Imaging Polymer Morphology Using Atomic Force Microscopy

Russell J. Composto
Materials Science and Engineering, and the Laboratory for Research on the Structure of Matter,
University of Pennsylvania

Agilent Web Seminar
October 24th, 2007
Case Studies:

1) Nanostructures assembled from amphiphilic block copolymer films.

2) Surface segregation of nanoparticles in homopolymer and block copolymers
Amphiphilic Block Copolymer

Materials:
Poly( styrene-\textit{b-}tert- acrylic acid) (PS-\textit{b-}PAA)

Procedure:
• Spin-coat films from organic solvent
• Anneal at 130 °C
• Characterize:
  • Bulk: TGA and SAXS
  • Thin Film: FTIR-ATR, Ellipsometry, and \textit{AFM (aqueous, pH, solvent...)}

$ f_{\text{PAA}} = 0.19$

Hydrophilic PAA cylinders in Hydrophobic PS matrix
In Situ AFM in Aqueous Environment

- **AFM (PicoPlus, Agilent AFM)**

  (i) Magnetic AC (MAC) mode: intermittent contact mode

  (ii) Silicon cantilever w/ magnetic coating: \( k = 2.8 \text{ N/m} \), tip radius \(< 7 \text{ nm} \),
       \( f,\text{air} = 75 \text{ kHz} \), \( f,\text{aqueous} = 30 \text{ kHz} \)

  (iii) Liquid cell

  **(iv) In situ scan for at least 2h: Capture swelling of soft nanostructure**

- **pH Buffer Solutions:**

  (i) Sodium Phosphate Buffers: \( \text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4 \)

  (ii) pH range: 2.6 – 9.1

  (iii) Buffer strength: 20 mM
Nanostructures Assembled from Amphiphilic Block Copolymers

1. Morphology Evolution in aqueous medium (pH = 6) *(Nano Lett. 2006, 6, 282)*
   - Swelling dynamics
   - Reversibility

2. Effect of pH *(Macromolecules 2006, 39, 6063)*
   - Morphology dependence
   - Thickness and Contact angle vs pH

3. Swelling in organic solvent

4. Iron Oxide nanoparticle formation
Nanostructured PS-\textit{b}-PAA films (33 nm)

Grain Analysis (SPIP):

- Nearly hexagonal packing of cylinders, consistent with SAXS of bulk.
- Cylinder diameter: $23.7 \pm 2.7$ nm.
- Cylinder-to-cylinder spacing: 52.0 nm.

*Nano Lett.* **2006**, *6*, 282
Swelling in Water (pH ~ 6)

- Cylinders to Mushrooms.
- PAA domain diameter (D) increases from 23 ± 3 to 50 ± 7 nm.
- \( D \) (Mushroom) = cylinder spacing, i.e., PAA mushrooms cover surface.
- Enhanced hydrophilicity: Contact Angle (CA) decreases by ~ 30°.

*Nano Lett.* **2006, 6, 282**
Reversibility of Swelling

Swollen film reverts to original structure after annealing at 130 °C for 1d
pH-Response: **Three pH Regimes**

- **Low: pH < 4**
  - Hexagonal Packed Holes

- **Intermediate: 4 < pH < 6**
  - Hexagonal Packed Mushrooms

- **High: pH > 6**
  - Hexagonal Packed Depressions

---


All AFM images: 1 μm (0 – 15 nm)
Equilibrium film thickness as function of pH

- Overall thickness swells by $\sim 3x$
- Thickness dramatically increases near pH = 5 (pK$_a$ of acrylic acid = 4.3)
- Swelling is reversible

*Macromolecules* 2006, 39, 6063
Exposure to Toluene Vapor at 50 °C

- PS matrix swells slowly (relative to PAA in water).
- PS matrix covers PAA cylinders (high regions).
- Hydrophobicity increases. CA: 73°(dry) to ~ 90° (wet)

Note: CA for PS: ~ 90°
Synthesis of Nanoparticles in ABC Template

FeCl₃ Solution (2mM) → O₂ Plasma 10 min → Fe₂O₃ NP

- FeCl₃ Solution
- PAA (Polyacrylic Acid) and PS (Polystyrene)
- Time, t
- t = 10 min
- t = 60 min

Fe₂O₃ NP Dimensions
- d = 25.8 nm, h = 2.5 nm
- d = 30.3 nm, h = 2.3 nm

unpublished
Preparation of Ag NP in PMMA

Ag complex

Hhfac

\[
\text{Ag(CH}_3\text{COO)} + \text{HCHO} \rightarrow \text{CH}_3\text{COOH} + \text{Ag(hfac)}
\]


Ag complex

Hhfac

\[
\text{Ag(CH}_3\text{COO)} + \text{HCHO} \rightarrow \text{CH}_3\text{COOH} + \text{Ag(hfac)}
\]

Ag Nanoparticles (NP) in PMMA Films

5 wt% Ag-PMMA  10 wt% Ag-PMMA  20 wt% Ag-PMMA

Height

Phase

SPHERICAL  FACETED

NP formation vs self-assembly of BCP?

$L = \text{lamella period}$

Can we stabilize perpendicular morphology?
Morphology Evolution (2h)

- Addition of Ag reduces parallel lam.
- Long range order reduced by NP

• NP alignment on PMMA lamella

Morphology Evolution (48 h)

- Domain growth of parallel lamella “align” ⊥ lamellae

0 wt %

2 µm × 2 µm

- NP slow down growth of parallel grains
- NP rejected from parallel lamella

2 wt %

Effect of Ag Concentration

- Stabilize perpendicular morphology (short range).
- Arrange NP’s into linear arrays along PMMA stripes.

5 wt %

2 h

96 h

2 µm x 2 µm

Macromolecules, 2007, 40, 6316
Conclusions

• The Picoplus is a powerful tool for following phase transformations and self assembly in block copolymers.

• Can we “stimulate” transformations using functional tips?

• AFM is excellent tool for imaging surface segregating NPs.

• Can we determine “depth” of NPs using “hard” imaging?
Contributions / Acknowledgements

**Group Members**

- Chen Xu, PhD Candidate in Materials Science
- Ranjan Deshmukh, PhD August 2007.
- Jay Park, PhD Candidate in Materials Science

**Collaborators**

- Brad Wayland, Mike Fryd (Chemistry, Penn)
- Karen Winey (MSE, Penn)
- Song Xu (Agilent)

**Acknowledgements:**

- National Science Foundation: DMR, MRSEC and NBIC programs.
- ACS- Petroleum Research Foundation.
- National Institute of Health (biomaterials)
- Nanotechnology Institute (biomaterials)
- Colgate-Palmolive Company (biomaterials)
- Agilent (instrumentation)