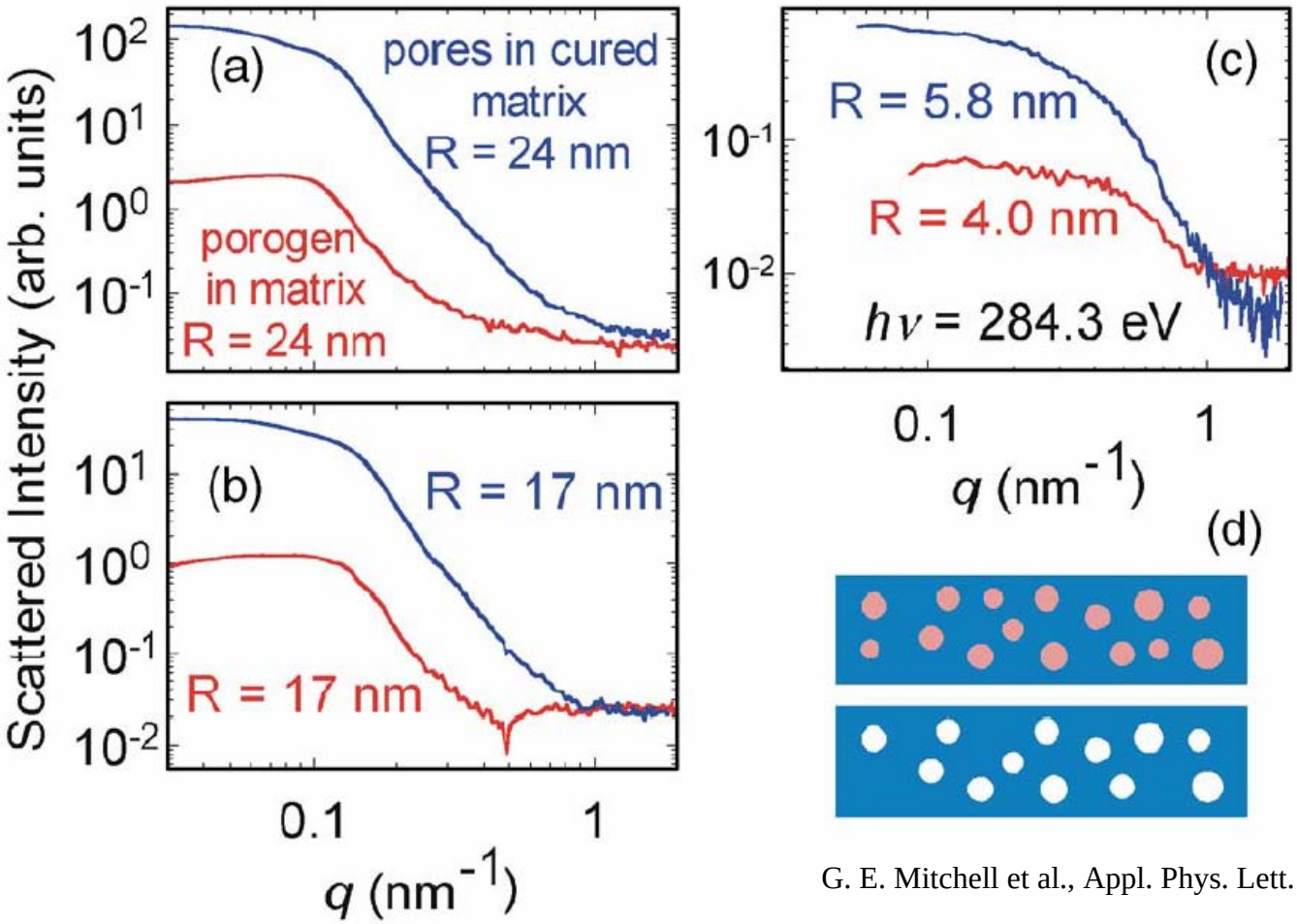
- Decreasing feature size in integrated circuits require lower dielectric constants for insulating layers to:
  - increase circuit speed, decrease power consumption, decrease crosstalk
- Adding pores to SiLK dielectric resin is used to decrease dielectric constant from 2.65 to 2.1 and less
- Future materials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



G. E. Mitchell et al., Appl. Phys. Lett. **89**, 044101 (2006)

* SiLK is a trademark of The Dow Chemical Company

Systematic variation in porogen size

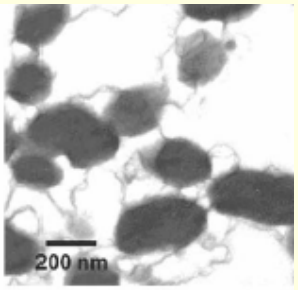


Smallest pores collapse

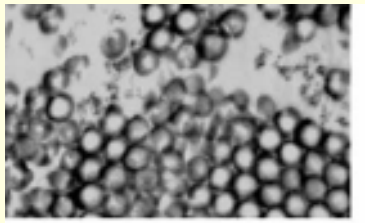
G. E. Mitchell et al., Appl. Phys. Lett. **89**, 044101 (2006)

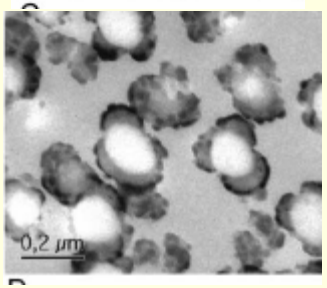
Still issues with background, need to improve instrumentation
Wouldn't be able to do the experiment with STXM, TEM, or SAXS. - Deuteration and SANS would work.

PMMA/P(BA-co-S)

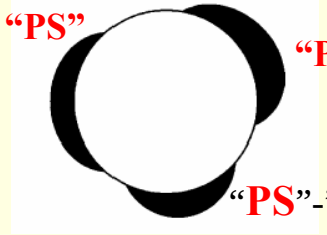


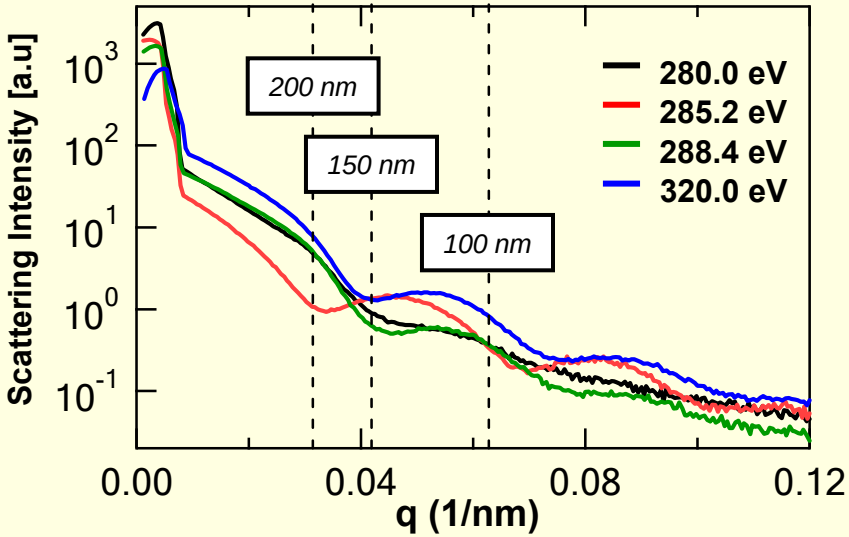
J.M. Stubbs,
D.C. Sundberg Polymer 46 (2005) 1125





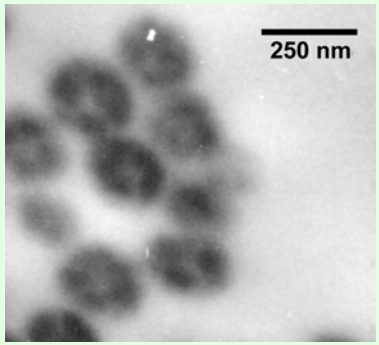
Idealized, "consensus" particle





➡ **"PS" effective radius larger than PMMA "radius"**

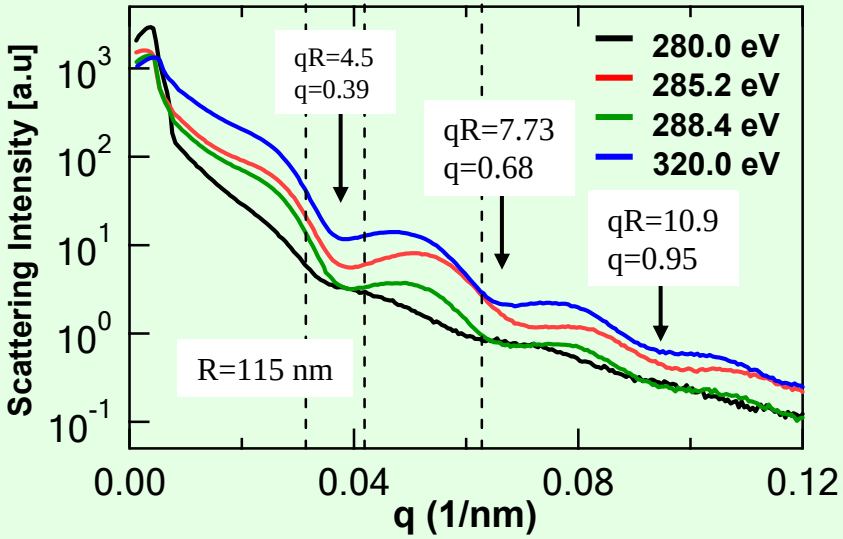
P(MA-b-MMA) / PS



(Figure courtesy J. Stubbs UNH)

Different process and composition

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

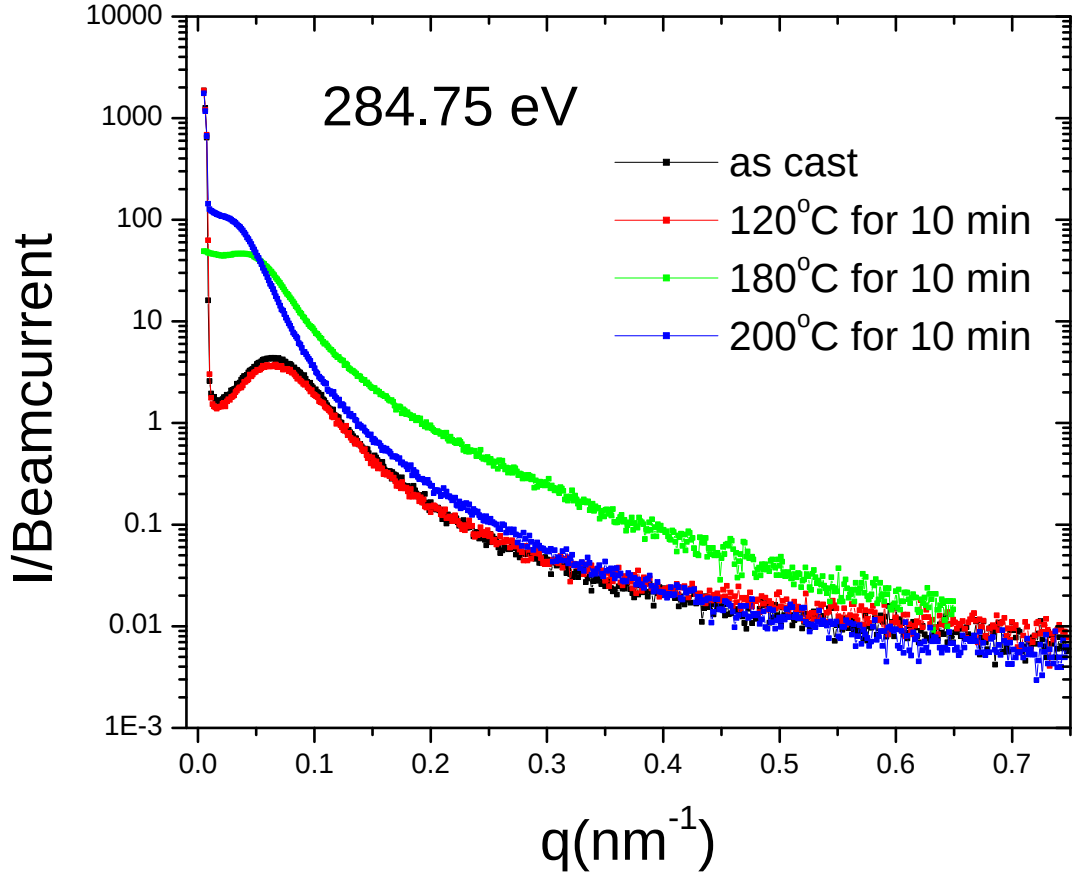


➡ **"PS" about same size than PMMA/acrylate!**
➡ **Scattering indicates PS is slightly more in center of nanoparticle relative to PMMA/P(BA-co-S)**

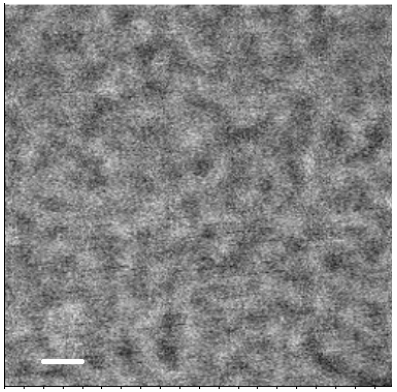
T. Araki et al. Appl. Phys. Lett. 89, 124106 (2006

All polymer Solar Cell:
PFB:F8BT cast from chloroform

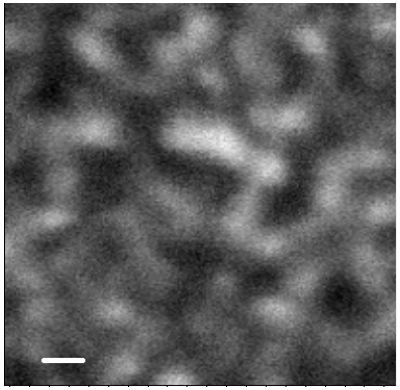
RSoXS



STXM



#0: As spun



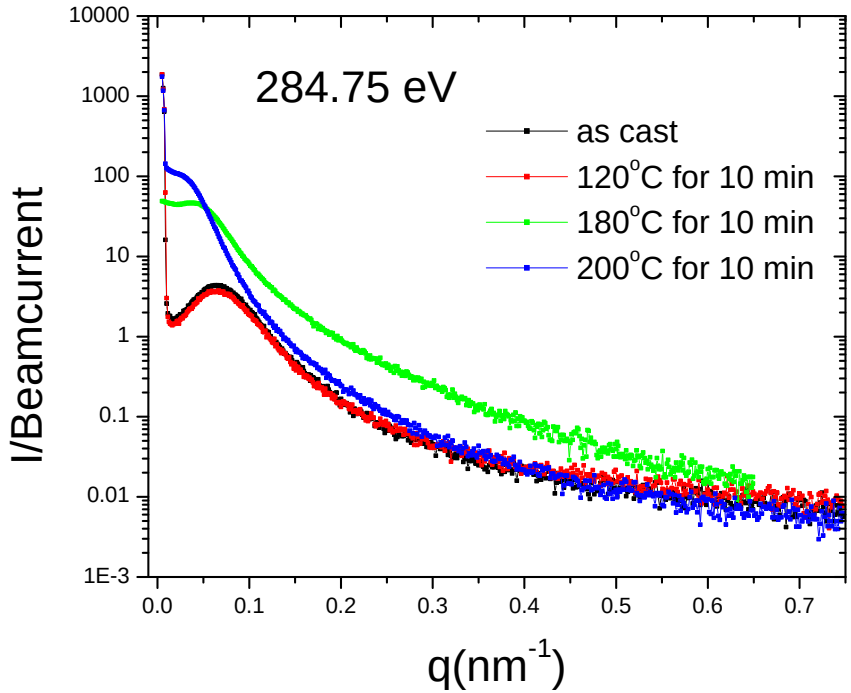
200 deg C annealed

Scale bar: 200nm

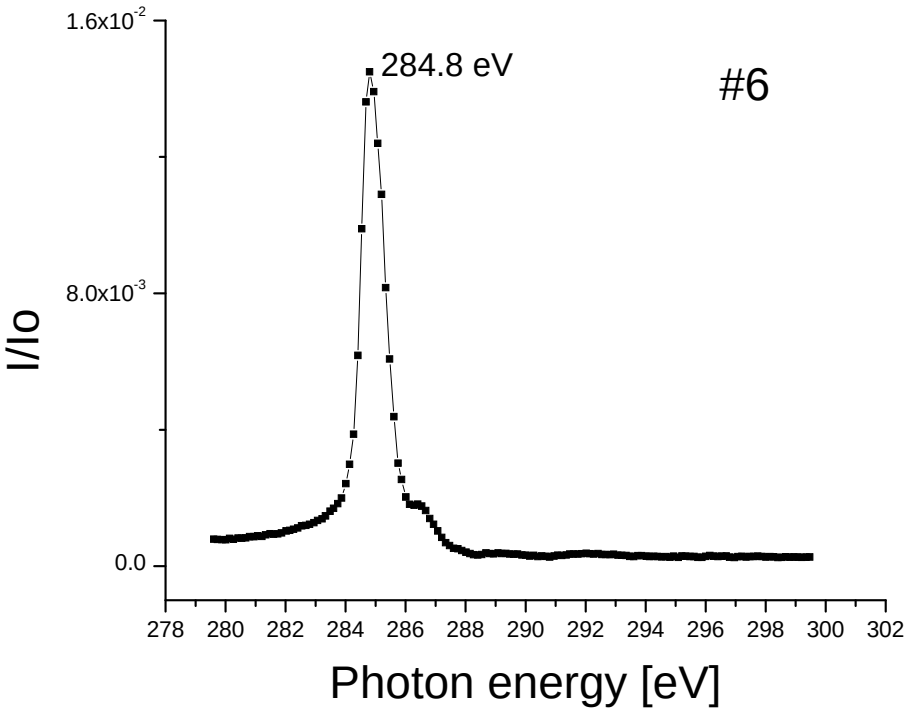
S. Swaratj, B. Watts, H. Ade, C. McNeill

All polymer Solar Cell:
PFB:F8BT cast from chloroform

RSoXS



Energy scans: 1deg off-axis



S. Swaratj, B. Watts, H. Ade, C. McNeill

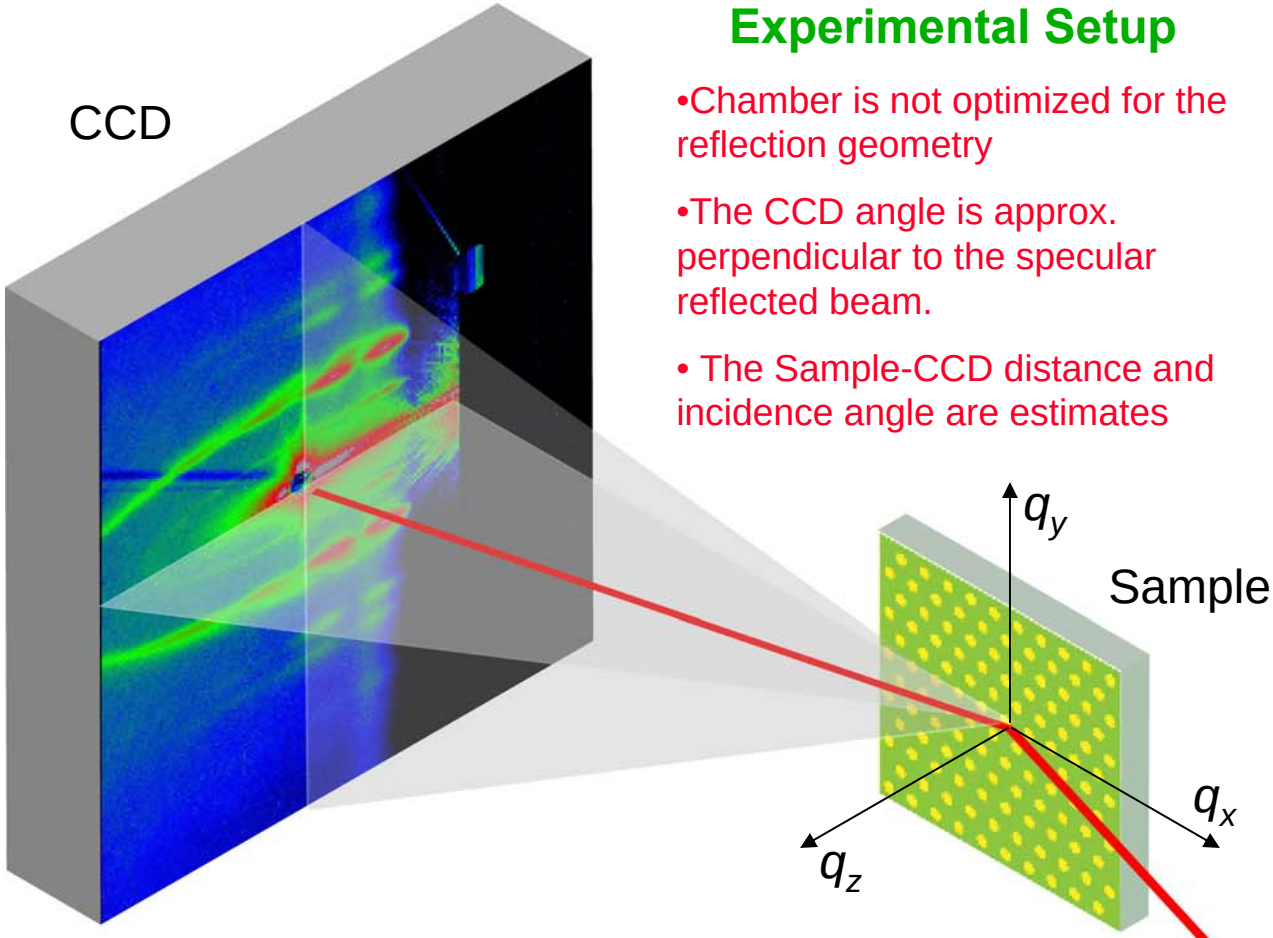
Resonant GISAXS on block copolymers

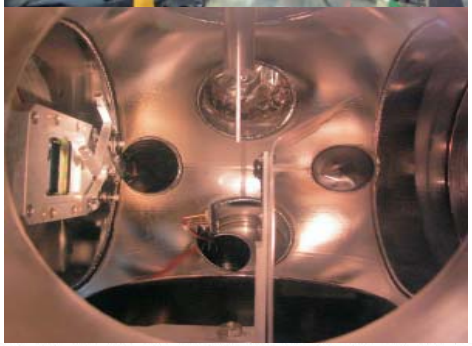
C. Wang, T. Araki, B. Watts, H. Ade (NCSU), A. Hexemer (LBNL)
S-J. Park, T.P. Russell (UMass), B.Schlotter (SSRL) C.Tang,
E.J.Kramer (UCSB)

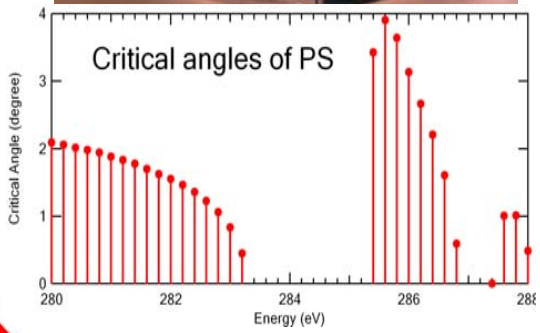
- **Goal**
  - **Use model systems (with two or three components) to establish utility and applicability of GIRSoXS**
  - **Can sensitivity of each component can be tuned by tuning photon energy?**
- **Experiment**
  - **Diblock and triblock copolymer thin films were prepared by S-J.Park, C. Tang**
  - **GIRSoXS experiment was carried at BL5-2 SSRL by C. Wang, B. Watts, T. Araki and B. Schlotter.**
  - **9 degree incident angle, i..e above critical angle - Not true GIRSoXS.**
- **Brief Summary**
  - **Basic quality of GIRSoXS data looks promising, but the instrument needs to be further optimized**
  - **Contrast variations and scattering intensity changes as a function of photon energy have been observed**
  - **Future experiments with three-component-systems with a photon energy dependent structure factor should be explored**

Experimental Setup

- Chamber is not optimized for the reflection geometry
- The CCD angle is approx. perpendicular to the specular reflected beam.
- The Sample-CCD distance and incidence angle are estimates







CCD area	1300 x 1340, 20 μm/pixel
CCD - Sample	~ 43 mm
Incident Angle	~ 9 deg (above critical angle)
Beam stop	15 um wire with a 200 um diameter epoxy bead. About 1 cm from the CCD

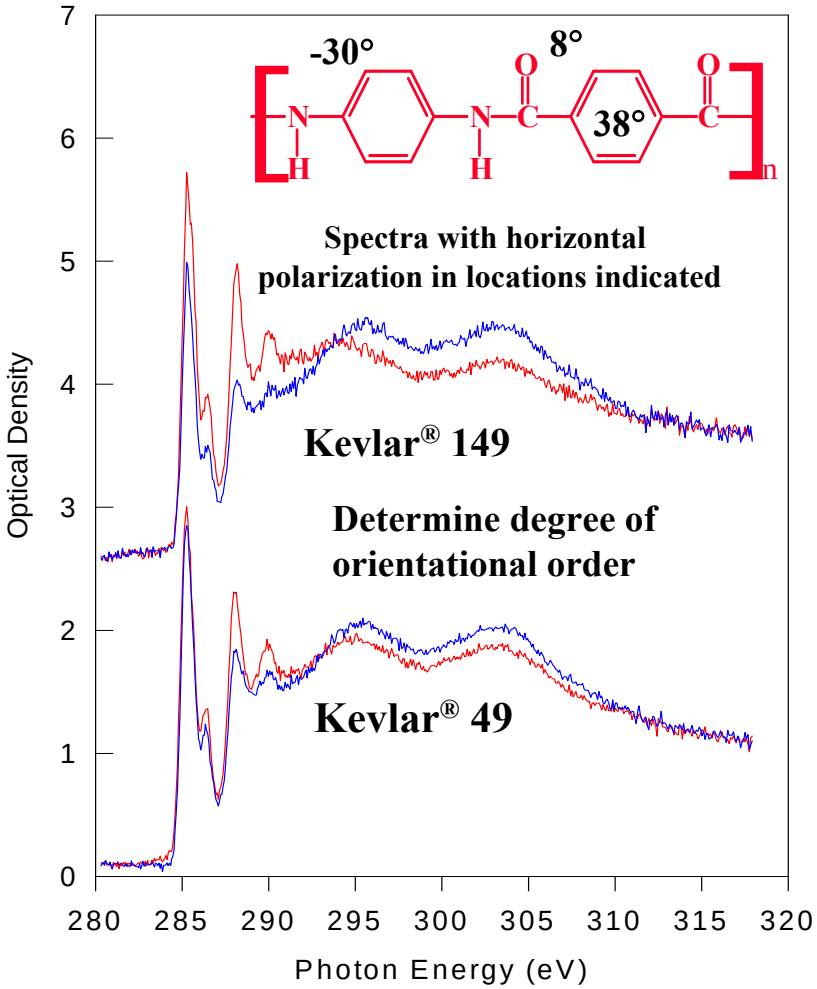
X-ray

Aperture (75 x 125 μm)

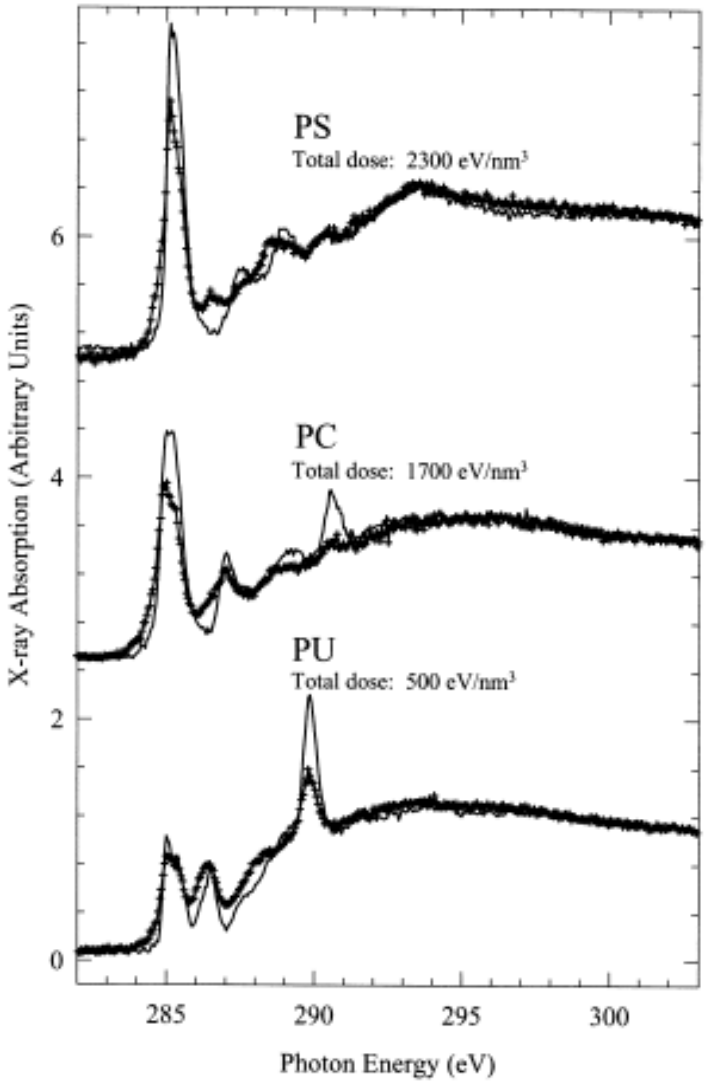
Beam size: ~400 μm x ~100 μm (H x V)

Use NSLS-II 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



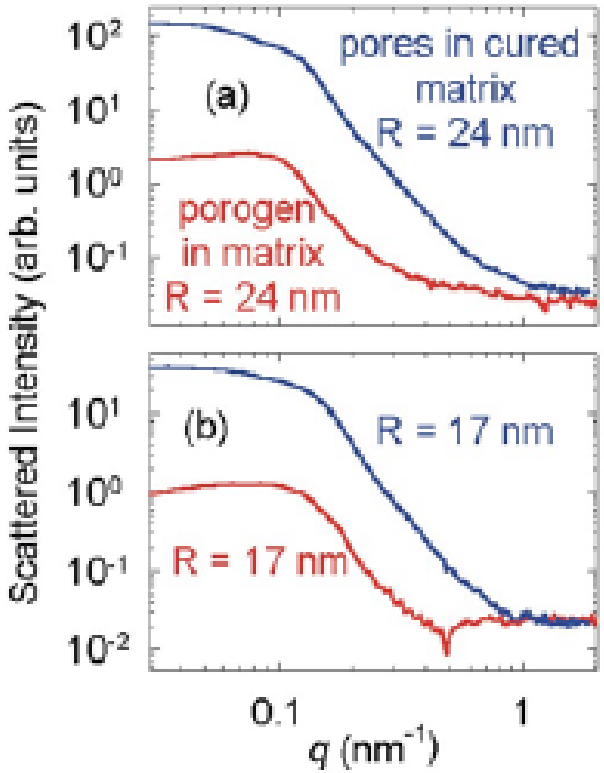
T. Coffey et al. J. Electron Spectroscopy 122 (2002) 65 –78

- **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 a "cross-over"?

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

- Combine low resolution STXM and RSoXS: Microbeam resonant scattering
  - Damage?

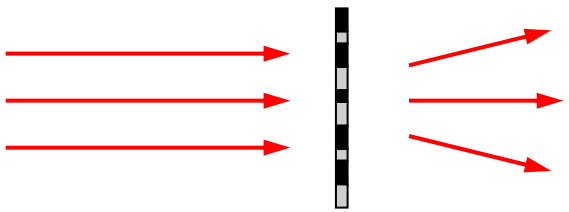


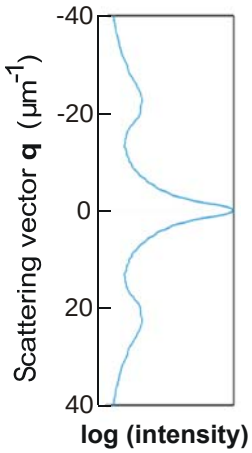
 Data: Beamline 6.3.2 ALS

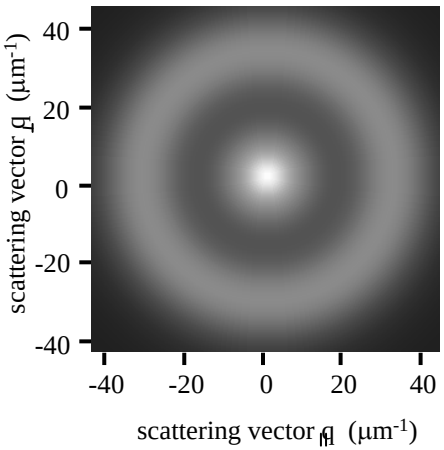
Incoherent vs. Coherent X-Ray Scattering

Small Angle Scattering

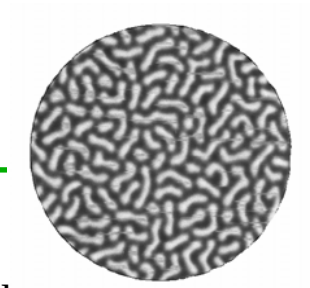
Coherence length larger than domains, but smaller than illuminated area





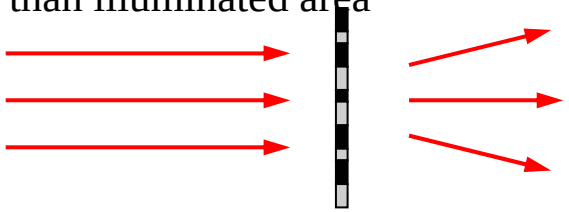


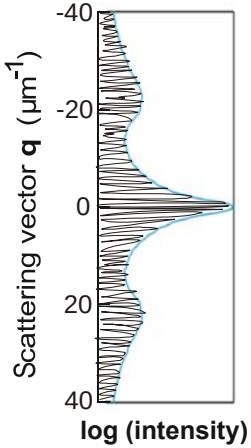
information about domain statistics

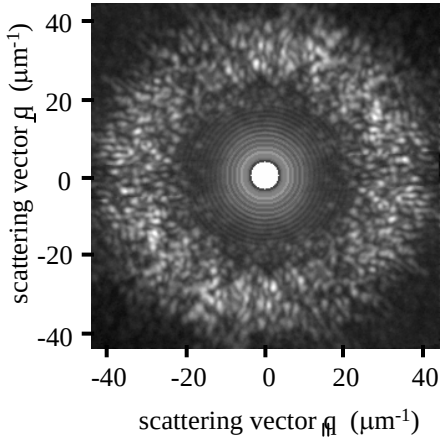


Speckle

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 !!!!

Other possibilities

- Resonant x-ray photon correlation spectroscopy?
  - R-XPCS
- Resonant coherent imaging?
  - Coherent imaging proposed by other workshop!
- Spatially resolved inelastic scattering?
  - Damage?
  - Sensible domain size?

Conclusions

- **NEXAFS microscopy and resonant reciprocal space techniques are excellent "compositional" tools with 1D, 2D, and 3D (tomography) spatial resolution well below 1 micron.**
- **C,N, O edges have feature-rich spectroscopy for organic materials.**
  - **Specificity**
  - **Many organic, soft condensed matter application will continue to benefit from these tools**
  - **Thin samples 100-2000 nm thick.**

- **Science opportunities**
  - **See Helmut Frey**

If we were a rich man?

- Bending magnet STXM workhorse
- Bending magnet RSoXR/RSoXR workhorse

- Microfocus RSoXS undulator beamline
  - Intensity at sample scales with brightness/coherence
  - Soft x-ray EPU beamline
- R-XCPS
  - Needs coherence
  - Soft x-ray EPU beamline

- ……..

Beamline design(s) most likely relatively conventional (except heatload). Most advances are in the endstations

Thank you for your attention!!!!

Thanks to members of my group:
B. Watts, S. Swaratj, T. Araki, and C. Wang

and
Bill Slotter, Jan Luning (Stanford). C. McNeill (Cambridge), A. Hexemer (ALS), A. Garcia, T.-Q. Nguyen, G. C. Bazan, K.E. Sohn, and E.J. Kramer (UCSB).