Resonant Soft X-Ray Scattering of Polymers: Initial Experiments and Application to new Material Development

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- **Scattering data acquired at the Center for X-Ray Optics (CXRO) X-ray beamline 6.3.2 at the ALS, which is funded by the DOE**
- STXM Data Acquired at BL 5.3.2 at the ALS

Overview

- **Proof of principal experiments**
  - Well separated spectral features
  - Demonstrate molecular bonding specificity
- **Application to new material development**
  - Subtle differences in spectral features provide sufficient contrast to study phase structure of 100 nm films
- **Future Applications**
  - With an enhanced beamline (ID with 2 D detection)

Energy Dependence

$$f(0,E) = f_1(E) + i f_2(E)$$

(forward scattering direction)

$$f_2(E) = \frac{\sigma_a(E)}{2 r_e \lambda}$$

Photoabsorption cross section

r_e = classical electron radius
λ = wavelength
c = speed of light
h = Plank's constant

Kramer's Kronig relation relates f_1 to f_2:

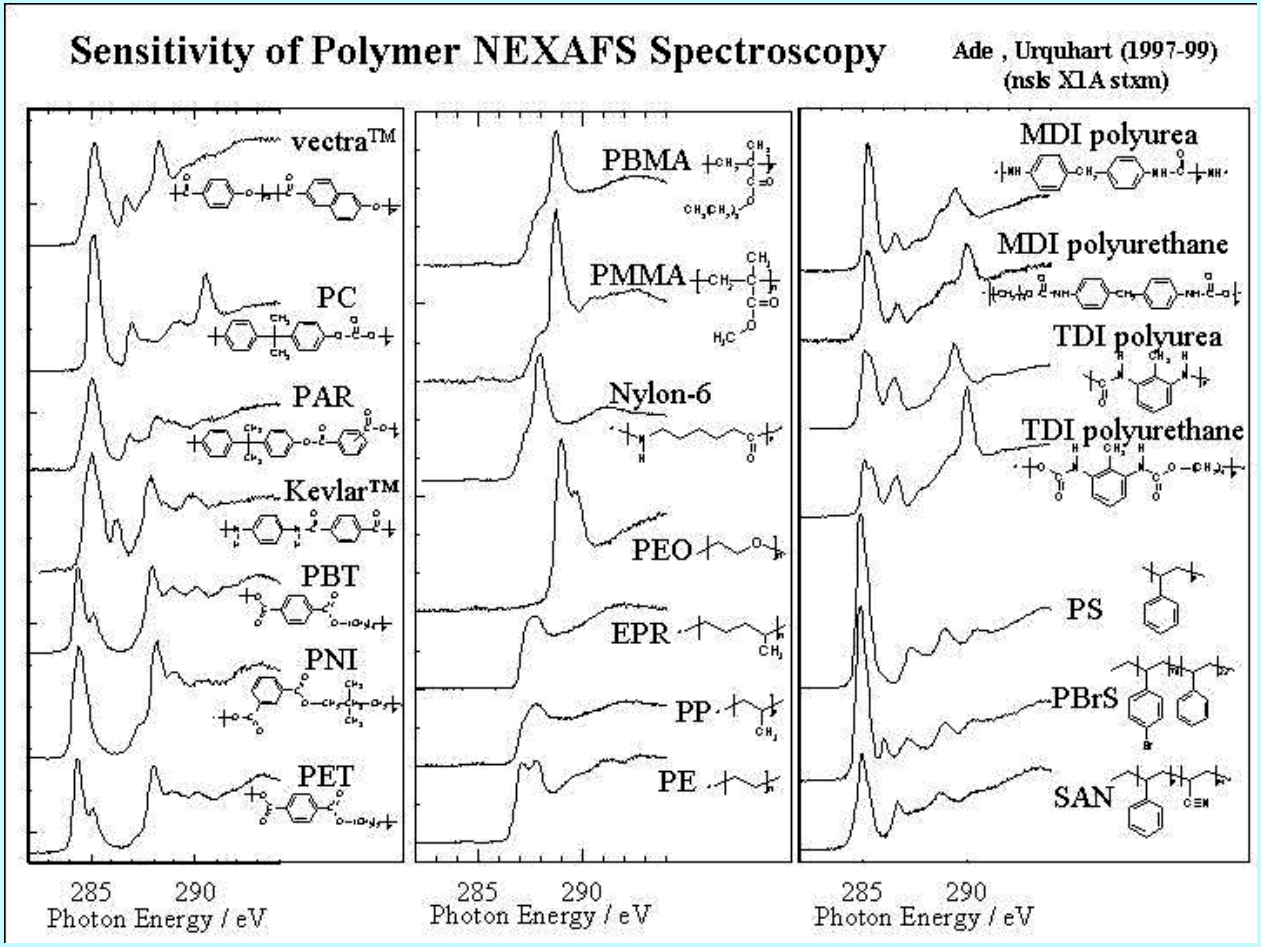
$$f_1(E) = Z - \frac{1}{\pi r_e hc} \int_0^\infty \frac{\varepsilon^2 - \sigma_a(\varepsilon)}{E^2 - \varepsilon^2} d\varepsilon$$

atomic number

$$n = 1 - \delta - i\beta = 1 - \frac{r_e \lambda^2}{2\pi} \sum_j n_j f_j$$

Near-edge x-ray absorption fine structure (NEXAFS) of the C K-edge

- Chemical sensitivity determined by the bonding environment
- Resonances can be 10 times stronger than the absorption edge
- Important for organic materials

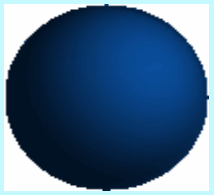


Proof of Principle Experiment

- Polystyrene (PS)

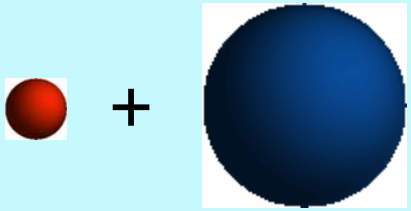
79 nm

- Polymethyl methacrylate (PMMA)

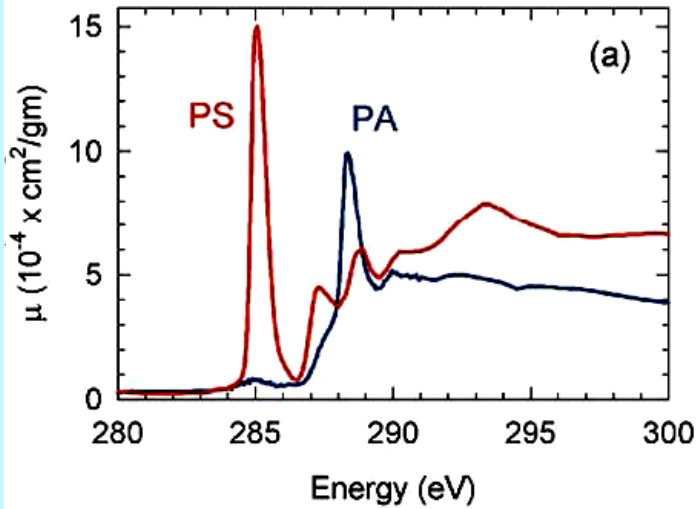


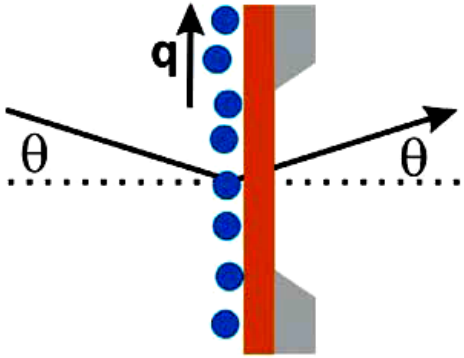
300 nm

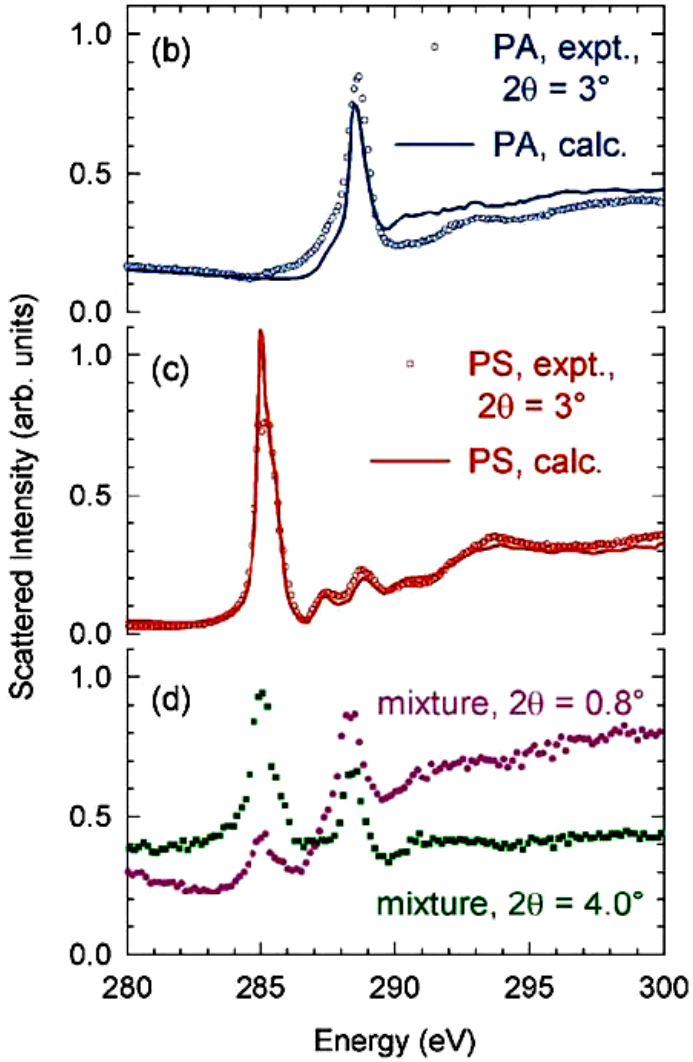
- Mix of both



Scattering Spectra
(Energy Scans)

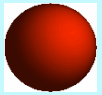




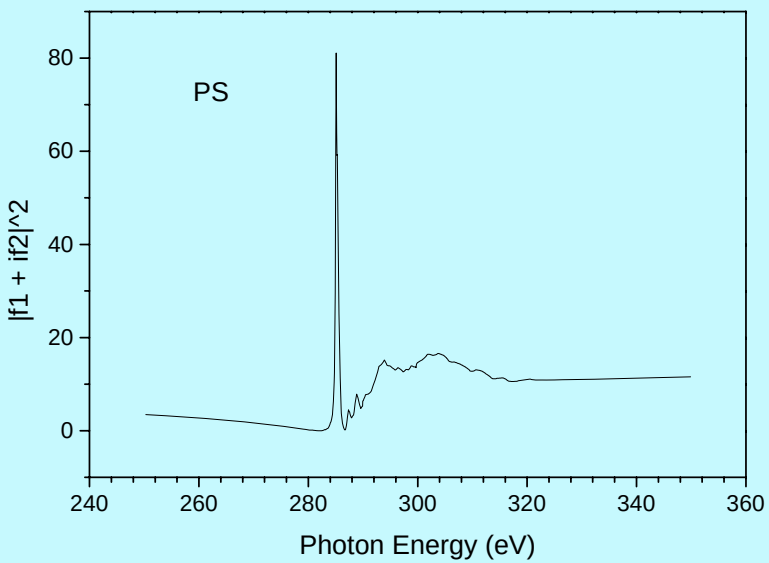


Proof of Principle Experiment

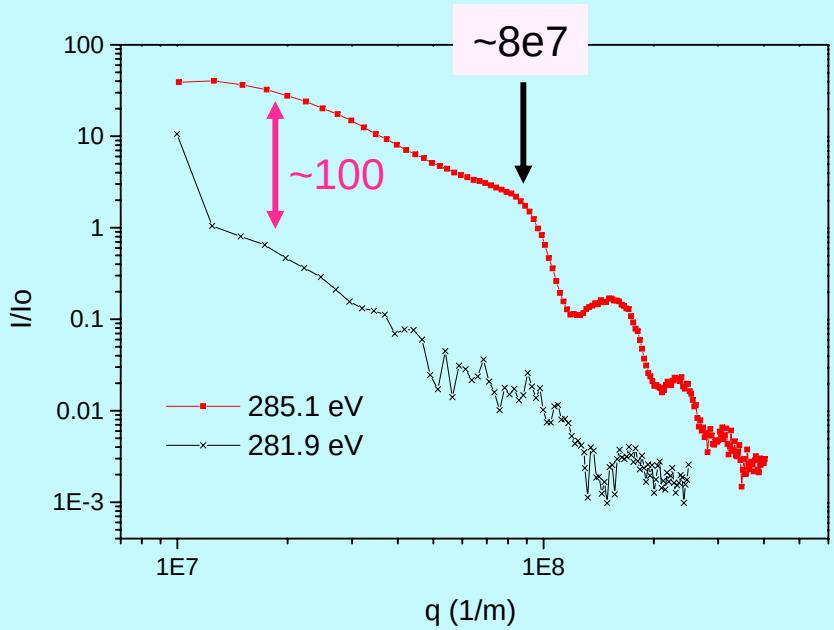
Polystyrene (PS)



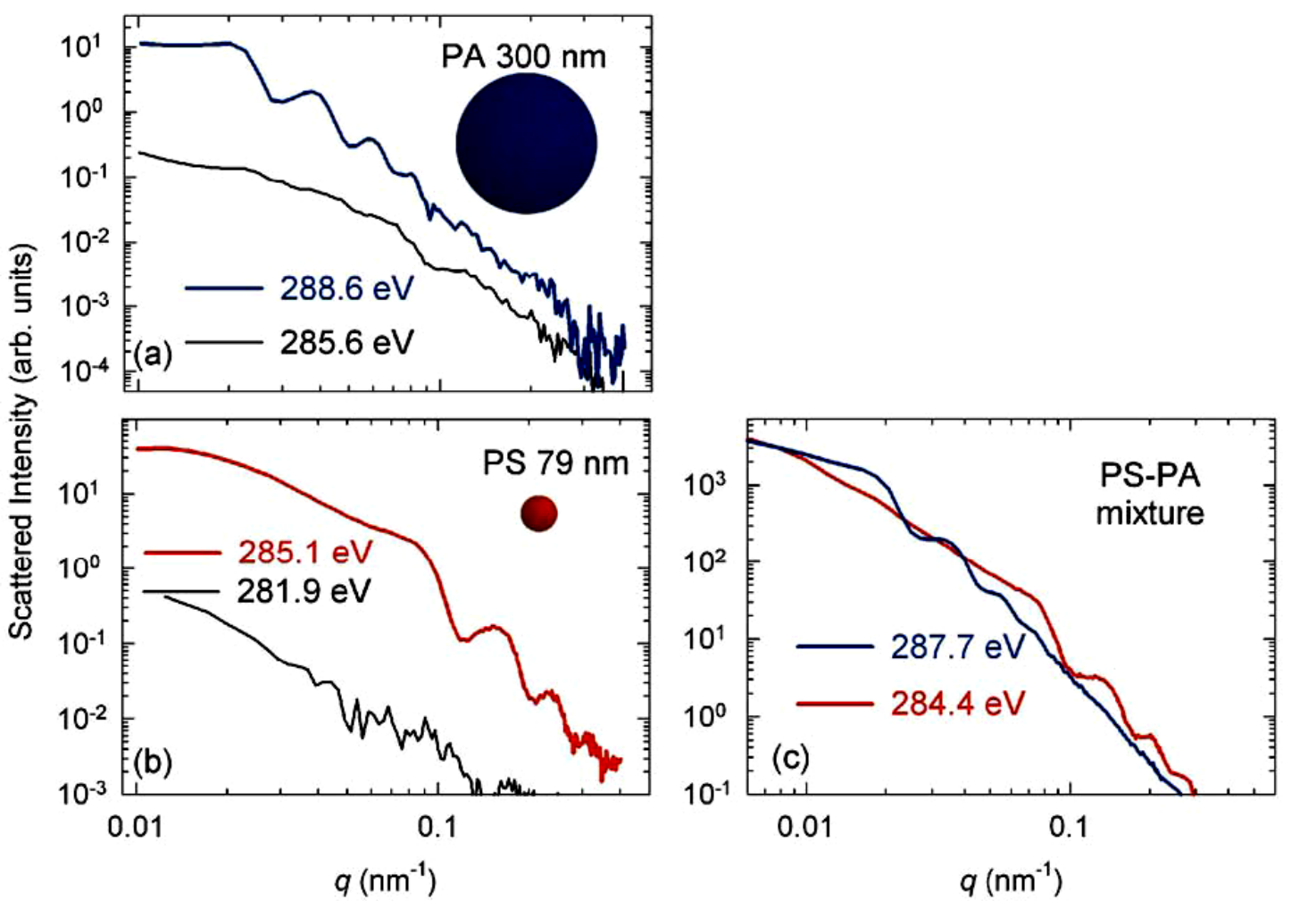
79 nm



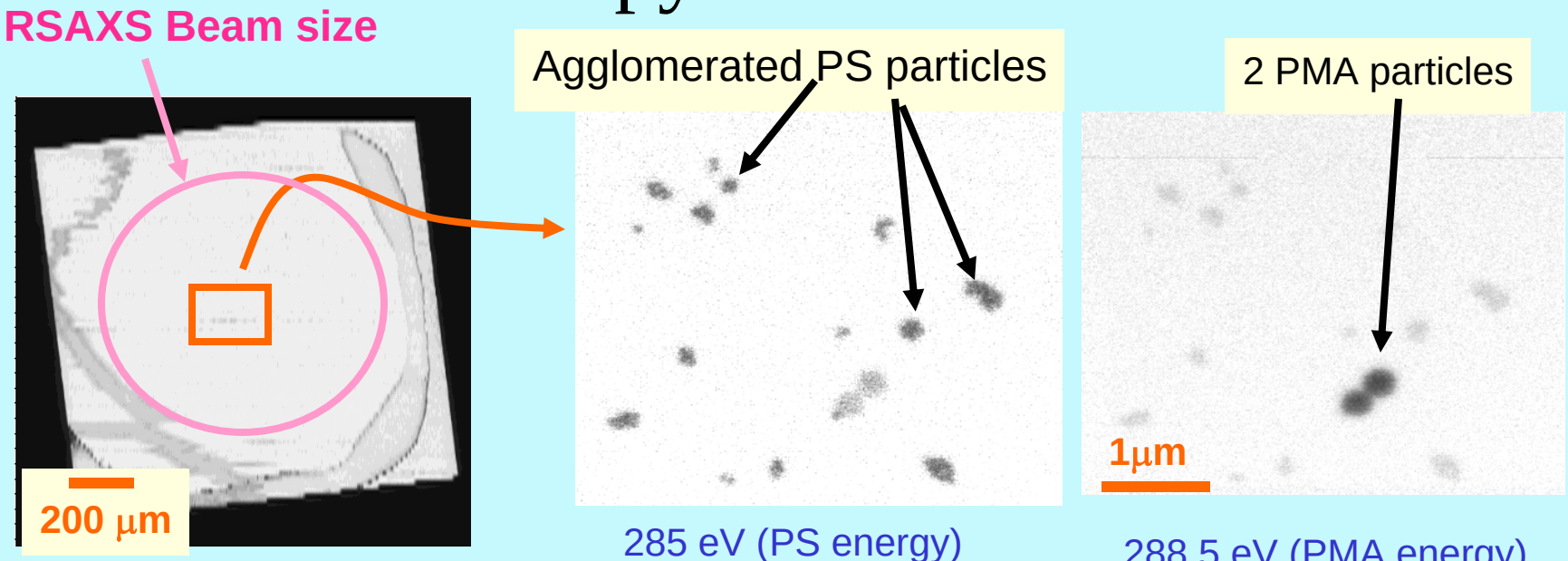
Tuning to the certain energies will switch on/off the scattering.



Scattering Patterns
(Angle Scans)



Scanning Transmission X-Ray Microscopy of Mixed PS / PMA

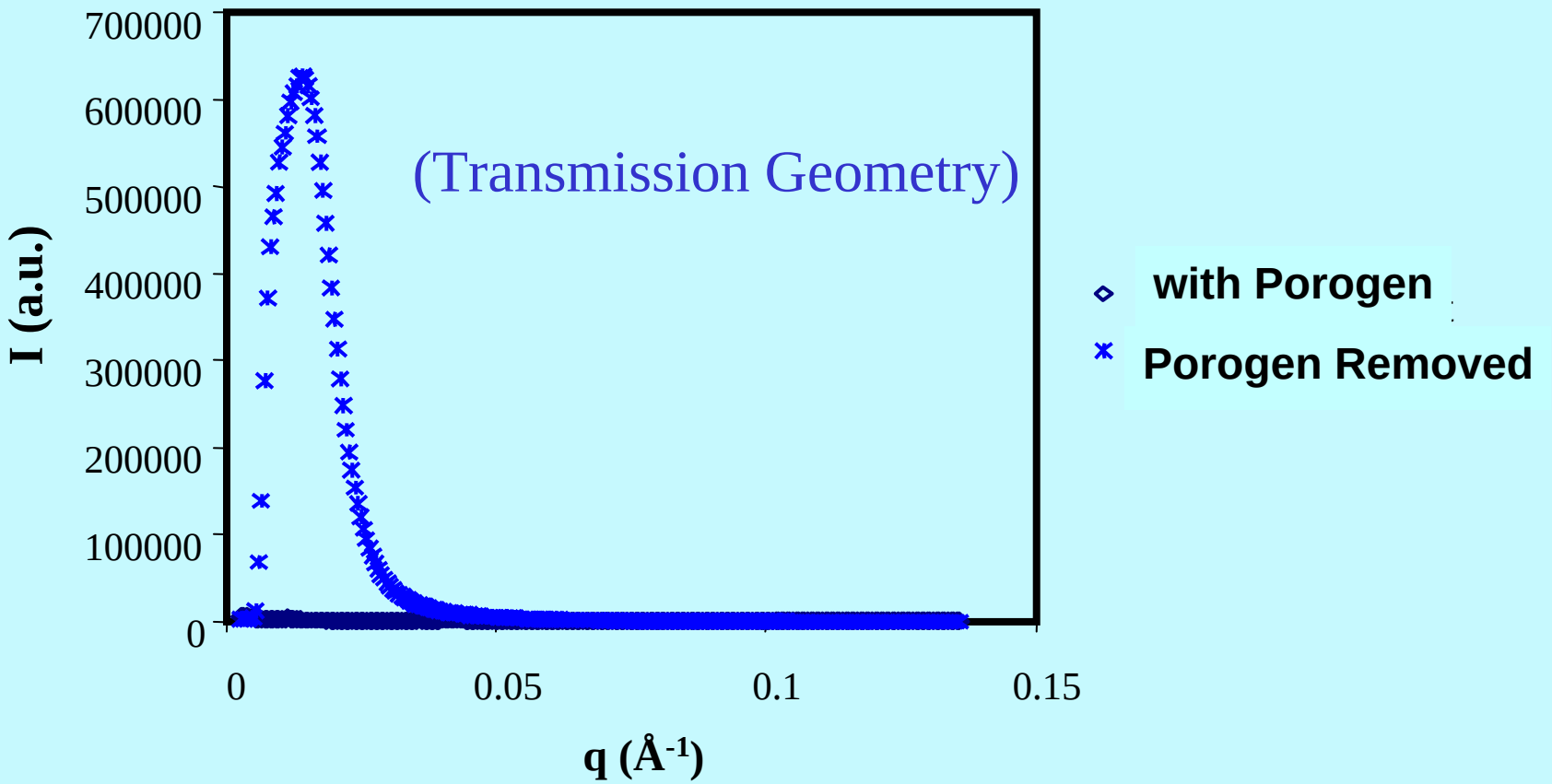


Densely populated area of sample

- Adequate signal even from very dilute samples
- Many more PS spheres than PMA spheres

Images measured with ALS BL 5.3.2 STXM

Conventional SAXS of Developmental Porous SiLK Resin



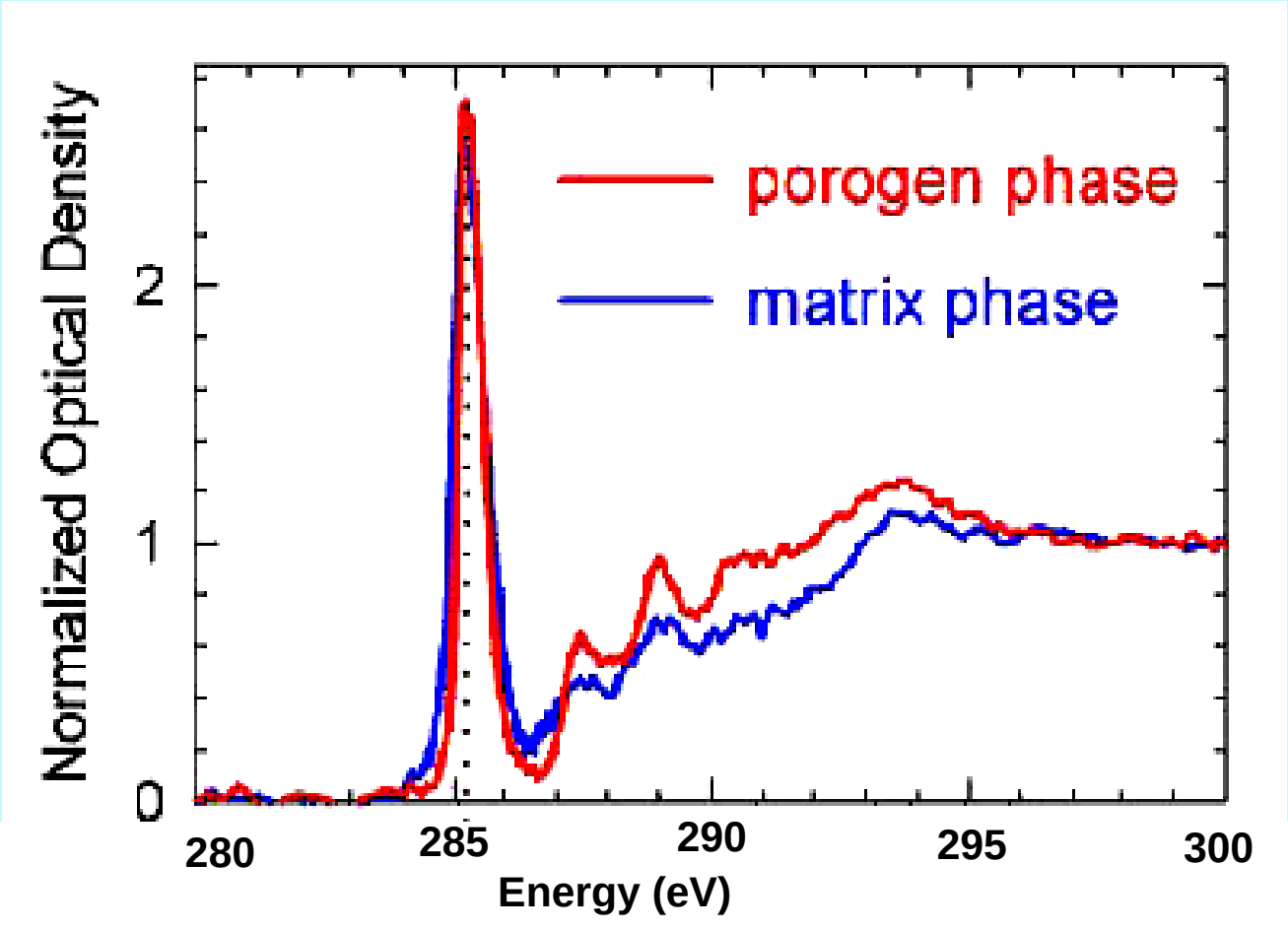
•porogen is invisible to hard x-ray SAXS (and TEM) => identical electron densities

Templating of Porogen to Make Porous SiLK* Resins

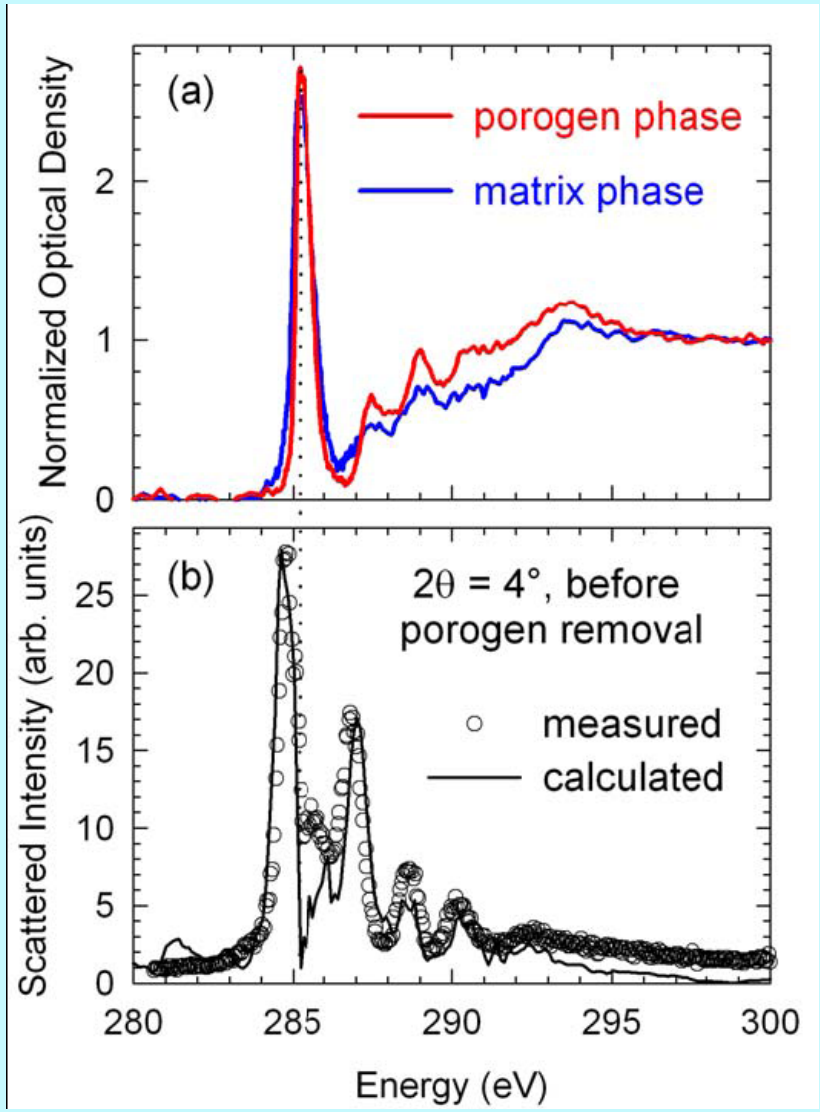
- Decreasing feature size in integrated circuits require lower dielectric constants for insulating layers to:
  - increase circuit speed, decrease power consumption, decrease crosstalk
- Adding pores to SiLK dielectric resin is used to decrease dielectric constant from 2.65 to 2.1 and less
- Future materials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

*** SiLK is a trademark of The Dow Chemical Company**

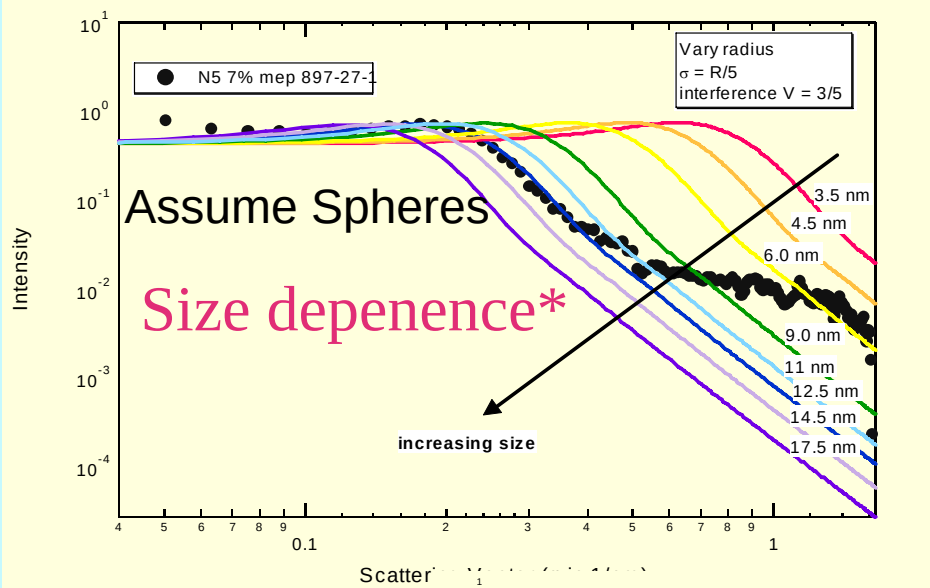
NEXAFS Spectra of SiLK® Resin Matrix and Experimental Porogen

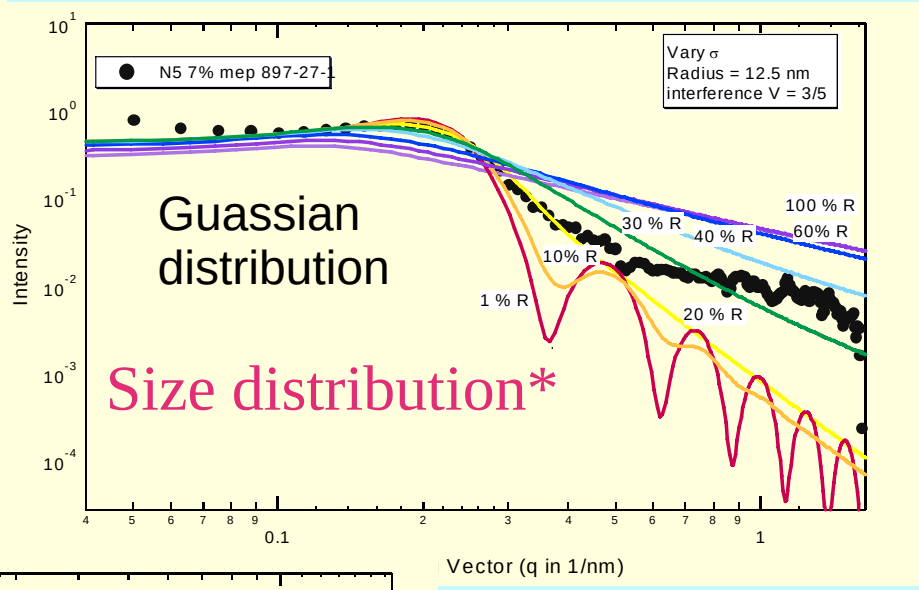


Scattering Energy Spectrum

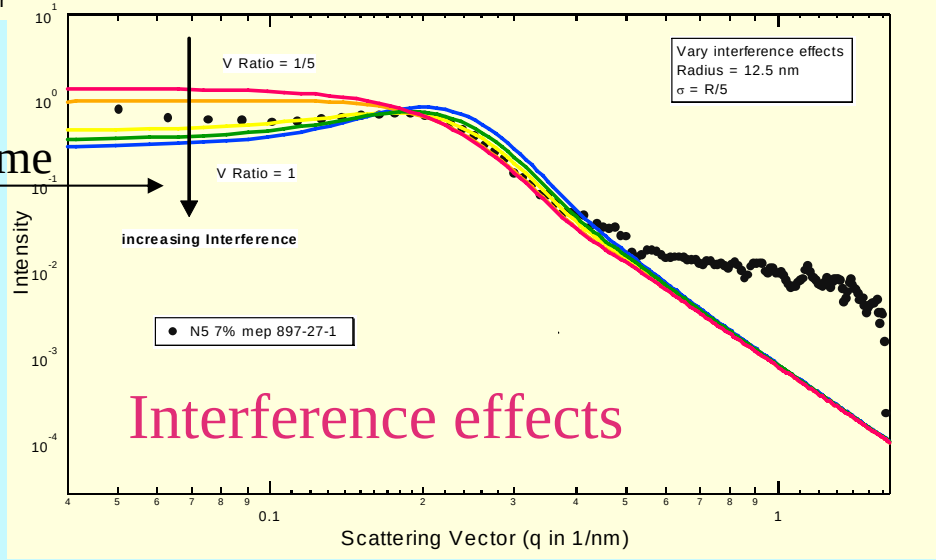


Data Analysis



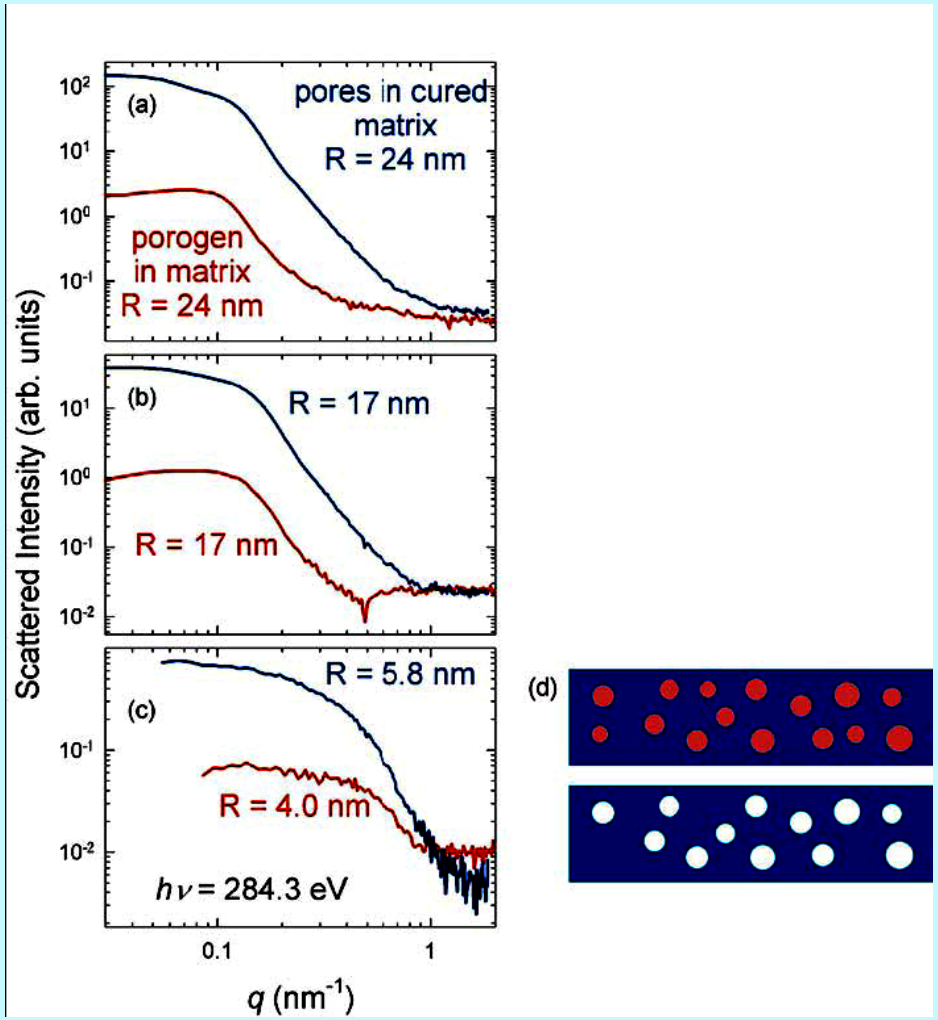


Increasing volume fraction



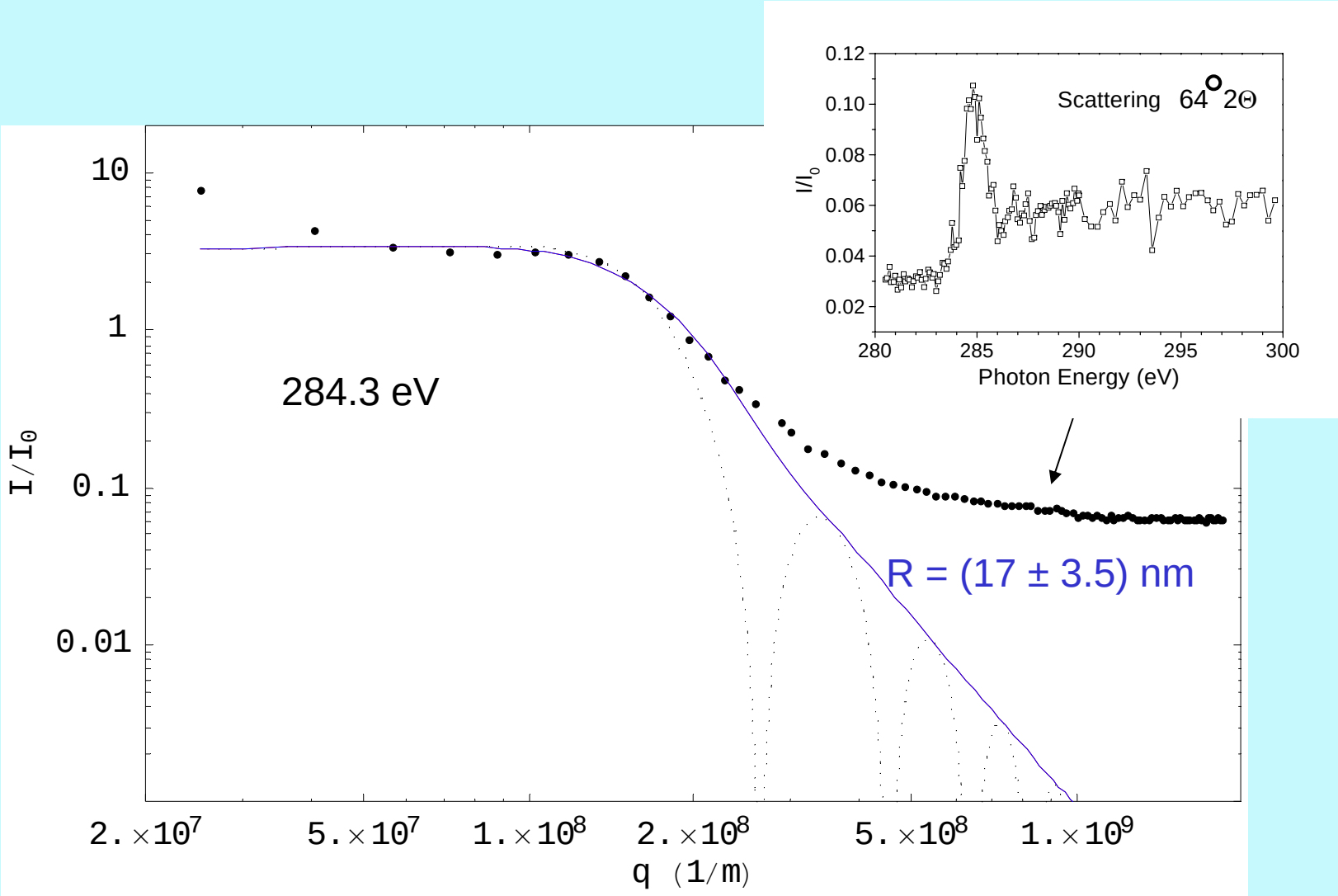
*Henke, and DuMond, J. Applied Physics, 26(1955)903.

Scattering of Porogen versus Pores

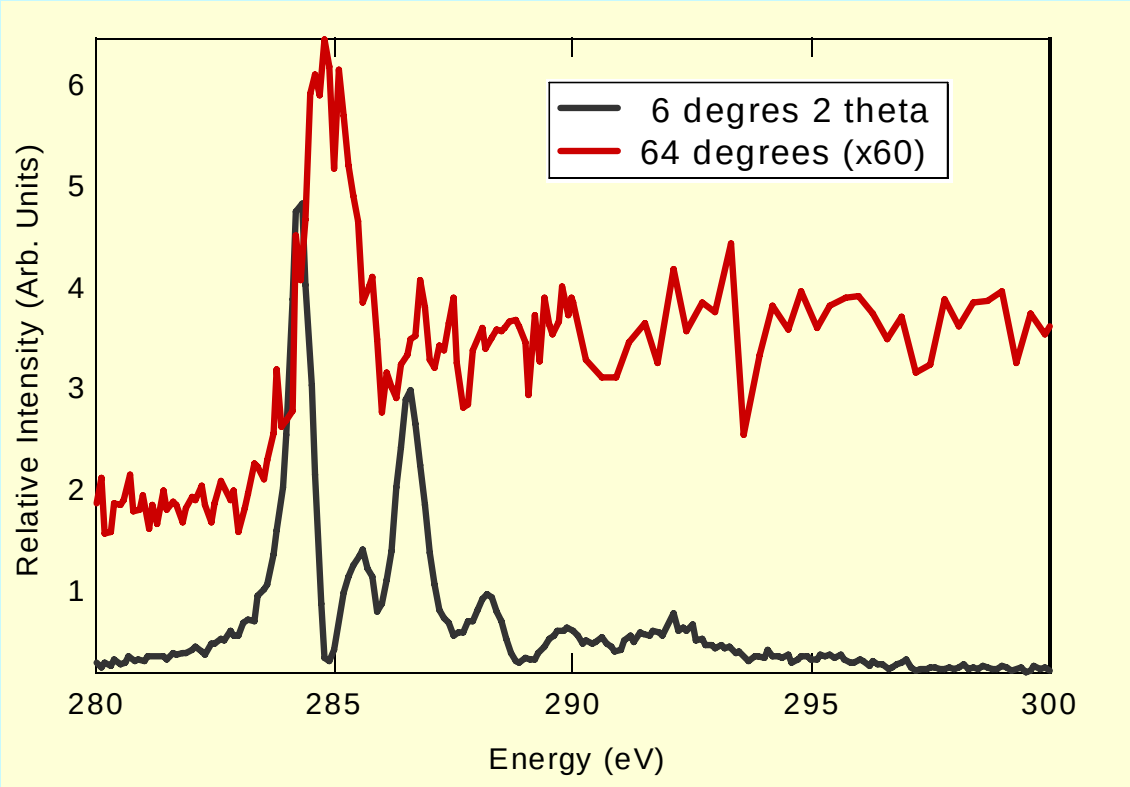


- Porous material has >10x higher scattering intensity than blends
- Larger porogens templated to same size pores
- Pores from smallest porogen were larger relative to porogen

Scattering at Large q



Resonant Scattering Intensity at Large scattering Angle



•Large angle scattering is from fluctuations within a single phase

Summary for Developmental Porous SiLK Materials:

- RSAXS provided capability to analyze porogen containing films unavailable with conventional SAXS because of increased scattering intensity at resonant energies

- Comparison of data before and after removal of porogen indicated the size of pores in films are similar to the size of porogen precursors in most cases and that porogen was a separate phase before processing to remove porogen

- **Smallest pores collapsed due to insufficient rigidity of the matrix ➔ smaller pores require stiffer matrix**

Conclusions

RXS provides new capabilities for polymer analysis:

- Chemically sensitive (bonding specific) x-ray scattering able to differentiate scattering according to chemical composition of phases
- Provides contrast for scattering of materials where no contrast occurs by traditional methods
- Identification of Phases (qualitative analysis) and quantitative analysis of sizes in complex mixtures

Future Potential Applications

Undulator, high bandwidth
2D detector

- Thin films
- Polymer blends with more than two phases
- Polyurethane
- Blends of semicrystalline polymers
- Complex colloidal systems (more than two phases)
- Structured latex
- Fluctuations in crosslink density
- Phase segregation / reaction time dependence
- Add to STXM for analysis nano phase structure of micro-phases