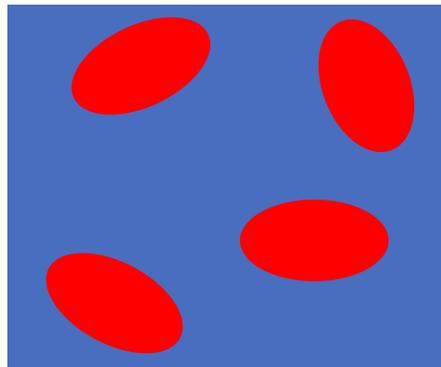


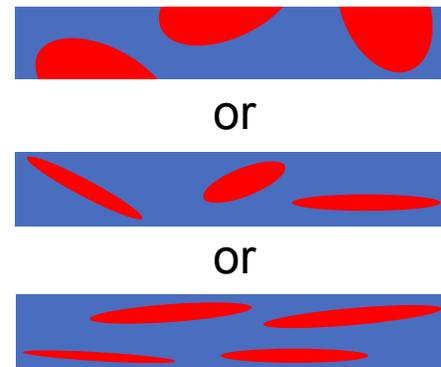
Thin Polymer Film Structure Using Resonant Soft X-ray Contrast Variation

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E. Bruce Orlor, Marilyn Hawley, Jeff Kortright

Los Alamos National Laboratory
Lawrence Berkeley National Laboratory



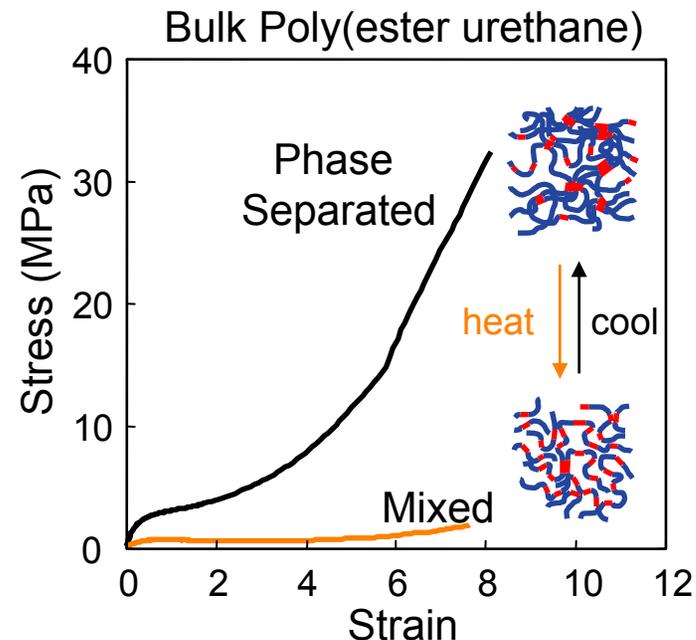
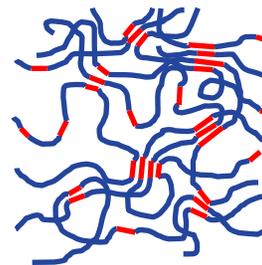
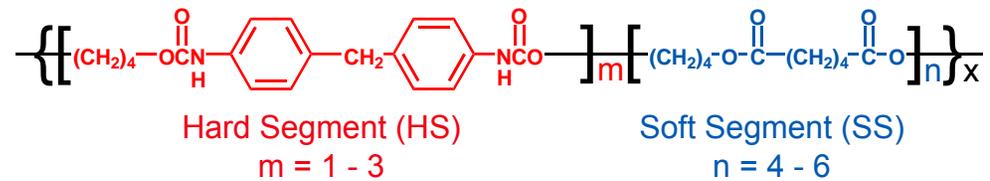
Bulk



Thin Film

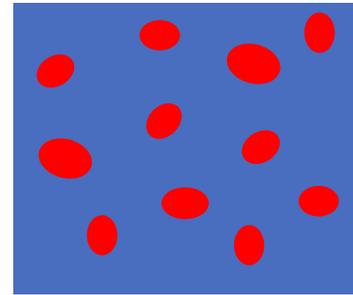
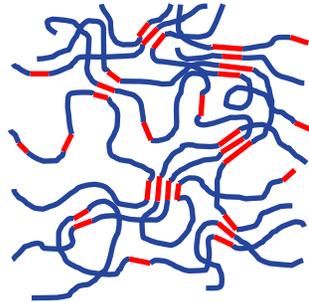
Poly(Ester Urethane)s: Morphology & Mechanics

- **Thin Film PESUs:**
Segmented block copolymers used as adhesives, binders, coatings
- **In bulk materials**
 - SANS results reveal phase separation of hard and soft segments
 - Hard domains act as crosslinks in soft domain matrix to give desirable mechanical properties
- Is morphology of thin film PESU similar to that of bulk?

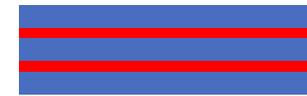
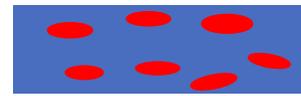


Morphology: Bulk vs. Thin Film

Bulk

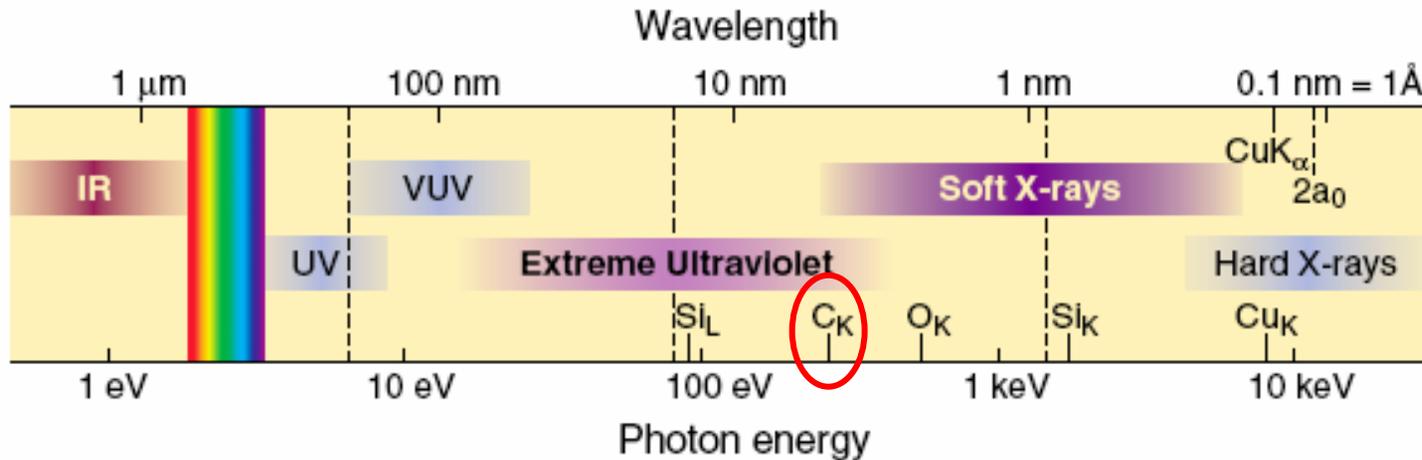


Thin Film



- Surface and interfacial forces can play a large role in determining morphology of thin films
- Morphological study of PESU thin films via scattering techniques is difficult
 - Contrast between domains is often weak
 - Small scattering volume in thin film gives weak signal
- Resonant soft x-ray scattering and reflectivity techniques are a new way to analyze thin polymer films
 - Contrast between light elements varies with energy
 - Structure & extent of phase separation in polymer films can be determined

What Are Soft X-rays & Why Are They Useful?



D. Attwood, *Soft X-rays and EUV Radiation*, Cambridge University Press: New York, 1999.

- Soft X-rays: Energy close to absorption edges of light atoms (C, N, O) where resonances in the atomic scattering factors occur
- Resonance techniques provide contrast mechanism to probe polymer structure
 - Performed at energies close to absorption edge of an element in the material
 - Previous experiments used high energy x-rays and heavy element labeling
- Investigation of unmodified polymers via resonance techniques is now possible
 - Requires thin films (100 - 500 nm)
 - Natural fit for phase-separating copolymers used in thin film applications (coatings, binders, adhesives, etc.)

Contrast Variation in Resonant Soft X-ray Scattering

- Scattering length density (ρ) depends on atomic scattering factors (f)
- Near absorption edge, real and imaginary parts of f (f' and f'' , resp.) vary strongly with energy
- Can calculate scattering length (b), scattering length density (ρ), and contrast ($\Delta\rho^2$) from f' and f'' :

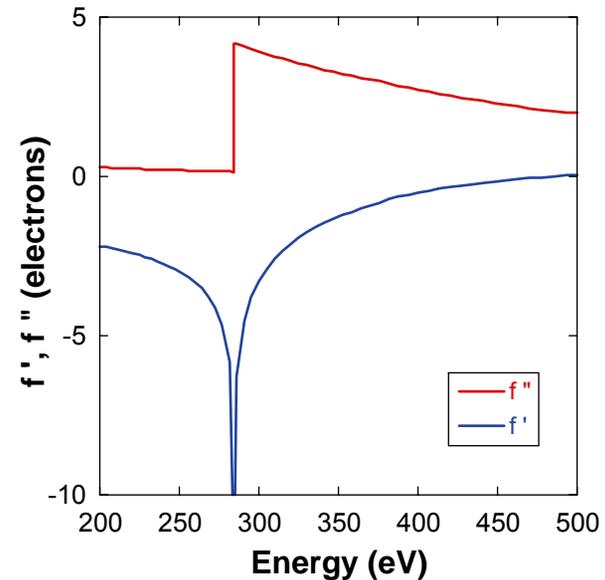
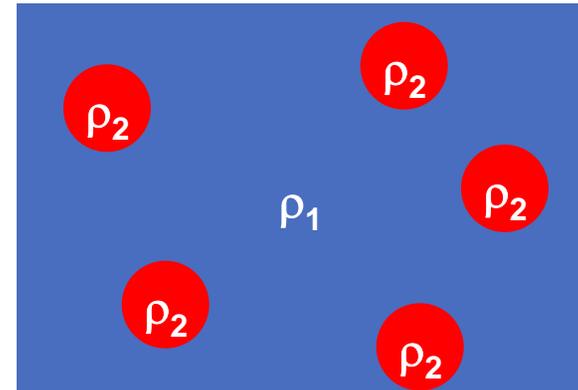
$$b(E) = (Z + f'(E) + if''(E))b_0$$

$$\rho_1 = \frac{1}{V_1} \sum_i^{\text{atoms}} b_i$$

$$\overline{\Delta\rho^2} = \Phi_1\Phi_2(\rho_1 - \rho_2)^2$$

$$I_S(Q) \propto \overline{\Delta\rho^2}$$

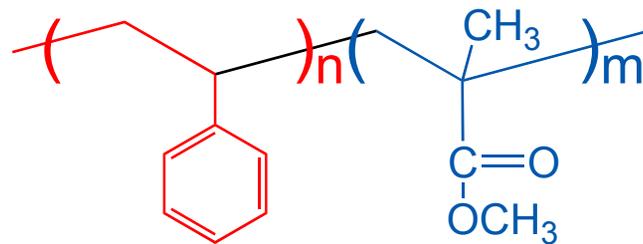
Phase-separated material:



Henke et al. *At.Data Nucl.Data Tables* **1993**, 54, 181.

Experimental: Two Phase-Separating Copolymers

- Poly(styrene - b - methyl methacrylate): 50:50 symmetric diblock; 42,000 g/mol (Polymer Source)
 - Readily forms well-defined lamellar morphology
 - Distinct differences in chemical make-up of the two blocks



- Poly(ester urethanes) (PESUs) with varying monomer ratios
 - Randomly alternating hard and soft segments phase-separate into domain structure that is not well-understood
 - Some differences in chemical make-up of hard and soft segments

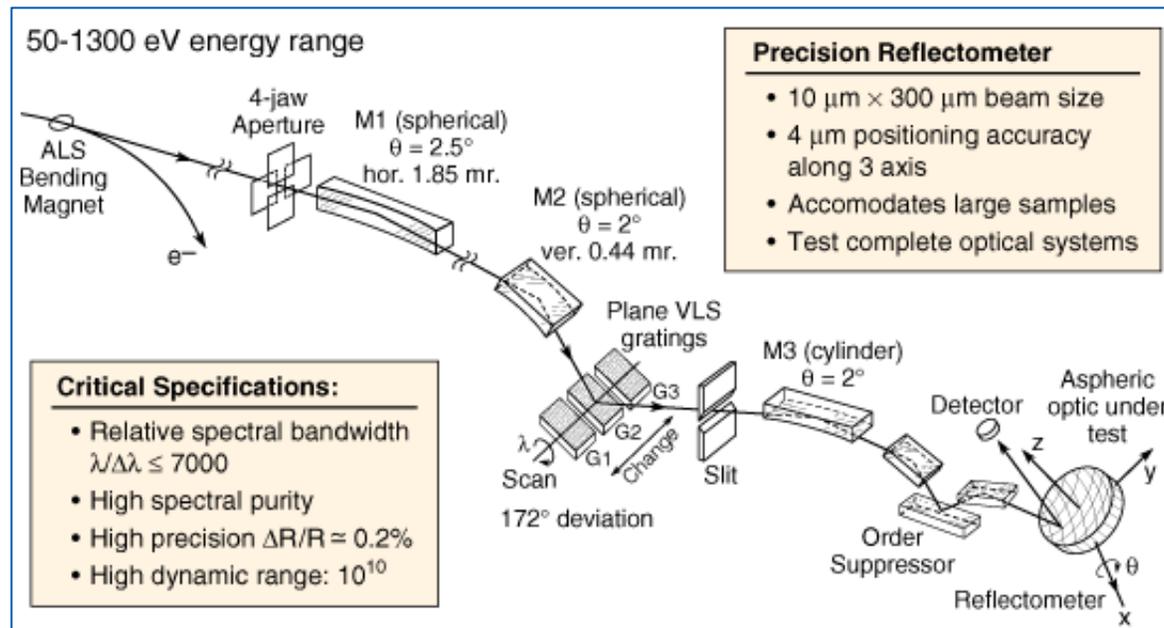


Hard Segment (HS)
m = 1 - 3

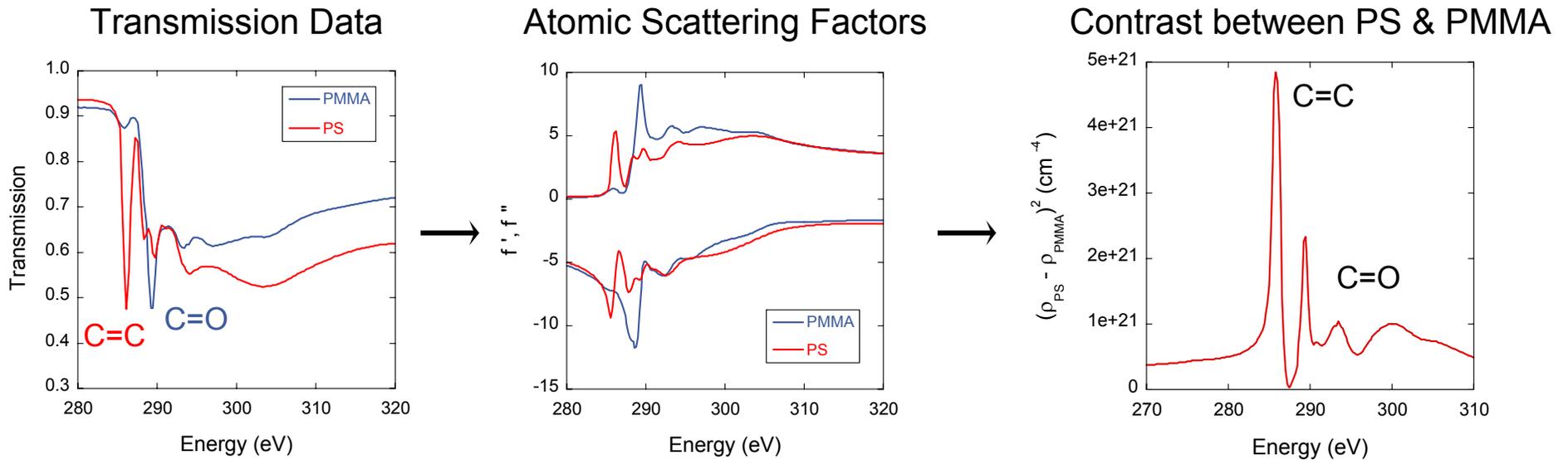
Soft Segment (SS)
n = 4 - 6

Thin Film Preparation and Scattering Experiments

- Copolymer solutions spin-cast to give 100 - 300 nm thin films, then annealed under vacuum
- Soft x-ray experiments done at ALS beamline 6.3.2 (bending magnet)
 - Energy range includes carbon absorption edge, ~284eV
 - Excellent energy resolution: ± 0.04 eV at 284 eV
 - Reflectometer endstation capable of transmission & reflectance modes



PS-PMMA Diblock: Contrast Between PS & PMMA



$$-\ln(T) = \mu(E) \rho_{mt}$$

$$\mu(E) = \frac{N_A}{M} \sum_i [x_i \sigma_{a,i}(E)]$$

$$\sigma_a(E) = \frac{2b_0 h c f''(E)}{E}$$

$$f_C''(E) = \frac{1}{x_C} \left[\frac{\mu(E) E M}{2b_0 h c N_A} - \sum_i^{atoms} x_i f_i''(E) \right]$$

$$f_C'(E) = \frac{2}{\pi} \int_0^\infty \frac{\epsilon f_C''(\epsilon)}{E^2 - \epsilon^2} d\epsilon$$

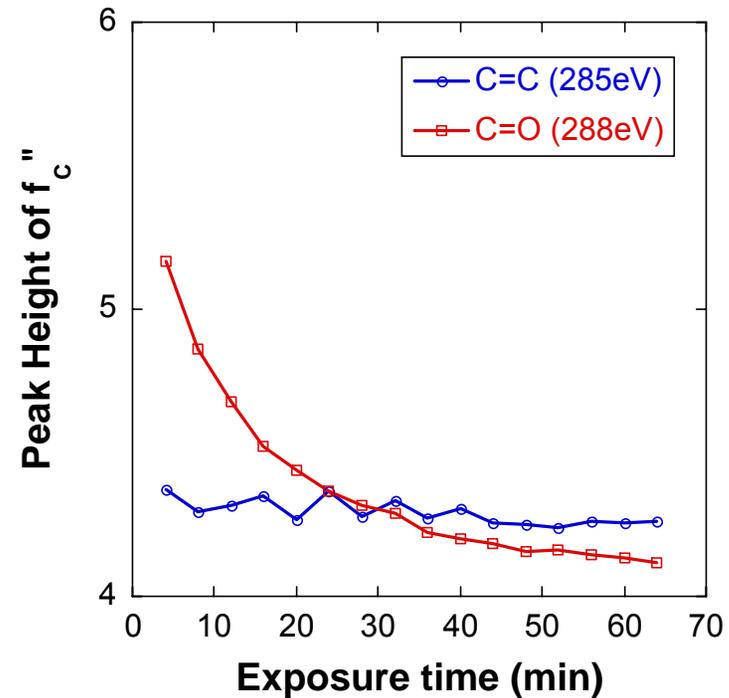
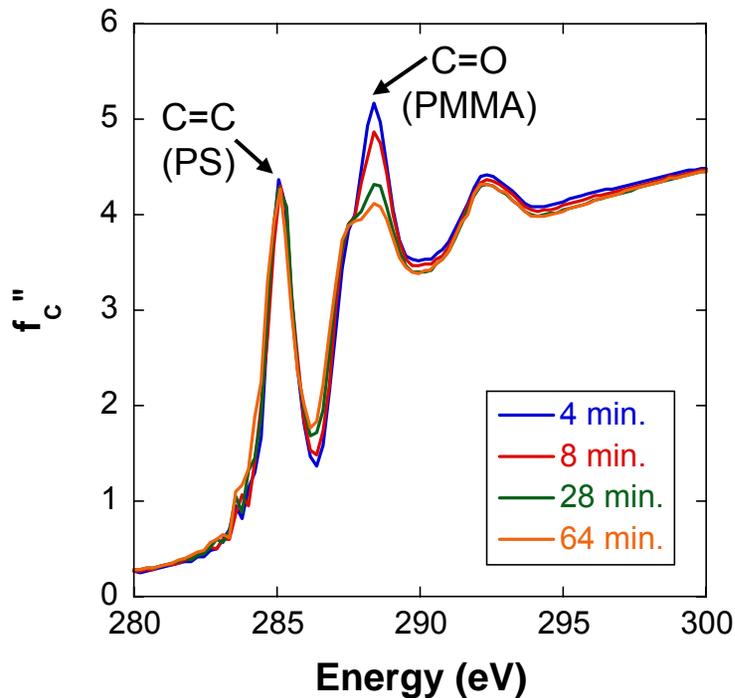
$$b_C(E) = \left(Z + f_C'(E) + i f_C''(E) \right) b_0$$

$$\rho = \frac{1}{V} \sum_i^{atoms} b_i$$

$$\overline{\Delta\rho^2} = \Phi_{PS} \Phi_{PMMA} (\rho_{PS} - \rho_{PMMA})^2$$

$$I_S(Q) \propto \overline{\Delta\rho^2}$$

Carbonyl Carbons Susceptible to Radiation Damage

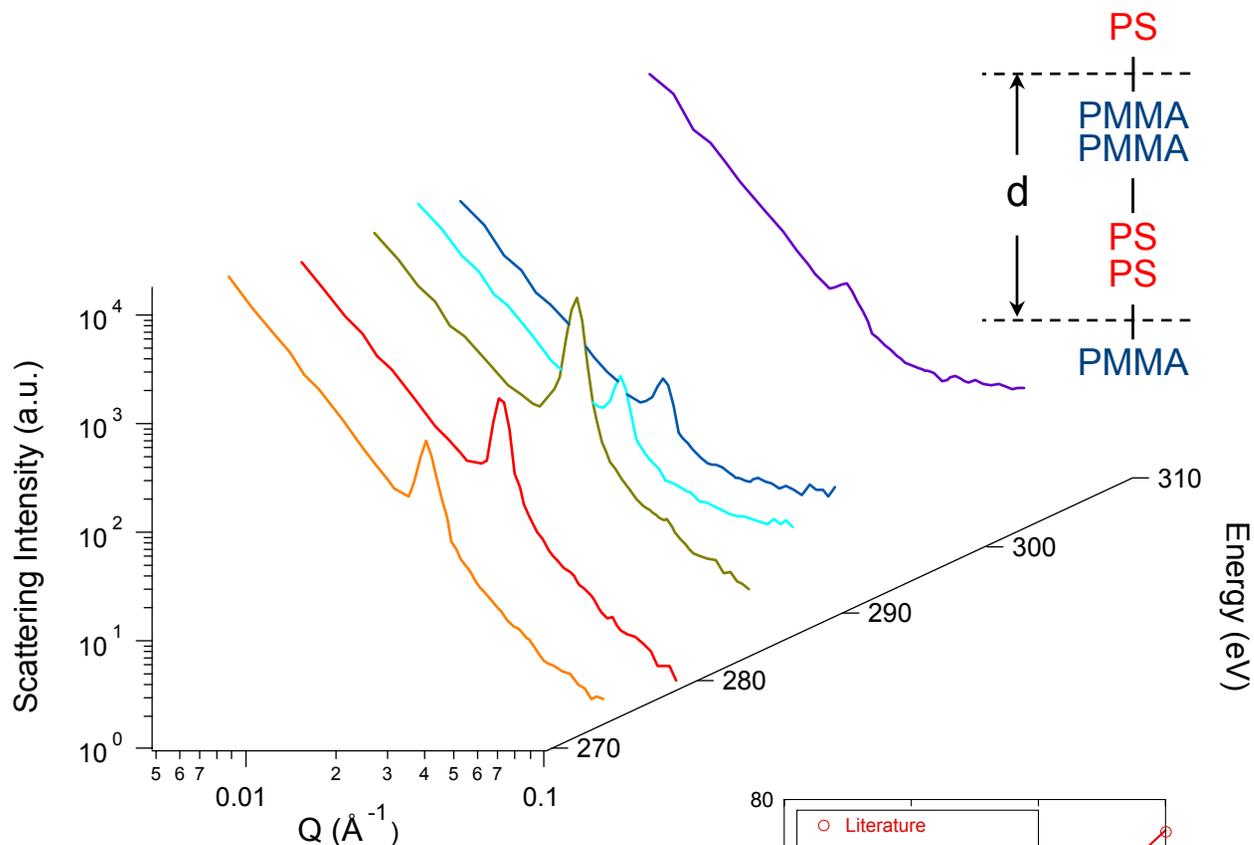


- Problem for multiple scattering experiments on one sample: Carbonyl carbons in PMMA ester group degrade upon exposure to soft x-rays
- Solution: Move to different spots on film for each scattering experiment (i.e., at each incident energy)

PS-PMMA Resonant Scattering Agrees with Expectations

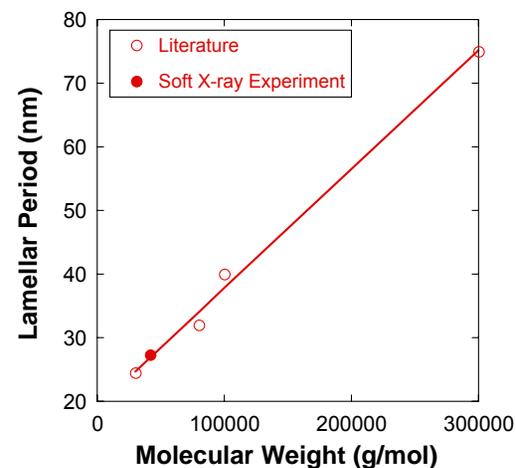
- Peak observed in scattering curves at all energies examined
- Peak intensity varies with incident x-ray energy
- Peak position gives lamellar spacing that agrees well with literature trends*

* Russell et al., *Macromolecules* **1989**, 22, 4600; Mayes et al., *Macromolecules* **1994**, 27, 749.

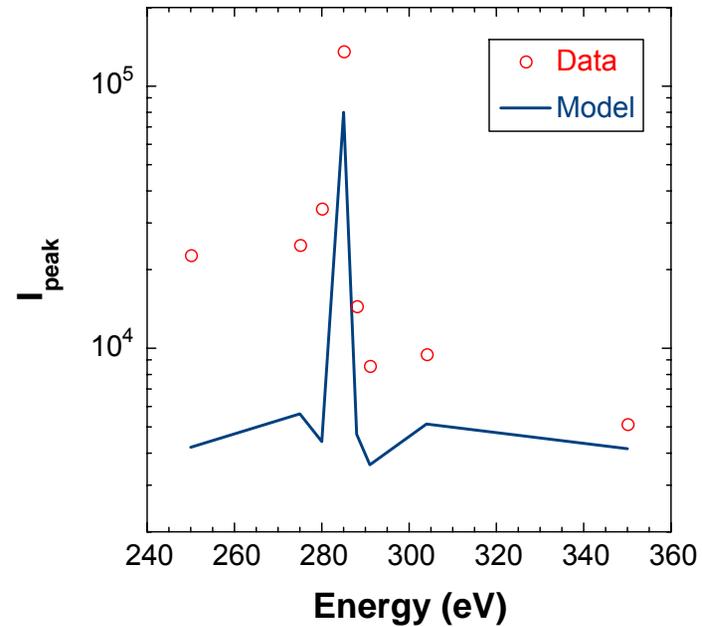
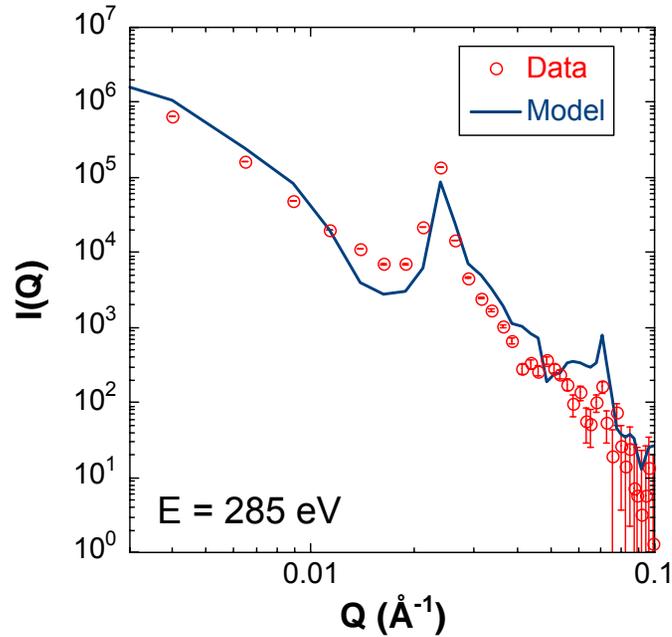


$$Q \approx 0.023 \text{ \AA}^{-1}$$

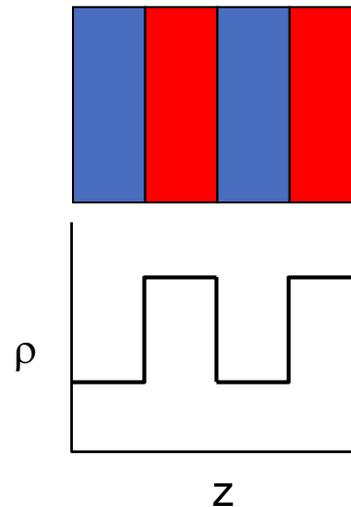
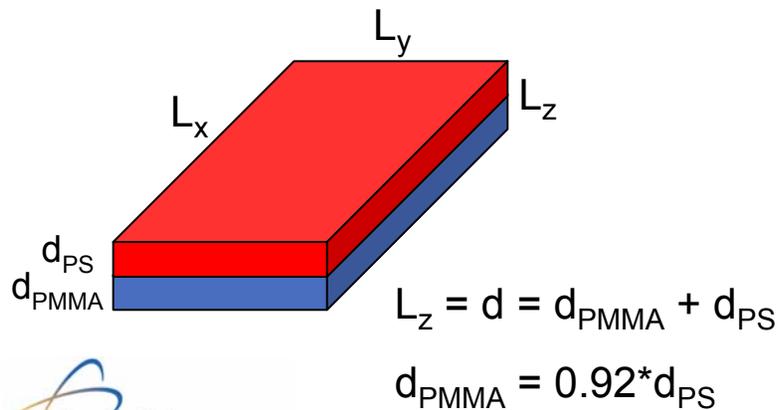
$$d = \text{lamellar period} \\ = 2\pi / Q \\ \approx 27.3 \text{ nm}$$



PS-PMMA Scattering Data Modeled as Stacked Sheets



$$I_S(Q) = \Delta\rho^2 \langle P(Q)S(Q) \rangle$$



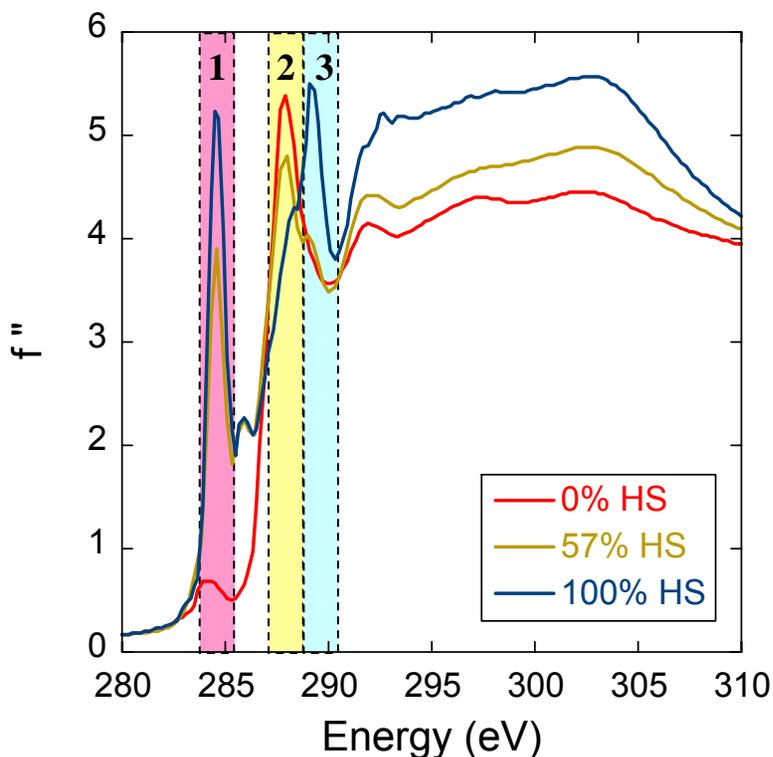
- $d_{PS} = 13.9 \pm 0.3 \text{ nm}$
- $d_{PMMA} = 12.8 \pm 0.3 \text{ nm}$
- $d = 26.7 \pm 0.6 \text{ nm}$
- $N = 8$
- $L_x = 104.6 \pm 2.2 \text{ nm}$
- $L_y = 41.6 \pm 1.1 \text{ nm}$

Spectra of Poly(Ester Urethane) Copolymers



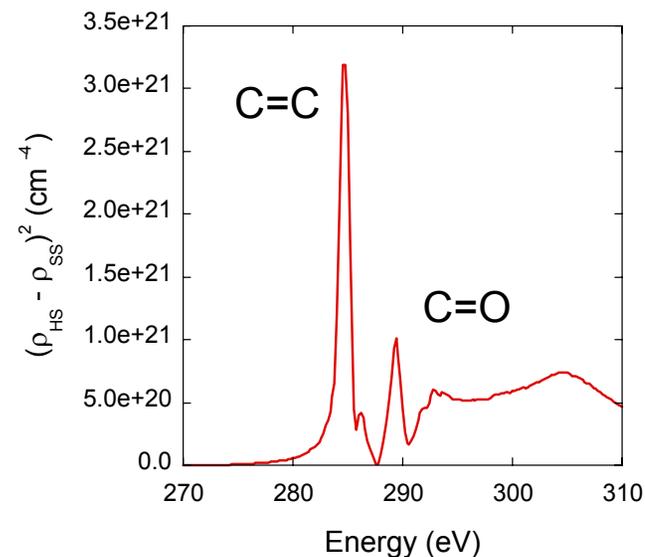
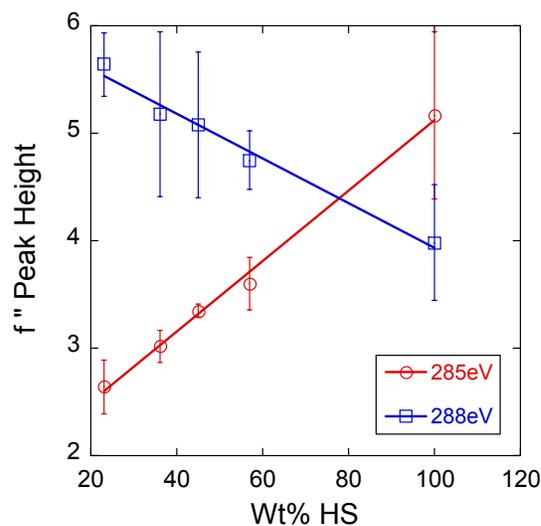
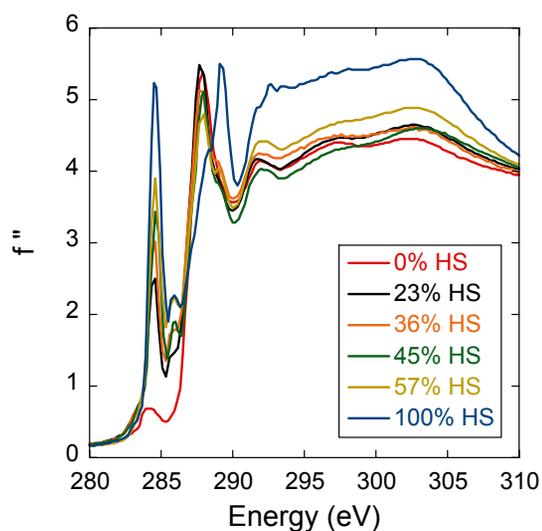
Hard Segment (HS)
m = 1 - 3

Soft Segment (SS)
n = 4 - 6



Peak	Approximate Energy (eV)	Assignment
1	285	1s → π*, C=C aromatic
2	288	1s → π*, C=O ester carbonyl
3	289	1s → π*, C=O urethane carbonyl

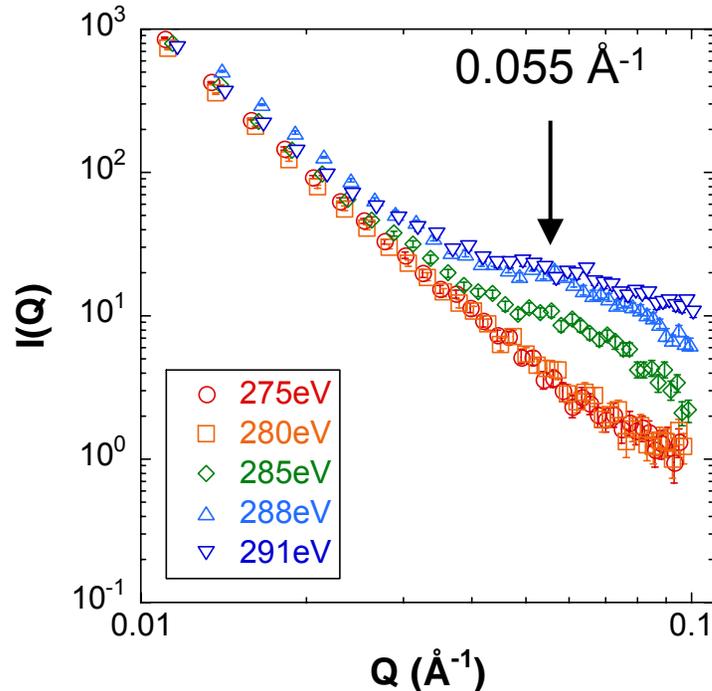
PESUs: Strong Contrast Between Hard and Soft Segments



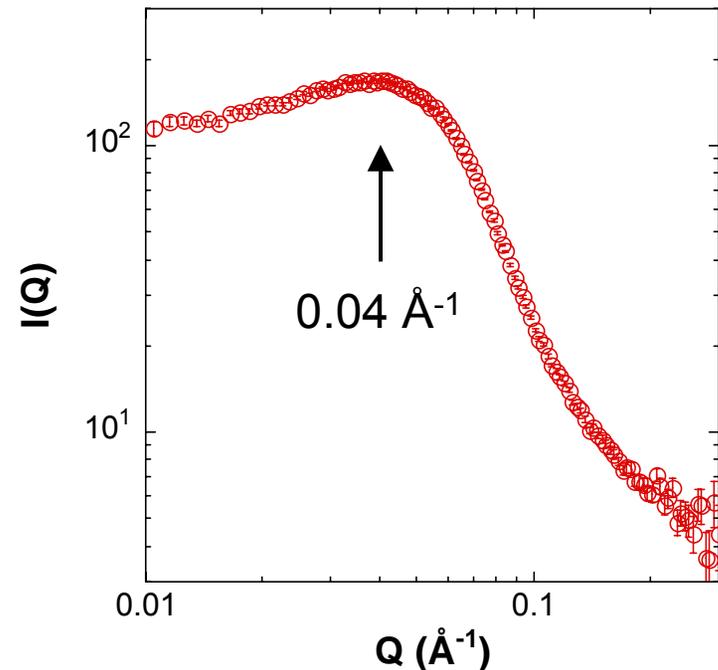
- Peaks representing key core to π^* transitions scale with %HS
- Contrast between hard and soft segments varies strongly with energy

PESU Scattering: Thin Film Differs from Bulk

Soft X-ray Data: 45% HS, 150 nm Film

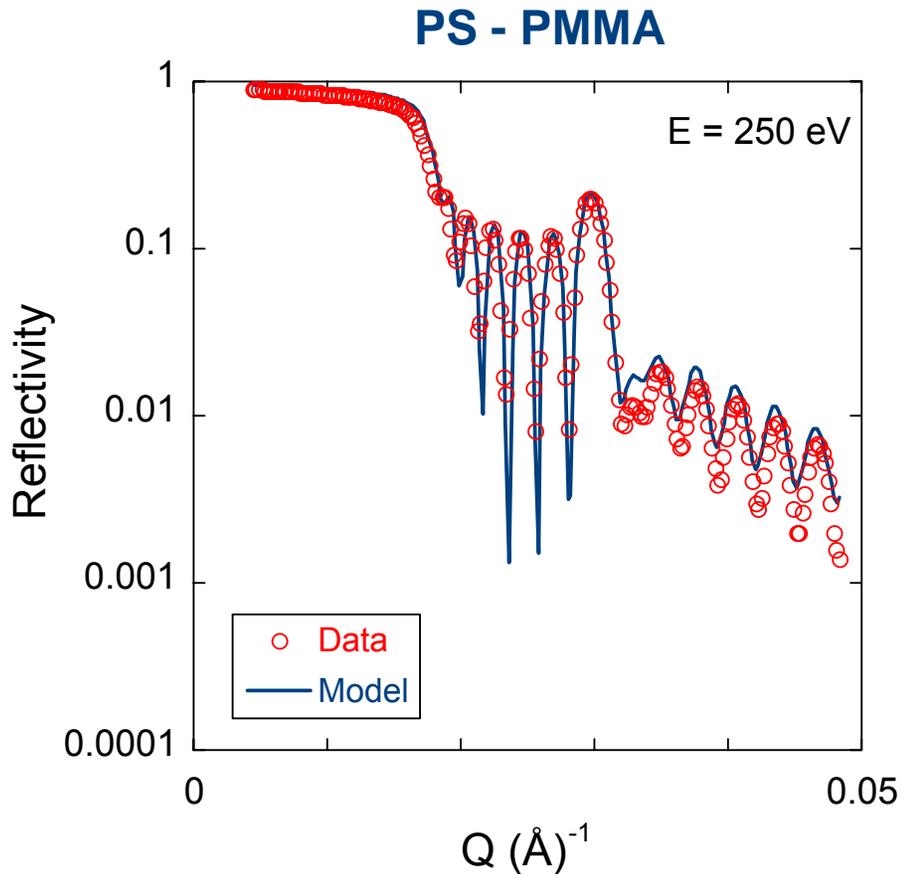


SANS Data: 45% d-HS, 0.2 mm Film



- SANS experiments with thicker films show peak reflecting domain spacing ~ 16 nm
 - Weak peak seen in soft x-ray data for thin films indicates different length scale, ~ 11 nm
 - Thin PESU films possess different domain structure than that seen in bulk materials
 - Weaker phase segregation?
- OR**
- In-plane phase-separated structure not easily seen with scattering?

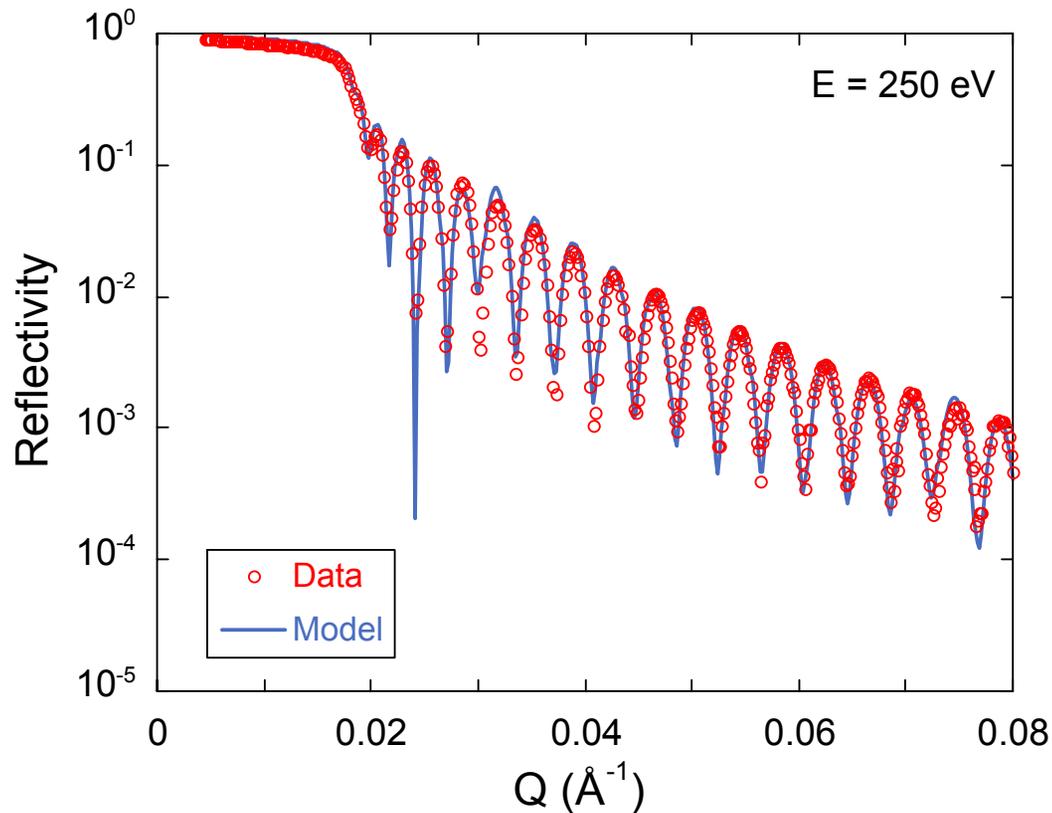
Soft X-ray Reflectivity: Probe in-plane structure



- Infinite sheets in x, y
- Scattering length densities & refractive index components calculated from PS & PMMA spectra
- Multilayer model:
 - Total thickness = 190.5 nm
 - Alternating PS & PMMA
 - $d_{\text{PS}} = 13.2 \text{ nm}$
 - $d_{\text{PMMA}} = 12.2 \text{ nm}$
 - $N = 7.5$
 - Si substrate



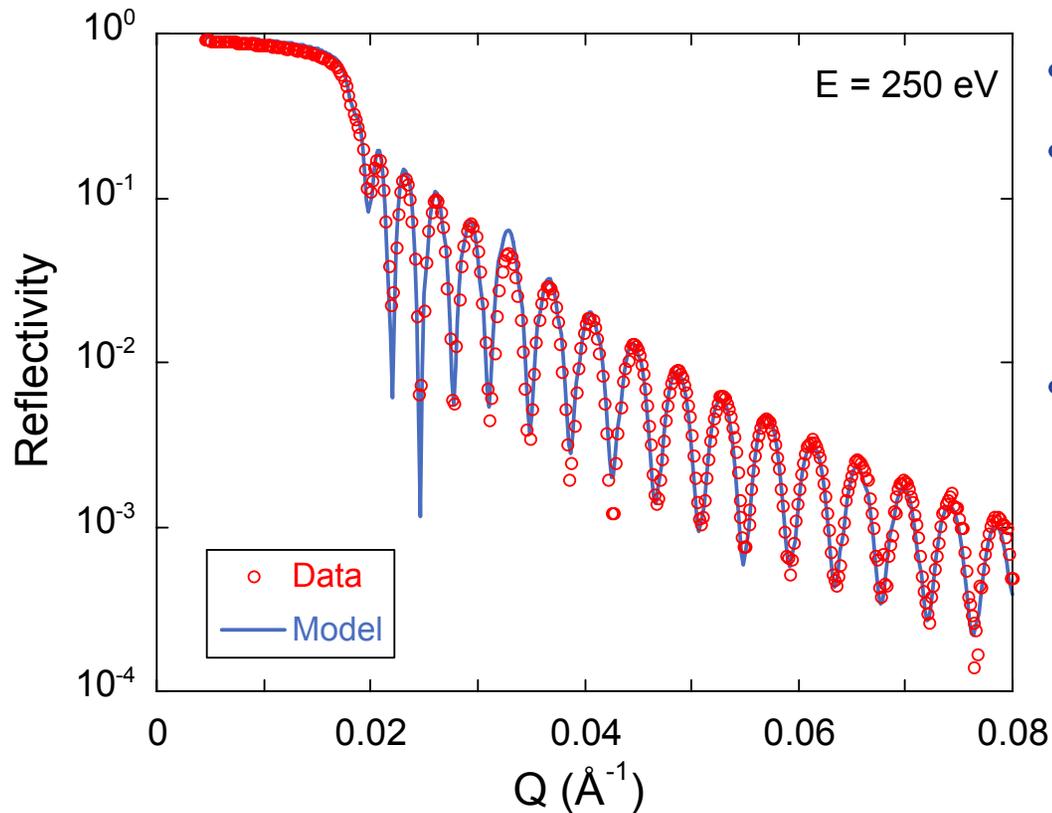
45% HS PESU Shows In-Plane Orientation



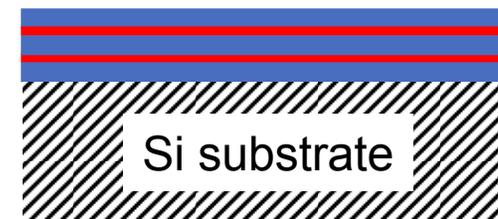
- Infinite sheets in x, y
- Scattering length densities & refractive index components calculated from 0% & 100% HS spectra
- Multilayer model:
 - Total thickness = 148.5 nm
 - Surface: 0% HS, 14.0 nm
 - Alternating 100% HS & 0% HS
 - $d_{100\text{HS}} = 13.8 \text{ nm}$
 - $d_{0\text{HS}} = 13.1 \text{ nm}$
 - $N = 5$
 - Si substrate



23% HS PESU Shows Strong In-Plane Orientation

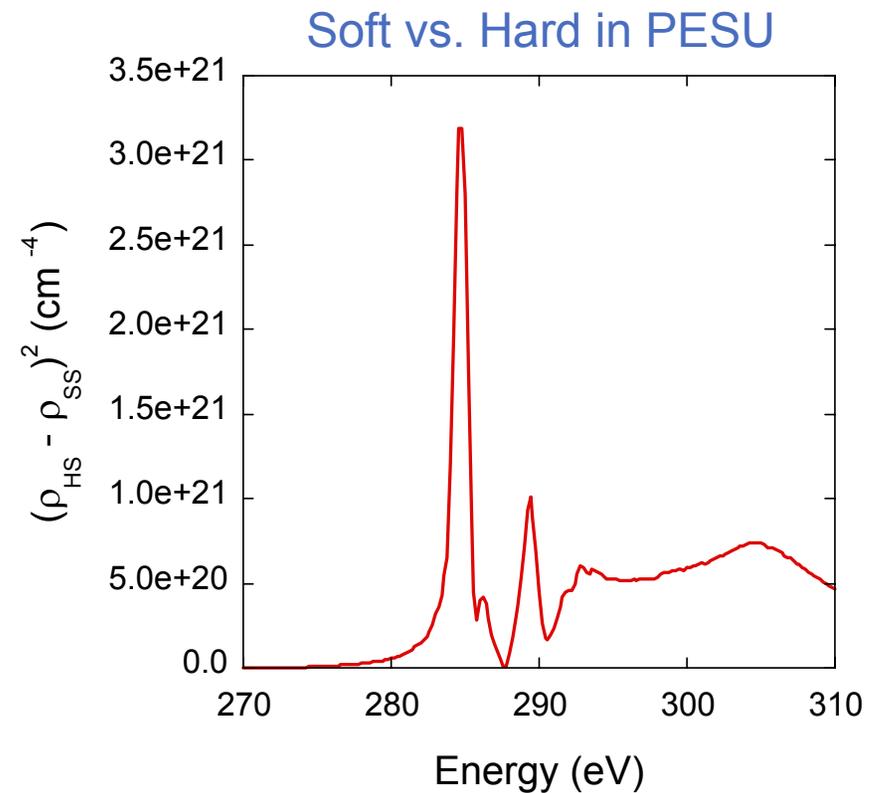
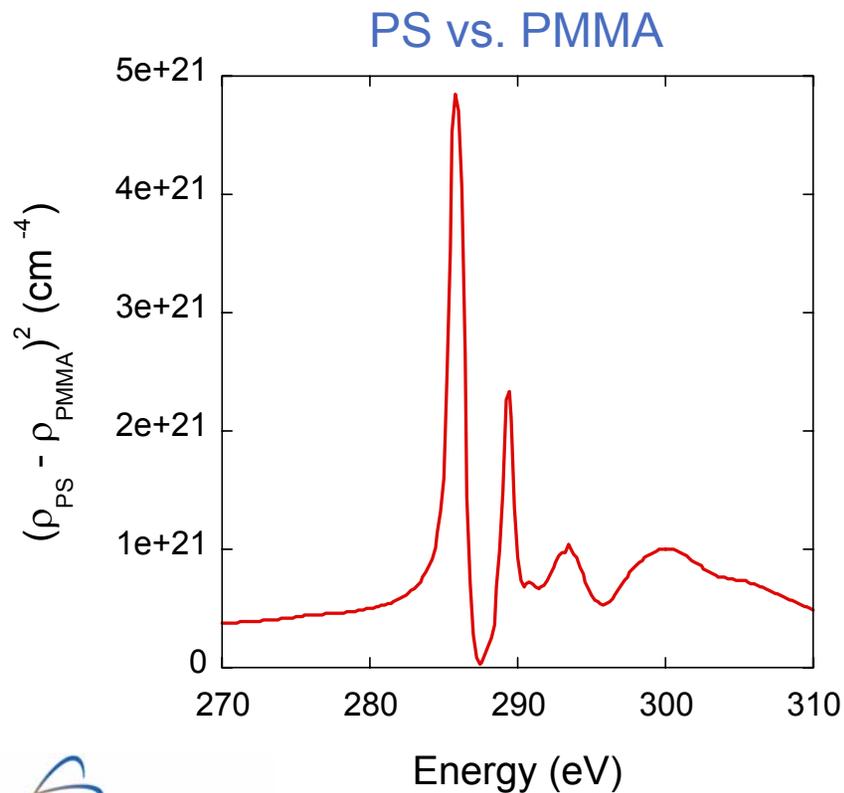


- Infinite sheets in x, y
- Scattering length densities & refractive index components calculated from 0% & 100% HS spectra
- Multilayer model:
 - Total thickness = 140.8 nm
 - Surface: 0% HS, 23.0 nm
 - Alternating 100% HS & 0% HS
 - $d_{100\text{HS}} = 7.15 \text{ nm}$
 - $d_{0\text{HS}} = 16.42 \text{ nm}$
 - $N = 5$
 - Si substrate



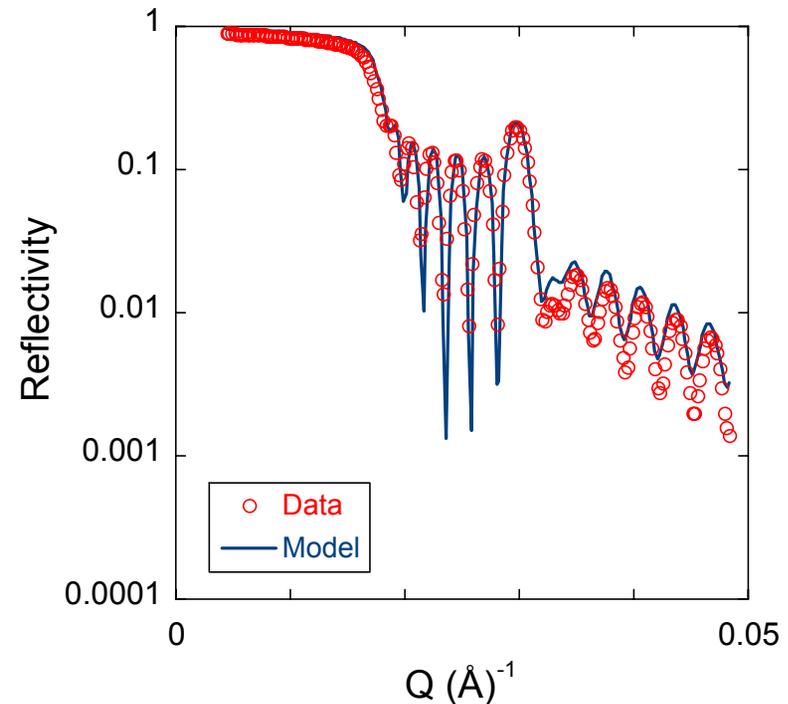
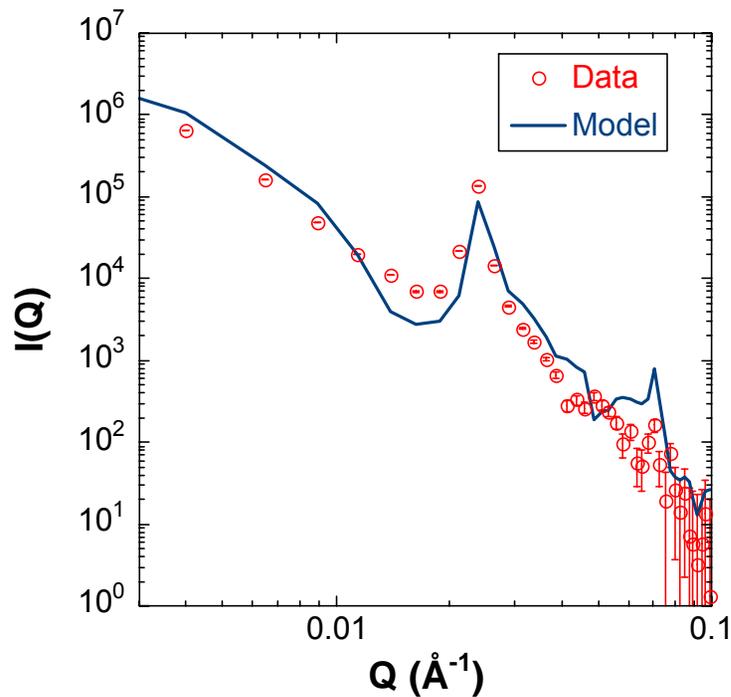
Summary

- Resonant x-ray scattering and reflectivity near carbon absorption edge are powerful methods for determining domain structure in polymer thin films
 - Contrast enhancement occurs at absorption edge
 - No need for chemical modification



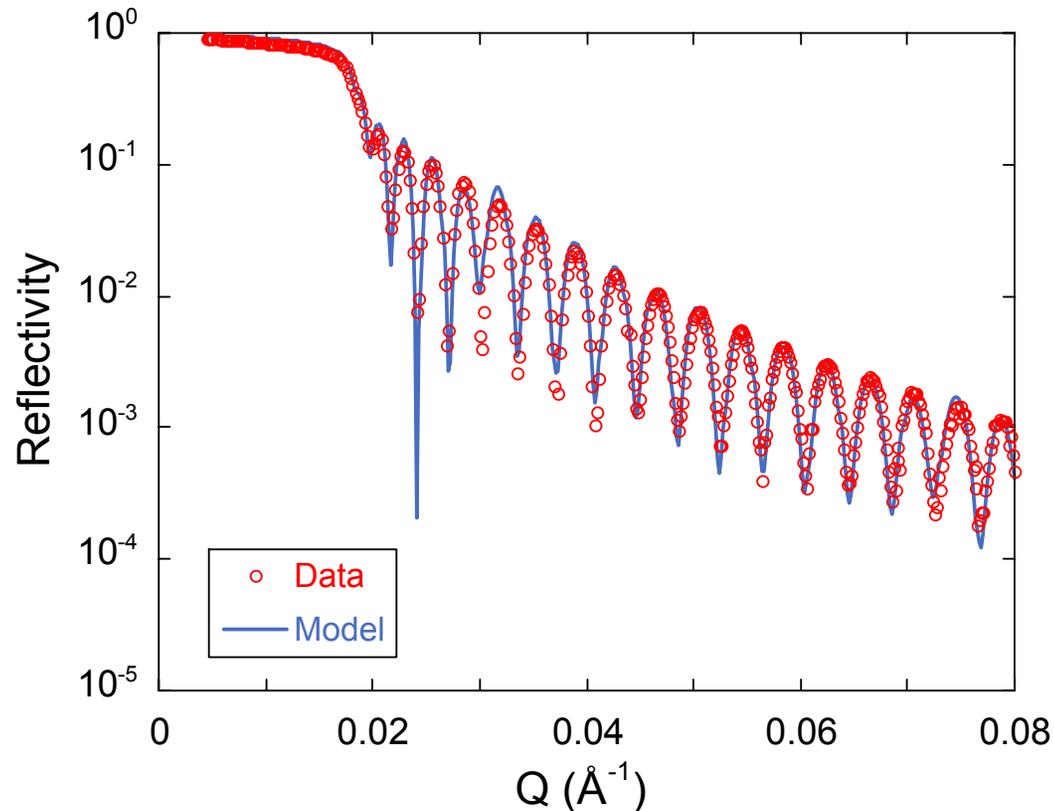
Summary

- Diblock copolymers demonstrate power of these new techniques
 - Peaks in scattering curves correspond to expected spacing and can be modeled to extract composition of each phase
 - Reflectivity data effectively probes in-plane structure



Summary

- Characterization of PESU copolymers with more complicated phase behavior appears promising
 - Features observed in transmission experiments scale with %HS
 - Scattering results indicate thin films possess different domain structure than that observed in bulk materials
 - Reflectivity results suggest strong in-plane orientation of domains



Acknowledgments

- Rich Spontak & Bin Wei, North Carolina State University
- Soft x-rays: Beamline 6.3.2, Advanced Light Source at Lawrence Berkeley National Laboratory, a DOE Basic Energy Sciences facility
- Neutrons: LQD beamline, LANSCE Division of Los Alamos National Lab, a DOE Basic Energy Sciences facility

Suggestions for New Beamline

- Desirable features from 6.3.2
 - Energy resolution: ± 0.04 eV at 284 eV
 - Precision goniometer that allows both transmission and reflection modes
- Sample environments
 - Temperature control
 - Cells for analysis of liquid samples
- Data acquisition
 - Calibration methods
 - Detection of background scattering due to fluorescence, Raman, etc.
 - Time-dependent measurements (e.g., kinetics)