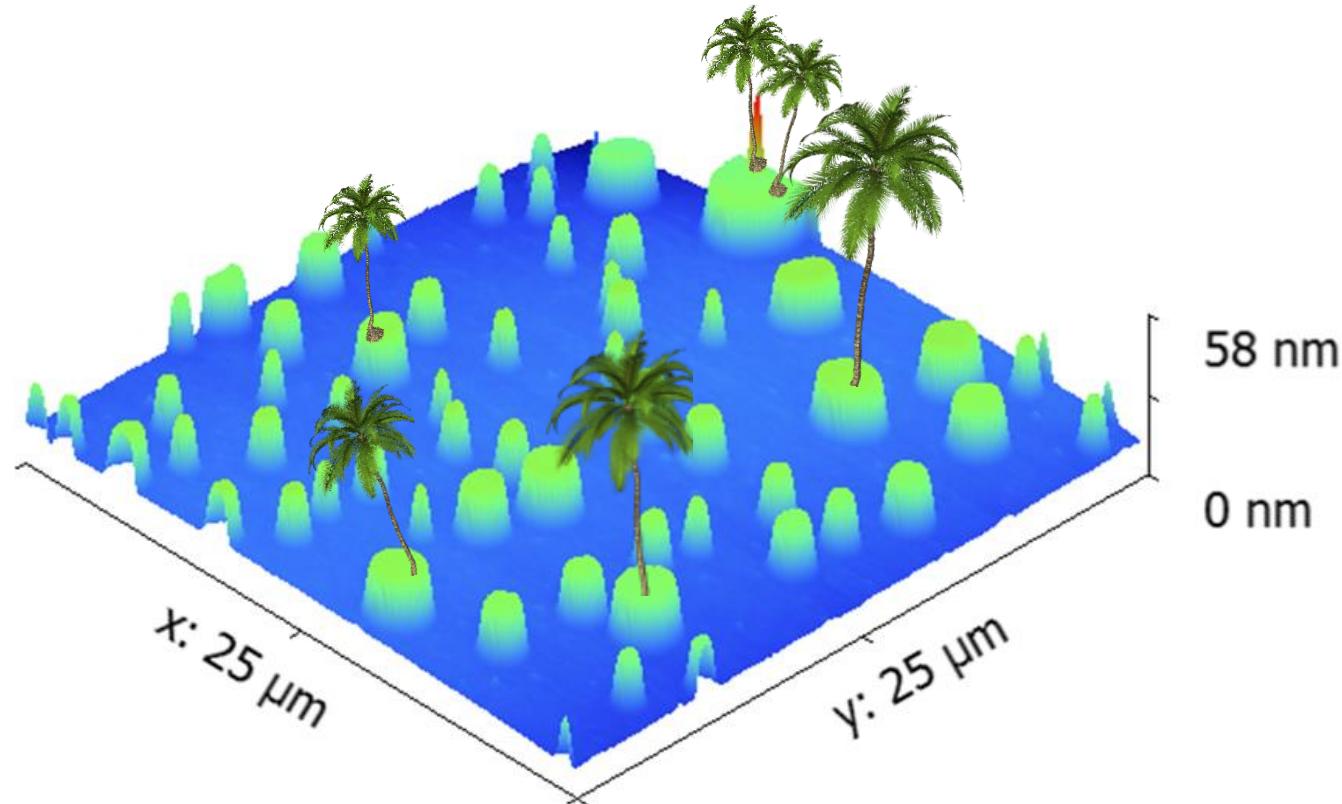


# Lecture 20

Chemical Engineering for Micro/Nano Fabrication

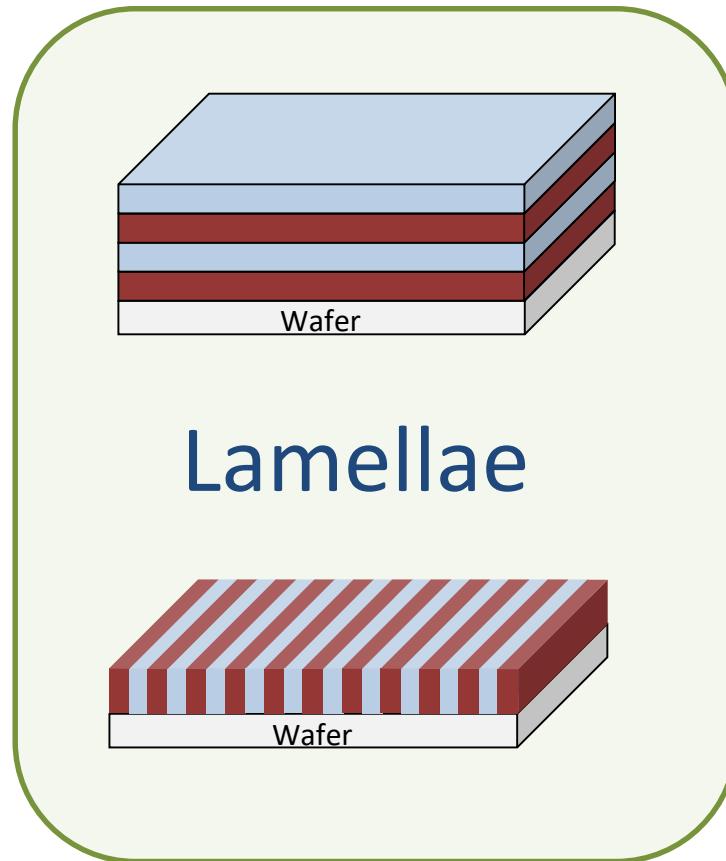


Islands??



# Block co-polymers

## Next....The Orientation Control Challenge

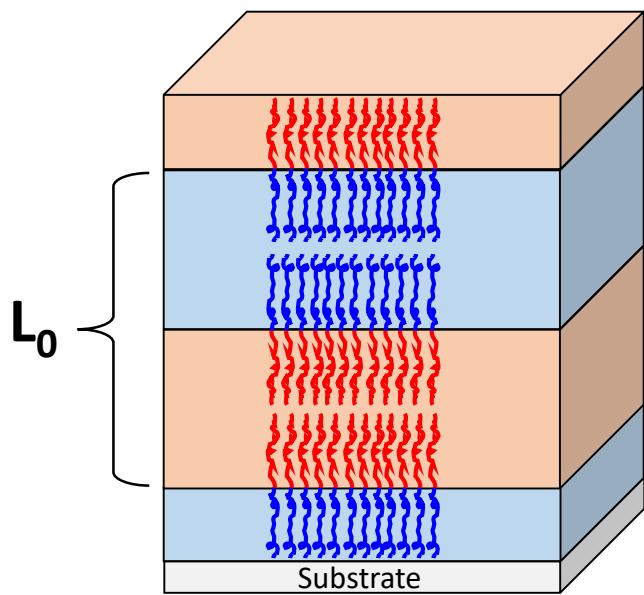
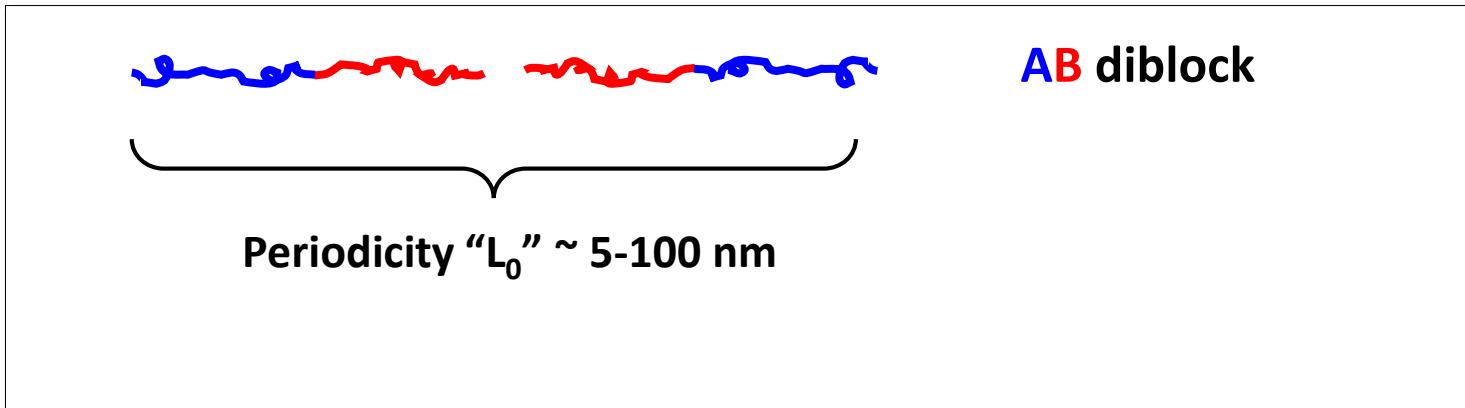


*Bates et al. Science* **338**, 775 (2012)

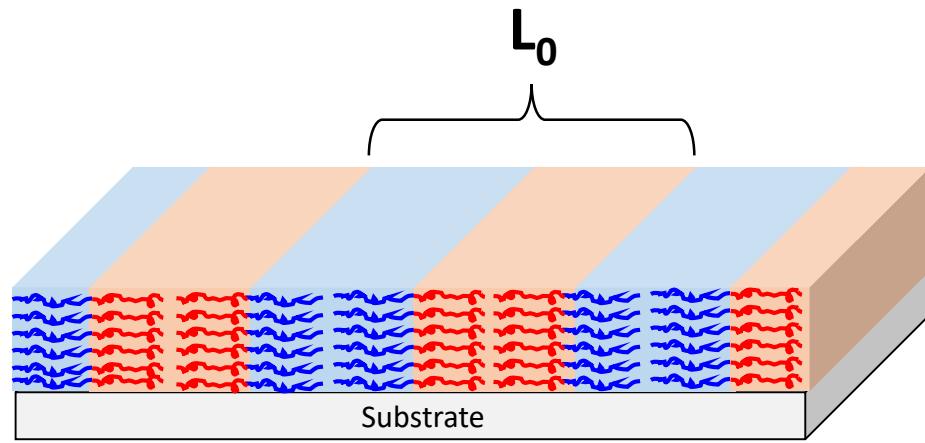
Maher et al. *Chem. Mater.* **2014**, *26*, 1471



# Block Copolymer Orientation



Parallel



Perpendicular



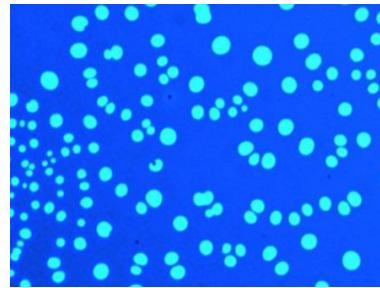
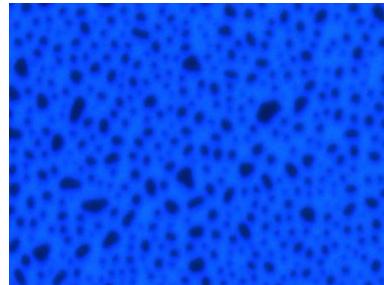
As cast film thickness >  $L_0$ ?

$2^*L_0$

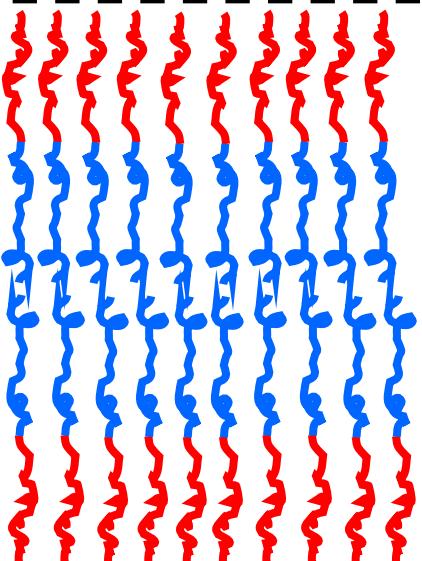
-----

Islands

$1.2^*L_0$



$1^*L_0$

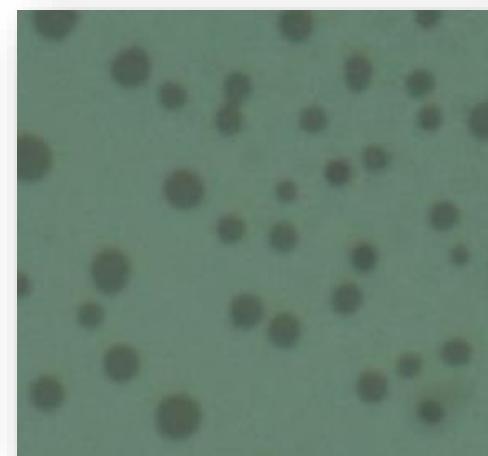
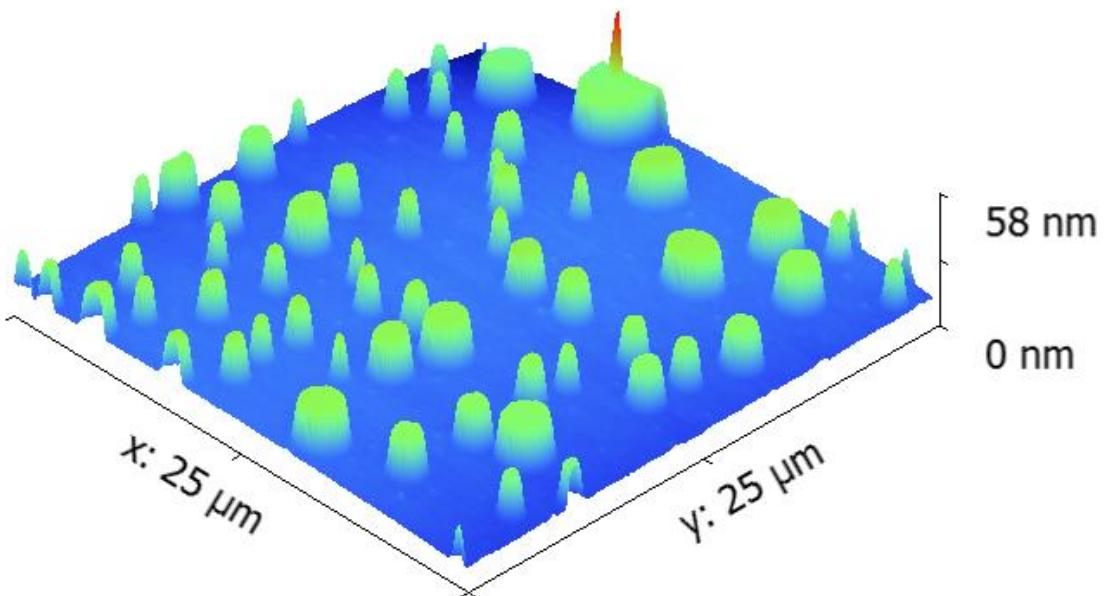


Surface Prefers Red Block



# The “island and hole” experiment

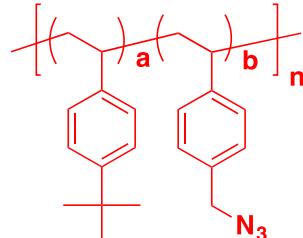
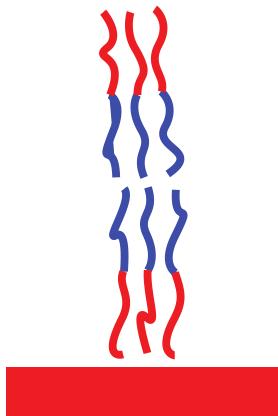
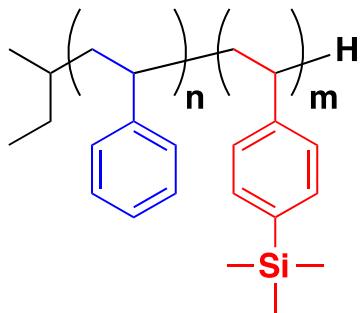
Structures are easily seen by optical microscopy



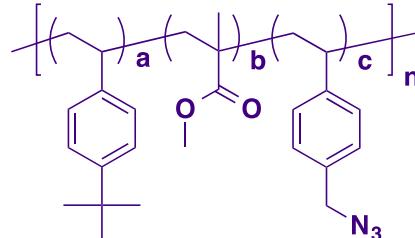
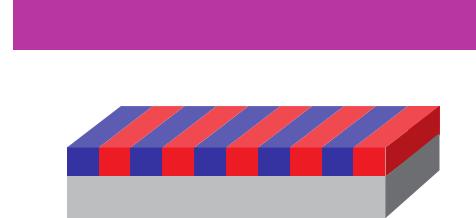
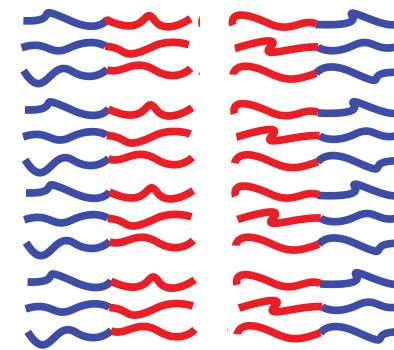
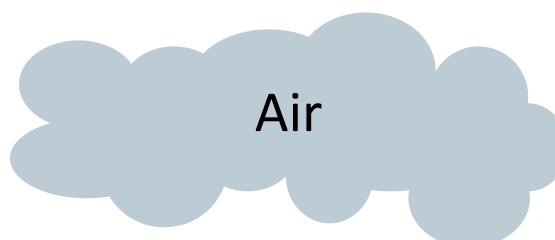
Islands



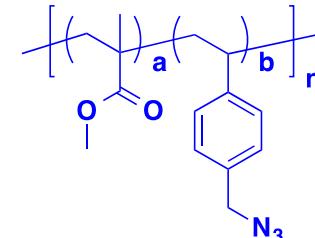
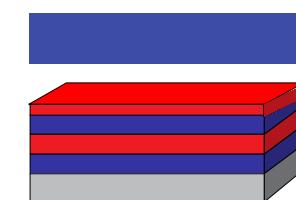
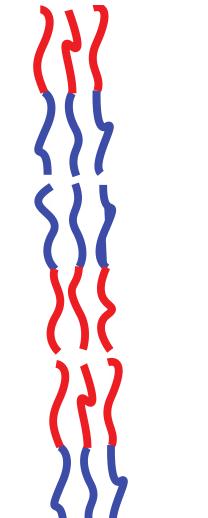
# Thin film orientation



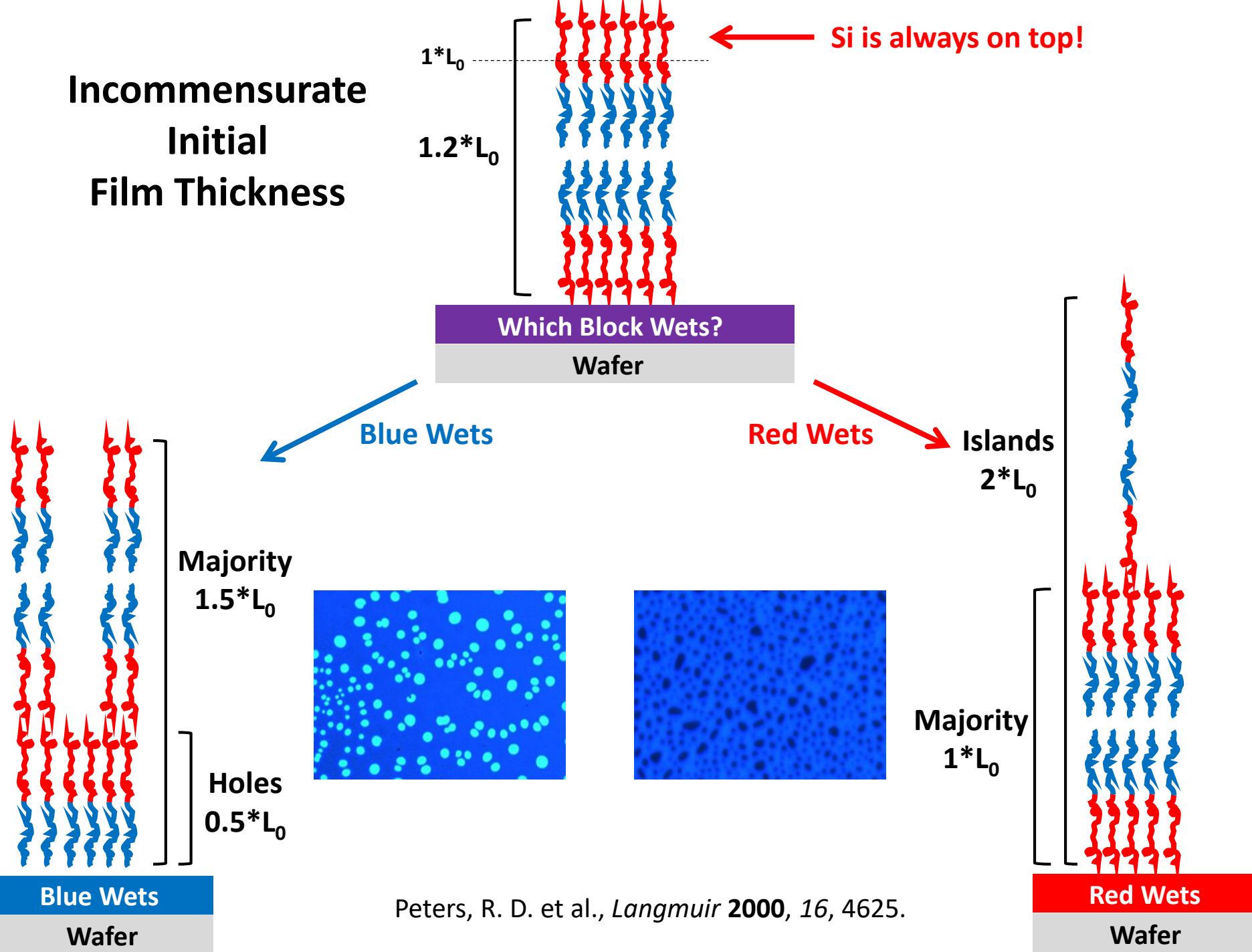
ChE 384T / 323



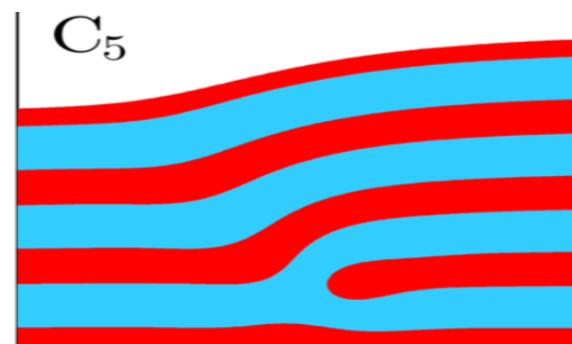
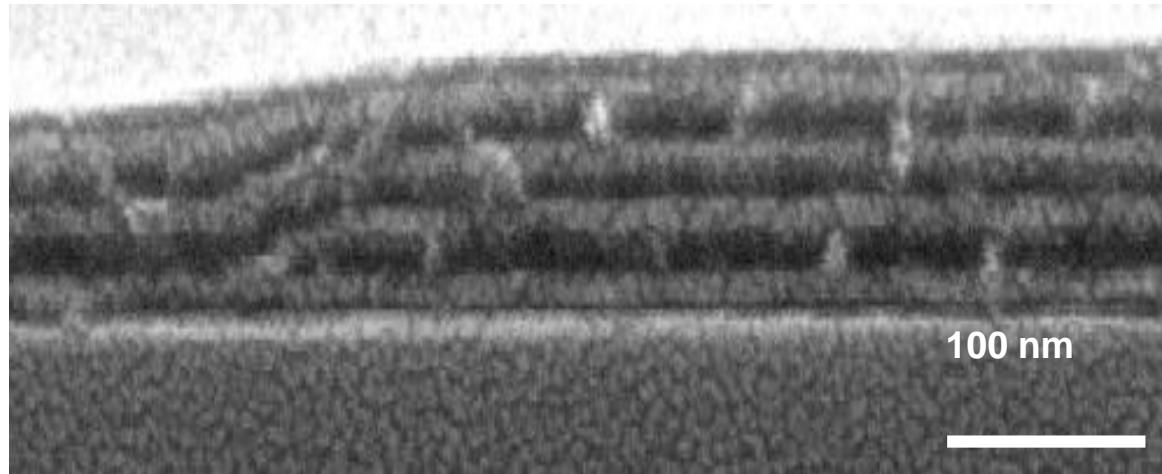
Bang et al. *Adv. Mater.* 2007, 19, 4552



# Incommensurate Initial Film Thickness



# Formation of Islands and Holes



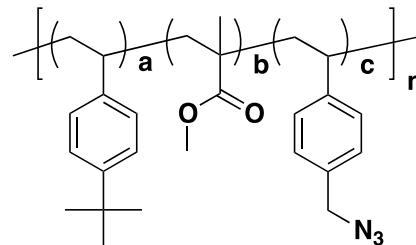
Maher, Michael, et al, JACS Nano **10(11)** 10152-10160 (2016)



# Finding the neutral composition

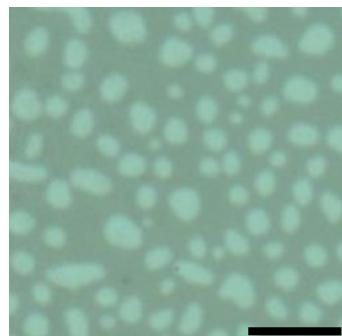
Surface treatment:

Initial BCB thickness:  $1.15 L_0$

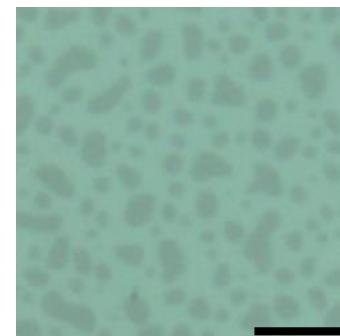


Percent PtBuS:

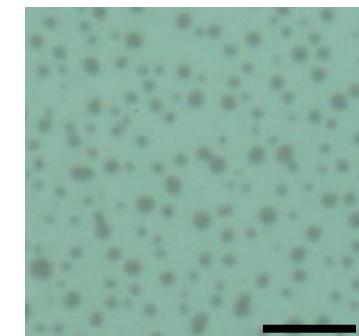
48%



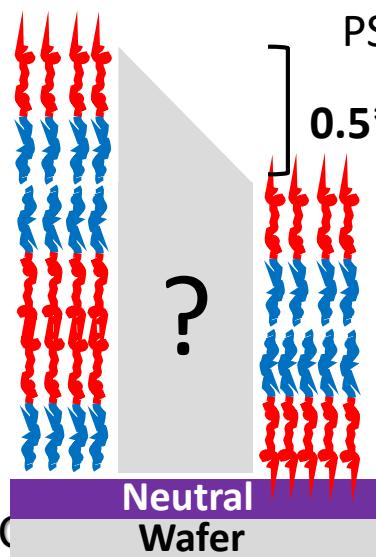
52%



65%



Result:

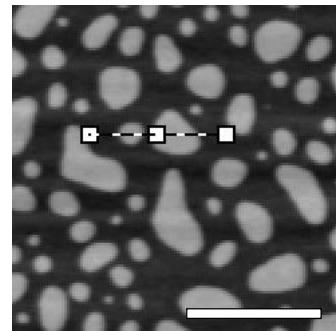


$1 L_0$  Holes  
PS wetting

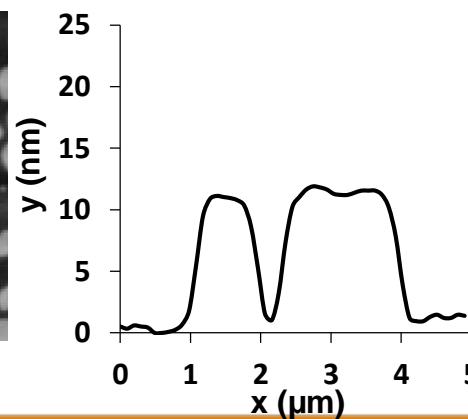
$0.5 * L_0$

$0.5 L_0$  Islands  
PS and PTMSS wetting!

$1 L_0$  Islands  
PTMSS wetting

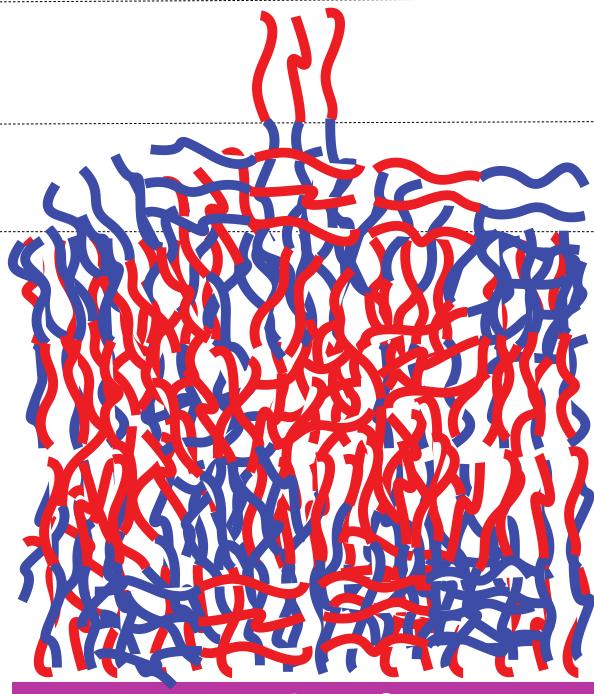
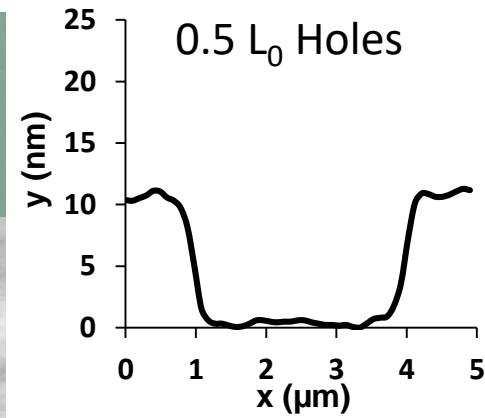
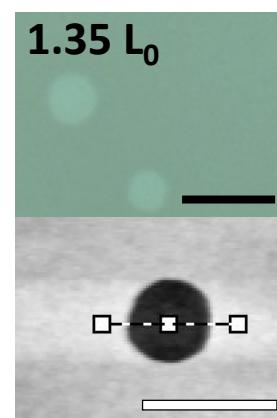
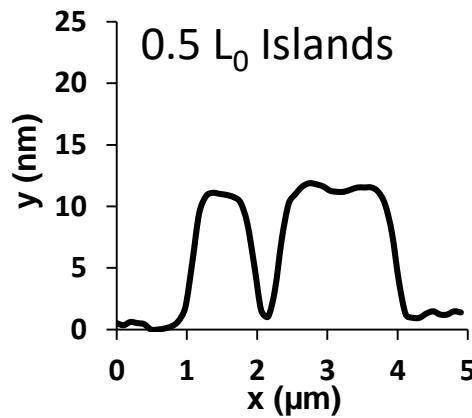
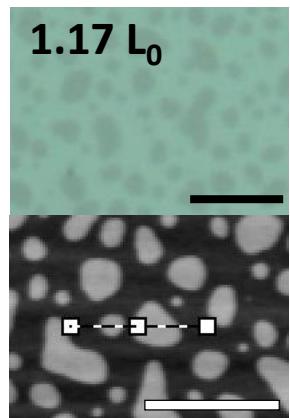


Scale bars are  $5 \mu\text{m}$

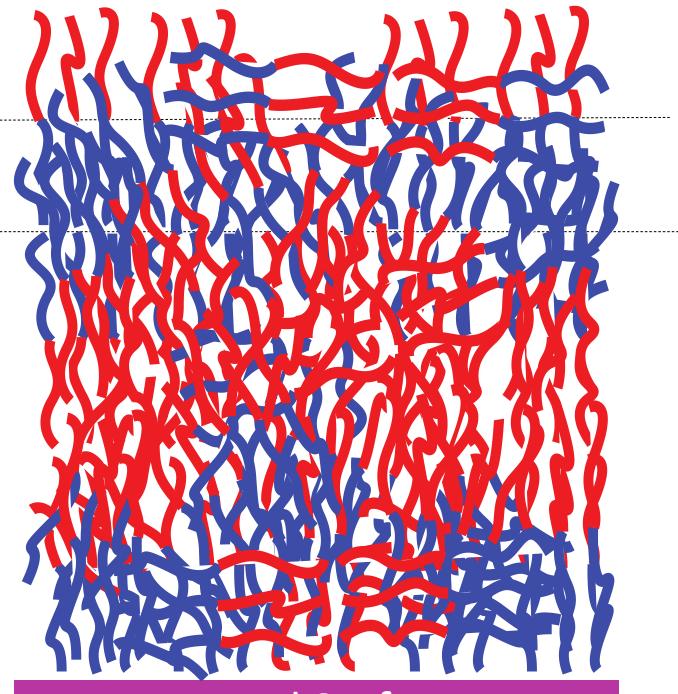


# Half $L_0$ features on a neutral surface

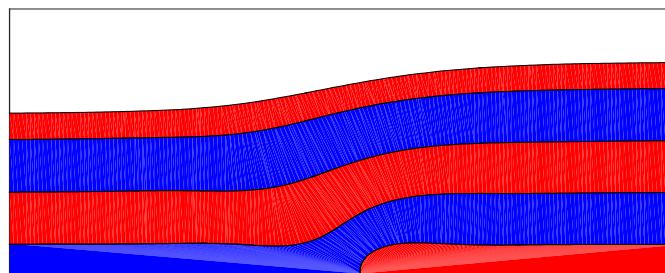
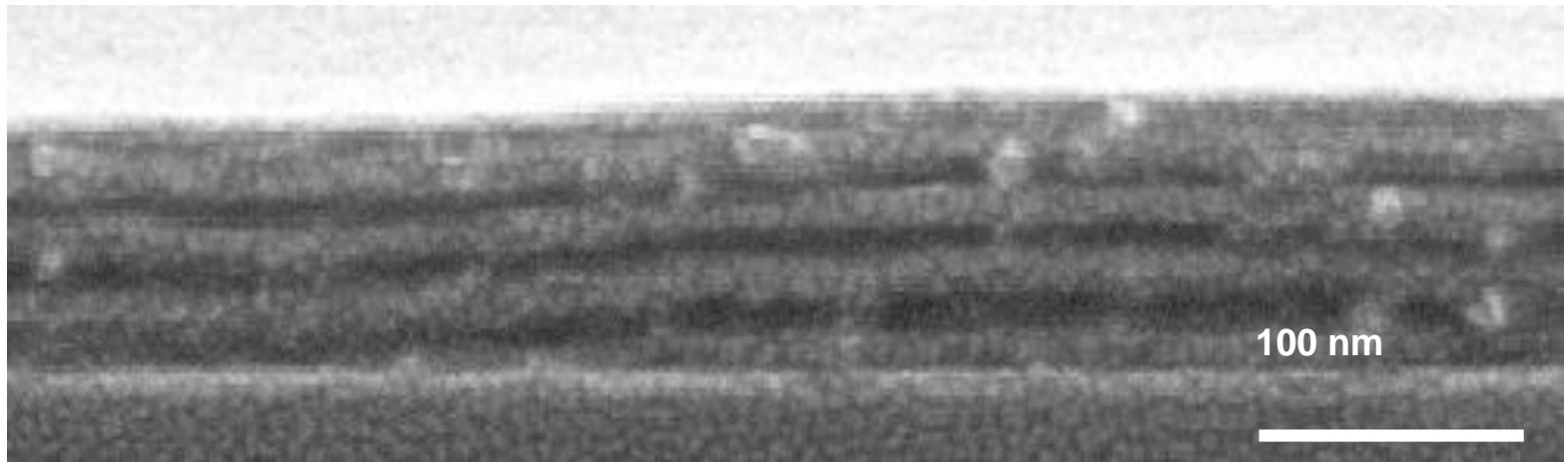
Kim et al. ACS Nano. 2013, 7, 9905.



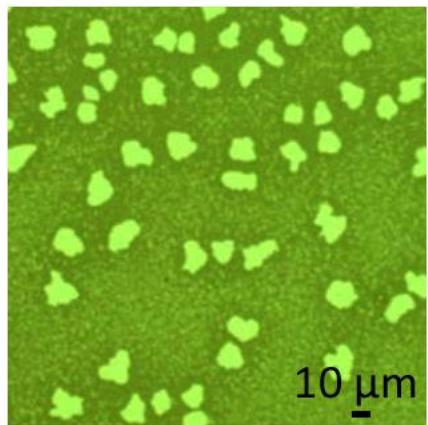
Scale bars are 5  $\mu\text{m}$



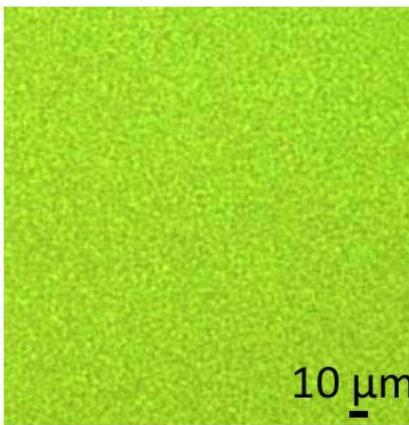
# Formation of $\frac{1}{2}$ Islands and holes on a neutral surface



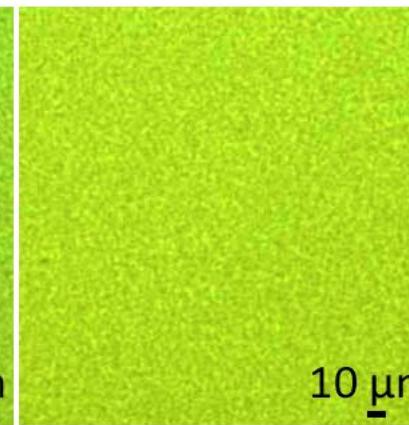
22%



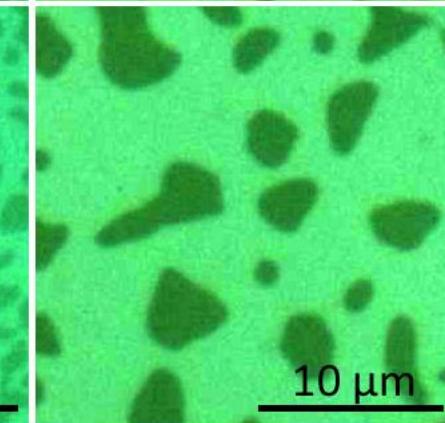
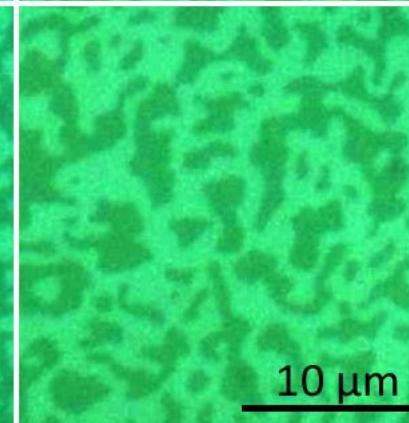
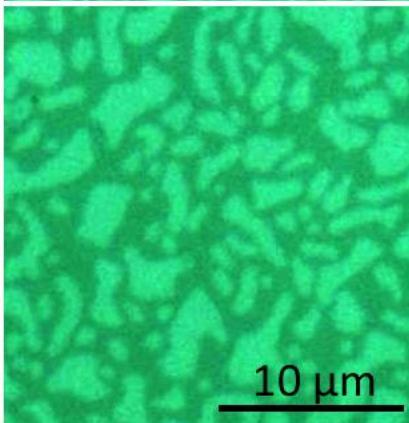
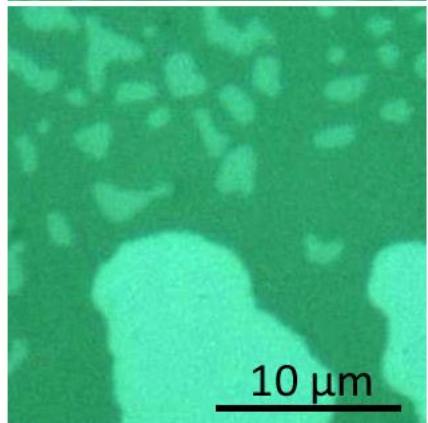
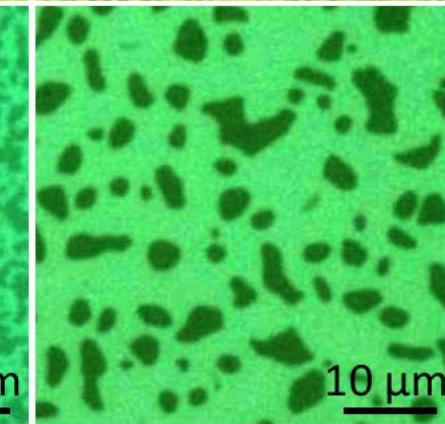
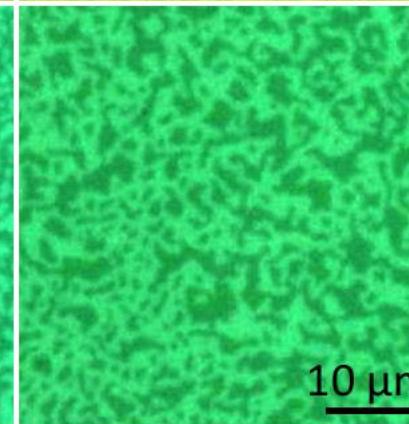
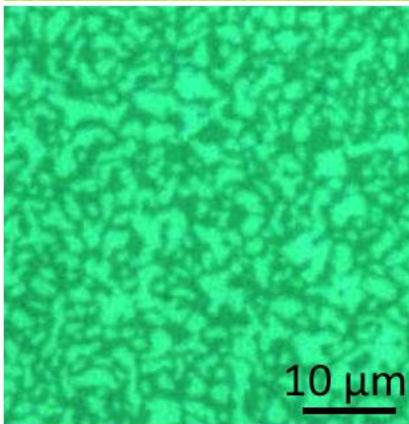
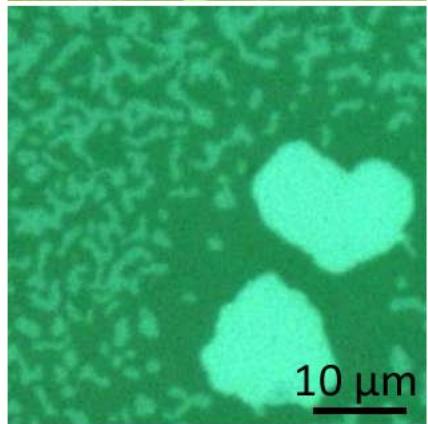
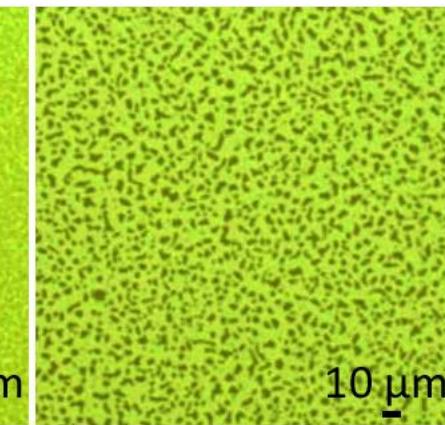
23%



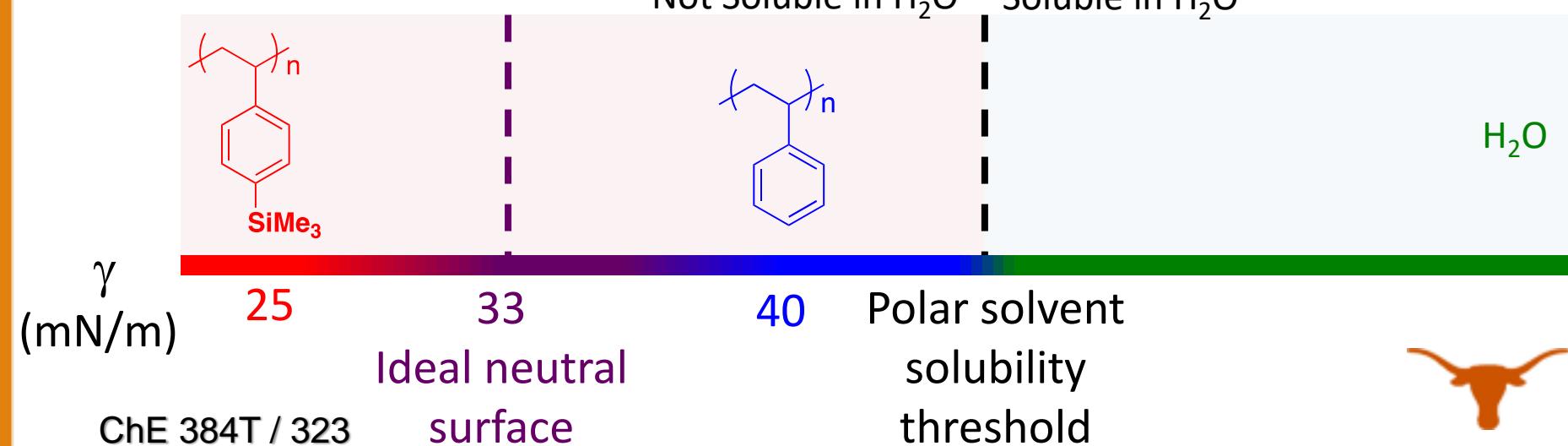
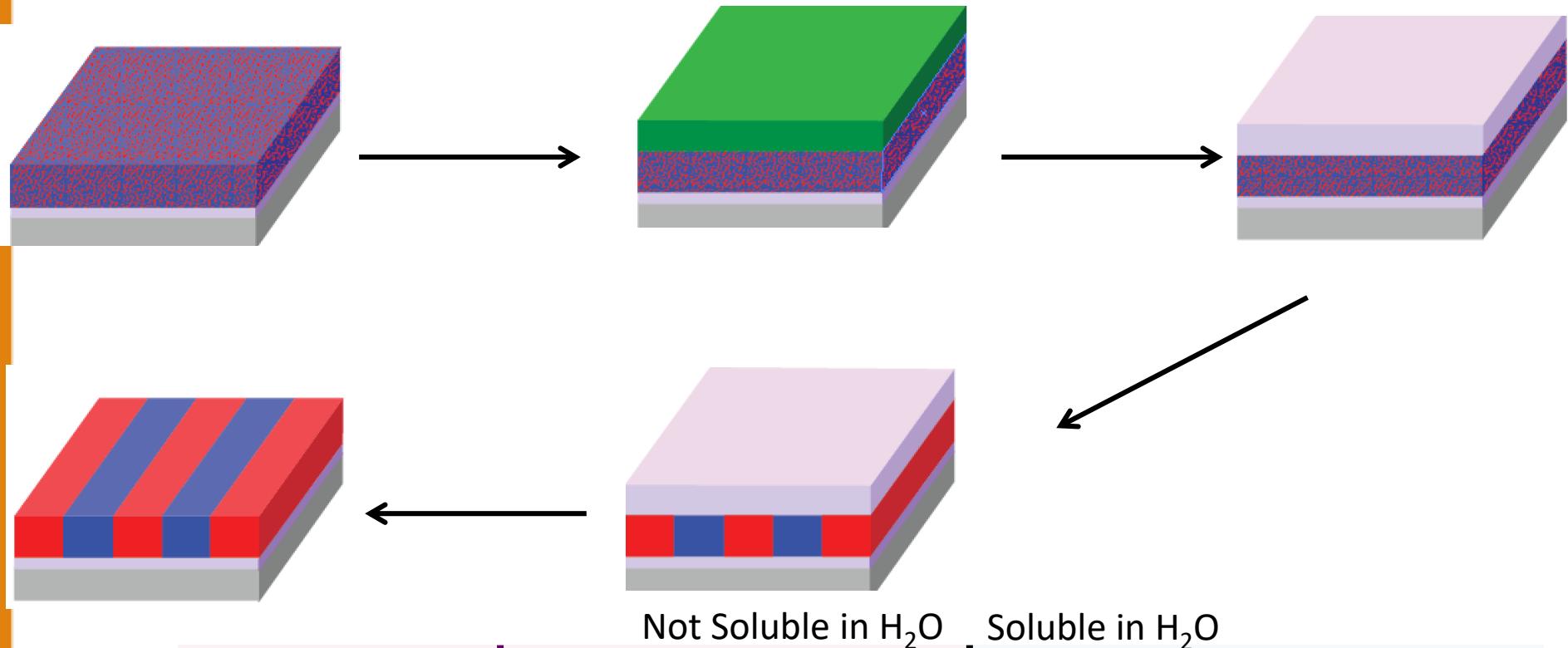
25%



28%



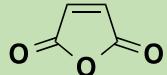
# Top Interface Challenge



# Top Coat Chemistry

## Requirements

1. Polarity switch

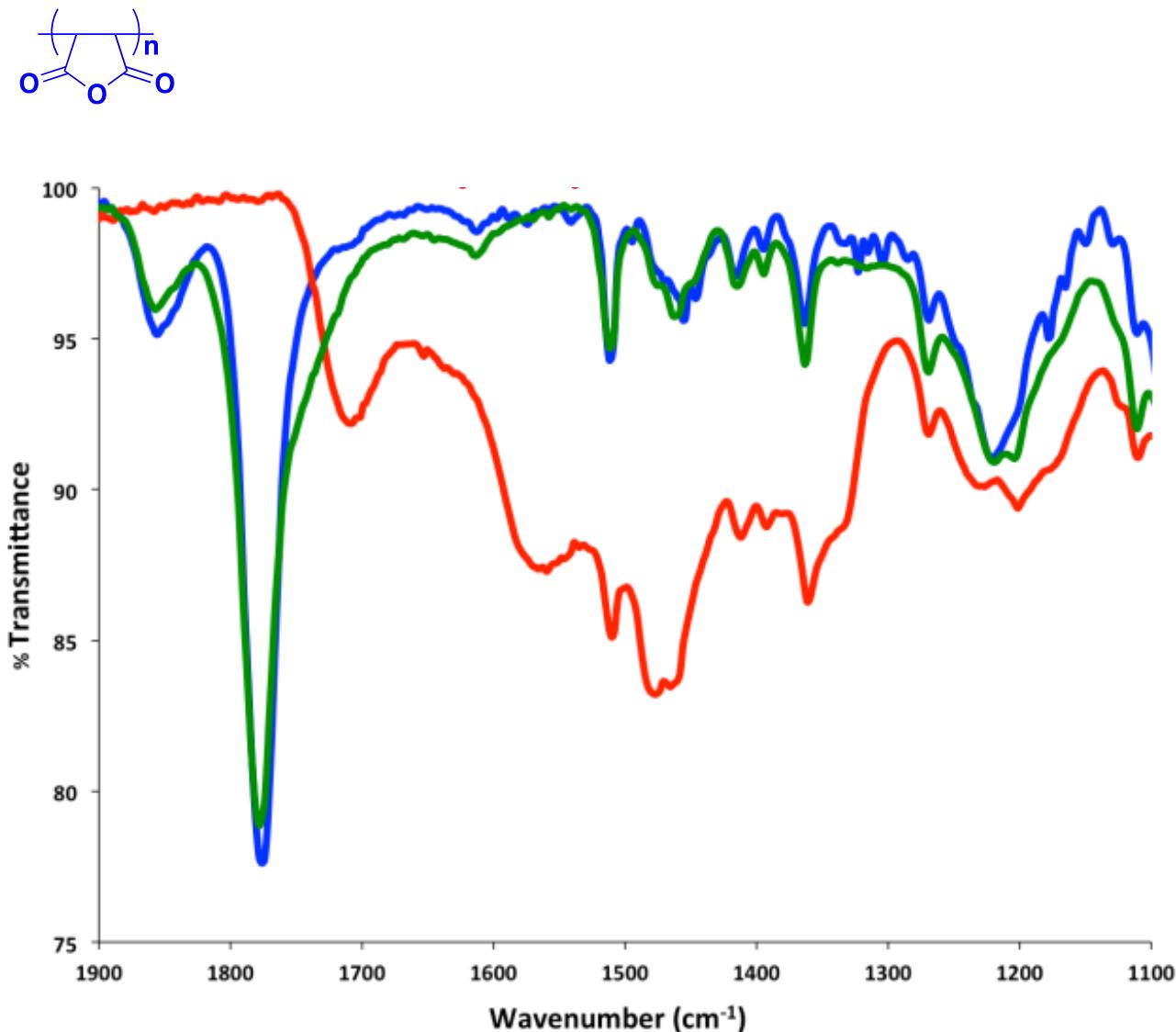


2.  $T_g$  greater than blocks

$$PS = 105 \text{ } ^\circ\text{C}$$

$$PTMSS = 135 \text{ } ^\circ\text{C}$$

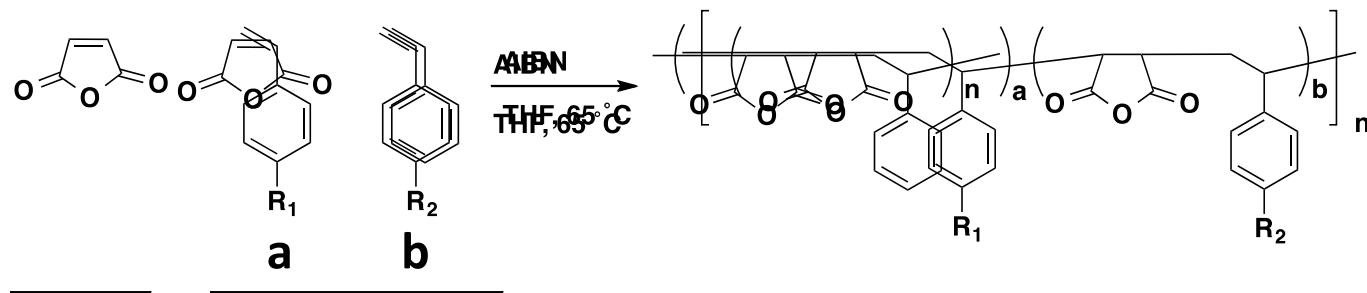
3. Surface energy control



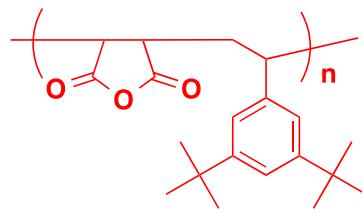
Maher, M., et al. *Chem. M*  
**2014**, 26, 1471

Bates, C., et al. *Science* **20**  
338, 775

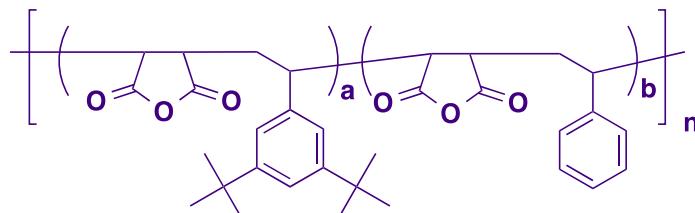
# Top Coat Design



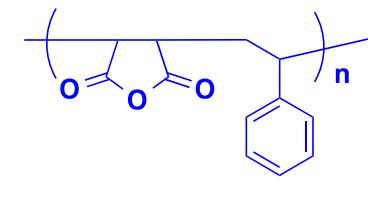
Mol fraction: 0.5       $a + b = 0.5$



PTMSS Preferential



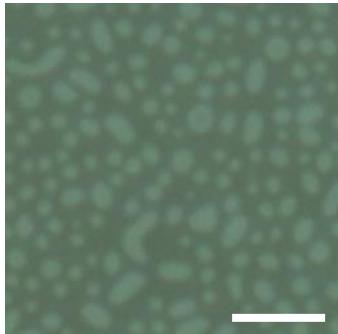
Neutral



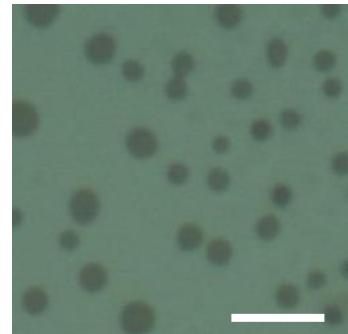
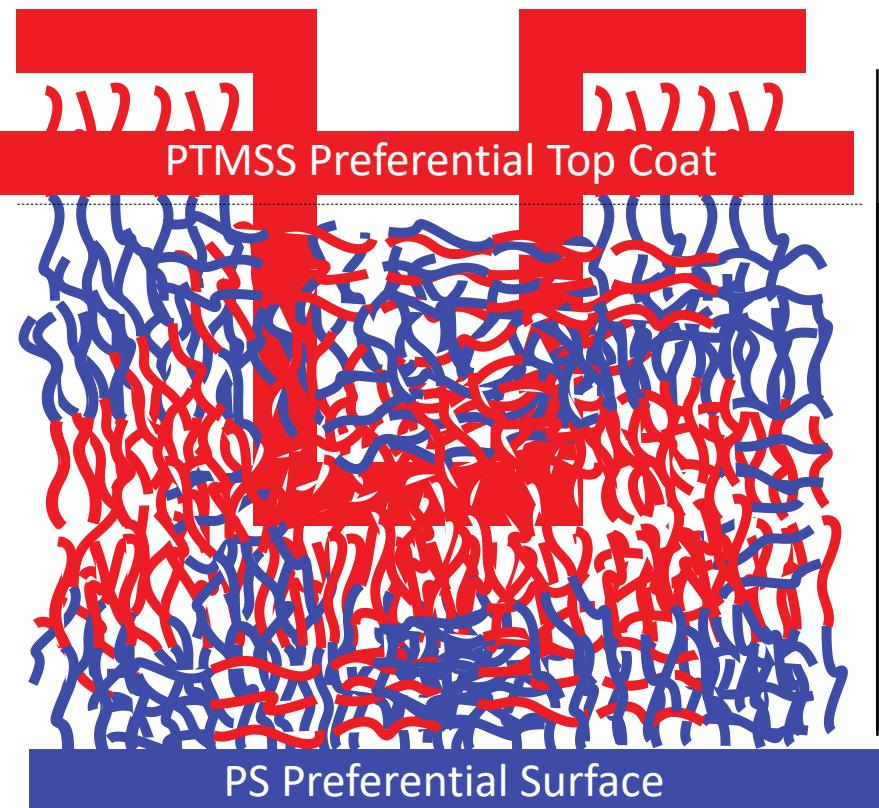
PS Preferential



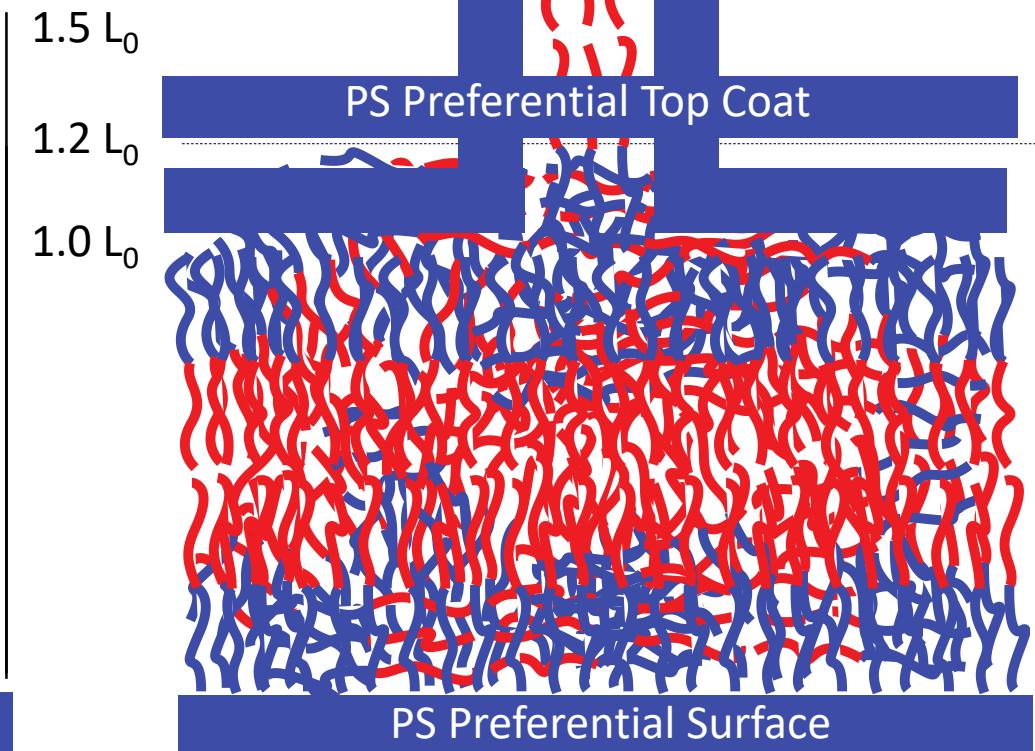
# Confined Island Hole test



Holes

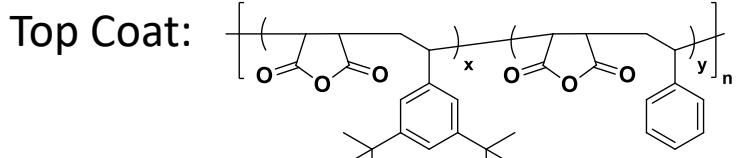


Islands

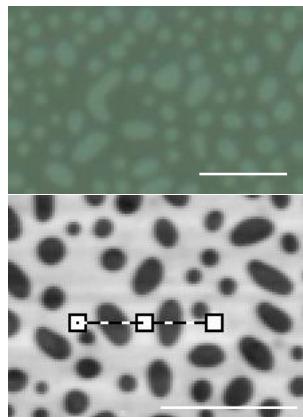


# Confined island hole results for 22 nm diblock

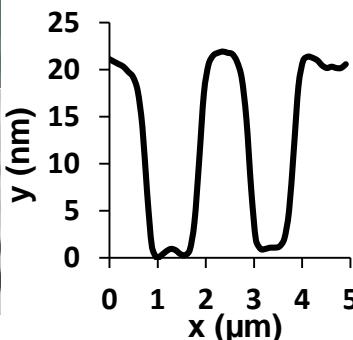
Initial BCP thickness:  $1.19 L_0$



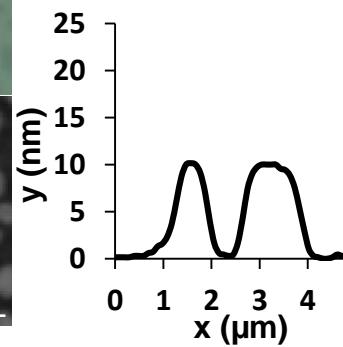
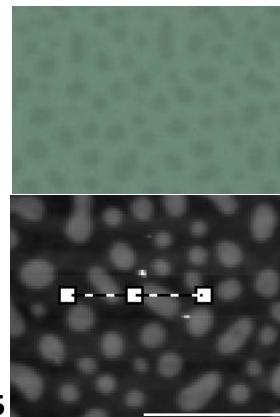
49% di-tBuS



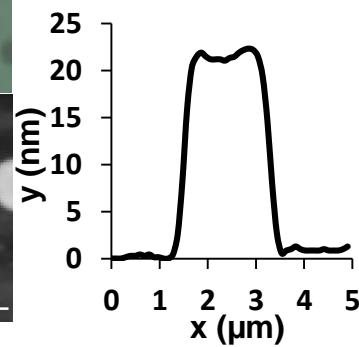
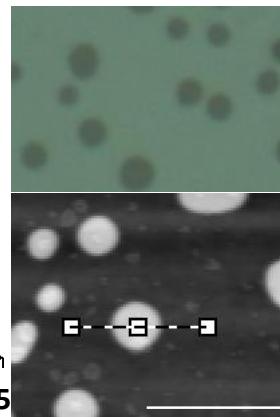
All scale bars = 5  $\mu\text{m}$



25% di-tBuS



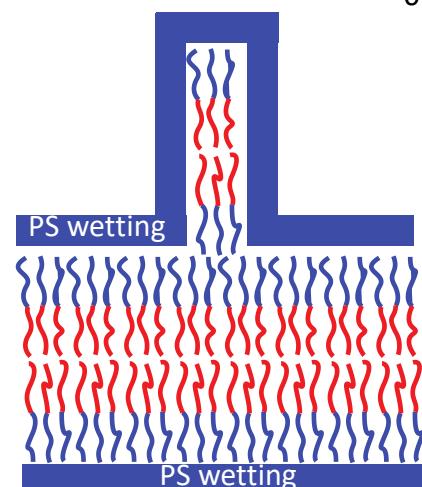
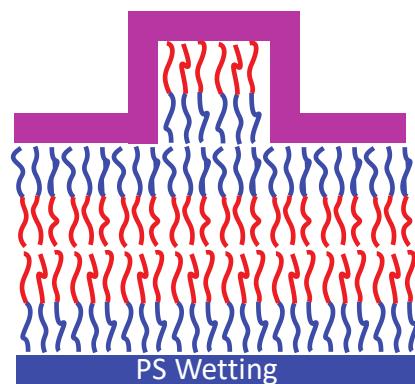
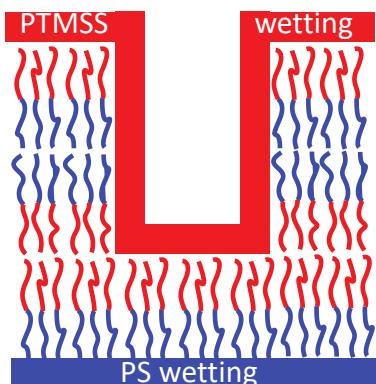
12% di-tBuS



22 nm holes =  $1 L_0$

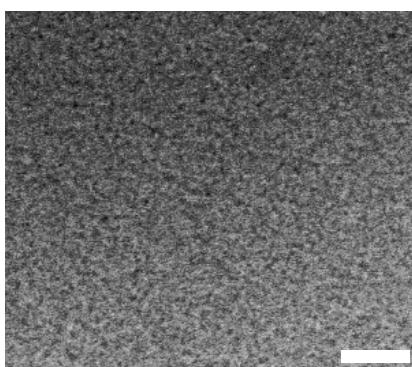
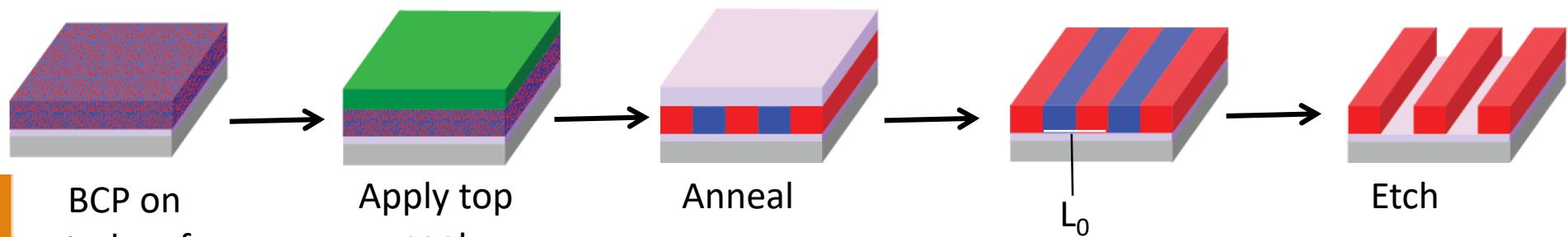
10 nm islands = 0.5  $L_0$

22 nm islands =  $1 L_0$

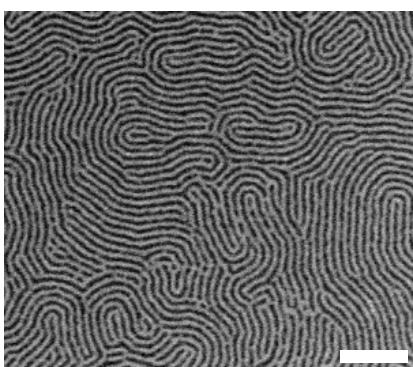


# Orientation Results

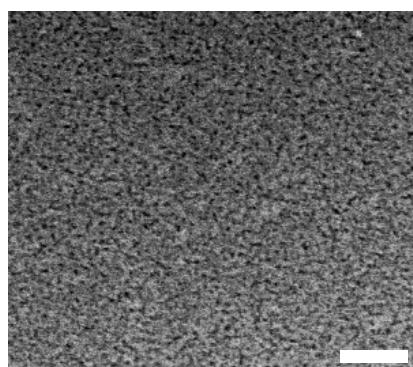
Maher et al. *Chem. Mater.* 2014, 26, 1471



$1.0 L_0$



$1.5 L_0$



$2.0 L_0$

$L_0$

PTMSS Preferential  
Interfaces

Etch

$3.0 L_0$

If both surfaces are truly neutral, alignment is perpendicular for all film thicknesses.