Probing 3-D Orientation in Templated Self-Assembly using Rotational SANS

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Templated Self Assembly of Block Copolymers

Challenges

• Difficult to “see” below the top surface

• Other applications will focus on complex 3-dimensional structures (Nanostructured membranes for energy applications, hierarchical assembly)

**SANS vs. NR of Thin Films**

**Small Angle Neutron Scattering**
- Measures structure parallel to the substrate
- Substrate must be neutron transparent with low adsorption, no SANS structure
- Optimal film thickness is on the order of mm’s, but 10 nm is possible.
- Analysis is performed in the limit of the Born Approximation
- Q vector is relative to beam only, substrate plane is irrelevant.

**Specular Neutron Reflectivity**
- Measures structure perpendicular to the substrate
- Substrate is smooth and flat, has relatively high scattering length density
- Characterization becomes challenging as film thickness > 200 nm.
- Limit of high interaction at low angle to limit of Born Approximation at very high angles
- Q vector is effectively defined by substrate plane.

SANS + NR together can provide parallel vs. perpendicular orientation map
Rotational Small Angle Neutron Scattering

- We convert from beam-coordinates \((q_x, q_y, q_z)\) to sample-coordinates \((Q_x, Q_y, Q_z)\) using a rotation matrix

\[
\begin{align*}
Q_x &= q_x \cos \omega - q_z \sin \omega \\
Q_y &= q_y \\
Q_z &= q_x \sin \omega + q_z \cos \omega
\end{align*}
\]
Rotational Small Angle Neutron Scattering

a) For each $\omega$:
   - Get SANS image
   - Box average $q_x$

b) Assemble the 1D slices:

c) Convert to sample reciprocal space

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Normalization of Scattering Volume

Path Length increases as sample is rotated

Implications:
1. Sample area measured is not constant
2. At high angles, reflection will no longer be negligible
3. Sample volume is increasing and must be normalized

Use invariance of \( I(qy) \) to normalize path length changes
Scattering Volume Normalization

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Lets look at a sample – Templated Assembly

BCP-filled Template as cast

dPS-b-PMMA
Lamellar Forming Morphology
Forms domains of approx. 20 nm size
Repeat period approx. 40 nm

BCP-filled Template after anneal @ T=160C for 1 hr

Diffraction Spots from template

Diffraction Spot from aligned BCP

Unaligned BCP

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"Top" and "Side" views from R-SANS

Normal Incidence (Qx-Qy plane)  Cross Section (Qx-Qz plane)
Templated Lamellae – 35 minutes

Temperature Data  Born Approximation Model

Vertical Lamellae

Horizontal Lamellae

Experimental Data

Born Approximation Model

Vertical Lamellae

$A_v = 0.42$

$s_v = 0.76$

$A_h = 4.0$

$s_h = 0.98$

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Templated Lamellae – 8 hours

Experimental Data

Born Approximation Model

$A_v = 0.20$
$s_v = 0.84$
$A_h = 3.5$
$s_h = 0.98$

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Neutron Reflectivity of Templated Assembly

XR techniques developed by Hae-Jeong Lee et al.
Kinetics of Ordering Lamellae

Problem: Need to fill in missing “wedge” of data for more accuracy.
“Invariant” Scattering – $I(qy)$

Scattering volume
- 20min
- 35min
- 1hr
- 2hr
- 3hr
- 8hr
- 72hr

Sample rotation $\omega$ (degrees)

Relative intensity

Short Anneal

Long Anneal

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Final Thoughts

Rotational SANS
• Developing Integral Equation model to describe $I(q)$ for all rotation angles
  • Wen-li Wu

• Filling in “Missing Wedge” with Off-specular Neutron Reflectivity
  • Brian Maranville, Sushil Satija, Chuck Majkrzak

• Striving to assess the role of dynamic scattering, substrate waveguiding, etc. to create quantitatively accurate models

• Potential to utilize the enhanced transmission scattering to measure confined systems with low $S/N$