Resonant scattering and reflectivity:
Initial application and developments for polymeric materials

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http://www.physics.ncsu.edu/stxm/

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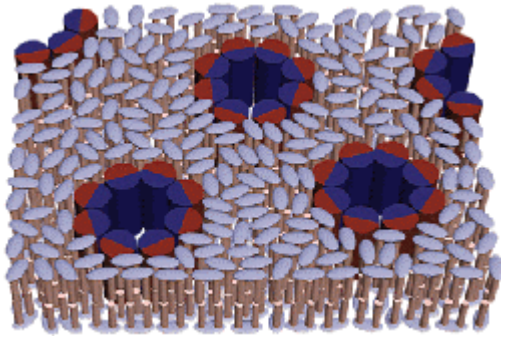
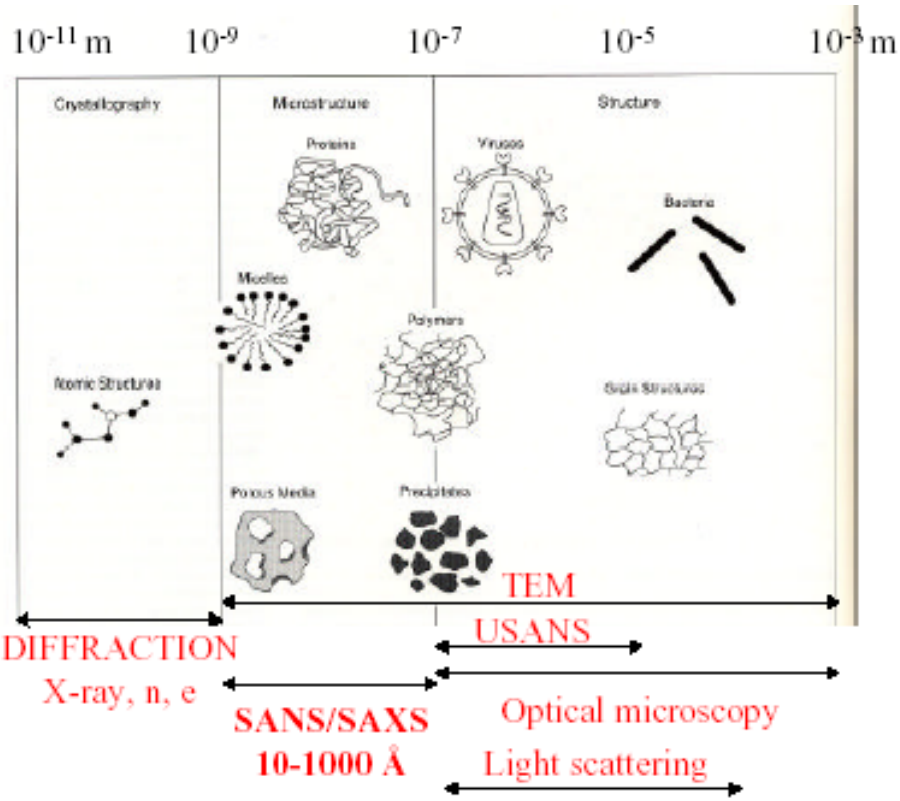
Potential of Soft X-ray Resonant Scattering



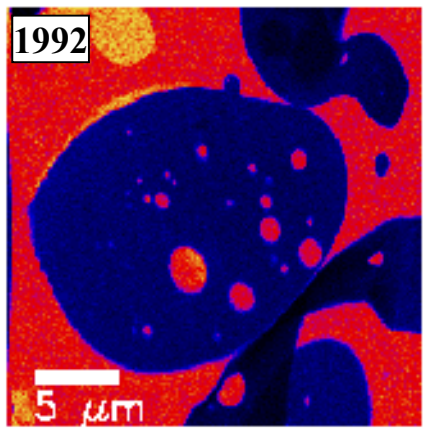
Neutron-scattering at IPNS, ANL…peptides (cylinders) inserting themselves in holes they form in a cell membrane.

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



From LANSCE Neutron Scattering A Primer

- **SXRS - complement to SANS, conventional SAXS? Hope YES**
  - **soft condensed matter characterization**
- **Real space info would be best, but**
  - **Contrast? Spatial resolution? Damage limits?**
    - **TEM needs stains**
    - **NEXAFS in STXM and PEEM limited to ~40 nm spatial resolution**
- **ALS strategic retreat 2004**
  - **Suggested dedicated optimized BM scattering line**
    - **Now aim for undulator!**



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

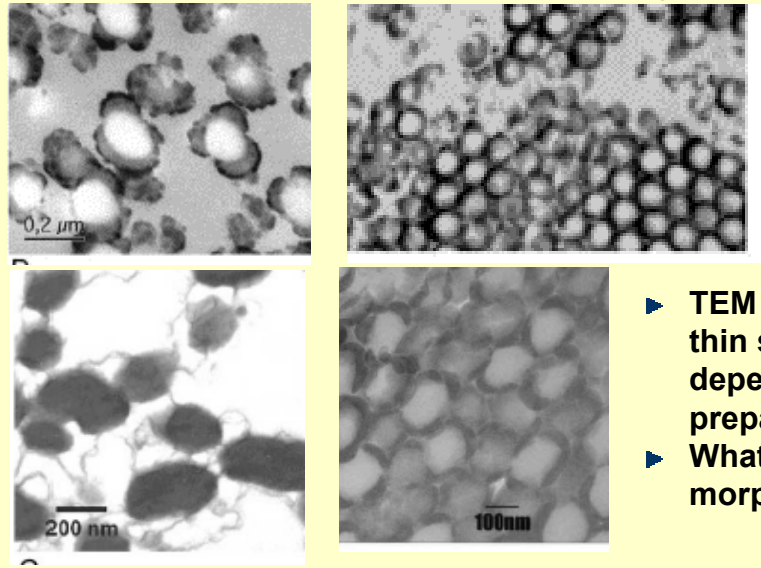
Soft x-ray resonant (anomalous) scattering of polymer nanoparticles

T. Araki, H. Ade (NCSU)

Supported by DOE (DE-FG02-98ER45737)

- Composite latex particles (two or more components) 20-300 nm in size have extraordinary range of applications
- Complex structure is difficult to characterize

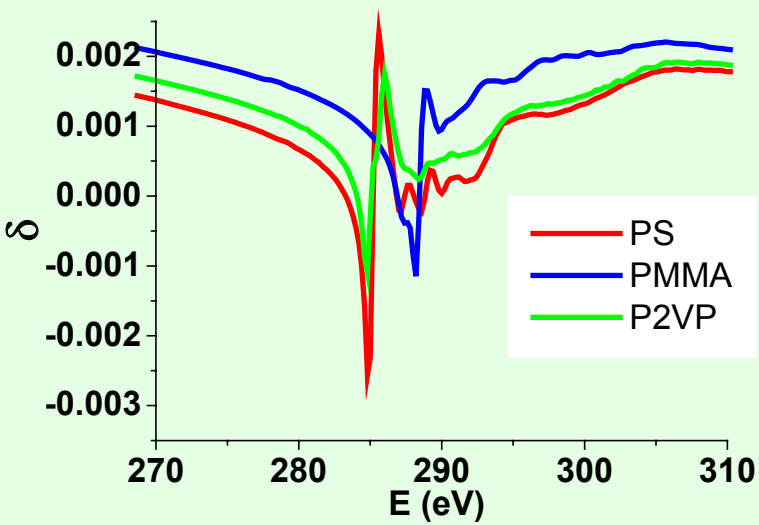
PMMA-"core"/P(BA-co-S) "shell" (designated JMS3-81)

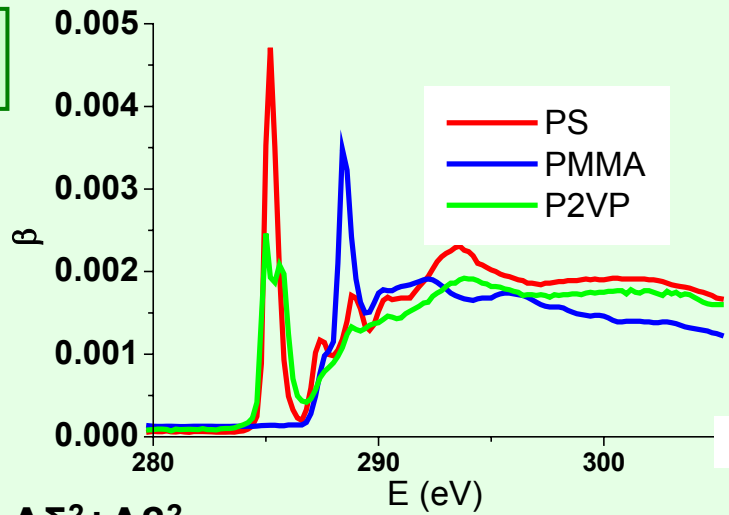


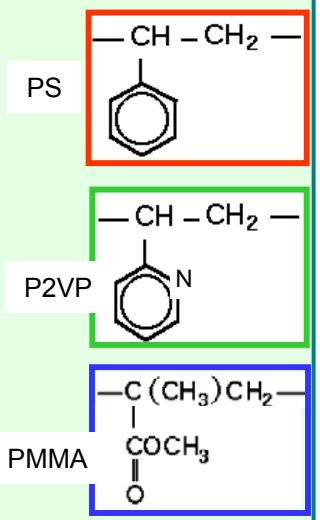
J.M. Stubbs, D.C. Sundberg Polymer 46 (2005) 1125

- TEM morphology of thin sections can depend on sample preparation
- What is the true morphology????

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



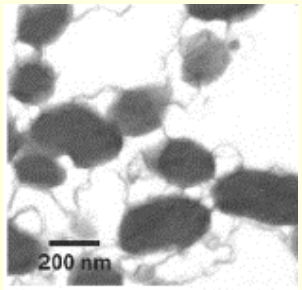




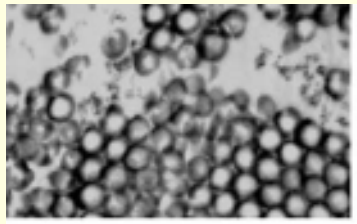
$I \propto \Delta\delta^2 + \Delta\beta^2$

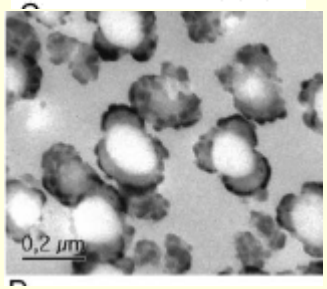
- Compositional information in scattering!!!!
- Huge potential as complementary tool!!!

PMMA/P(BA-co-S)

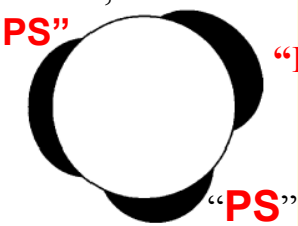


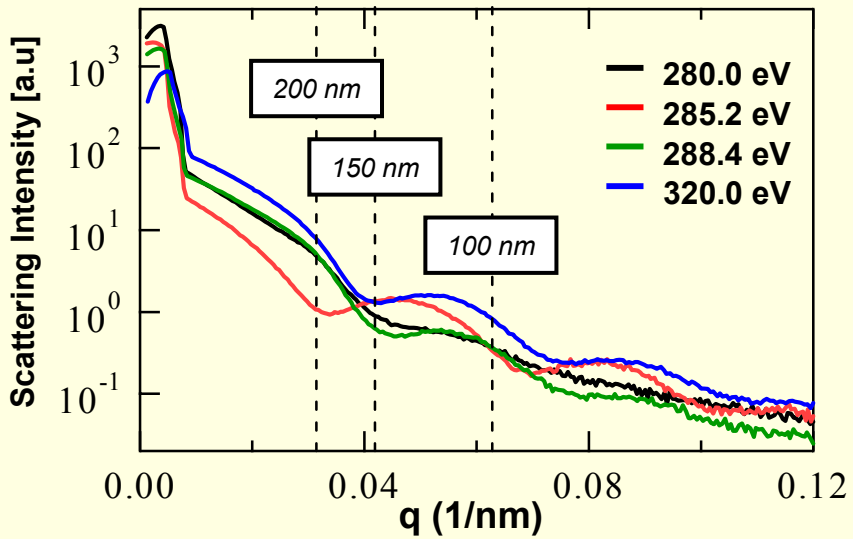
J.M. Stubbs,
D.C. Sundberg Polymer 46 (2005) 1125





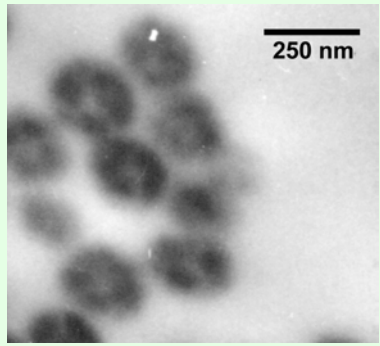
Idealized, "consensus" particle





➧ "PS" larger than PMMA!

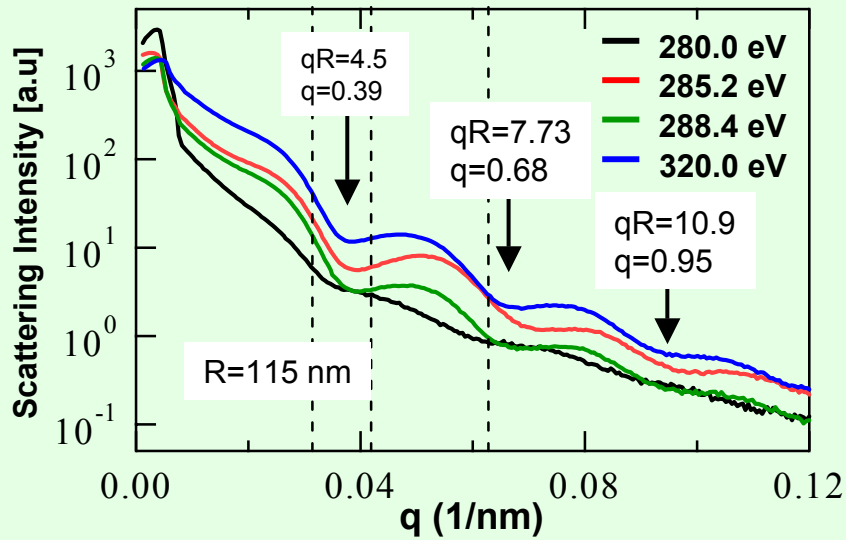
P(MA-b-MMA) / PS



(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!

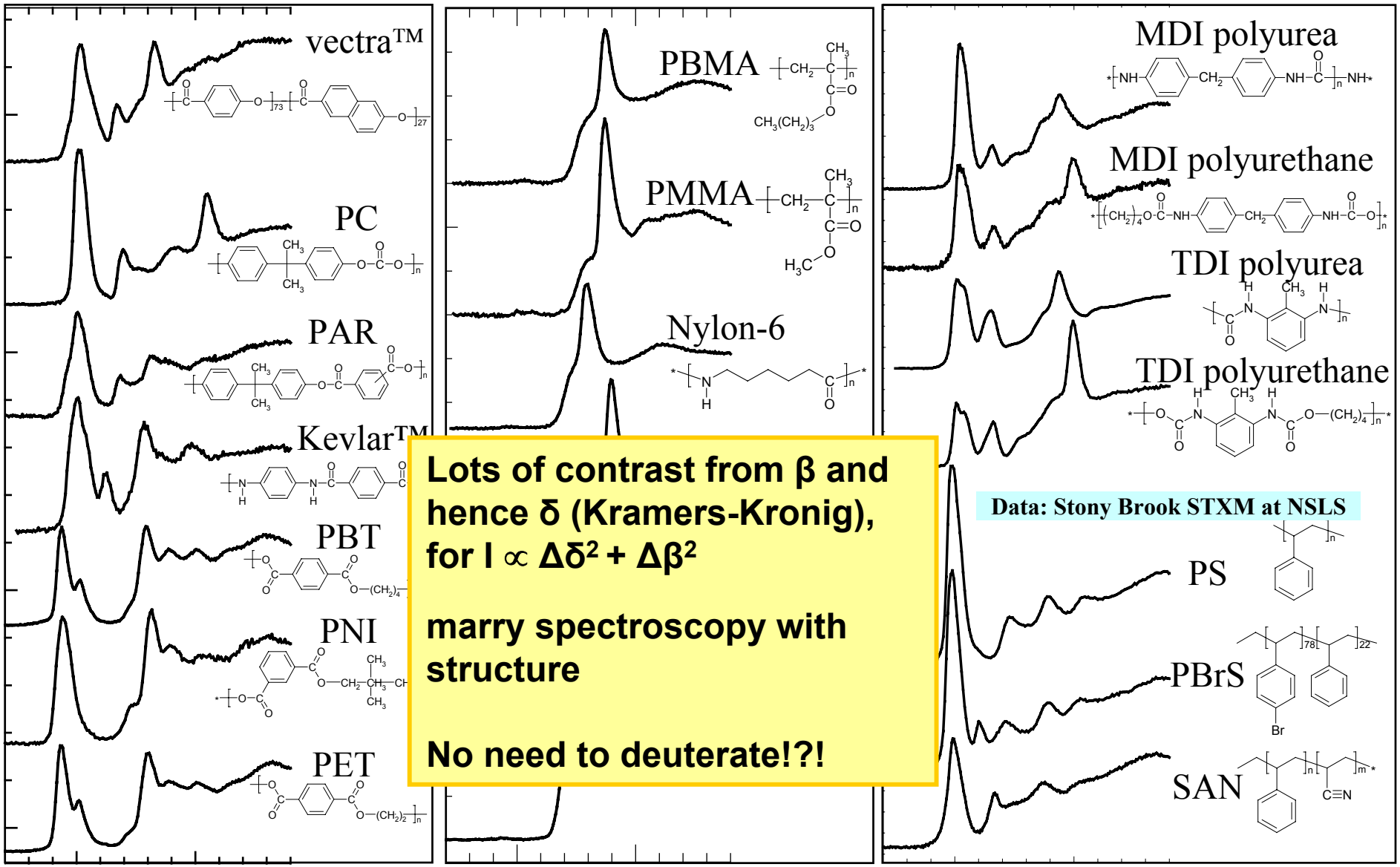
➧ Scattering indicates PS is slightly more in center of nanoparticle relative to PMMA/P(BA-co-S)

First results from structured polymer samples

samples provided by J. Stubbs, D. Sundberg (UNH), Data: Araki, BL6.3.2. ALS, Berkeley

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

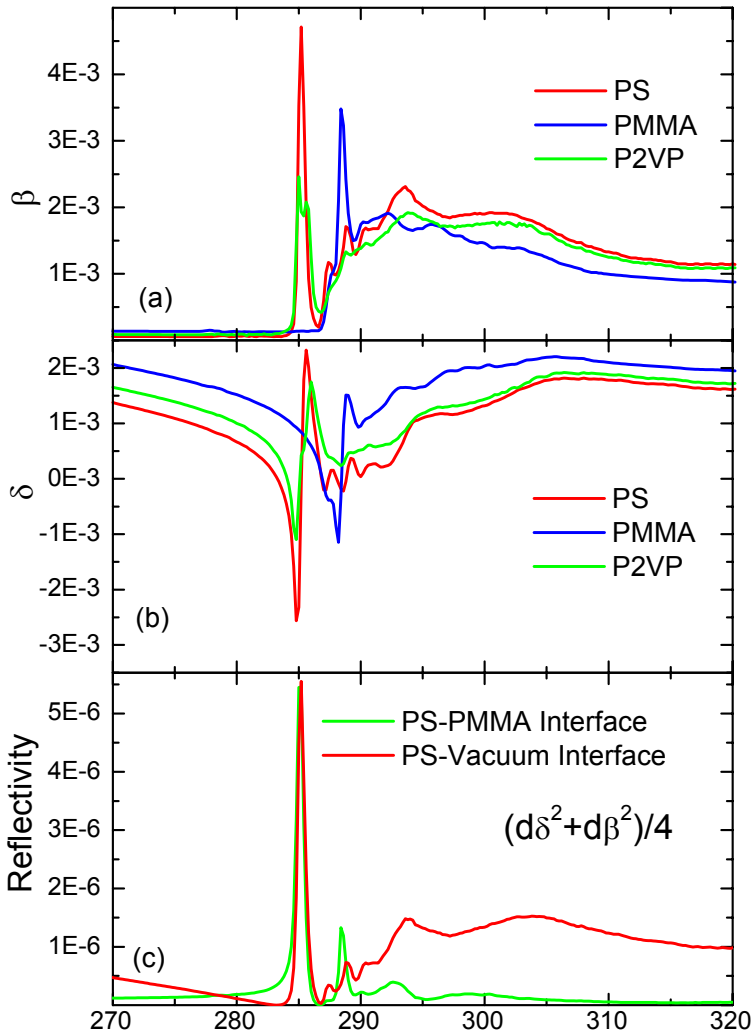
marry spectroscopy with structure

No need to deuterate!?!

Data: Stony Brook STXM at NSLS

Soft X-ray Resonant Reflectivity

C. Wang, T. Araki, H. Ade



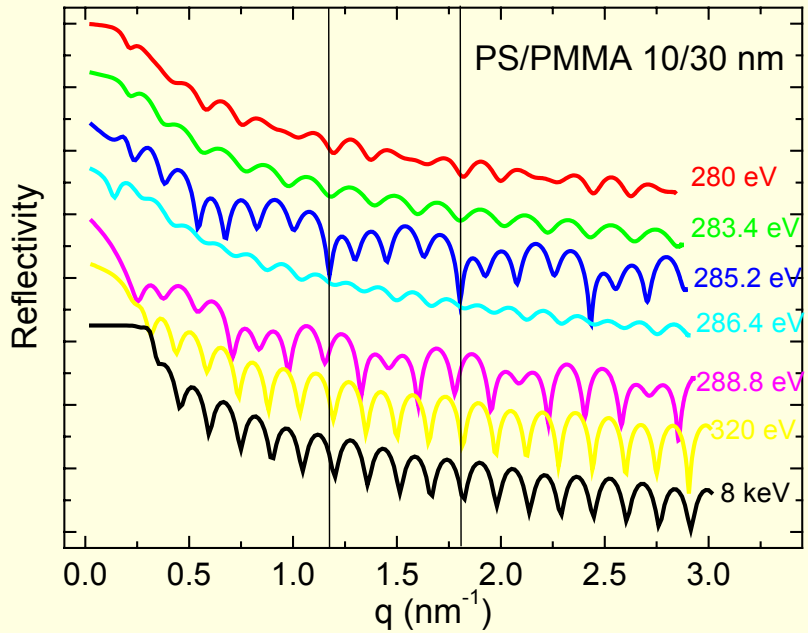
Can use large angles, hence, get good q-range

Reflectivity at the PS/PMMA interface is relate 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

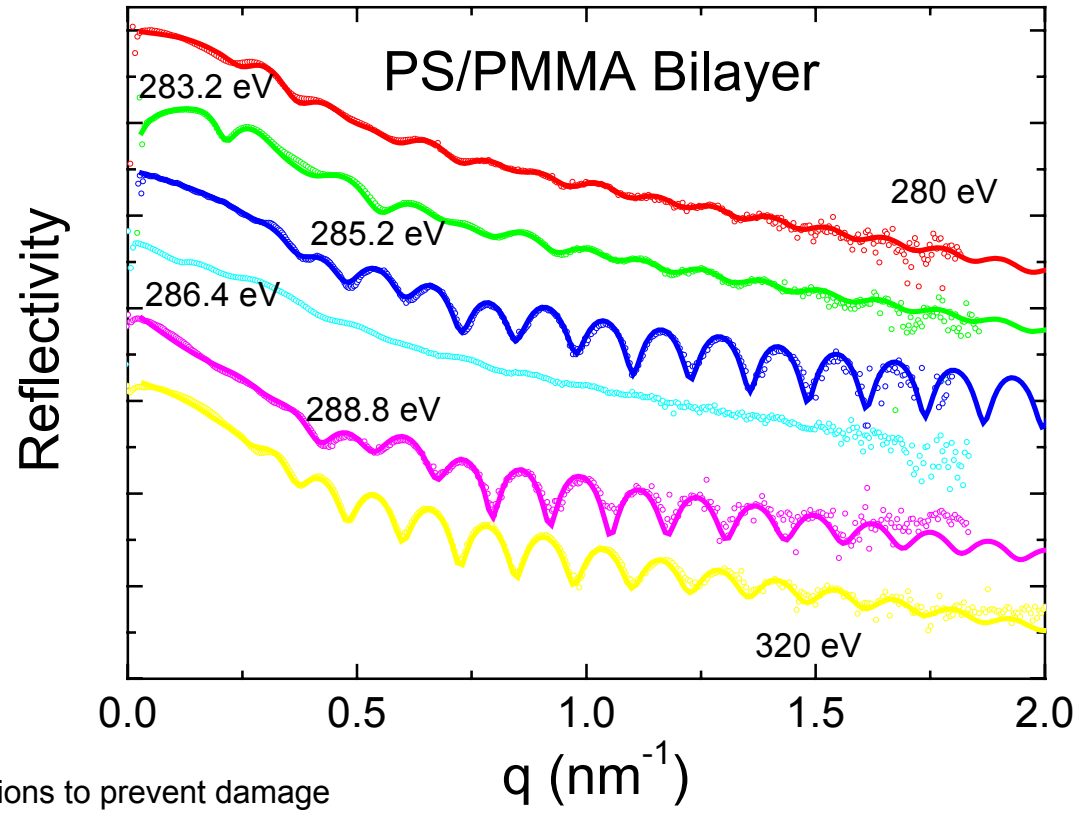
Soft X-ray Resonant Reflectivity

Our first experiments

C. Wang, T. Araki, H. Ade

Complementary Tool to Neutrons and hard X-rays

- Observed strong photon energy dependence
- Need to reduce uncertainty for δ and β
- Energy calibration needs to be improved



Different energies from different sample locations to prevent damage

E(eV)	d_{PS}(fit)	d_{PMMA}(fit)	σ_{sur}(fit)	σ_{int}(fit)
280	18.42	31.21	0.66	1.90
284.3	17.59	30.60	0.72	1.89
285.2	17.02	30.79	0.69	1.92
288.8	17.57	31.21	1.02	1.93
320	17.66	30.87	1.18	2.36
average	**17.65**	**30.94**	**0.85**	**2.0**

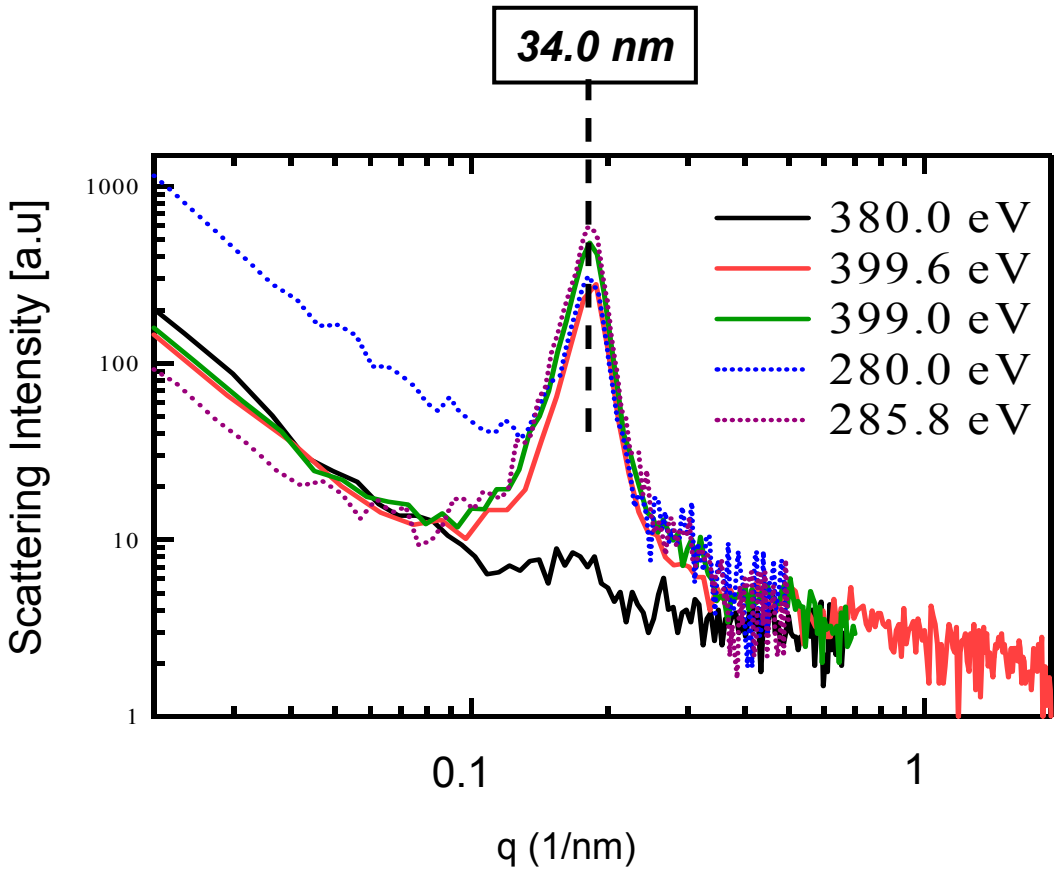
- Average thickness d of PS/PMMA bilayer is 17.7 nm / 30.9 nm.
- Surface roughness = 0.85 nm
- Interface roughness = 2.0 nm.
- 1.8 nm SiO_2 layer with 0.4 nm roughness was also considered in the fitting.

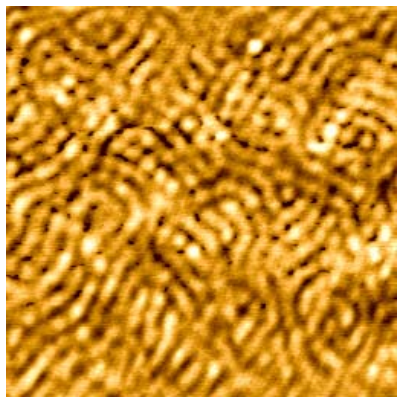
Data: Araki, BL6.3.2. ALS, Berkeley

One interesting experiment

- **Dynamics at the PS/PMMA interface**
  - **Combine correlation spectroscopy (S. Sinha) with layer contrast tuning.**
  - **PS on top of PMMA. Turn PS reflection off!**

Scattering from block copolymers PS-b-P2VP





Spherical/lamellar phase

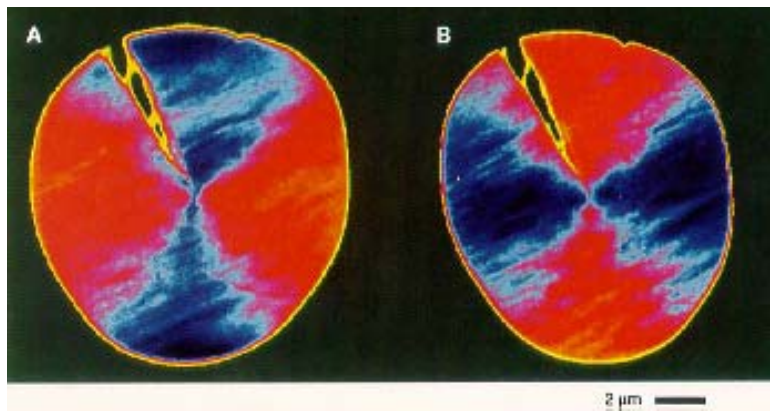
Φ = ~30 nm

Conclusions of preliminary results

- **High, tunable contrast**
- **Compositional 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**

- **Contrast from orientation!?**



NEXAFS microscopy sensitive to orientation

Technological requirements/challenges

- **Multichannel detection**
  - **Large angular range**
- **Carbon edge particularly interesting for soft matter**
  - **Beamline/instrument should work well at that energy**
- **EPU best**
  - **Orientation, composition**

- **Time resolution!?**
- **Environmental control!?**

Post Doc hire by 1/1/2006
Need good applicants