Template Directed Assembly of Polymer Blends into Nonuniform Geometries at Multiple Length Scales

NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing (CHN)

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Team Strength and Capability

NEU: Directed assembly, MEMS, fabrication, nanoscale contamination control

Semiconductor & MEMs fab

- 7,000 ft^2 class 10 and 100 cleanrooms
- 6 inch completer wafer fab, nanolithography capabilities

UML: High volume polymer processing and assembly

UNH: Synthesis, self-assembly

Plastics processing labs

- **20,000 ft^2 +**
- **Compounding and forming equipment**

Center for High-Rate Nanomanufacturing

A unique partnership

Fully-equipped synthetic labs

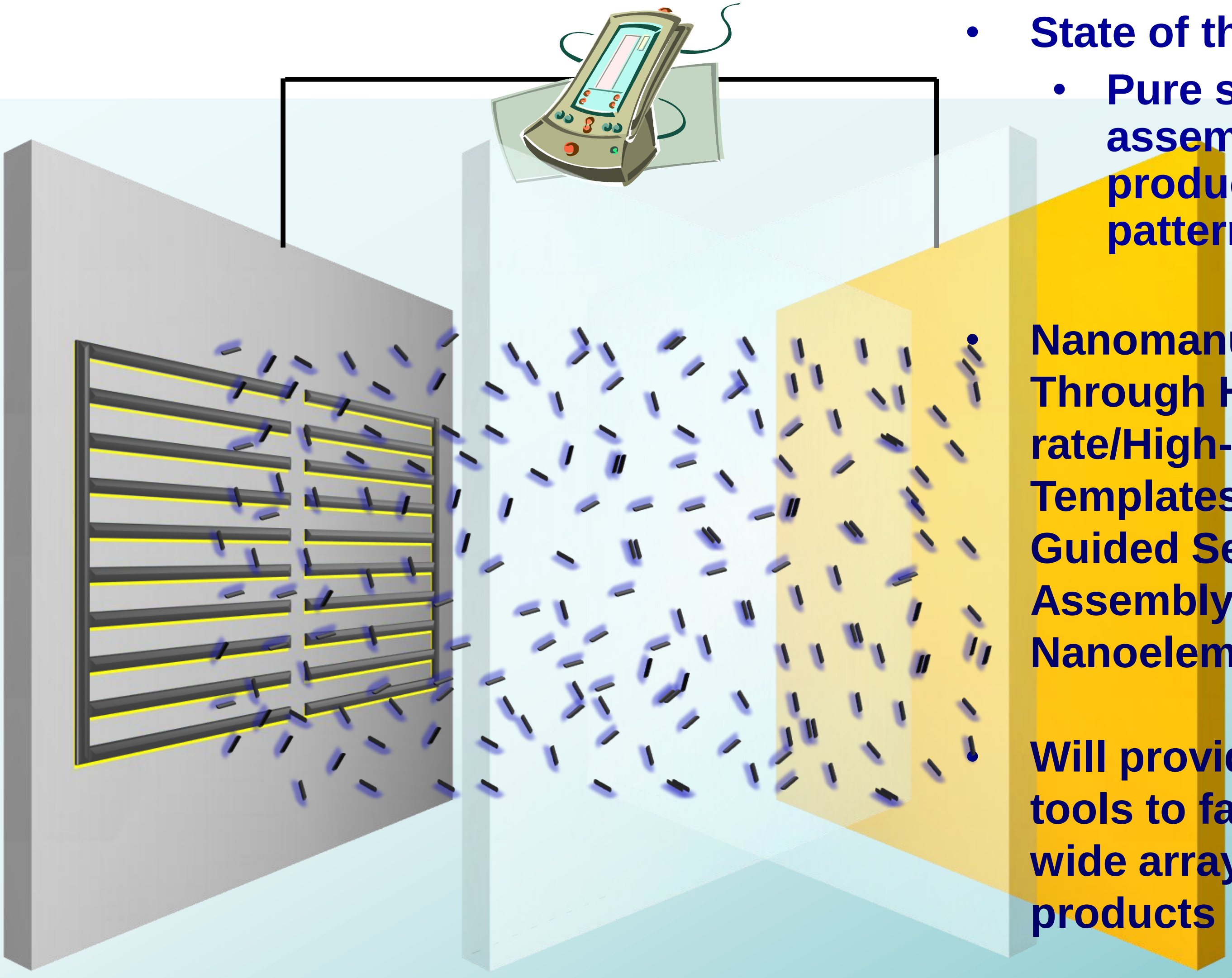
- **10,000 ft^2 +**

Director: Ahmed Busnaina, NEU

Deputy Director: Joey Mead, UML, Associate Directors: Carol Barry, UML; Nick McGruer, NEU; Glen Miller, UNH; Jacqueline Isaacs, NEU,

Group Leader: David Tomanek, MSU

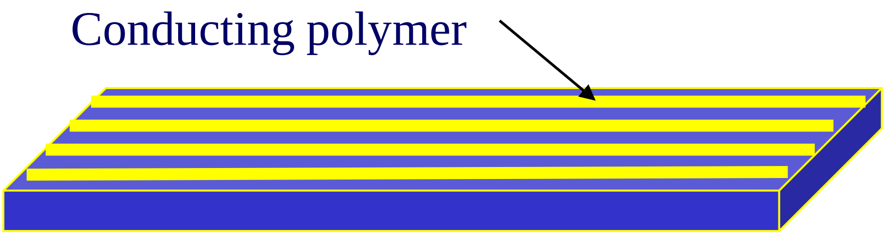
How Does Directed Assembly and Transfer Work?



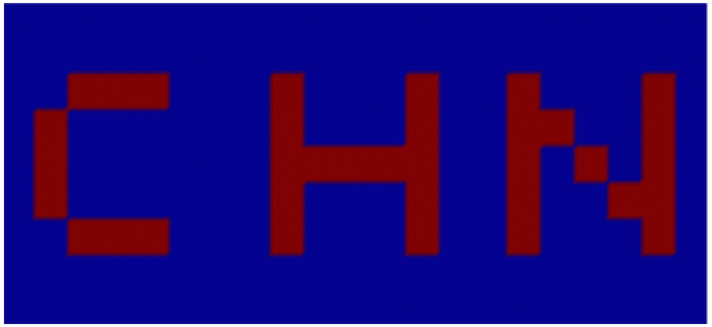
- State of the Art:
  - Pure self-assembly produces regular patterns
- Nanomanufacturing Through High-rate/High-volume Templates for Guided Self-Assembly of Nanoelements
- Will provide the tools to fabricate a wide array of products

Directed Self-Assembly of Polymers

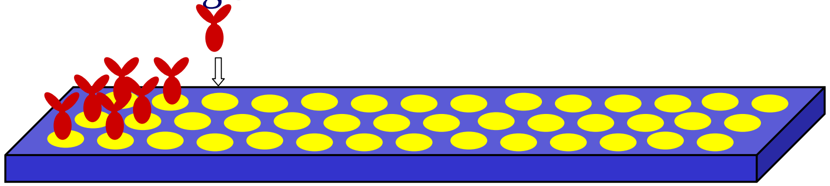
Flexible Electronics



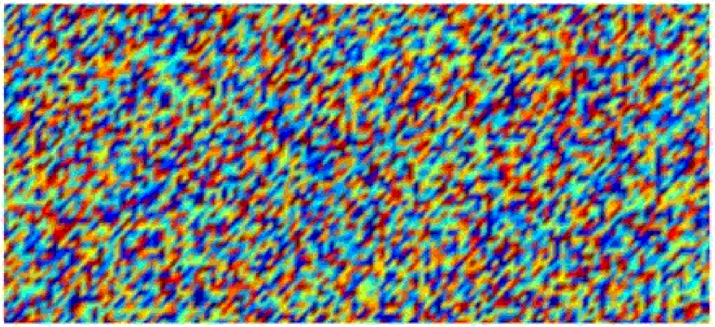
(Nano-)Template:



Biosensors
(radiation, cancer, anthrax, etc.)



Resulting concentration:

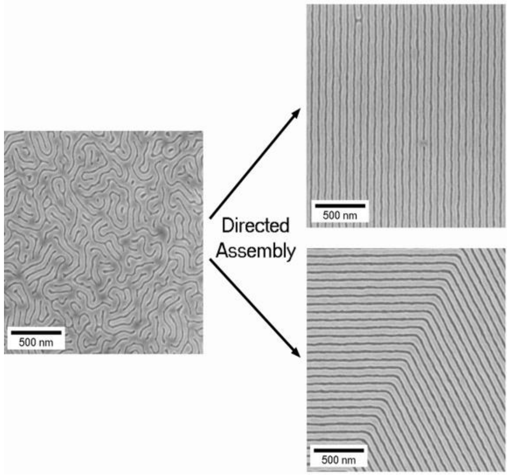


Kazmer, UML

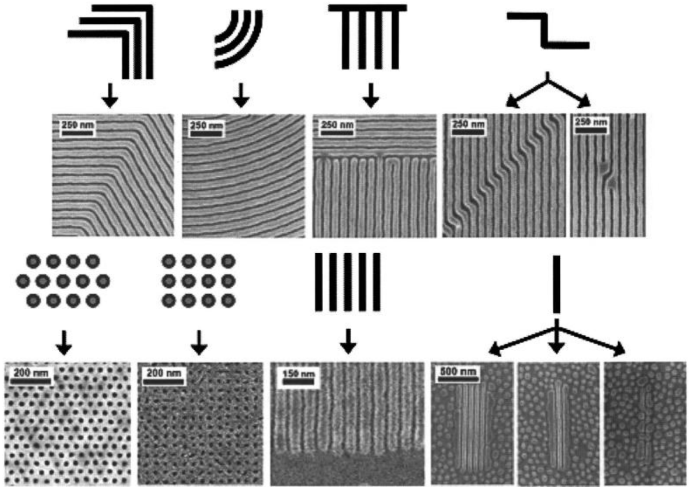
State of the Art
Directed Assembly of Block Copolymers

- Template directed assembly of block copolymers into nanopatterns with long range order
- Annealing often necessary
- Preparation of non-uniform structures challenging - homopolymers may be required
- Patterning reported to require ith 10% variation between phase domain size and pattern periodicity

PS-b-PMMA



PS-b-PMMA/PS/PMMA



PS-b-PMMA/PS/PMMA Blend

*Nealy et al., Nature **424**, 411-414 (2003), Science **308**, 1442-1446 (2005)*
Nealey et al., Journal of Vacuum Science Technology B, 25(6), (1969-1975), 2007

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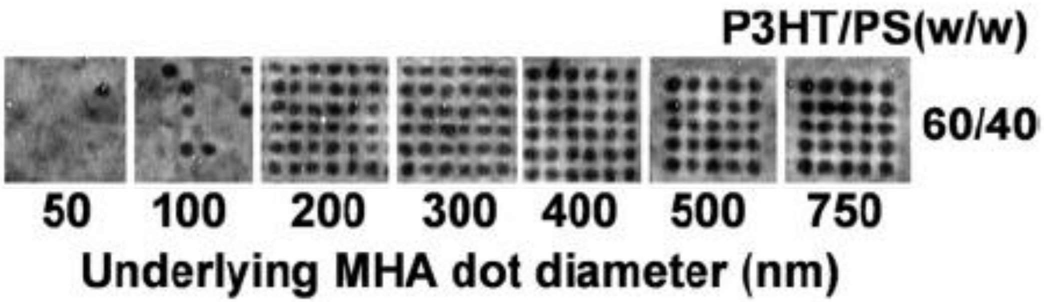
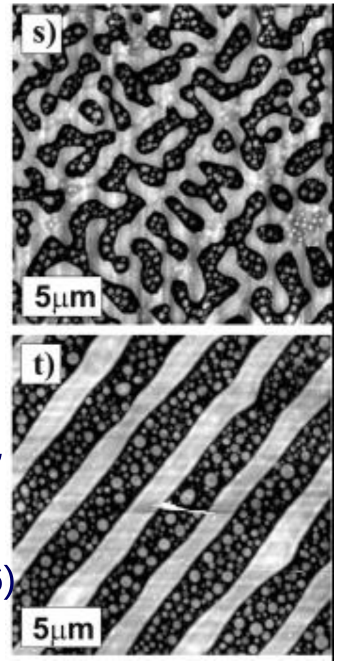
State of the Art
Directed Assembly of Polymer Blends



D. Coffey & D. Ginger, JACS, 2005, 127, 4564

SAM: hexadecanethiol [$HS(CH_2)_{15}CH_3$]
poly(2-vinylpyridine), polystyrene
J. Raczkowska, et al., *Macromolecules,* 2005**,** *38,* 8486

Surface Science, 600, 1004-1001 (2006)



Polymer Blends

- Wide range of materials
- Nonuniform patterns and simultaneous multi-scale assembly possible
- Best results occurred when phase domain size and pattern periodicity were commensurate – not quantified

Polymer Blend Morphology Control

Patterned Polymer Structure

Approach 1

Heterogeneous Assembly

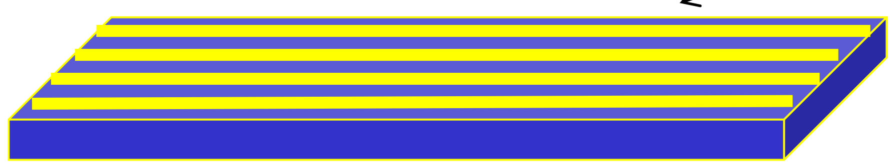
Assemble both polymers in single step on template

Approach 2

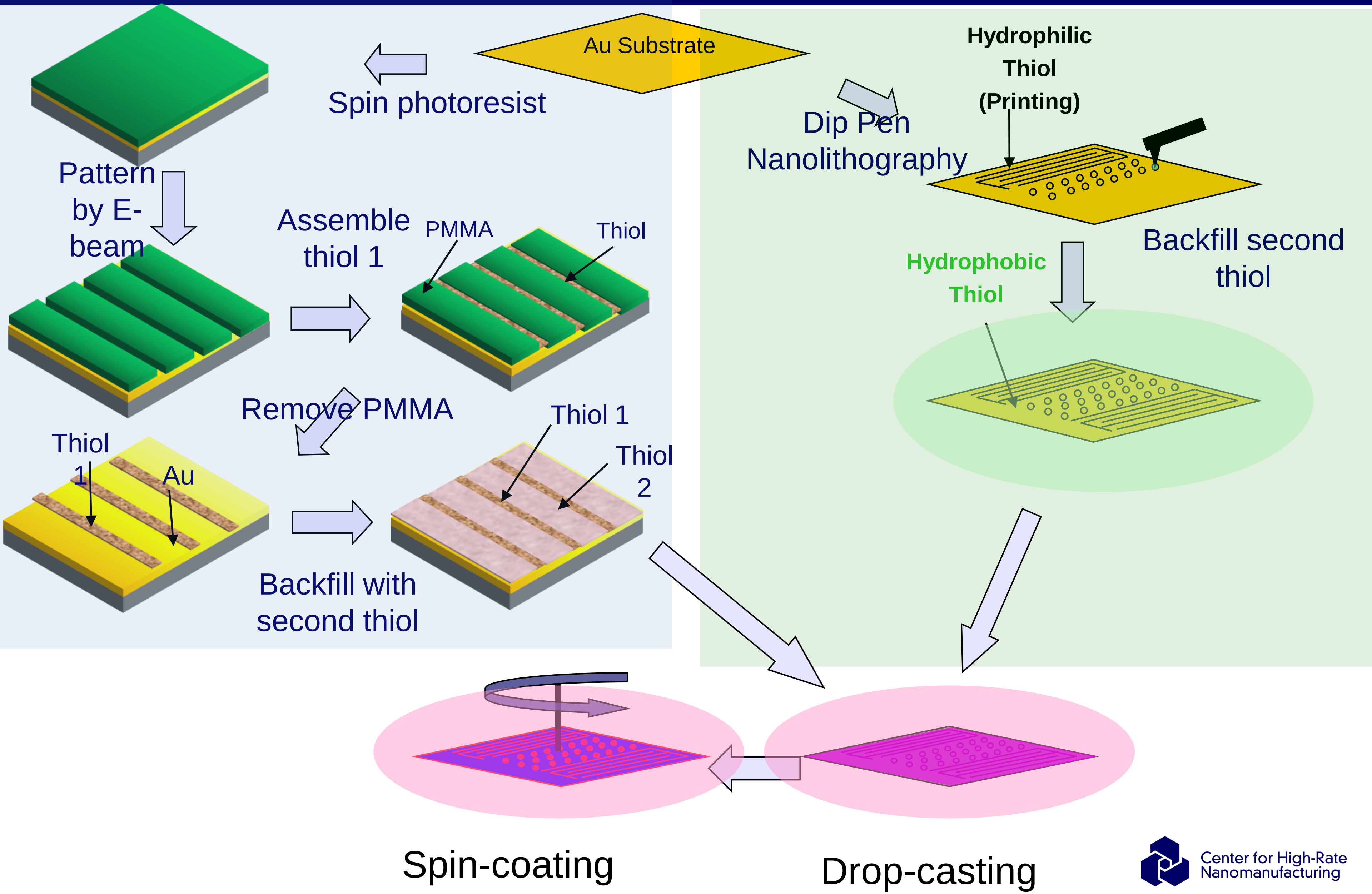
Homogeneous Assembly

Assemble single polymer on template

Transfer



Chemically Functionalized Templates



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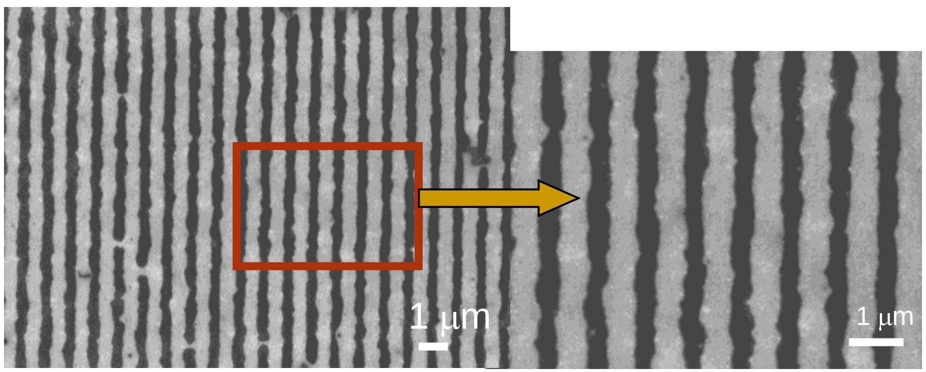
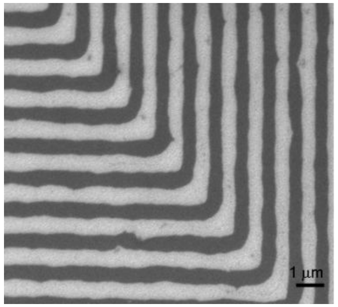
Heterogeneous Assembly of Polymer Blends - Polystyrene and Polyacrylic Acid (PS/PAA)

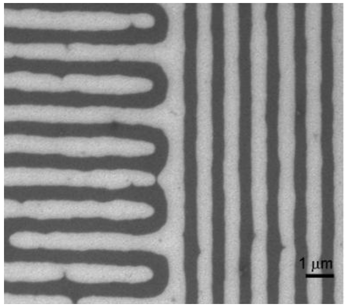
Polymer blends assembled in 30 s

- **No annealing**
- **Process conditions are critical for good assembly**
- **Non-uniform patterns**

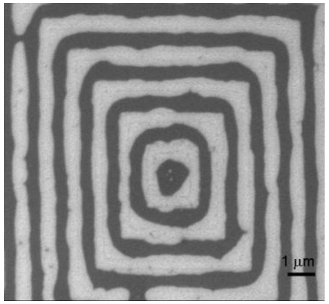




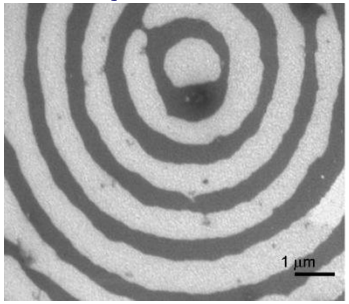
90˚ bends



T-junctions



Square arrays



Circle arrays

PS assembled on nonpolar areas (light); PAA assembled on the polar regions (dark)

Wei, M. L. Fang, J. Lee, S. Somu, X. Xiong, C. Barry, A. Busnaina, and J. Mead, *Advanced Materials*, 21(7), 735 (2009).

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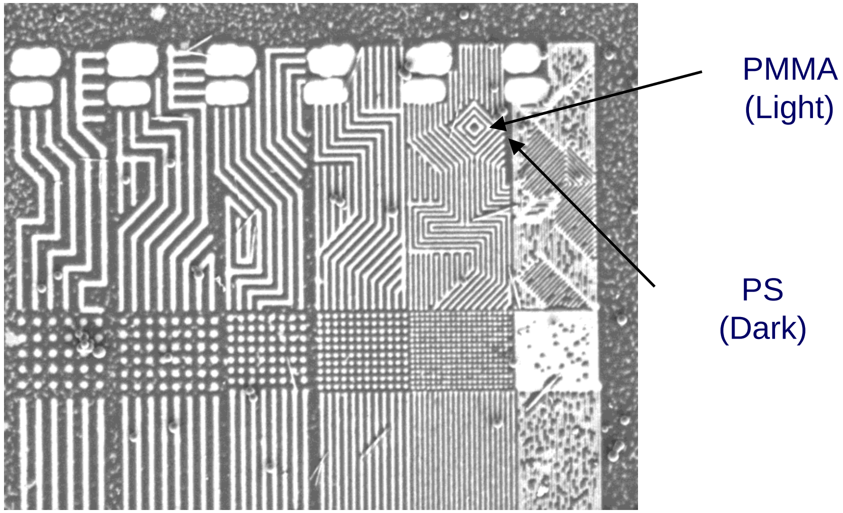
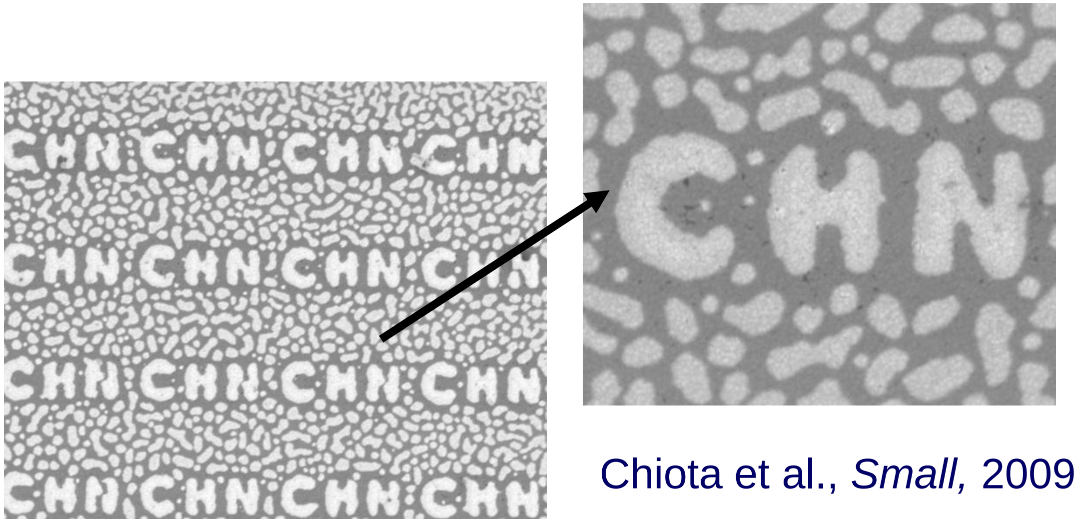
Multi-scale Patterned Polymer Blends

- Chemically functionalized templates assemble PS/PMMA polymer blends into non-uniform geometries.
- Polymer domains were patterned from 300 nm down to 100 nm on *the same template*.

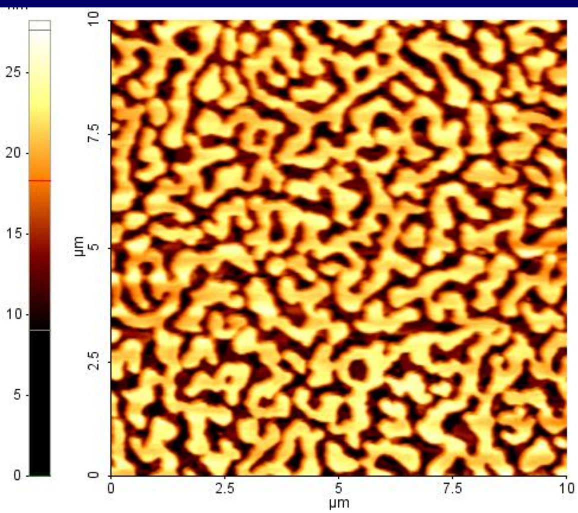
PS/PMMA (50/50 ratio)





Chiota et al., *Small,* 2009 Dec;5(24):2788-91

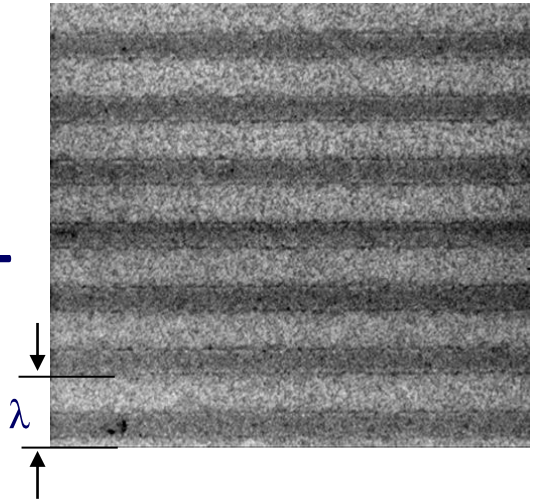
Commensurability



AFM topography images of PS (18k)/PAA(2k) blends 3000 rpm, 30s,

R -characteristic length = 993 nm

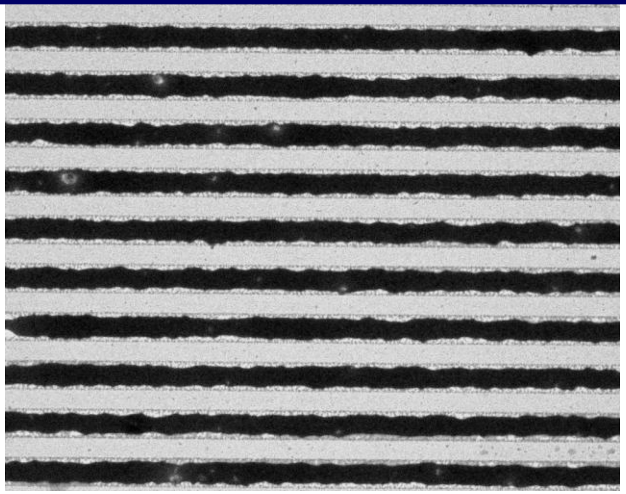
+



SEM images of chemically heterogeneous patterns

λ- pattern periodicity (pitch) = 1000nm

=



Directed assembly of PS/PAA blend on chemically heterogeneous patterns

- Characteristic length, R, is related to the domain sizes

Commensurability

- Relation between phase domain size and pattern periodicity, *λ* (pitch)

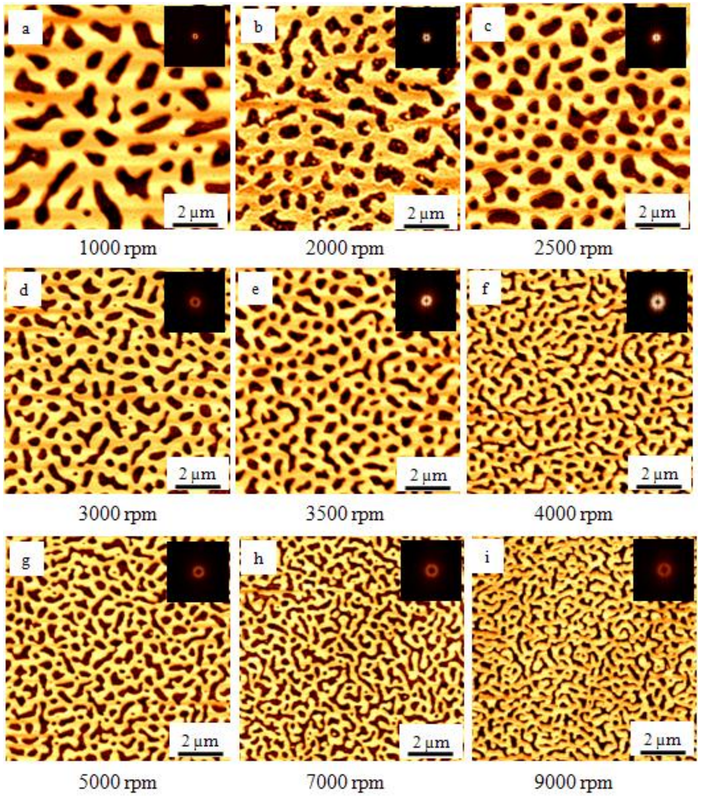
- Block Copolymers[1]
  - Requires domain size and *λ* to be within 10% of each other

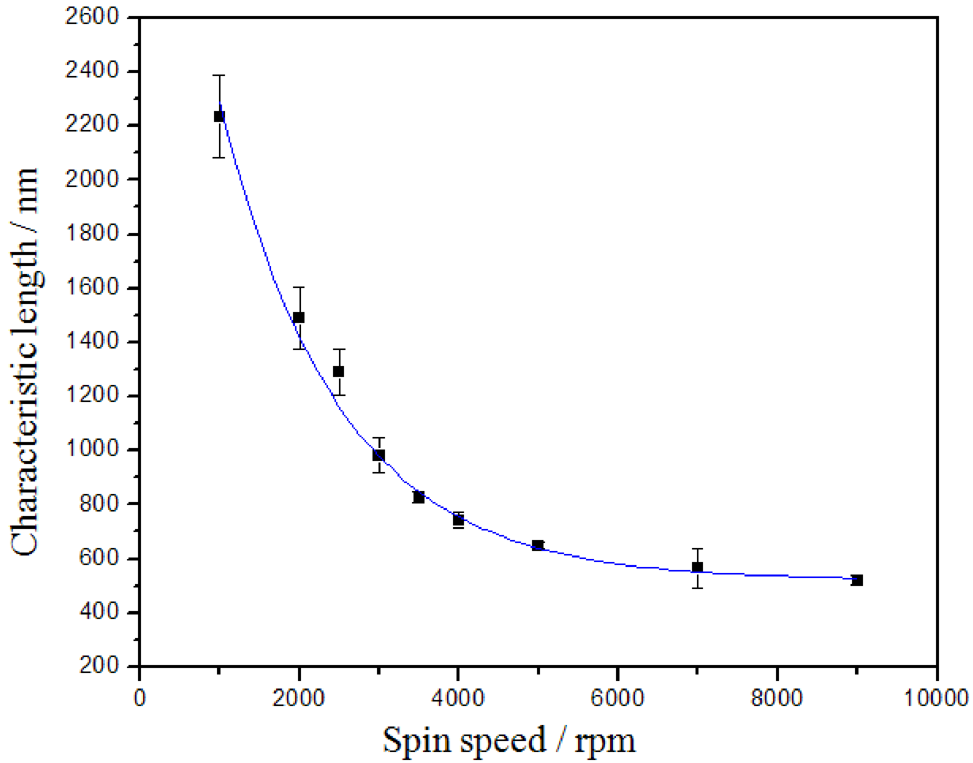
- Blends[2]
  - Well-ordered directed morphology formed when the characteristic length (*R*) (unpatterned) was commensurate with pattern periodicity (*λ*), i.e., *R*~ *λ*
  - Pattern periodicities micron-scale - relationship not quantified

- How to control domain size?
  - Spin Speed
  - Solution Concentration

[1] *Nealey et al., Journal of Vacuum Science Technology B, 25(6), (1969-1975), 2007*
[2] *Raczkowska, et al., Macromolecules 2005, 38, 8486*

Effect of Spin Speed on Domain Size



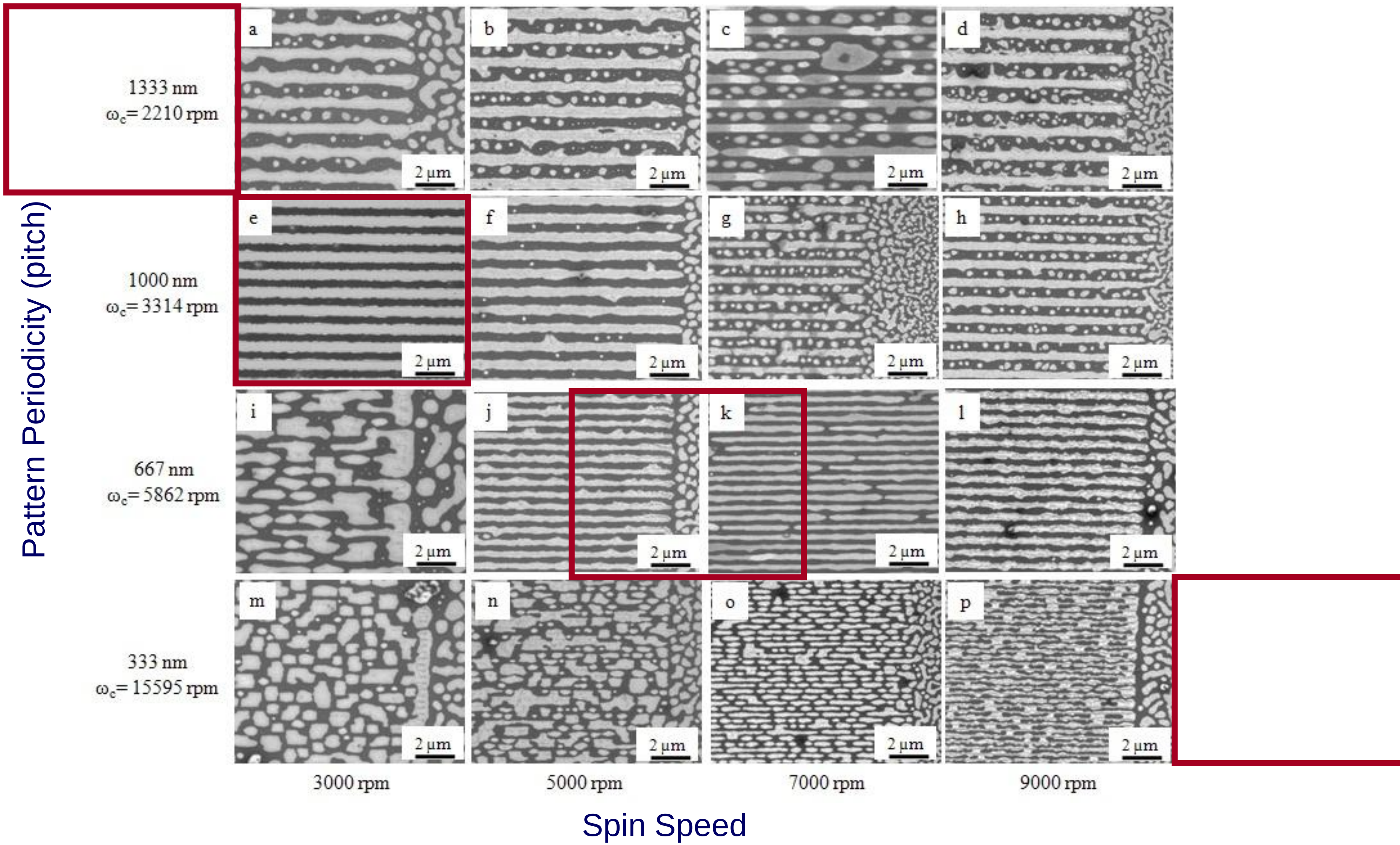


Characteristic length (R) dependence on spin speed and concentration → $R=k\omega^{\alpha}c^{\beta}$ (k denotes constant, ω is the spin speed and c is the solution concentration).

*Raczkowska, et al., Macromolecules 2005, **38**, 8486*

Concentration 1% PS/PAA

Effect of Spin Speed for Different Periodicities



PS/PAA blends using alternative MUAM/ODT patterns with various periodicities: ω_c stands for the critical spin speed for each pattern periodicity. Conc. 1%

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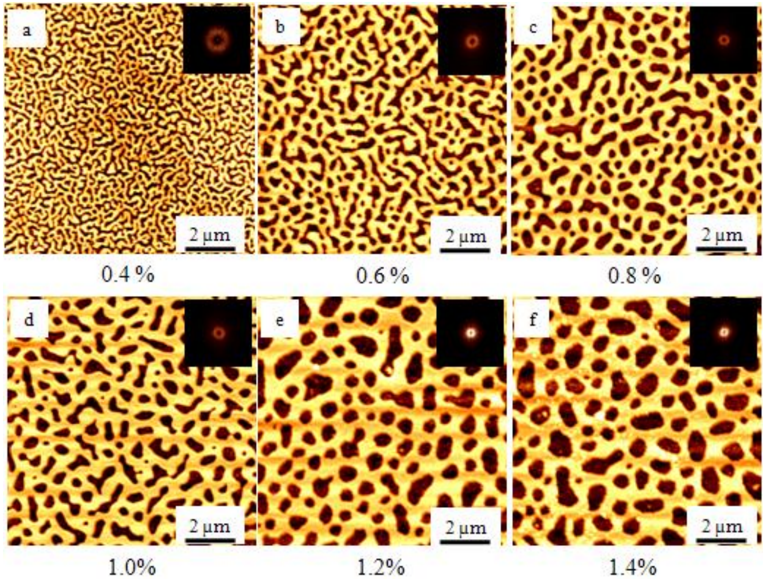
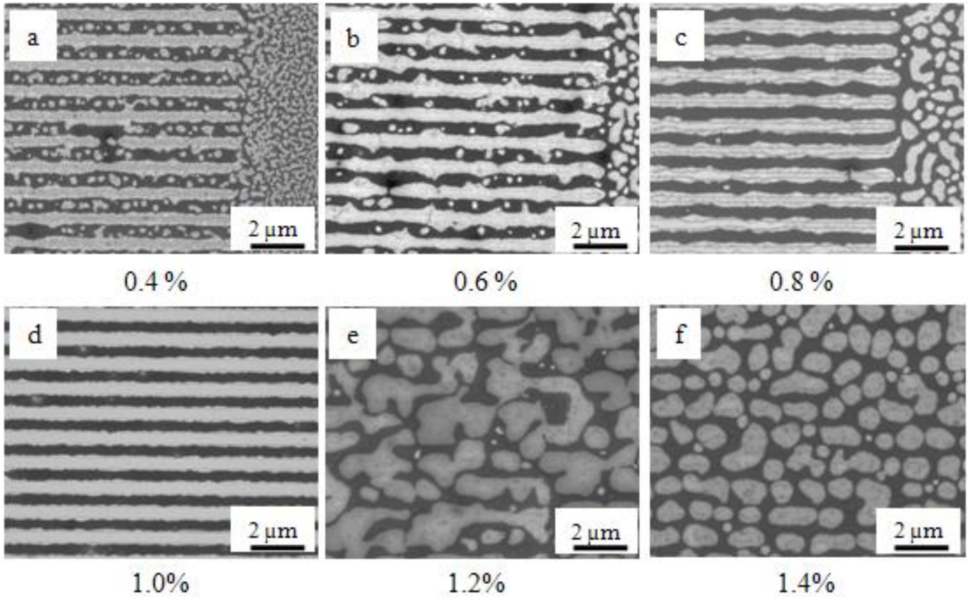
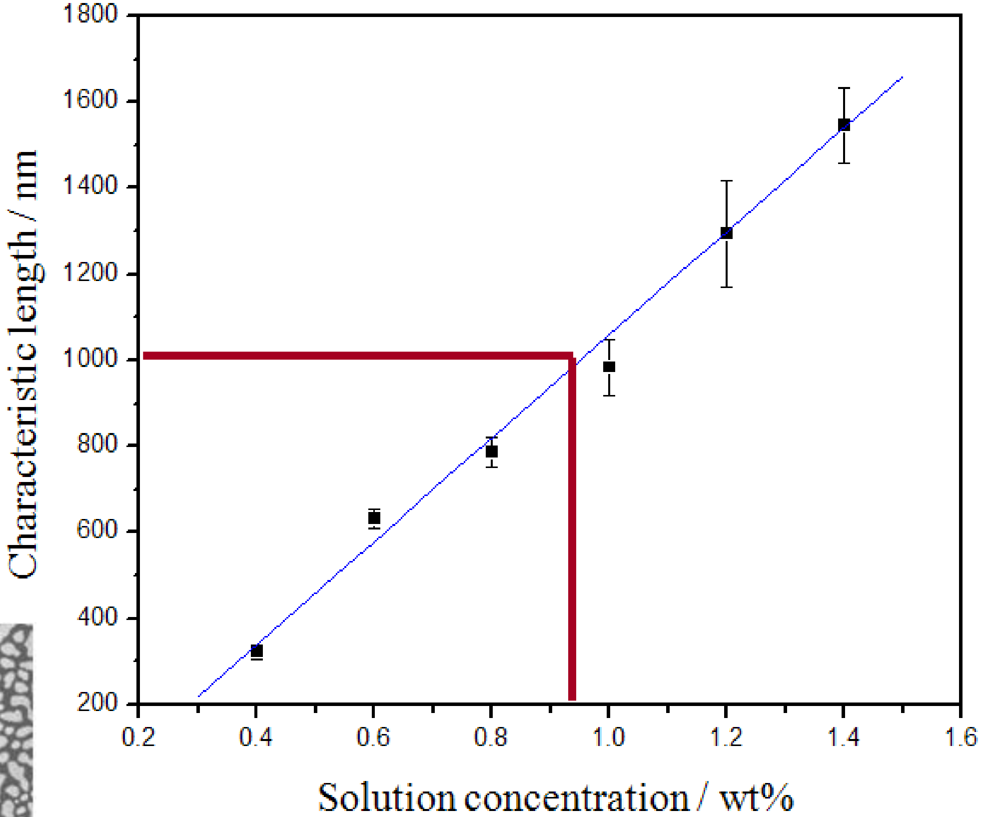
Effect of Solution Concentration on Domain Size







PS/PAA on the MUAM/ODT with 1000 nm periodicity. The dark regions are PS domains and the grey regions are attributed to PAA domains.

Spin speed 3000 rpm

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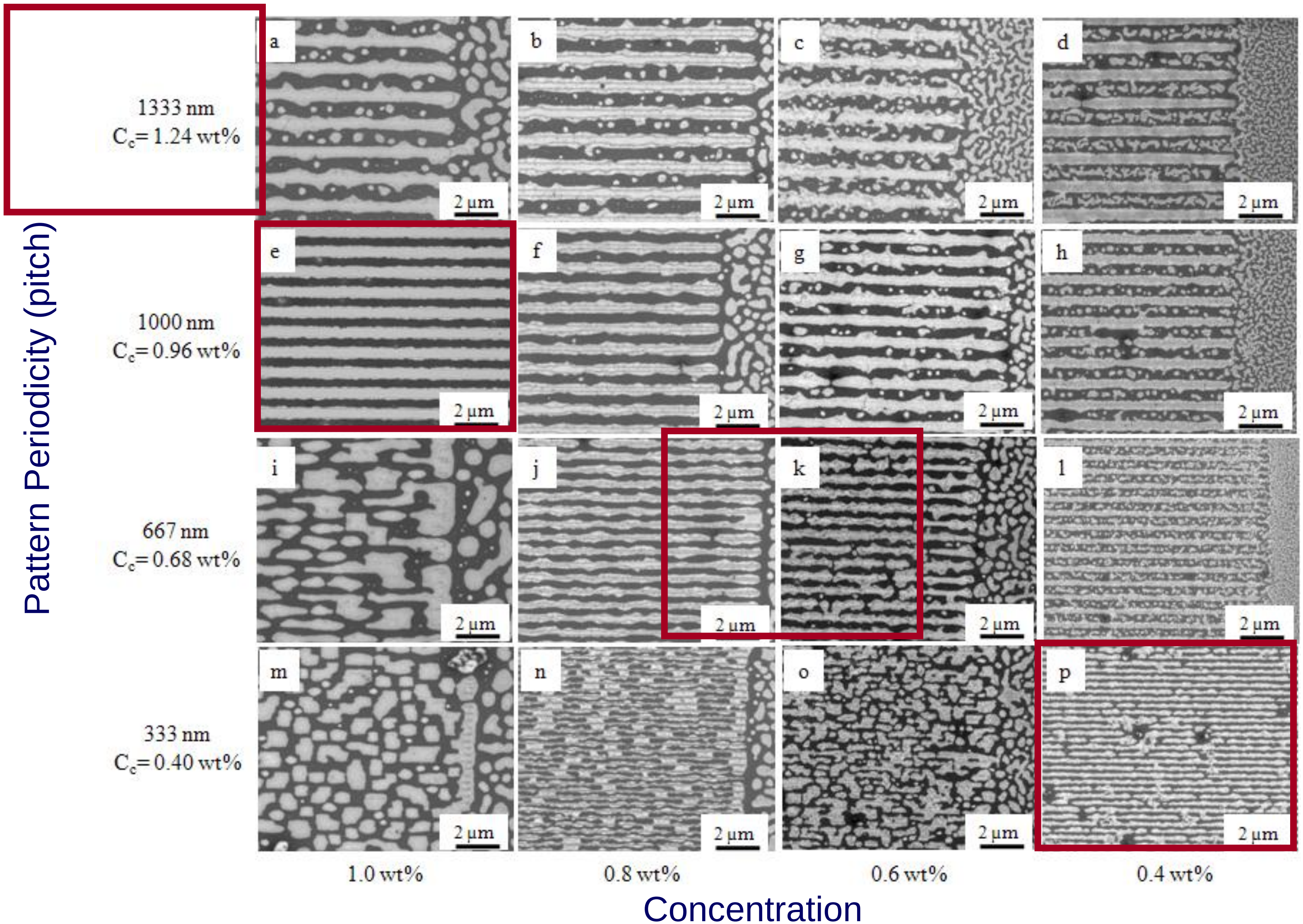
Effect of Solution Concentration for Different Periodicities



PS/PAA blends using alternative MUAM/ODT patterns with various periodicities: C_c stands for the critical solution concentration for each pattern periodicity. 3000 r

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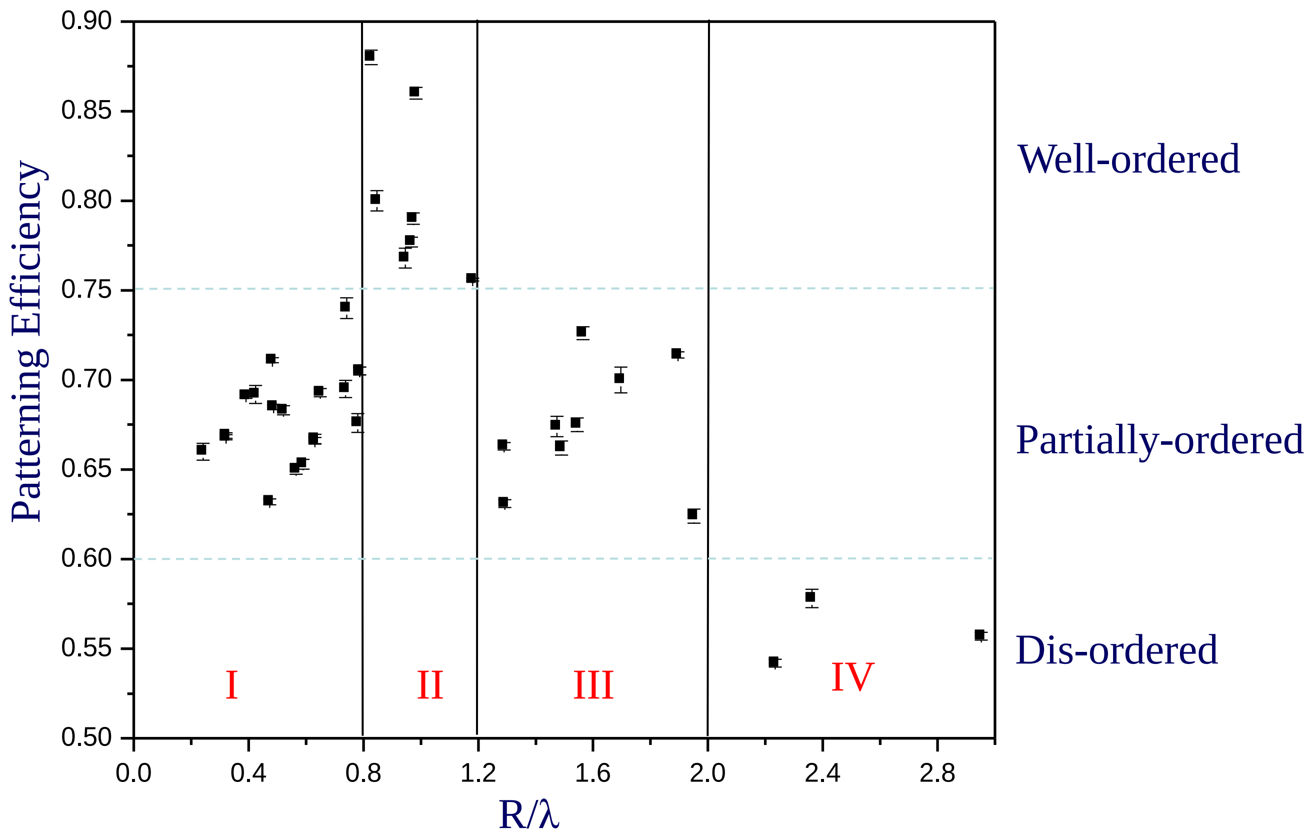
Commensurability



- Patterning efficiency (*Ep*) (dimensionless parameter)
  - When *Ep* is 0.5, morphology not directed and is isotropic.
  - When *Ep* is 1, morphology is perfectly patterned
- When 0.8<R/**λ** <1.2 well ordered patterns are formed, which corresponds to commensurability of 20% for assembly of polymer blends

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Polymer Blend Morphology Control

Patterned Polymer Structure

Approach 1

Heterogeneous Assembly

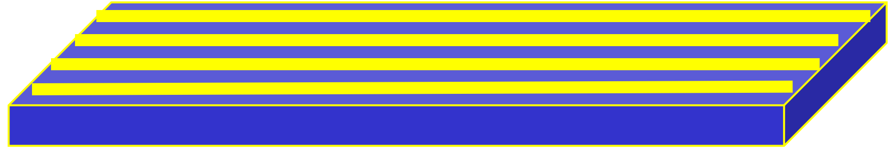
Assemble both polymers in single step on template

Approach 2

Homogeneous Assembly

Assemble single polymer on template

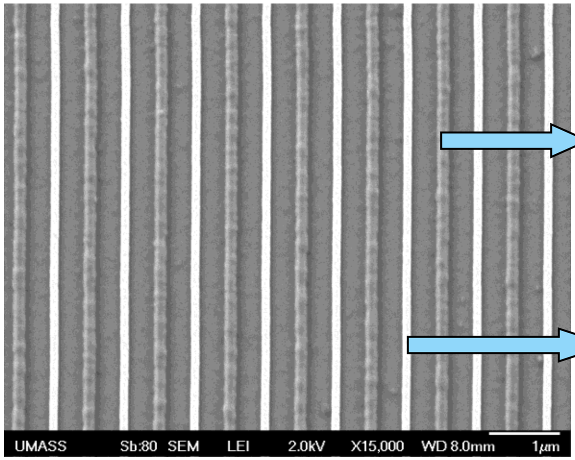
Transfer

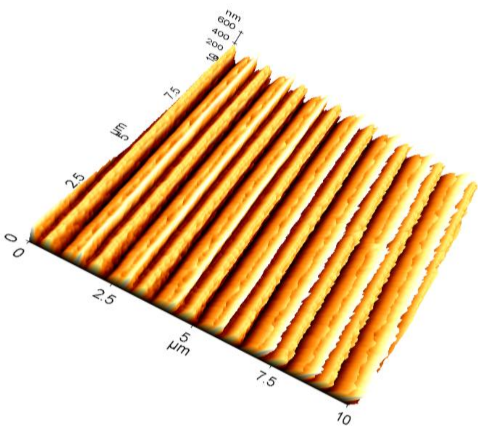


Assembly of Conducting Polymers using Nanowire Templates

Pattern Dimension	:	Gold Line width 100 nm Pitch 500 nm

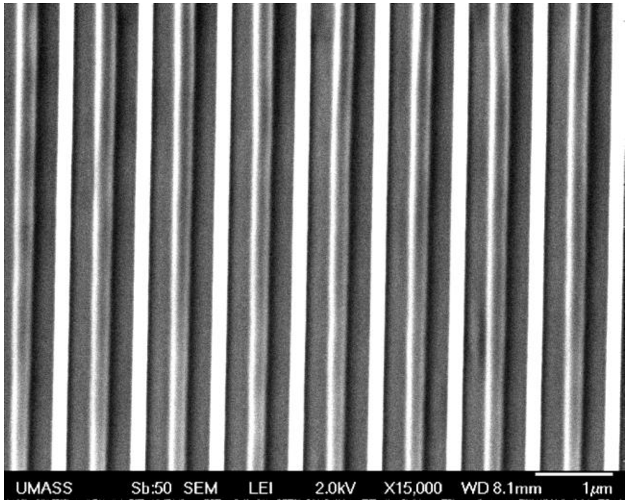
DC, 2 V 1 min

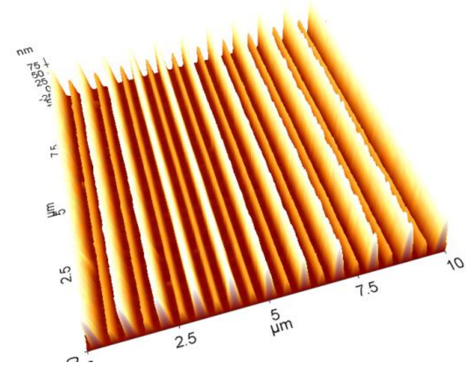




150 nm width, 160 nm height, and 100 μm length

AC, 2V, 100 Hz, 1 min





140 nm width, 50 nm height, and 100 μm length

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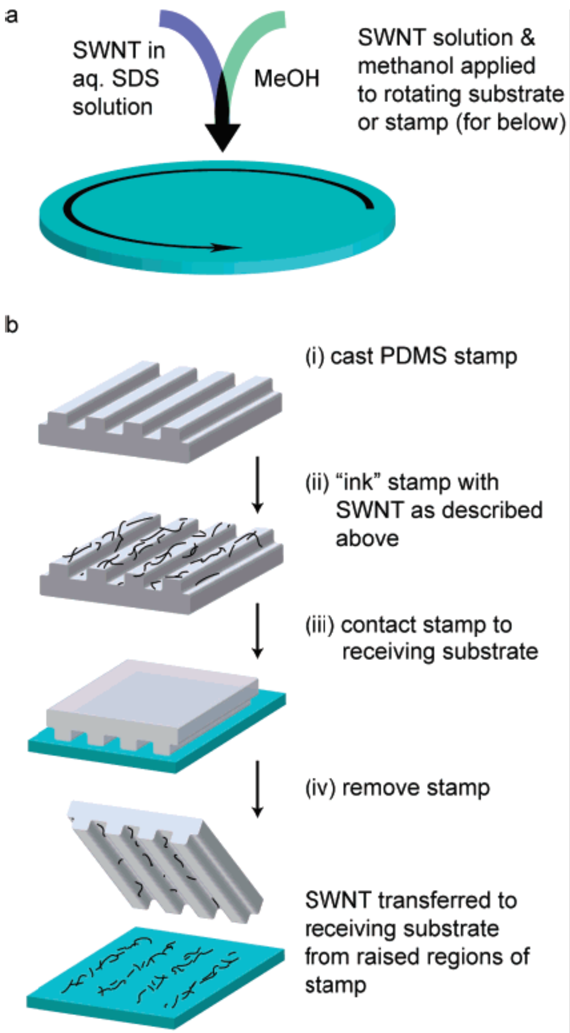
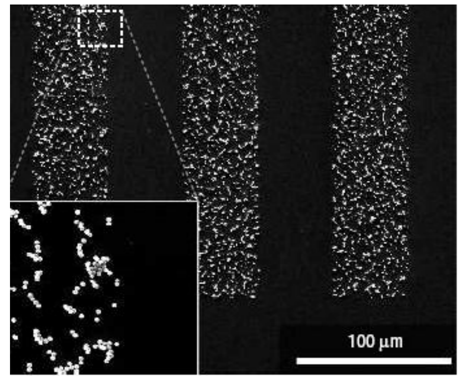
Transfer
State of the Art

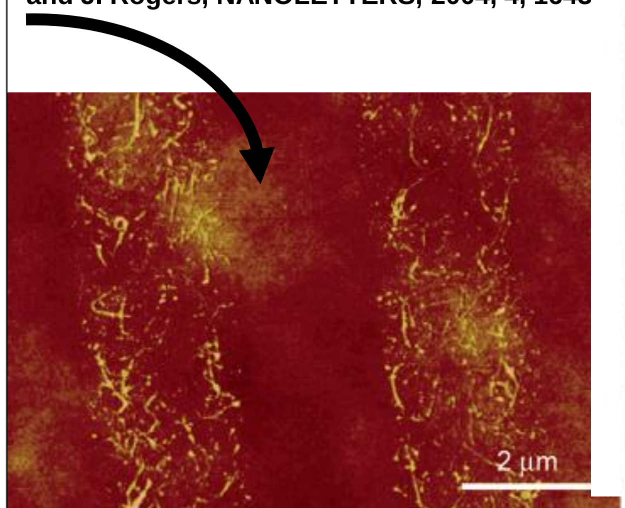


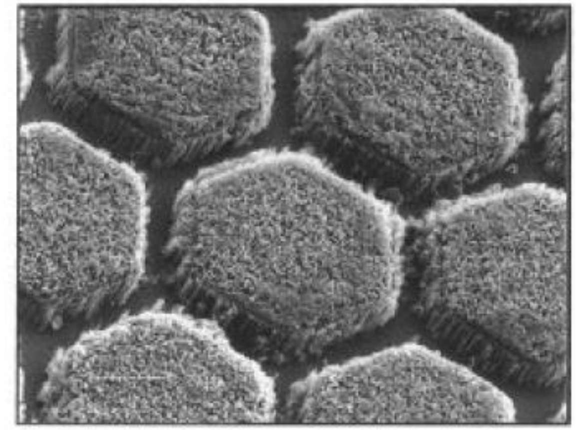
M. MEITL, Z. ZHU, V. KUMAR, K. LEE, X. FENG, Y.GANG Y. HUANG, I. ADESIDA, R. NUZZO AND J. ROGERS, Nature Materials VOL 5 JANUARY 2006

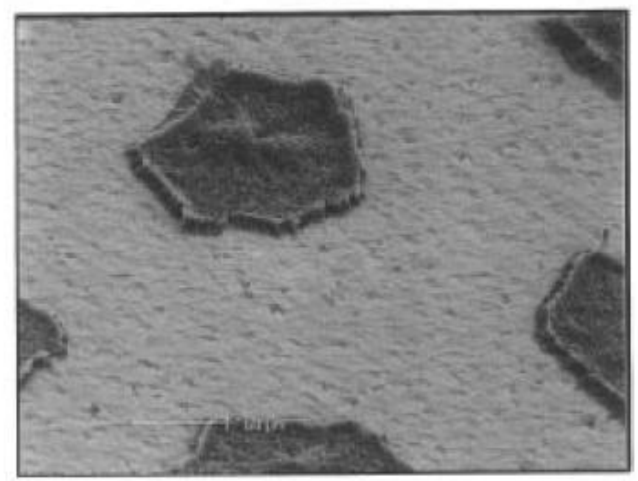


Silica nanoparticles

M. Meitl,| Y. Zhou, A. Gaur, S. Jeon, M. Usrey, M. Strano, and J. Rogers, NANOLETTERS, 2004, 4, 1643







S. Huang, L. Dai, and A. Mau, *J. Phys. Chem. B* (1999), *103,* 4223

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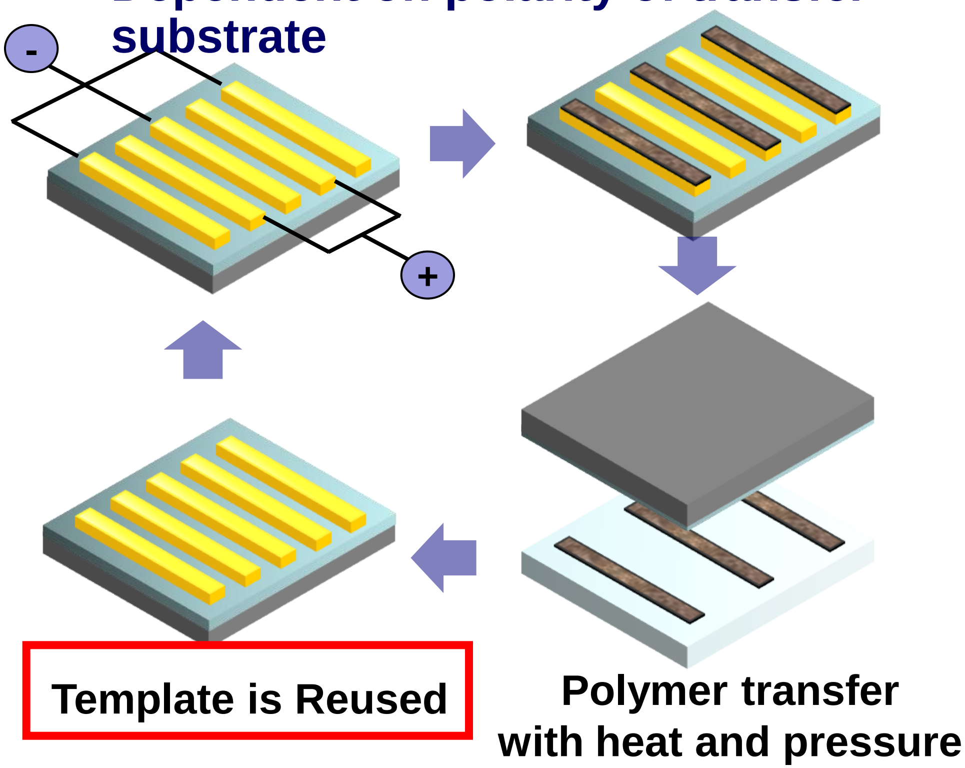
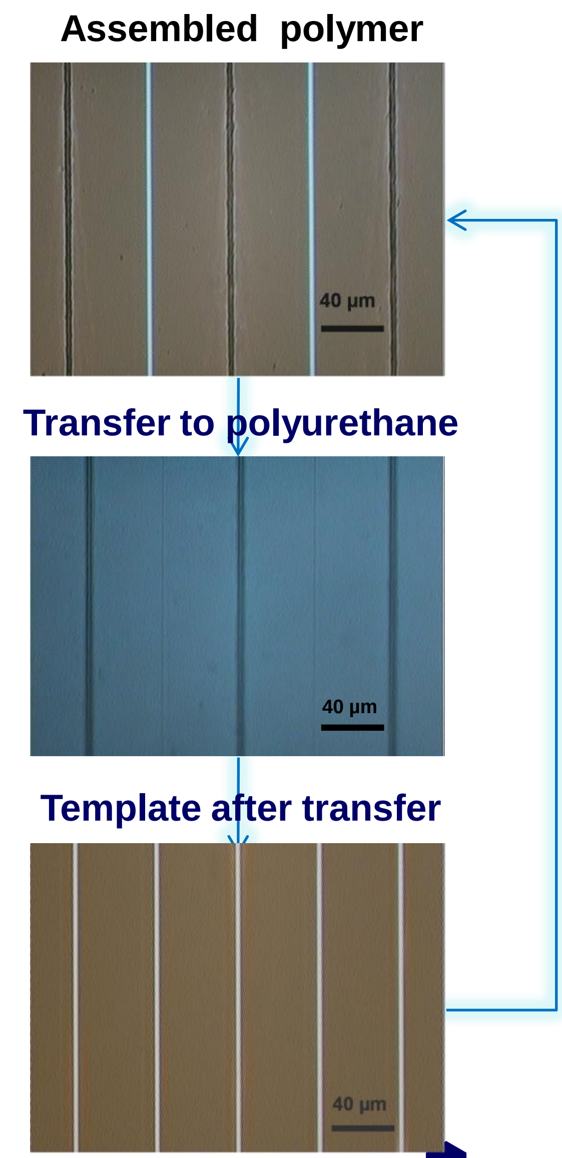
Electrophoretic Assembly and Transfer

- **Precise directed electrophoretic assembly of conductive polymer - polyaniline (PANI)**
  - **Requires 10 volts for < 1 minute**
  - **Template design critical for assembly into patterns**
- **Transfer of polymer wires onto substrates**
  - **Dependent on polarity of transfer substrate**



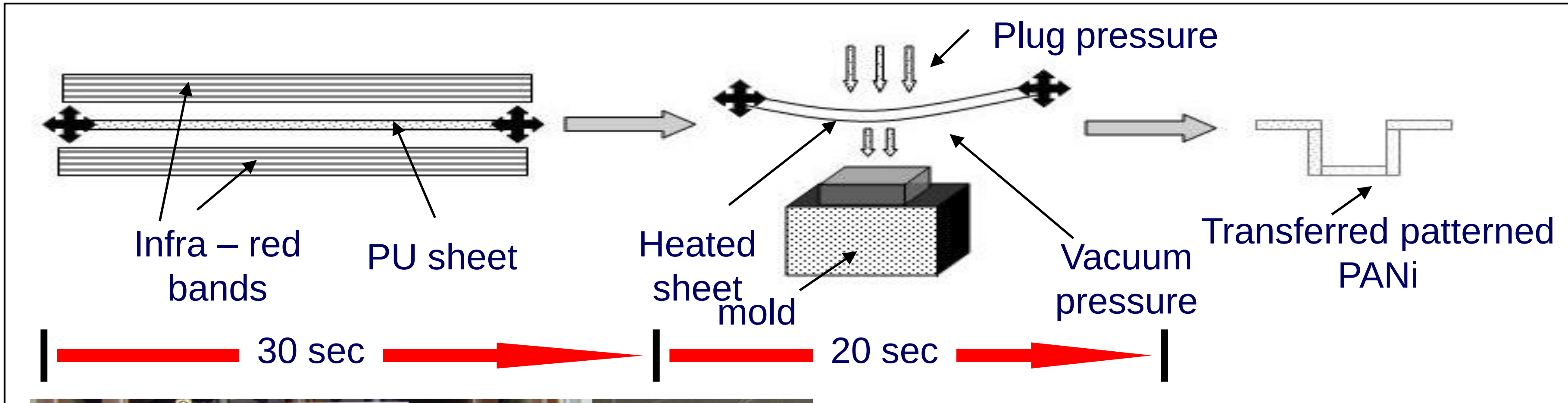


Wei et al., J. of Macromolecular Rapid Comm., 27, 2006

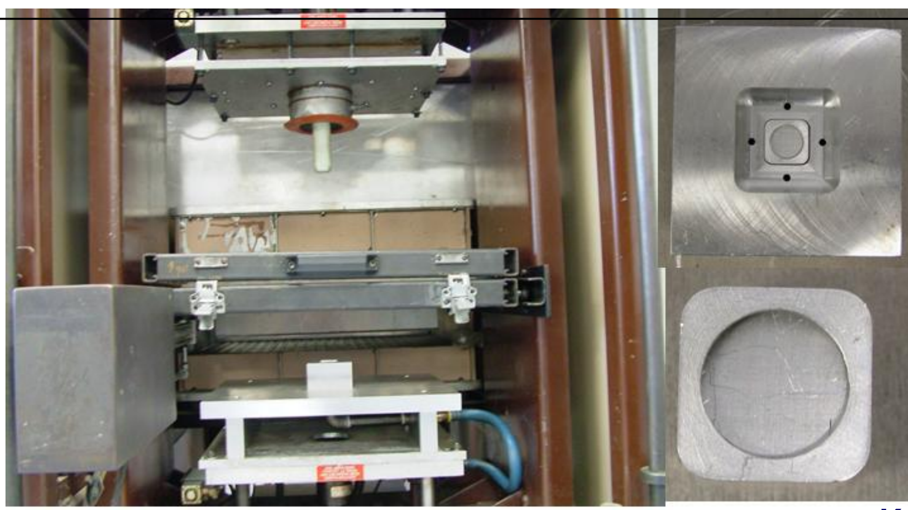
Scale up of Transfer Process

Transfer of conducting polymer and CNTs

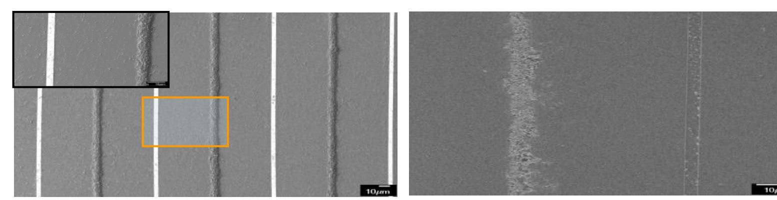
- Transfer time 10 s, total cycle time 40 s



Thermoforming mold sketch



Thermoforming machine and mold picture

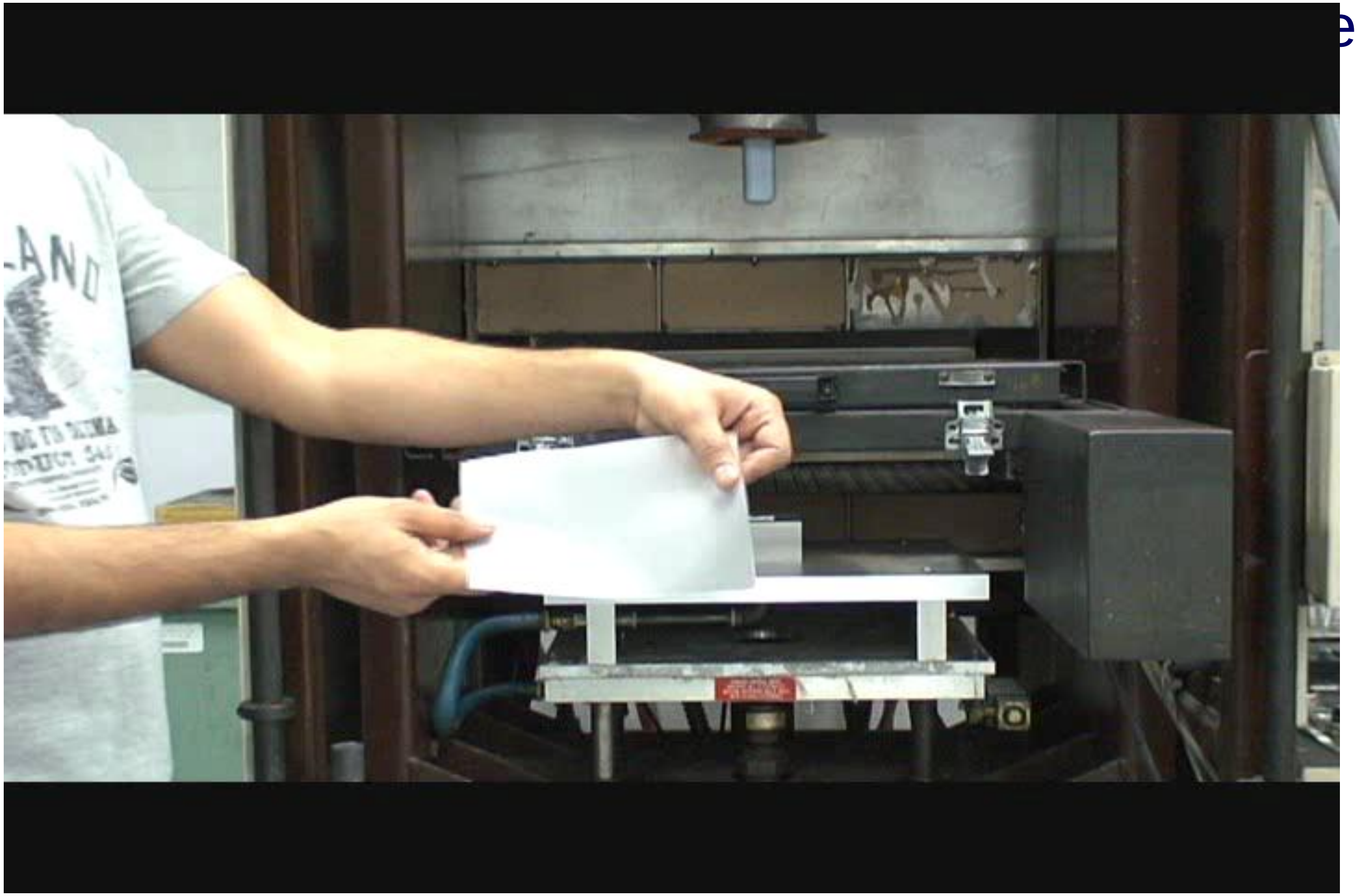


CNTs deposited on patterned structure at 20 V in 15s

Pattern transferred at 179º C in 15 s at 30mm Hg

Kumar, M. Wei, C. M. F. Barry, S. Orroth, A. Busnaina, J. Mead, Proc. An Tech. Conf. Soc. Plast Eng, 2008

Transfer using Thermoforming Process



Summary

- High rate assembly and transfer processes for polymer blends (<1 min)
- Heterogeneous Assembly
  - Control of domain sizes for PS/PAA blends using spin speed or solution concentration.
  - When the variation between characteristic length and pattern periodicity was within 20%, well-ordered replication of patterns was achieved
  - Pattern size down to 100 nm
  - Non-uniform geometry and multi-scale in one step fashion
- Homogeneous Assembly and Transfer
  - Directed assembly of conducting polymers
  - Complete transfer to flexible substrate by thermoforming
  - Cycle time 50 seconds

Acknowledgements

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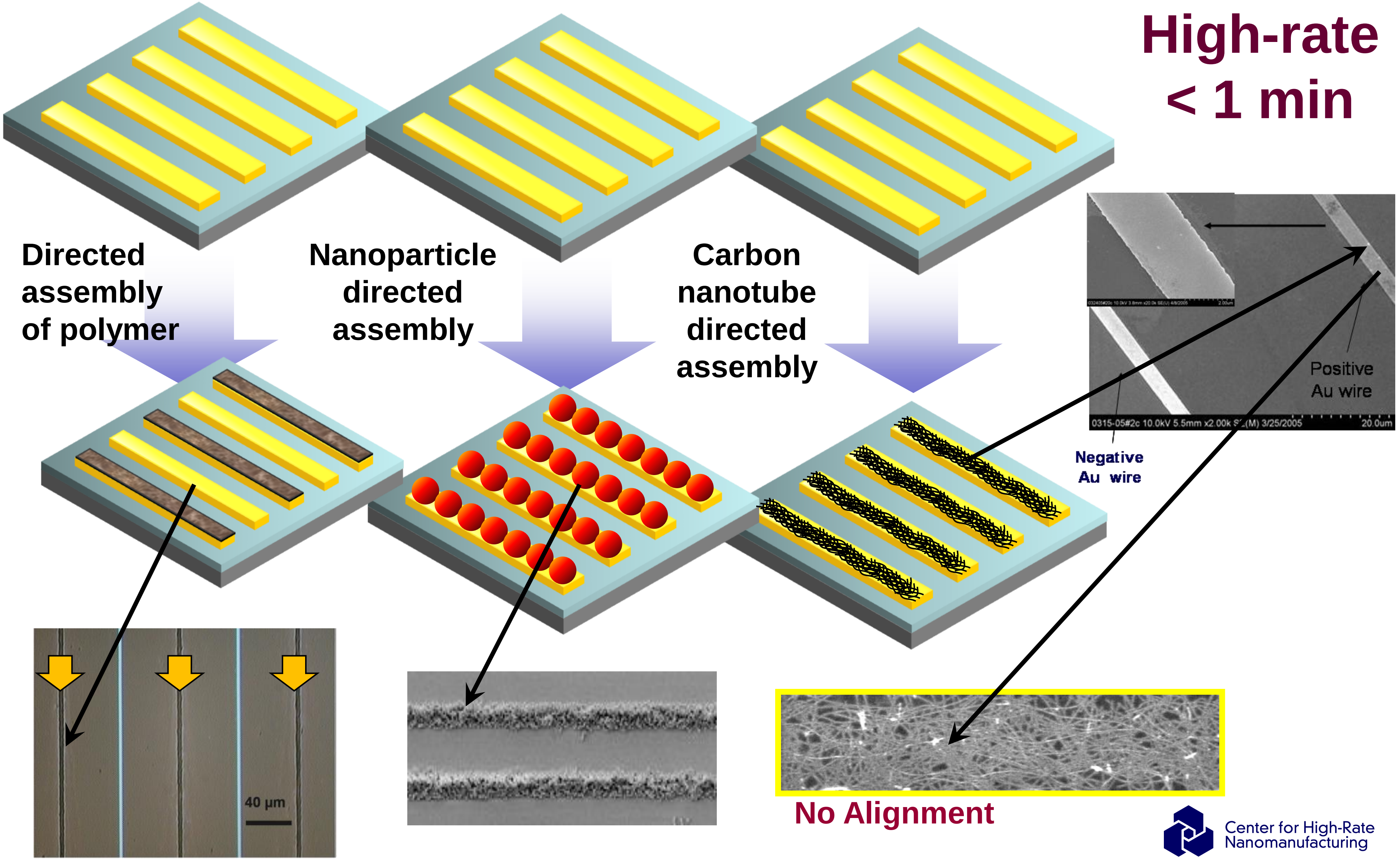
Nanowire Template Directed Assembly Using Electric Fields or Chemical Functionalization



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Nanotrench Template Directed Assembly Using Electrophoresis or Chemical Functionalization