Imaging Polymer Morphology Using Atomic Force Microscopy

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Agilent Web Seminar

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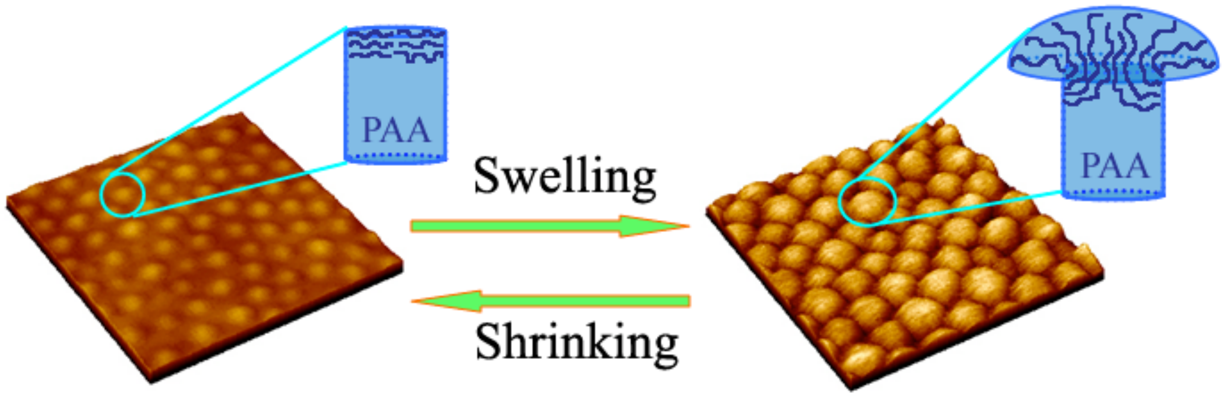
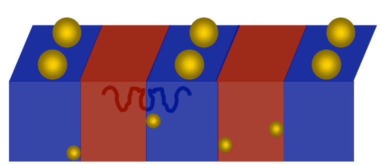
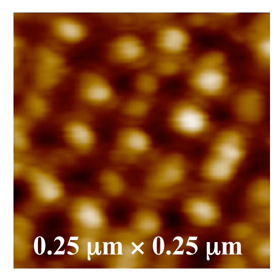
Case Studies:

1) Nanostructures assembled from amphiphilic block copolymer films.



2) Surface segregation of nanoparticles in homopolymer and block copolymers

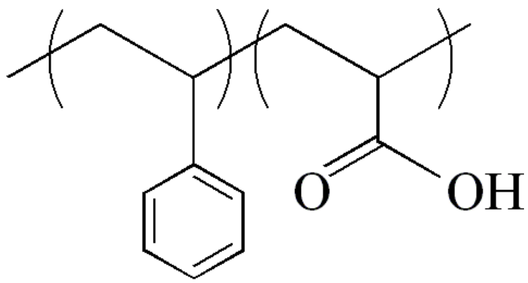




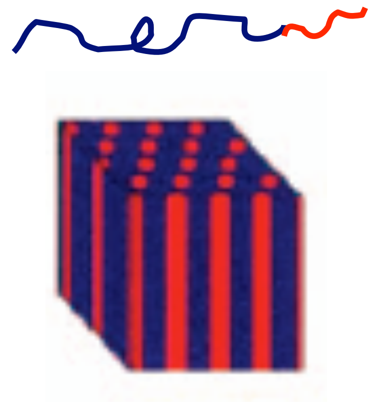
Amphiphilic Block Copolymer

Materials:

Poly(styrene-*b*-*tert*-acrylic acid) (PS-*b*-PAA)



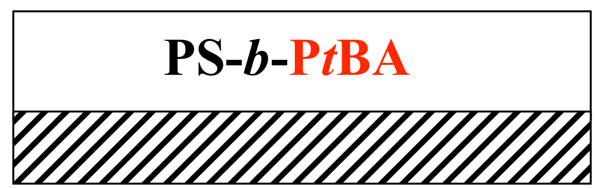
$f_{PAA} = 0.19$



Hydrophilic PAA cylinders in Hydrophobic PS matrix

Procedure:

- Spin-coat films from organic solvent
- Anneal at 130 °C
- Characterize:
  - Bulk: TGA and SAXS
  - Thin Film: FTIR-ATR, Ellipsometry, and ***AFM (aqueous, pH, solvent…)***



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 N/m, tip radius < 7 nm, f (air) = 75 kHz, f (aqueous) = 30 kHz

(iii) Liquid cell

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

- **pH Buffer Solutions:**

(i) Sodium Phosphate Buffers: $H_3PO_4/NaH_2PO_4/Na_2HPO_4$

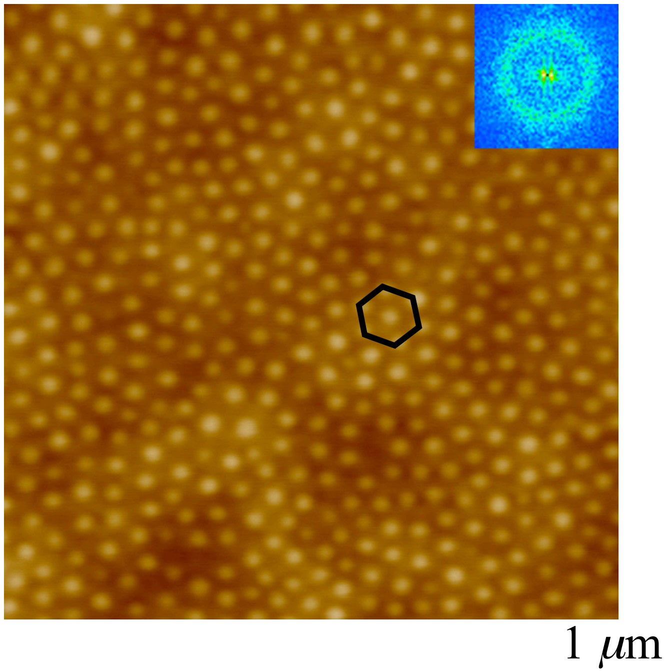
(ii) pH range: 2.6 – 9.1

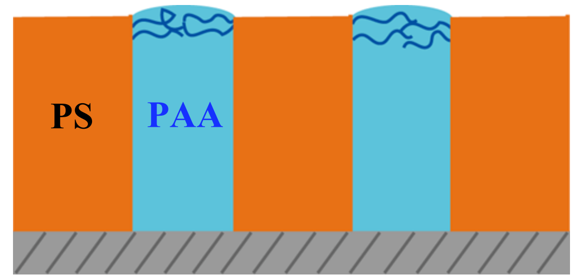
(iii) Buffer strength: 20 mM

Nanostructures Assembled from Amphiphilic Block Copolymers

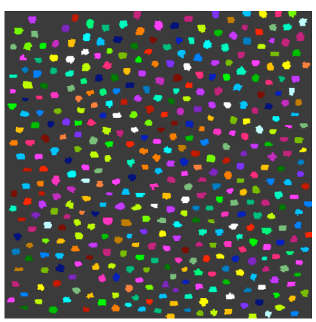
1. Morphology Evolution in aqueous medium (pH = 6) (*Nano Lett*. **2006**, *6*, 282)
   - Swelling dynamics
   - Reversibility
2. Effect of pH (*Macromolecules* **2006**, *39*, 6063)
   - Morphology dependence
   - Thickness and Contact angle vs pH
3. Swelling in organic solvent
4. Iron Oxide nanoparticle formation

Nanostructured PS-*b*-PAA films (33 nm)





Grain Analysis (SPIP):

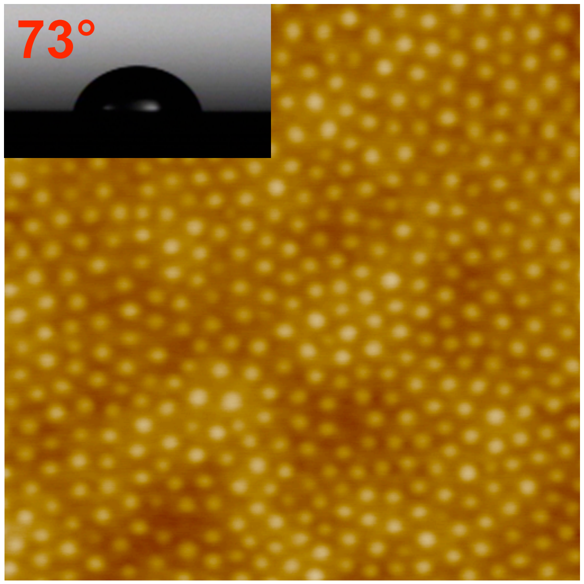


- Nearly hexagonal packing of cylinders, consistent with SAXS of bulk.
- Cylinder diameter: 23.7 ± 2.7 nm.
- Cylinder-to-cylinder spacing: 52.0 nm.

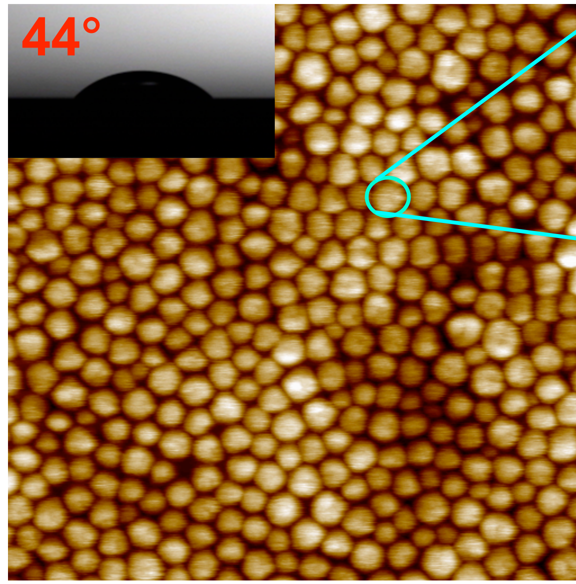
Nano Lett. **2006**, *6*, 282

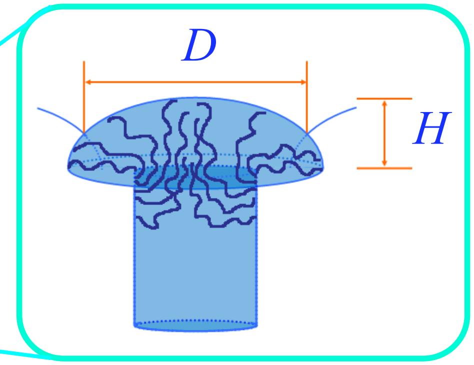
Swelling in Water (pH ~ 6)

0 min

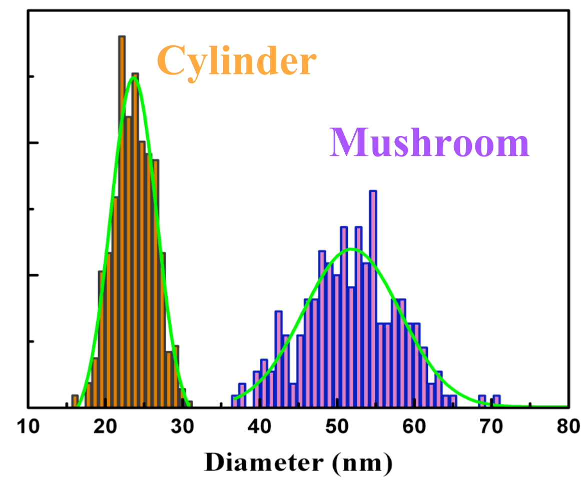


120 min





1 μm (0 – 20 nm)

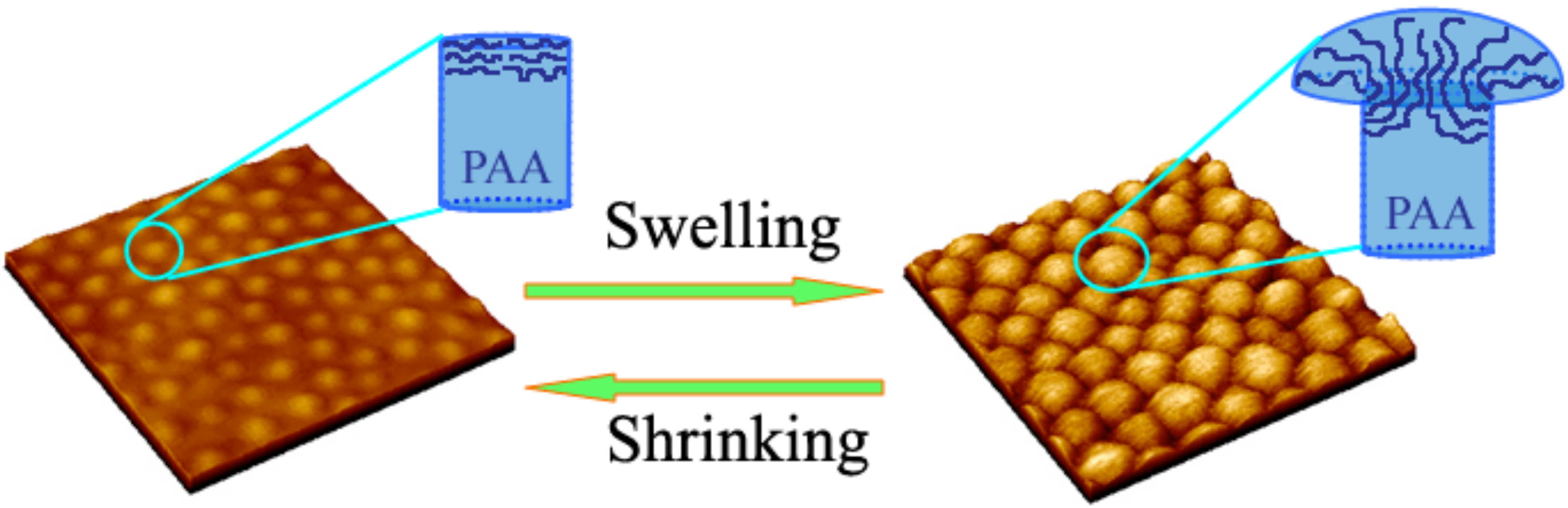


- Cylinders to Mushrooms.
- PAA domain diameter (D) increases from **23** ± 3 to **50** ± 7 nm.
- *D* (Mushroom) = cylinder spacing, i.e., PAA mushrooms cover surface.
- Enhanced hydrophilicity: Contact Angle (CA) decreases by ~ 30°.

Nano Lett. **2006**, *6*, 282

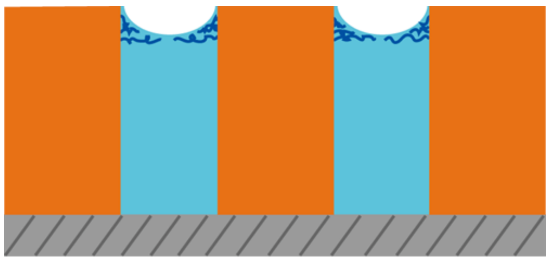
Reversibility of Swelling

Swollen film reverts to original structure after annealing at 130 °C for 1d

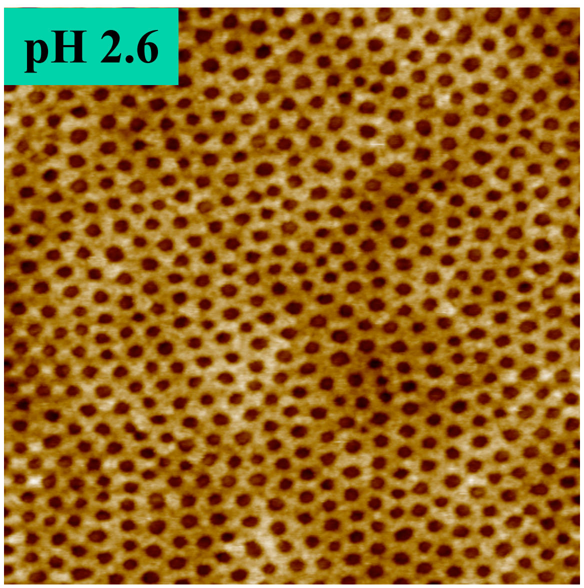


pH-Response: Three pH Regimes

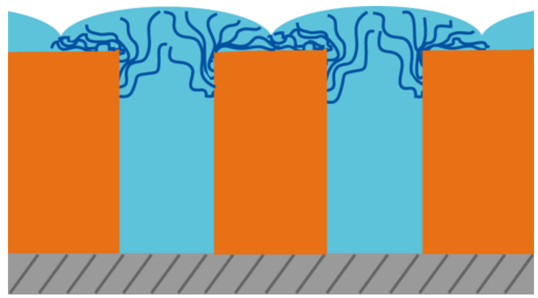
Low: pH < 4



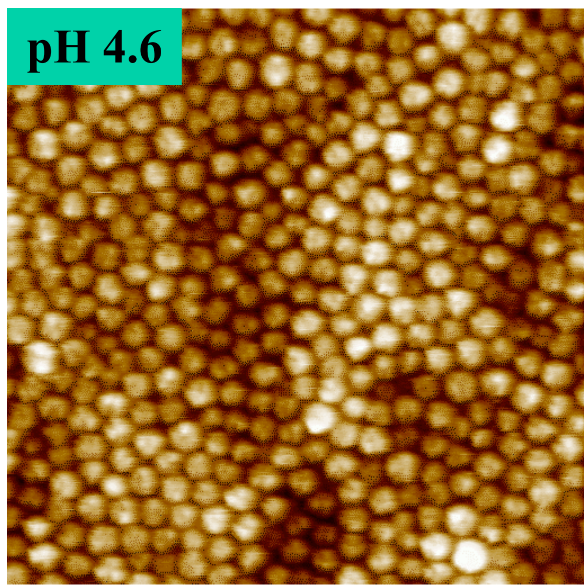
Hexagonal Packed Holes



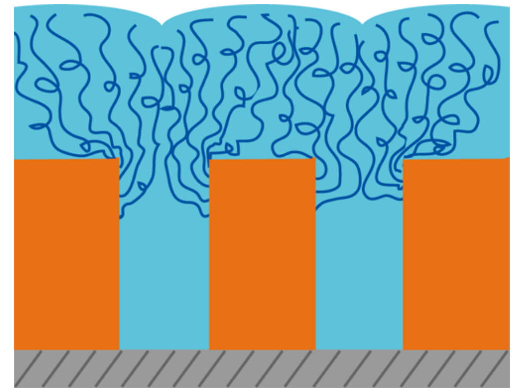
Intermediate: 4 < pH < 6



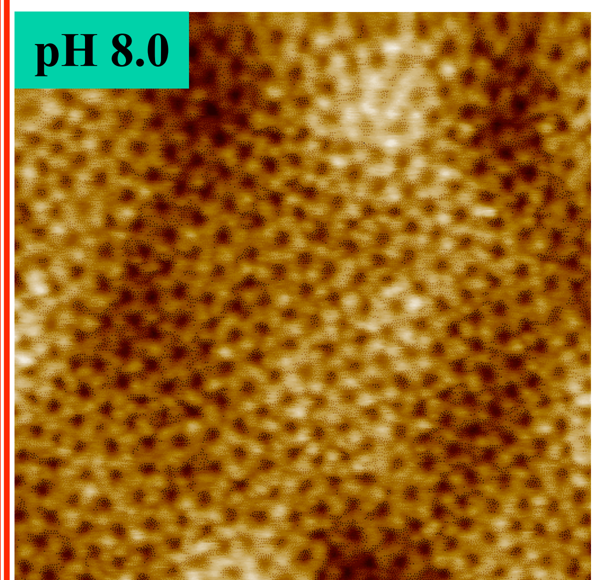
Hexagonal Packed Mushrooms



High: pH > 6



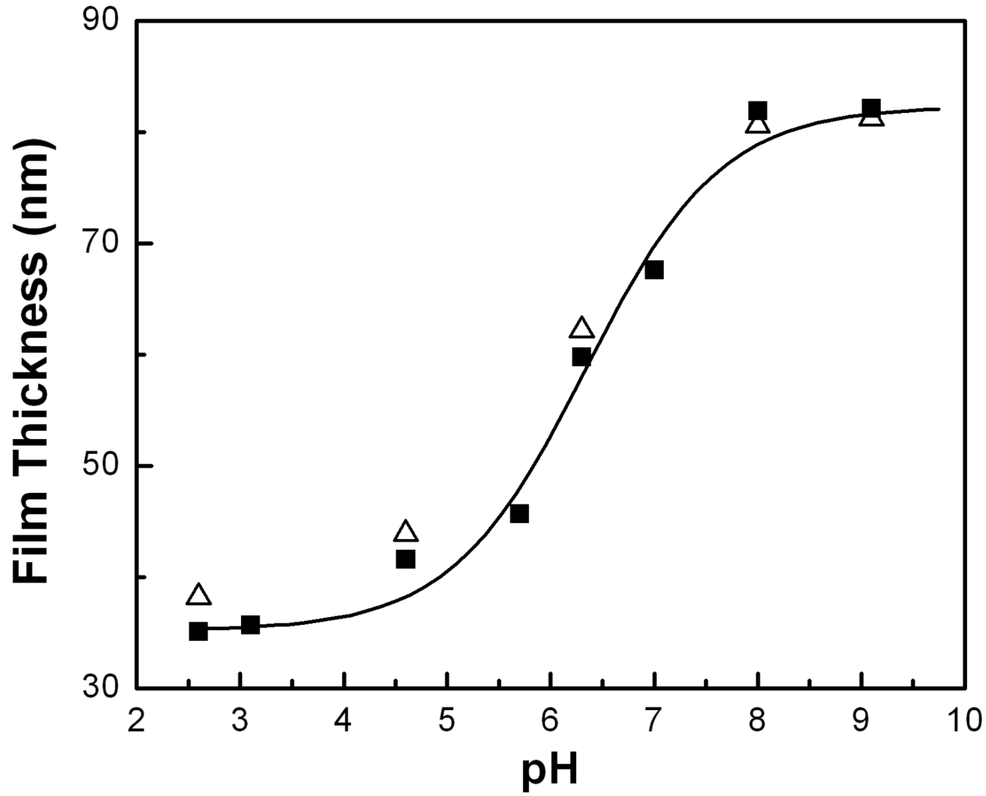
Hexagonal Packed Depressions



Xu, C. et al, *Macromolecules* **2006**, *39*, 6063.

All AFM images: 1 μm (0 – 15 nm)

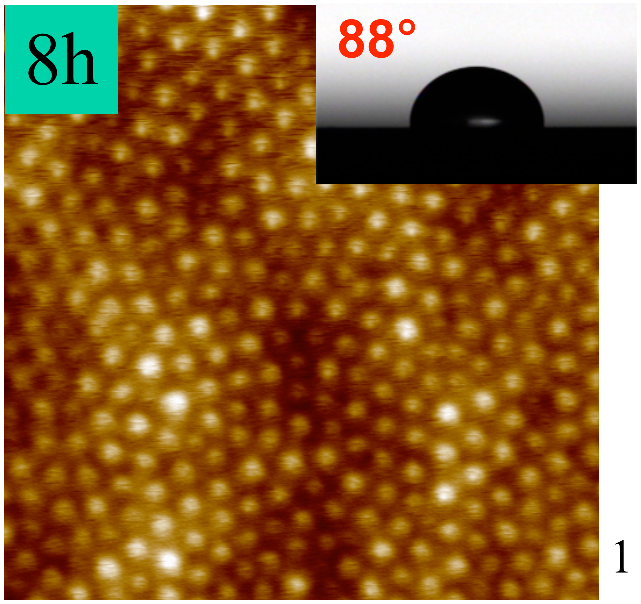
Equilibrium film thickness as function of pH



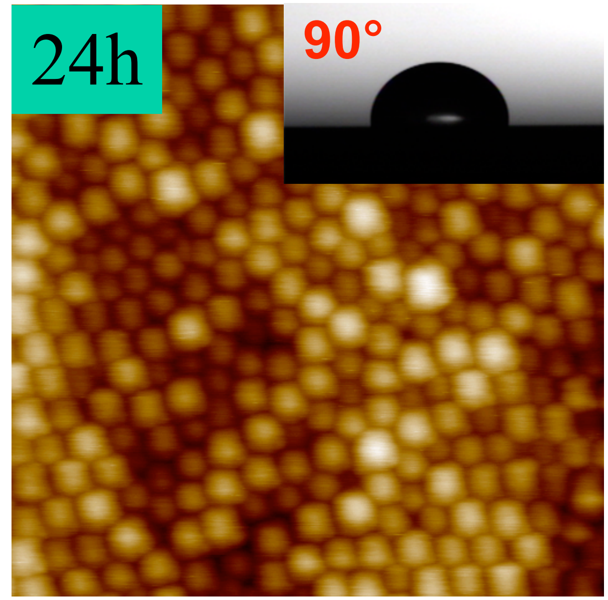
- Overall thickness swells by ~ 3x
- Thickness dramatically increases near pH = 5 (pK_a of acrylic acid = 4.3)
- Swelling is reversible

Macromolecules **2006**, *39*, 6063

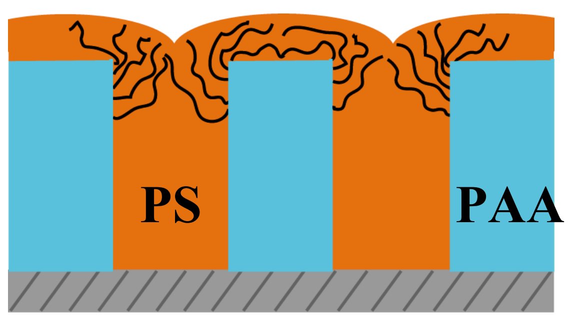
Exposure to Toluene Vapor at 50 °C



1 μm (0 – 10 nm)



- **PS matrix swells slowly (relative to PAA in water).**
- **PS matrix covers PAA cylinders (high regions).**

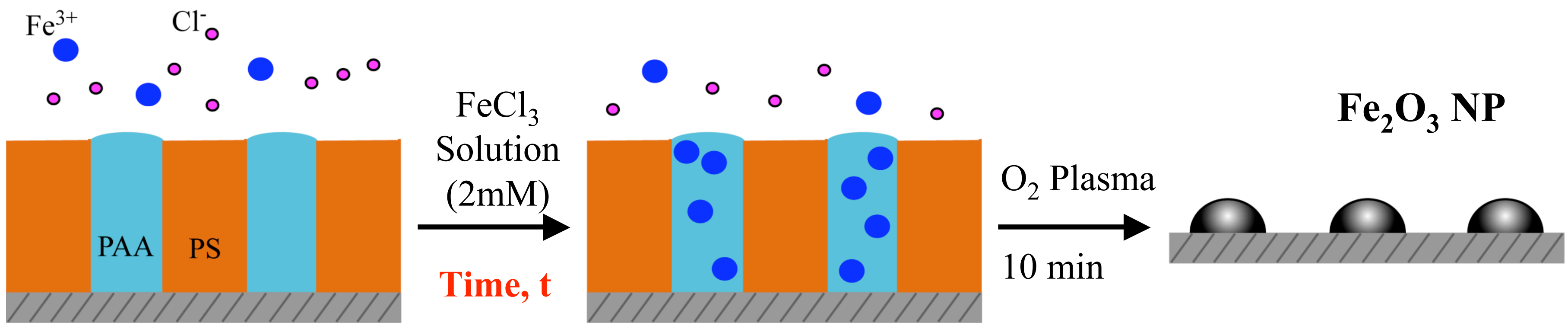


- **Hydrophobicity increases. CA: 73°(dry) to ~ 90° (wet)**

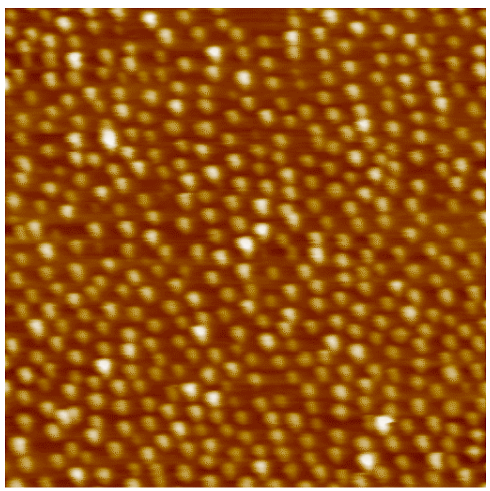
unpublished

Note: CA for PS: ~ 90°

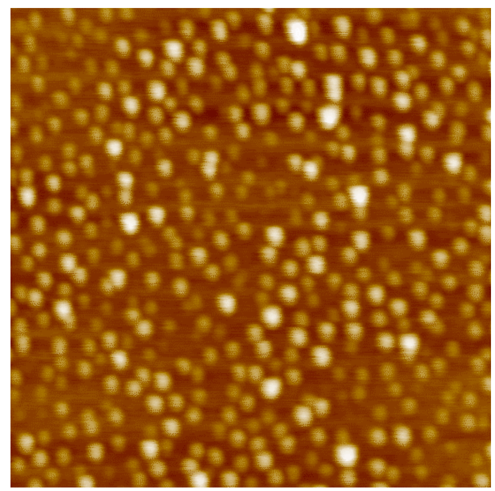
Synthesis of Nanoparticles in ABC Template



t = 10 min



t = 60 min



1 μm (0 – 10 nm)

Fe_2O_3 NP Dimensions

d = 25.8 nm, h = 2.5 nm

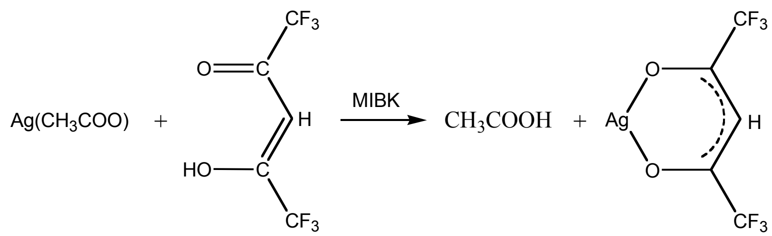
d = 30.3 nm, h = 2.3 nm

unpublished

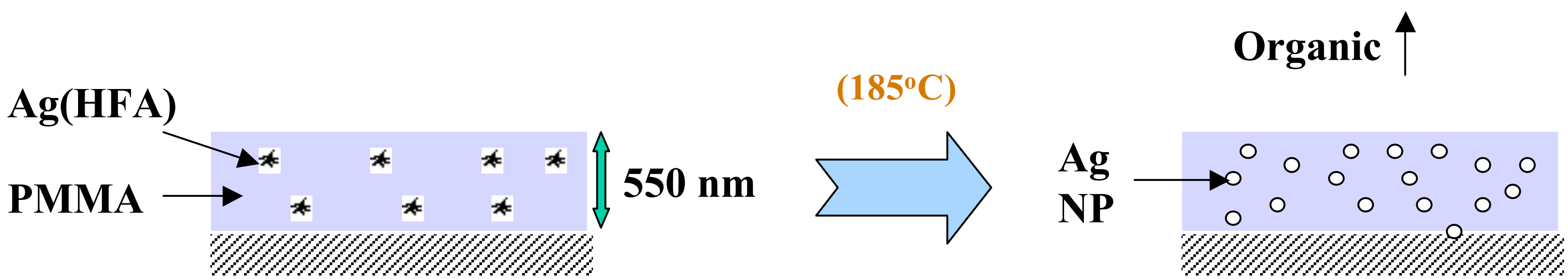
Preparation of Ag NP in PMMA

Ag complex

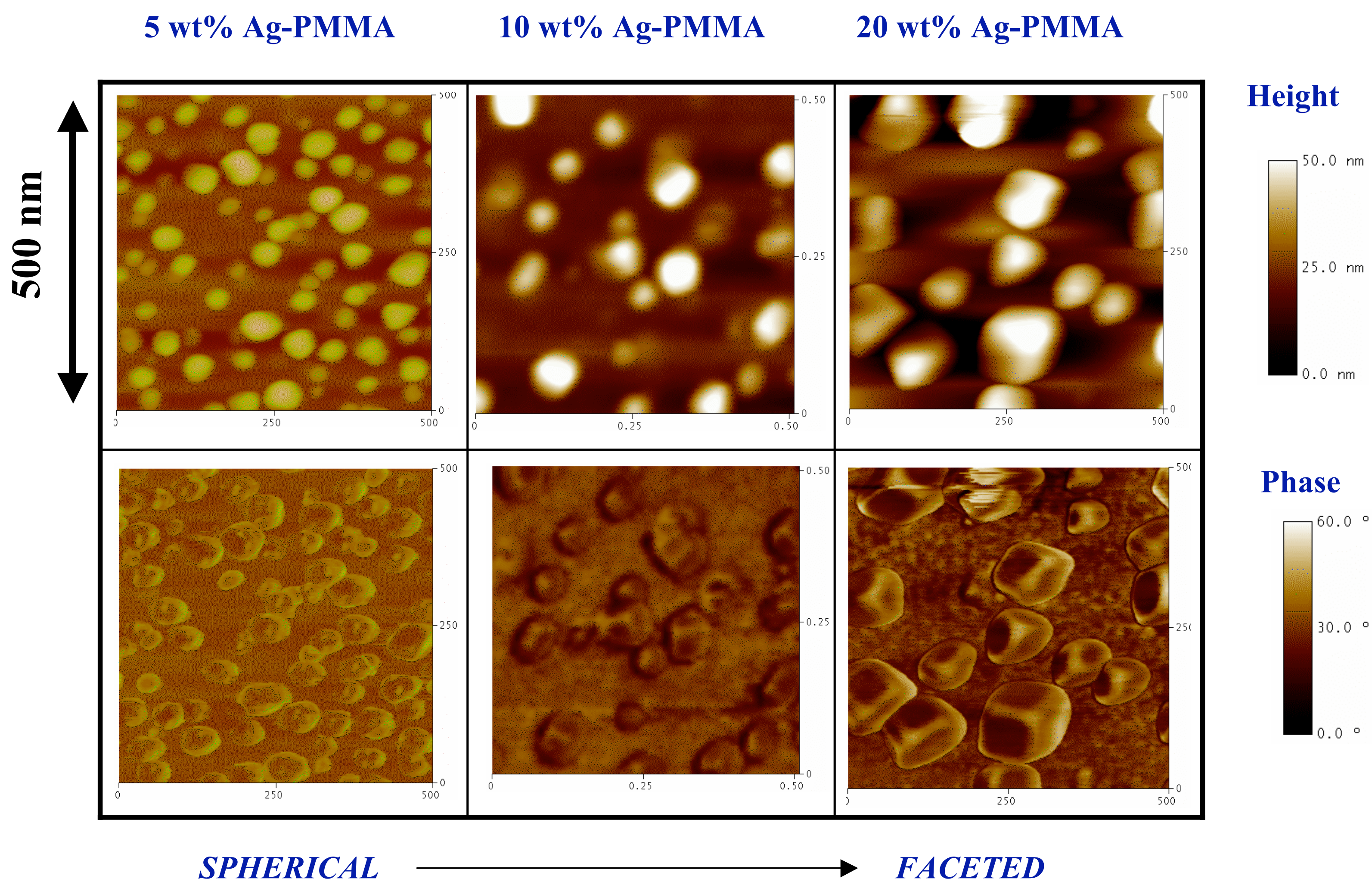
Hhfac **Ag(hfac)**



Rubira, et al. *Chem. Mater*. (1994)

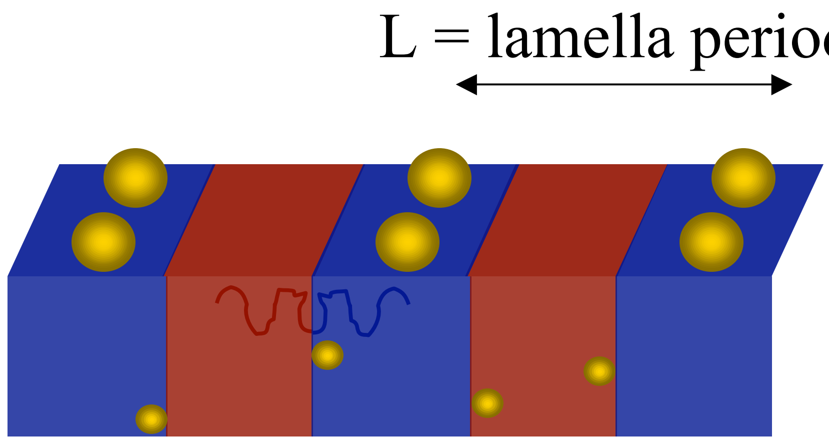


Ag Nanoparticles (NP) in PMMA Films



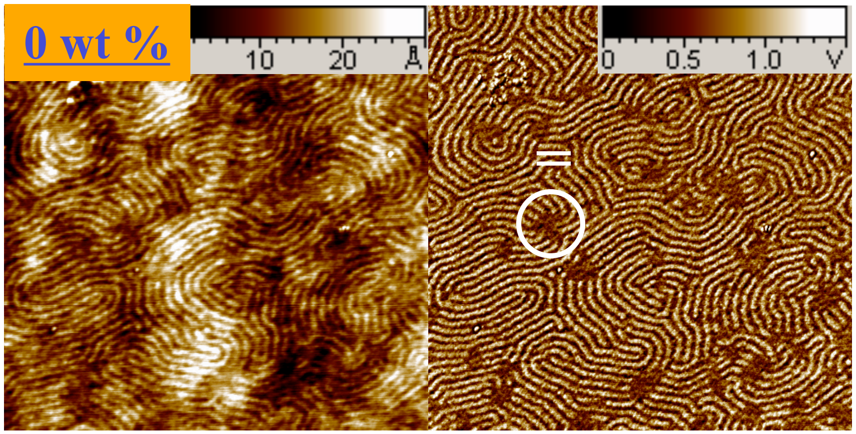
Deshmukh & RJC, *Chem. Mater.* (2007)

NP formation vs self-assembly of BCP?

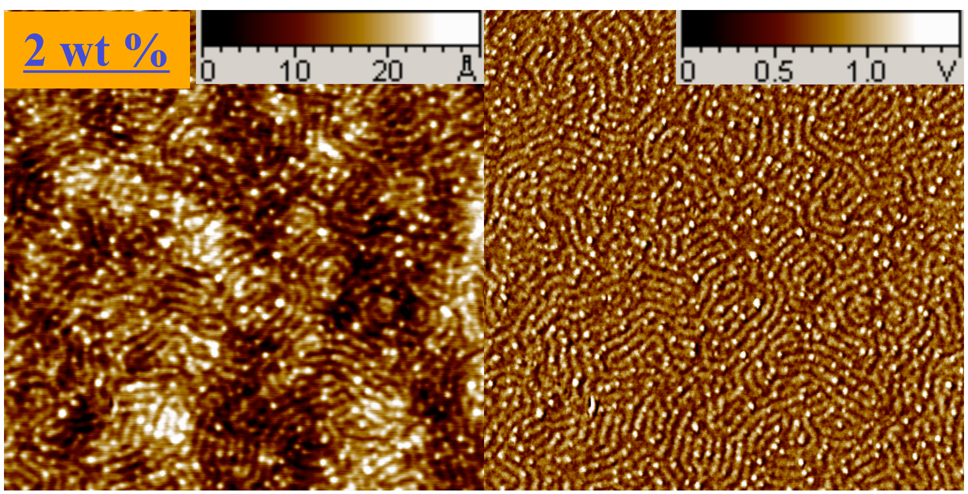


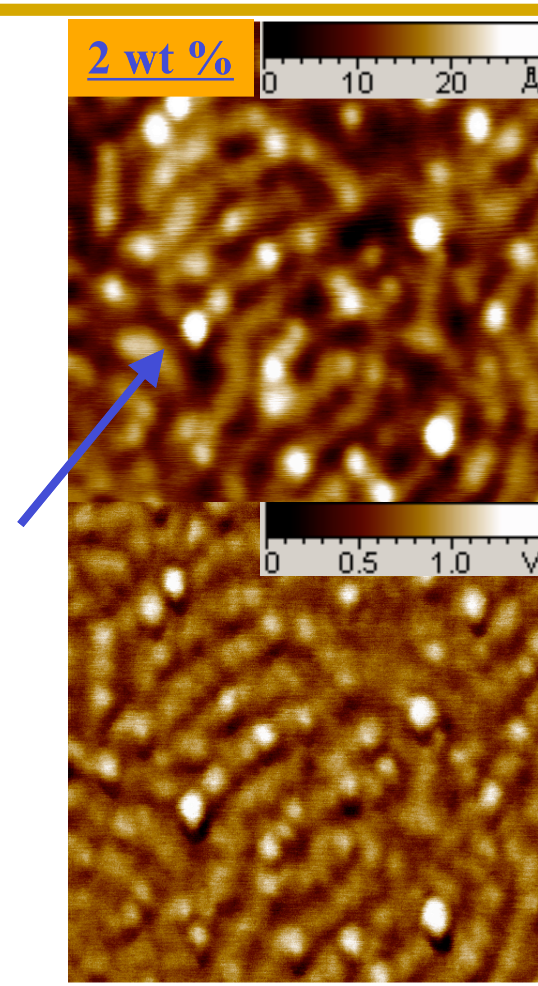
Can we stabilize perpendicular morphology?

Morphology Evolution (2h)



2 μm × 2 μm





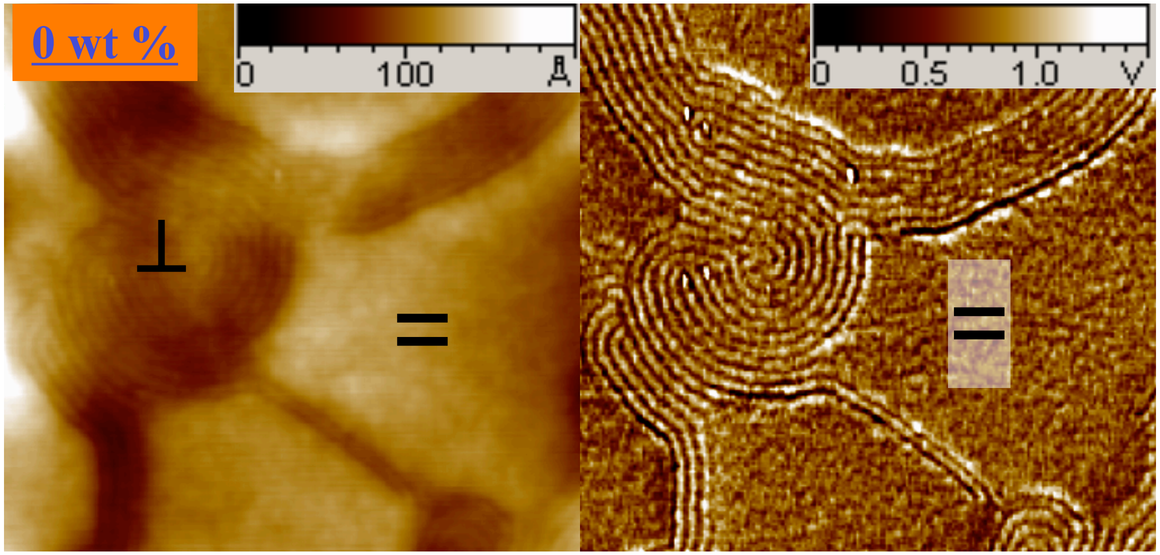
500 nm × 500nm

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

- NP alignment on PMMA lamella

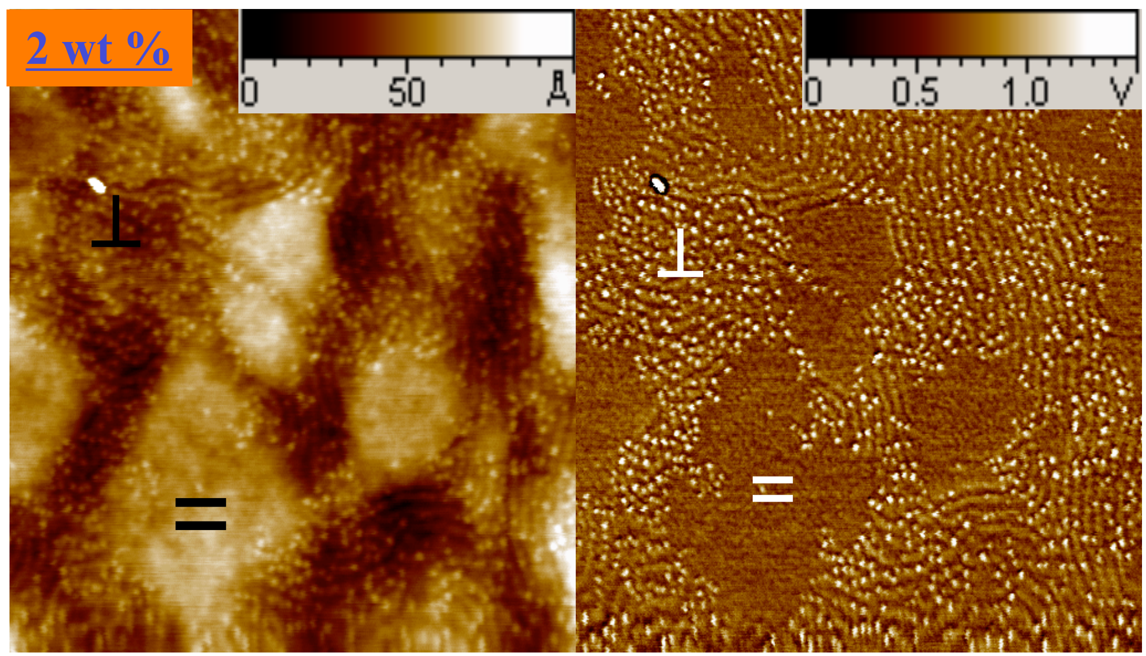
Deshmukh et al, *Macromolecules,* 2007, 40, 6316

Morphology Evolution (48 h)



- domain growth of parallel lamella “align”
  ⊥ lamellae

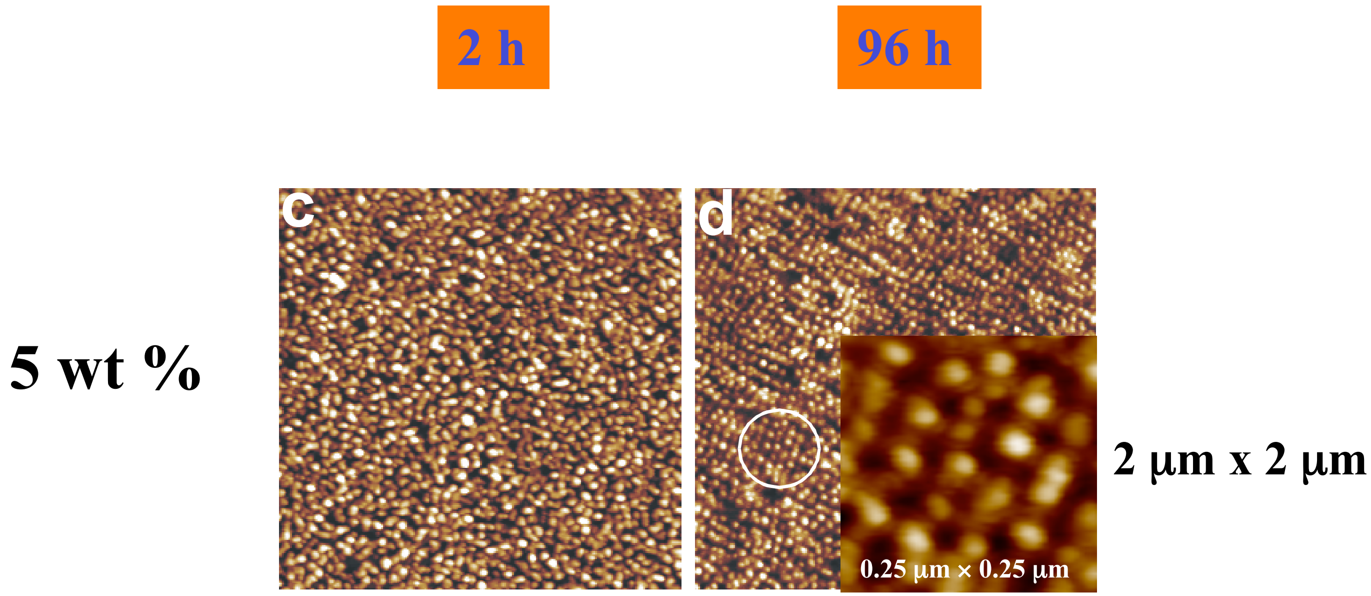
2 μm × 2 μm



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

Deshmukh et al, *Macromolecules,* 2007, 40, 6316

Effect of Ag Concentration



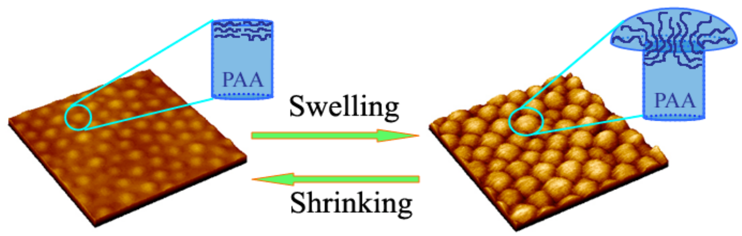
- Stabilize perpendicular morphology (short range).
- Arrange NP's into linear arrays along PMMA stripes.

Macromolecules, **2007, 40, 6316**

Conclusions

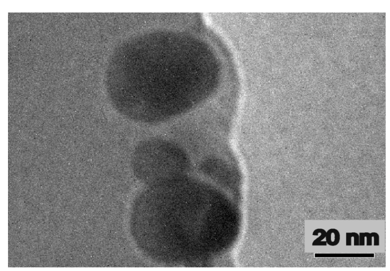
- The Picoplus is a powerful tool for following phase transformations and self assembly in block copolymers

- Can we “stimulate” transformations using functional tips?



- AFM is excellend tool for imaging surface segregating NPs.
- Can we determine “depth” of NPs using “hard” imaging ?

NP Wetting



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)

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