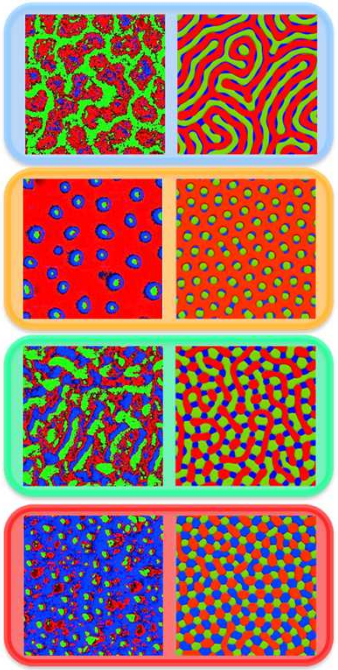
SAND2016-2965C

Exceptional service in the national interest

Sandia National Laboratories



Phase Behavior of Self-Assembled Ternary Polymer Brushes

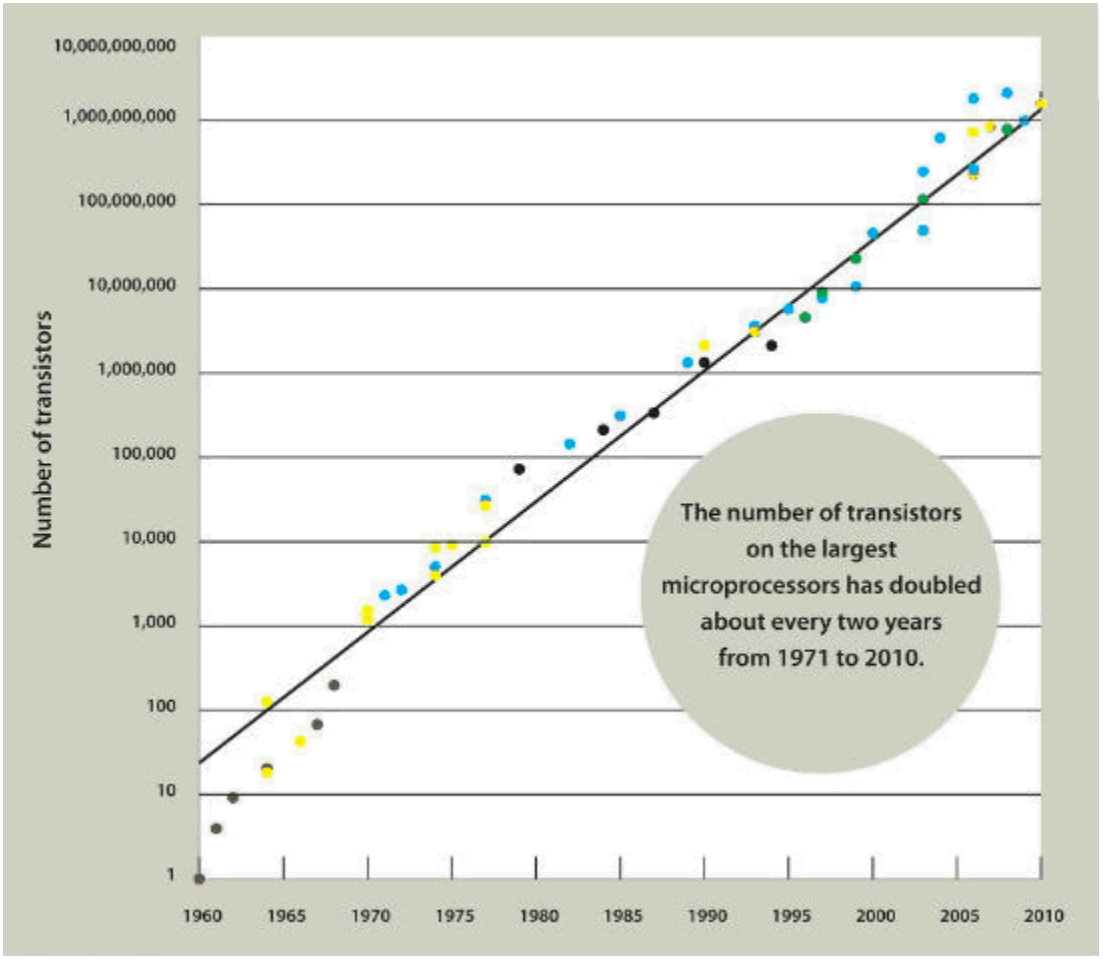
Chester K. Simocko, Amalie Frischknecht, Dale Huber
Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, NM

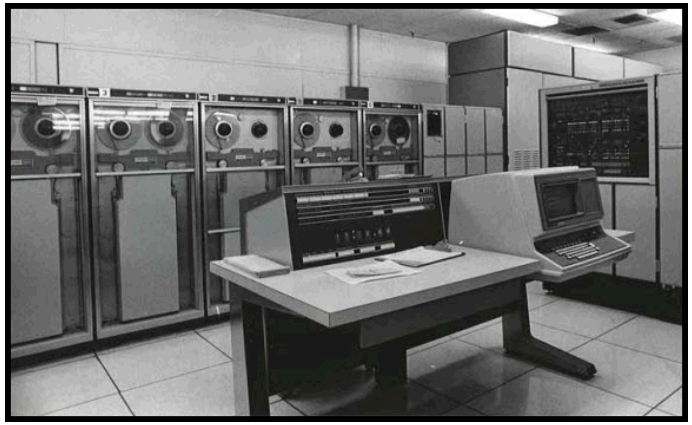
U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Smaller and Smaller

Sandia National Laboratories





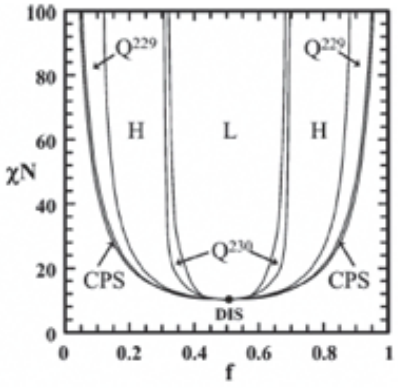
http://www.computerhistory.org/atchm/moores-law50-the-most-important-graph-in-human-history/

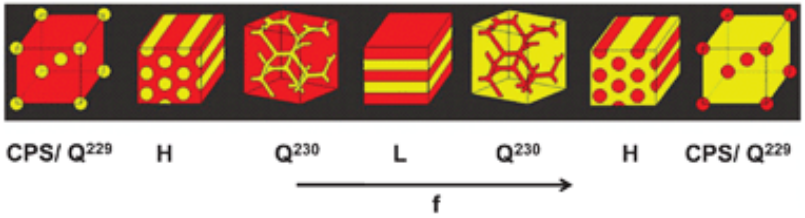
Block Copolymer Self- Assembly

Sandia National Laboratories

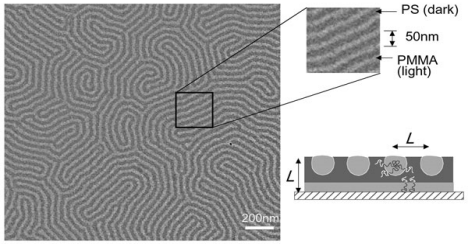
Block copolymers

- Two or more polymer blocks bound into a single chain
- Behave as immiscible polymer blends
- Due to covalent binding, phase separation is limited





Polymer A Polymer B



Block copolymers can self-assemble into a variety of microstructures.

Two main parameters determine what microstructure the block copolymer adopts

- f= polymer fraction
- χN = segregation force
  - χ = interaction parameter
  - N = number of repeat units

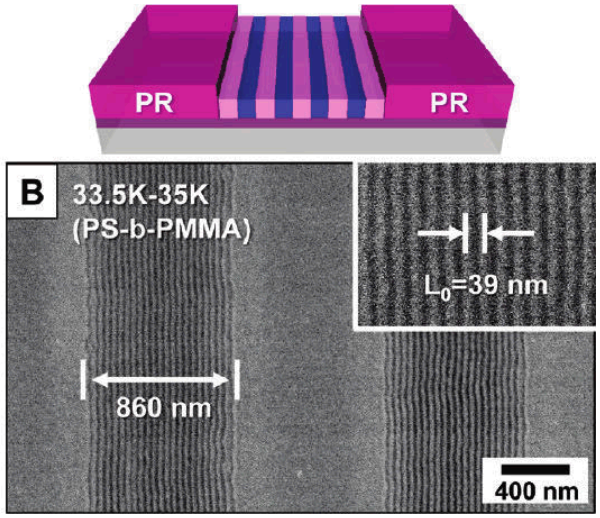
Phase separation occurs at $\chi N \approx 10.5$

Lopes, W.A.; Jaeger, H.M. *Nature*, 414, 735
Orilall, M.; Wiesner, U. *Chem. Soc. Rev.*, 2011, 40, 520–535

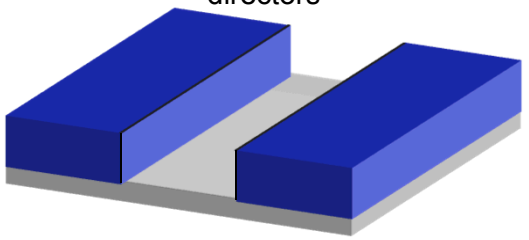
Block Copolymer Lithography

Polymer Lithography

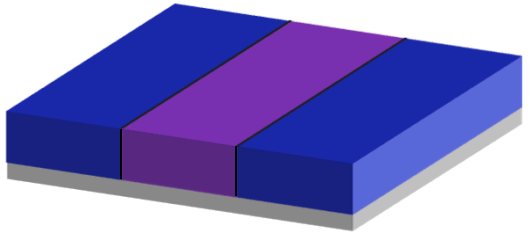
- Microscale directors are patterned on the surface
- Block copolymers are spin coated onto the pattern
- Annealing the block copolymer allows the different polymers to phase separate



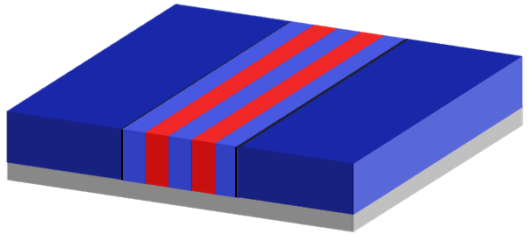
1. Template microscale directors



2. Spin coat block copolymers



3. Anneal to induce phase separation



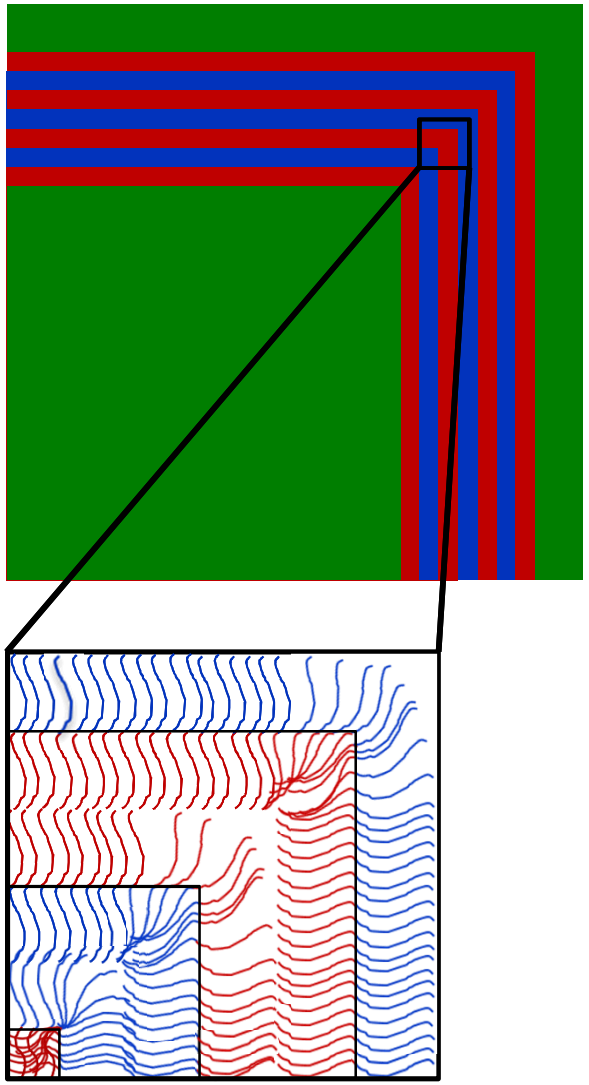
Jeong, S.J. *et al., Nanoletters,* ***2009,*** *9(6),* 2300

Drawbacks of Block Copolymer Lithography

Sandia National Laboratories

Drawbacks

- Difficult to purify
- Not bound to the surface, can be washed or abraded off
- Lateral phase separation can only be achieved on planar surfaces
- Certain architectures can be difficult to achieve without the use of triblock copolymers

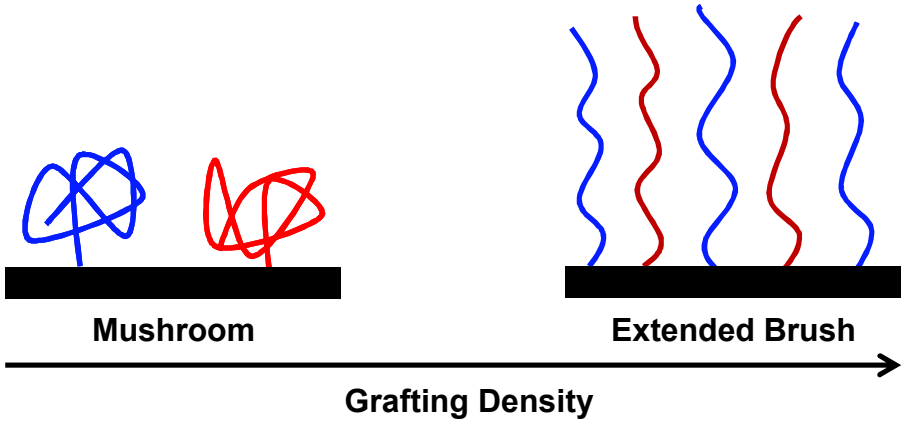


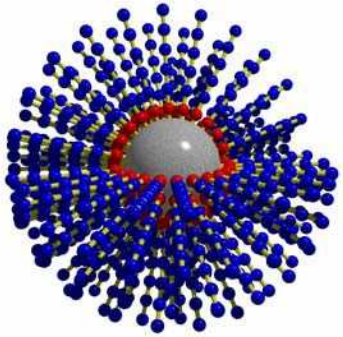
So how do we solve these problems?

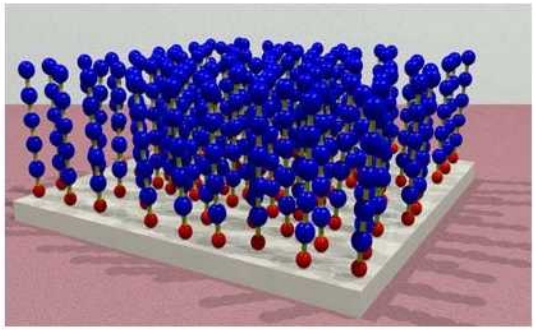
Mixed Polymer Brushes

Polymer Brushes

- Polymers attached to a surface
- Grafting density controls polymers conformation
  - Low density – Mushroom
  - High density – Extended Brushes







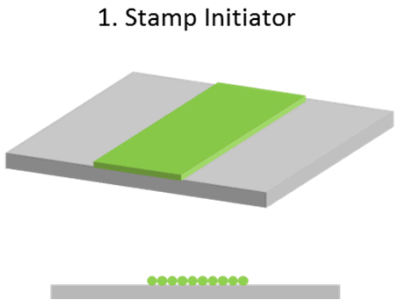
Mixed Polymer Brushes

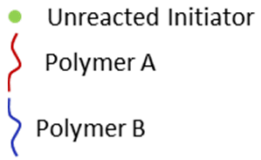
- Phase separate similar to block copolymers
- Allows for patterning on many different surface geometries and features
- Mechanically and physically more robust than block copolymers due to covalent binding to the surface

Matyjaszewski, K.; *ATRP on Surfaces, http://www.cmu.edu/maty/atrp-how/procedures-for-initiation-of-ATRP/atrp-from-surfaces.html*

Brush Lithography

Like block copolymers, mixed polymer brushes can also take advantage of polymer lithography

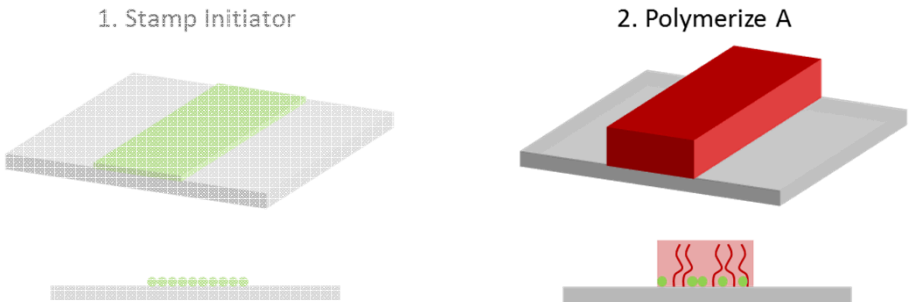




US Patent #8,652,768, Huber and Frischknecht.

Brush Lithography

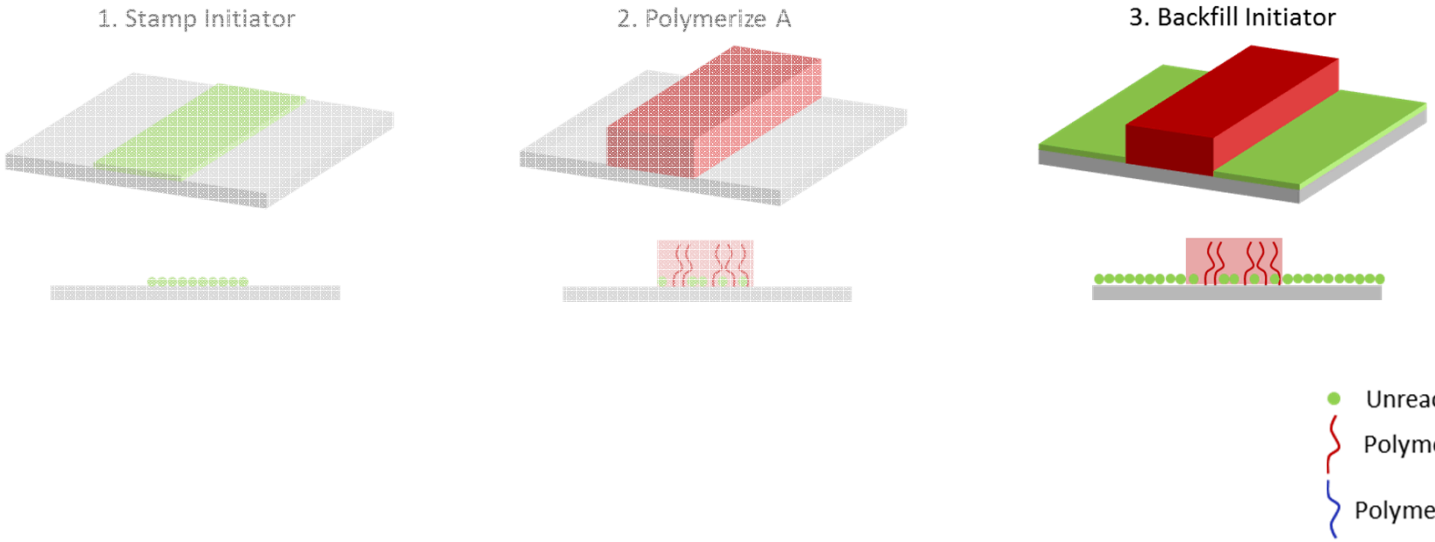
Like block copolymers, mixed polymer brushes can also take advantage of polymer lithography



US Patent #8,652,768, Huber and Frischknecht.

Brush Lithography

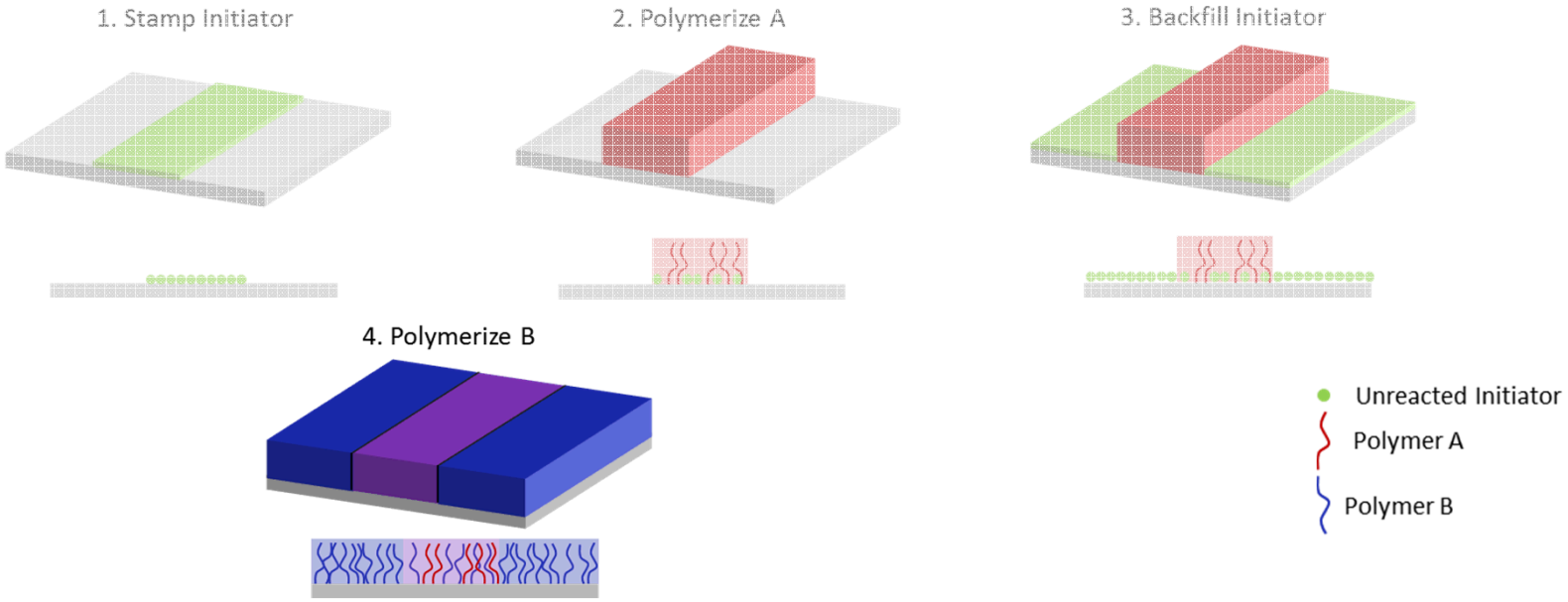
Like block copolymers, mixed polymer brushes can also take advantage of polymer lithography



US Patent #8,652,768, Huber and Frischknecht.

Brush Lithography

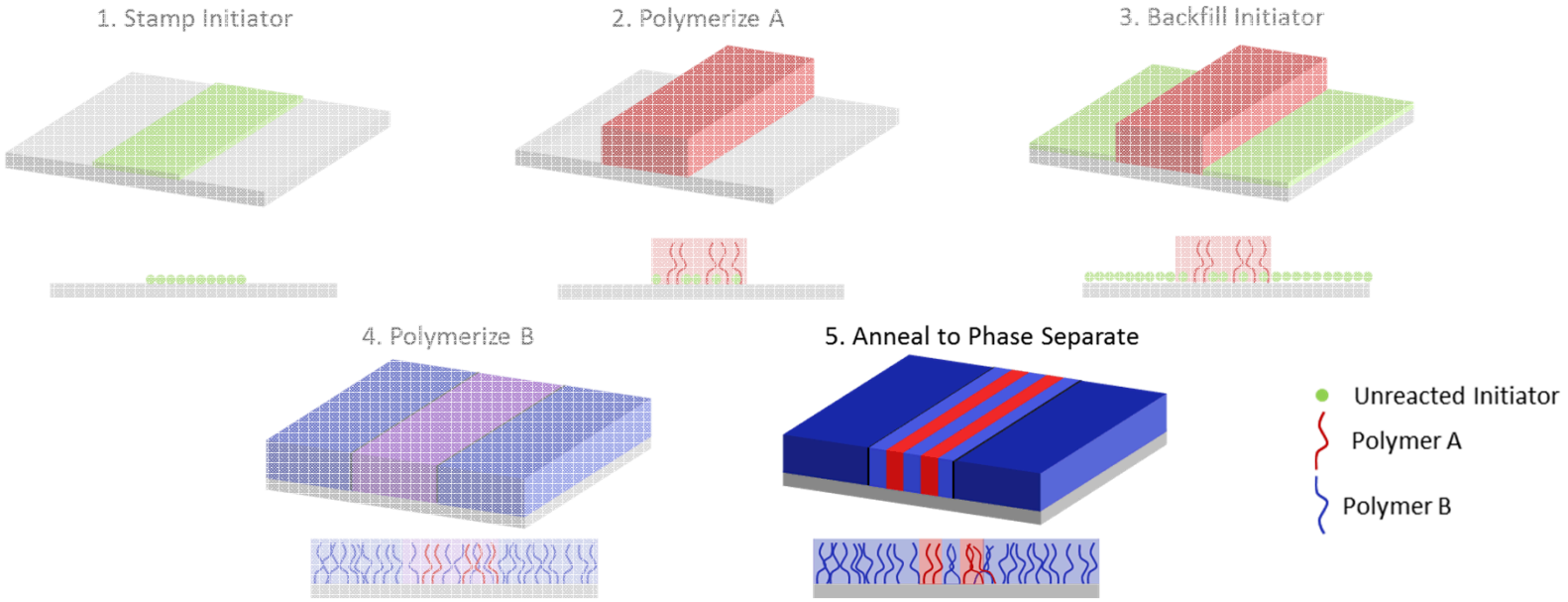
Like block copolymers, mixed polymer brushes can also take advantage of polymer lithography



US Patent #8,652,768, Huber and Frischknecht.

Brush Lithography

Like block copolymers, mixed polymer brushes can also take advantage of polymer lithography



But first we need to study the phase behavior of the brushes

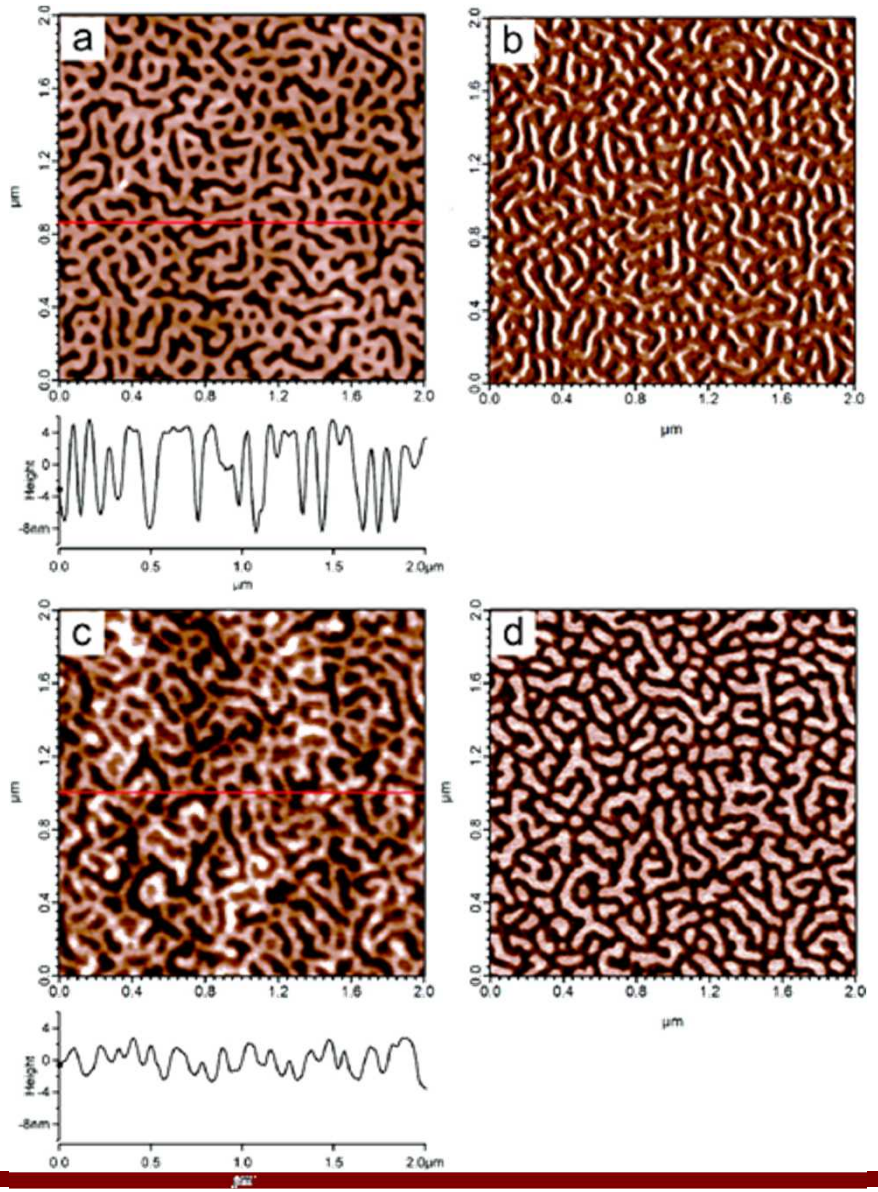
US Patent #8,652,768, Huber and Frischknecht.

Self-Assembly of Binary Polymer Brushes

Sandia National Laboratories

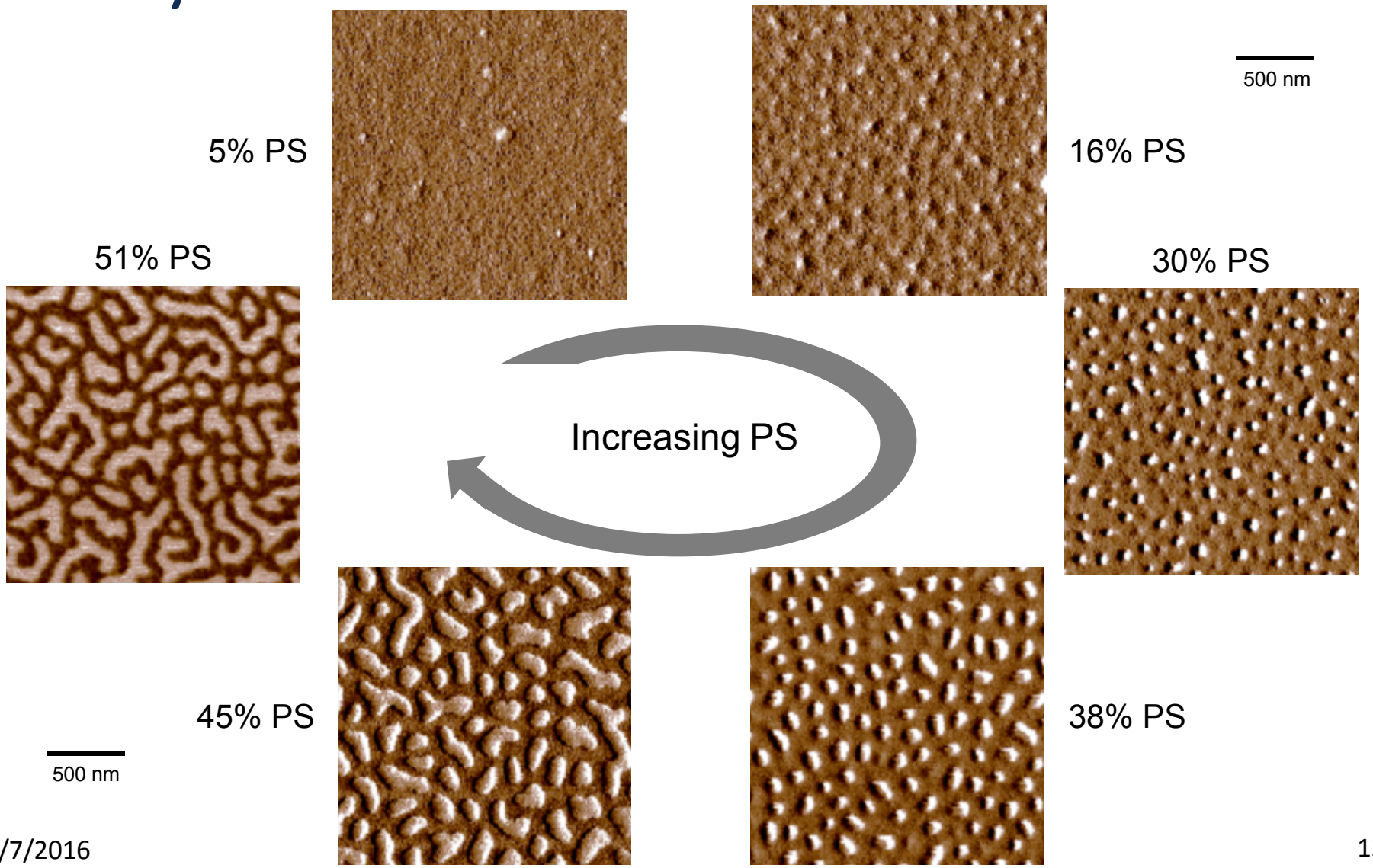
Brush Characterization

- Brushes were synthesized from poly(methyl methacrylate) (PMMA) and polystyrene (PS)
- Solvent vapor and thermally annealed
- AFM was used to analyze phase behavior
- Annealing reduced surface roughness and increased phase contrast
- A number of phase morphologies were observed based the polymer composition of the brush



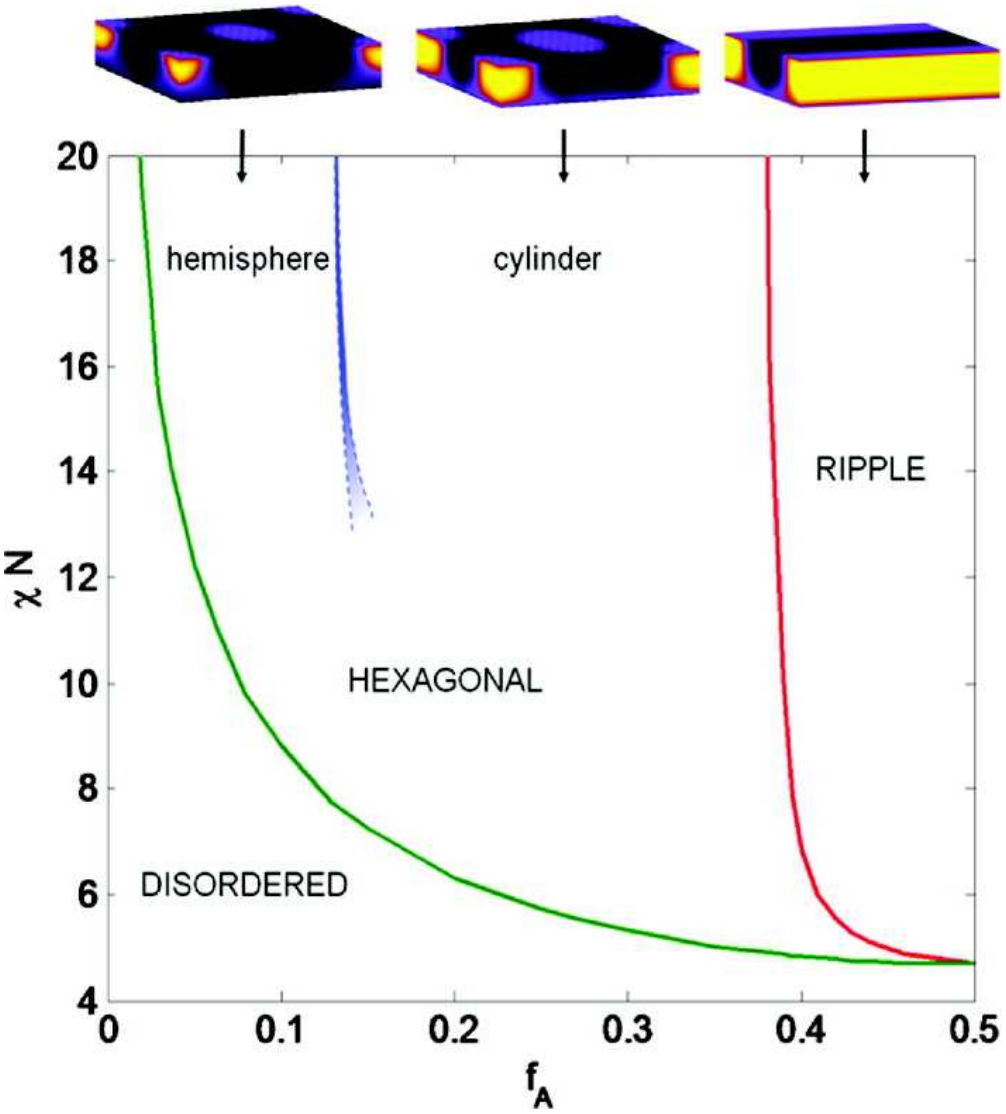
Price, A.P.; Hur, S.M., Fredrickson, G.H.; Frischknect, A.L.; Huber, D.L.. *Macromolecules.* 2012, *45,* 510-524

Controlling Self-Assembly of Binary Polymer Brushes



Price, A.P.; Hur, S.M., Fredrickson, G.H.; Frischknect, A.L.; Huber, D.L.. *Macromolecules.* 2012, *45,* 510-524

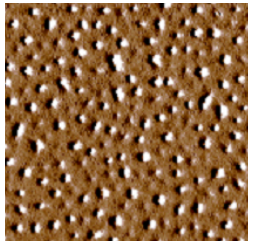
Phase Diagram



5% PS

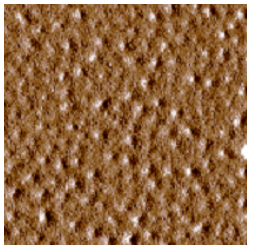
Disordered

30% PS



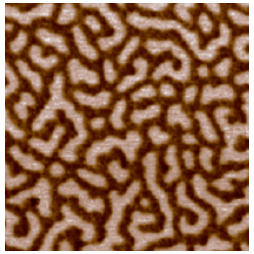
Cylinder

16% PS



Hemisphere

51% PS



Ripple

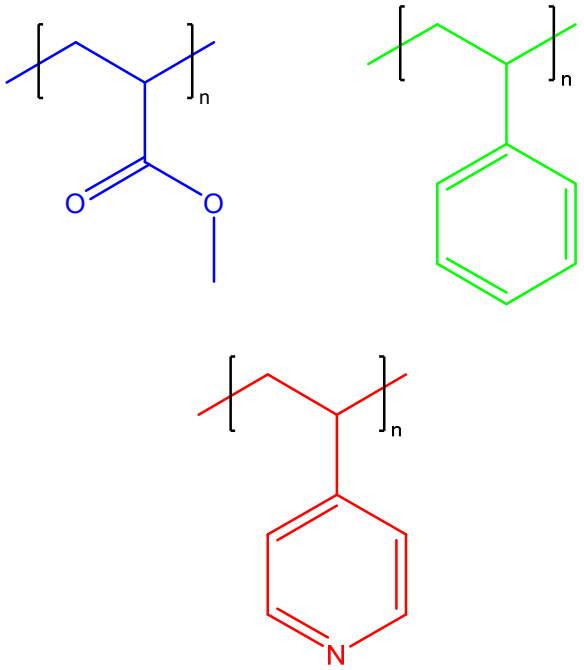
Self Consistent Field Theory (SCFT) predicts a number of phase regimes

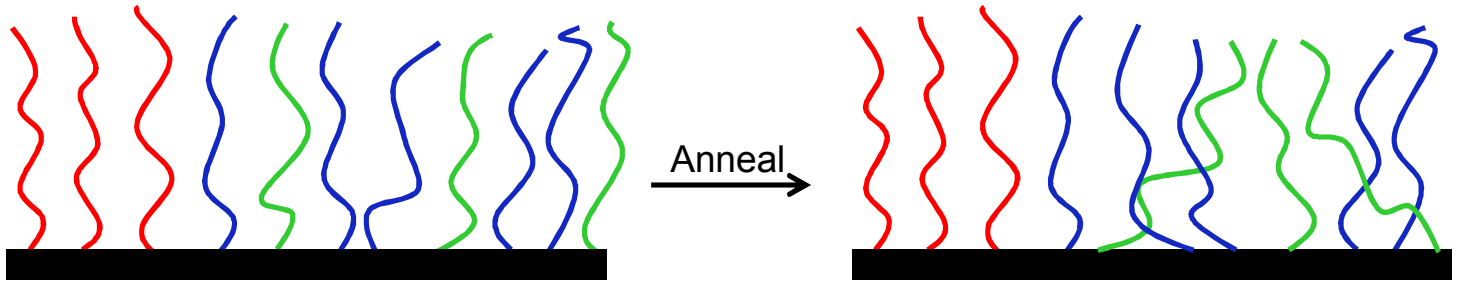
Price, A.P.; Hur, S.M., Fredrickson, G.H.; Frischknect, A.L.; Huber, D.L.. *Macromolecules.* 2012, *45,* 510-524

Ternary Polymer Brushes

Ternary Brushes

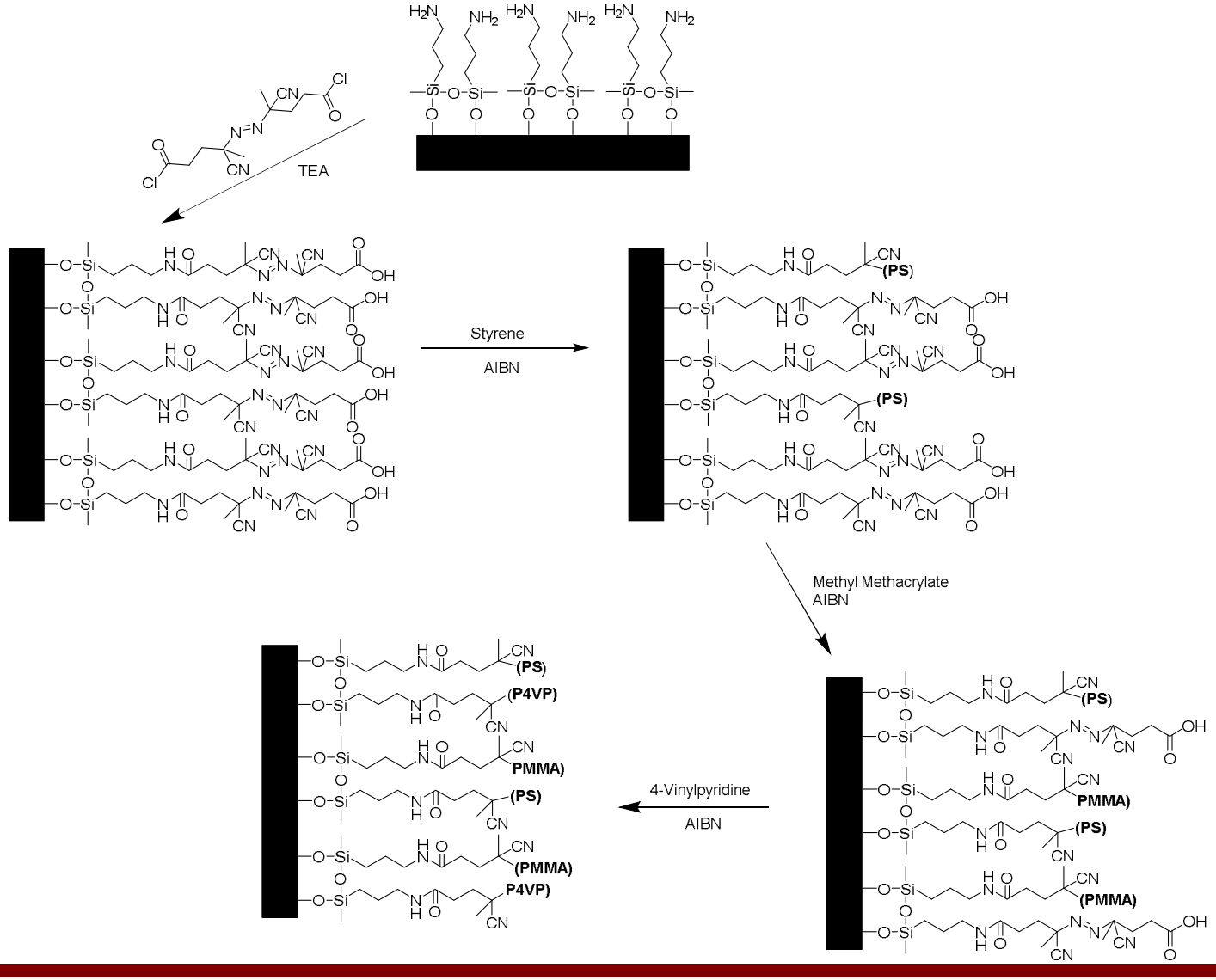
- Consists of PMMA, PS, and P4VP
- Strongly segregating system
  - $\chi N_{PS\text{-}PMMA} \approx 18$
  - $\chi N_{PMMA\text{-}P4VP} \approx 65$
  - $\chi N_{PS\text{-}P4VP} \approx 320$
- AFM was used to analyze phase behavior
- Results in varied and unique phase regimes
- Correlate results with SCFT and create a complete phase diagram





Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Surface Initiated Growth of Ternary Polymer Brushes

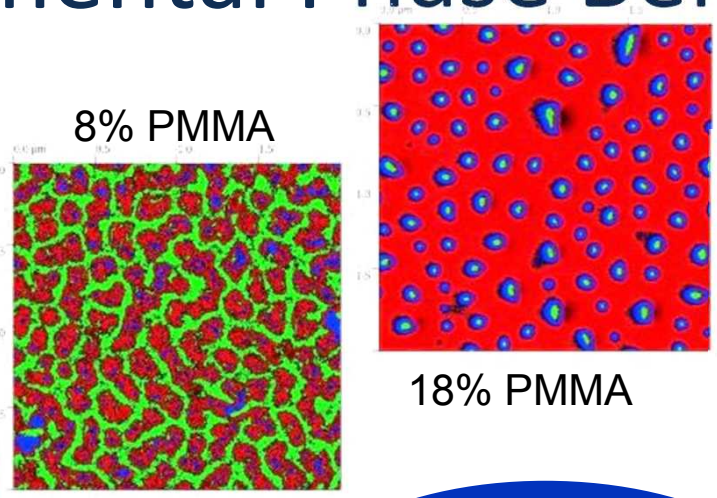


Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Experimental Phase Behavior

Sandia National Laboratories

PMMA
PS
P4VP

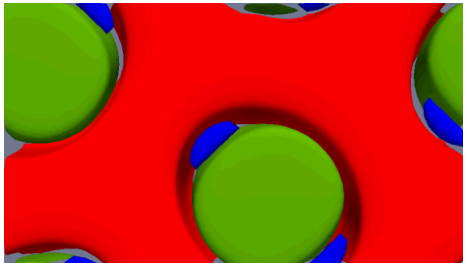


Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA



Decorated Cylinder

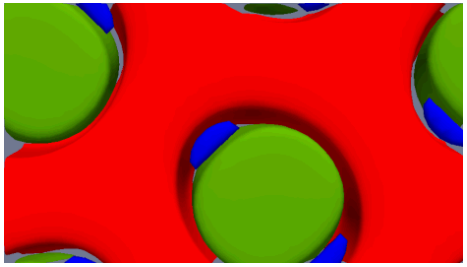
PMMA
PS
P4VP

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA



Decorated Cylinder

10% PMMA

Decorated Ripple

Increasing PMMA

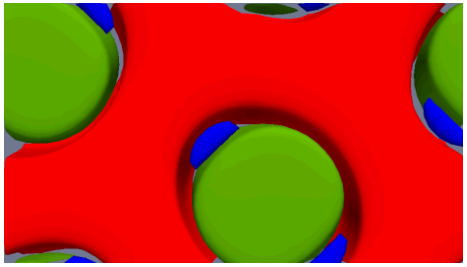
PMMA
PS
P4VP

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA

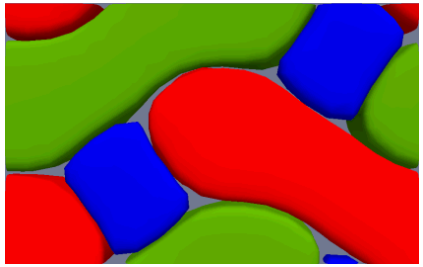


Decorated Cylinder

10% PMMA

Decorated Ripple

20% PMMA



Basket Weave

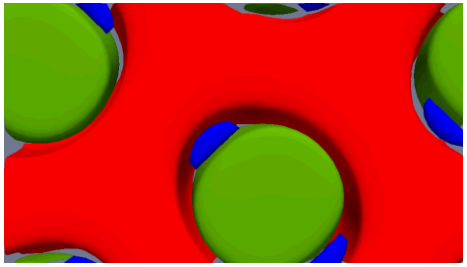
PMMA
PS
P4VP

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA

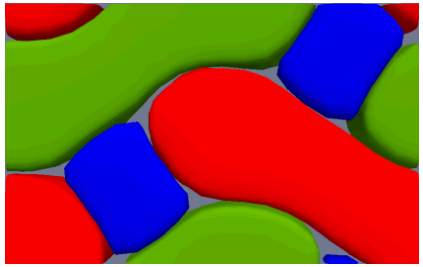


Decorated Cylinder

10% PMMA

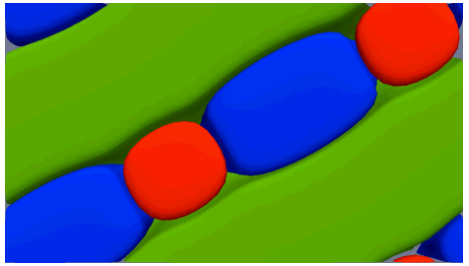
Decorated Ripple

20% PMMA



Basket Weave

30% PMMA



Segmented Ripple

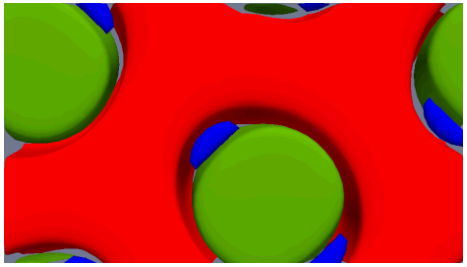
PMMA
PS
P4VP

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA

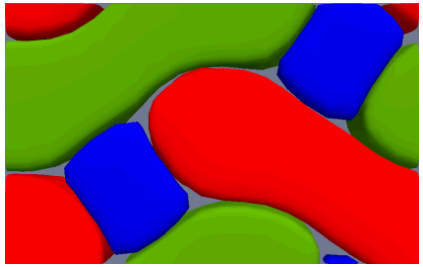


Decorated Cylinder

10% PMMA

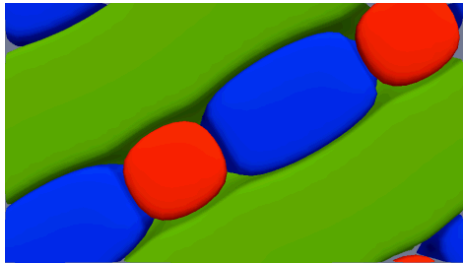
Decorated Ripple

20% PMMA

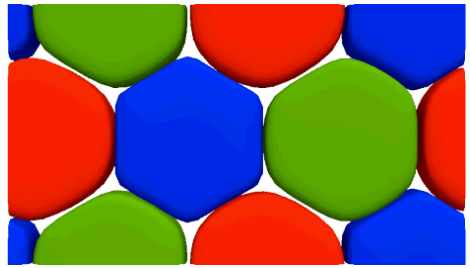


Basket Weave

30% PMMA



Segmented Ripple



Checkerboard

33% PMMA

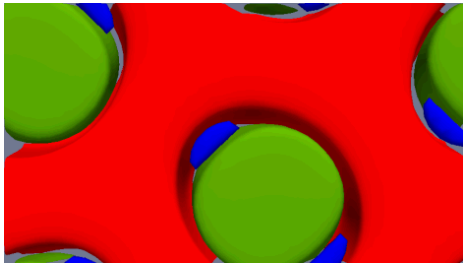
PMMA
PS
P4VP

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA

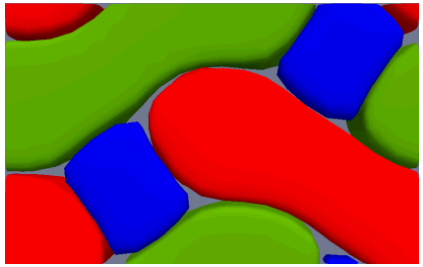


Decorated Cylinder

10% PMMA

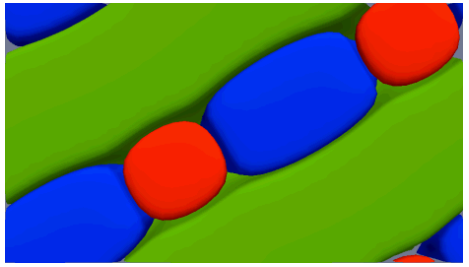
Decorated Ripple

20% PMMA



Basket Weave

30% PMMA

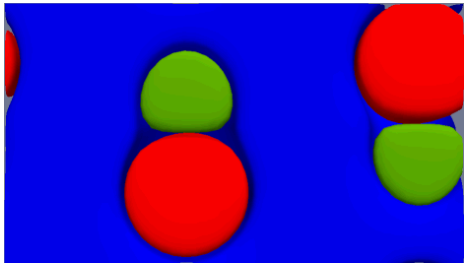


Segmented Ripple

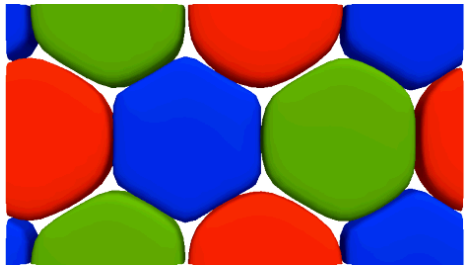
PMMA
PS
P4VP

Increasing PMMA

70% PMMA



Lobed Cylinder



33% PMMA

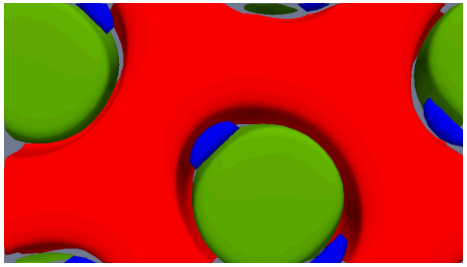
Checkerboard

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

SCFT Simulations of Ternary Brushes

Sandia National Laboratories

10% PMMA

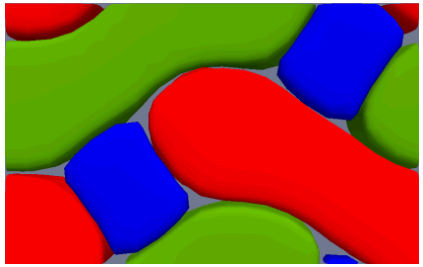


Decorated Cylinder

10% PMMA

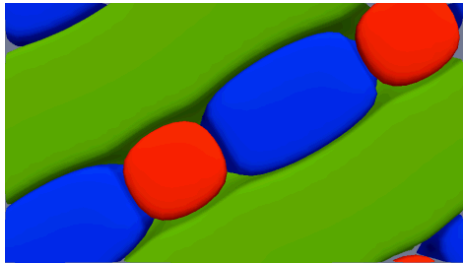
Decorated Ripple

20% PMMA



Basket Weave

30% PMMA

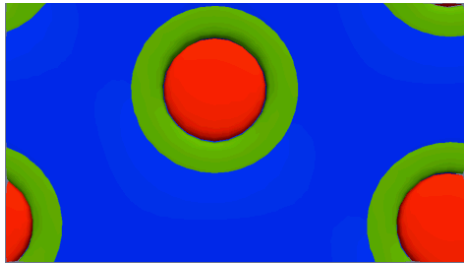


Segmented Ripple

PMMA
PS
P4VP

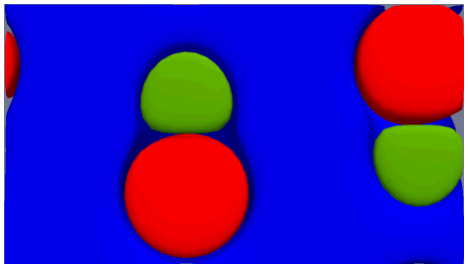
Increasing PMMA

Ringed Cylinder

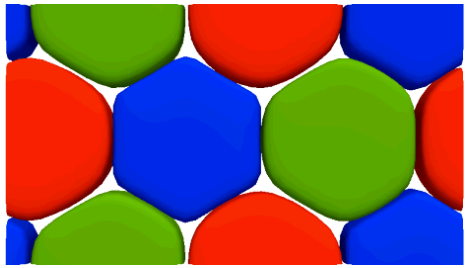


80% PMMA

70% PMMA



Lobed Cylinder

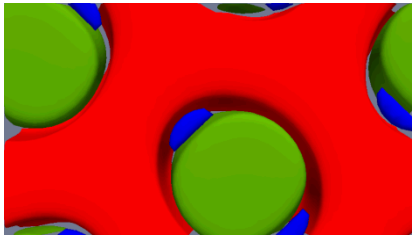
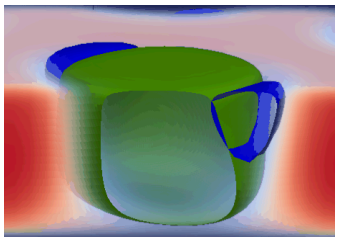
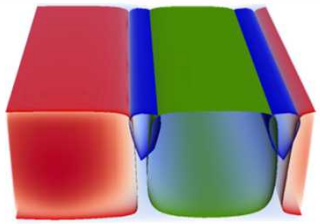
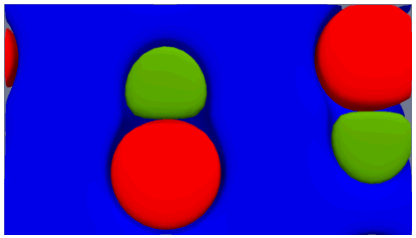
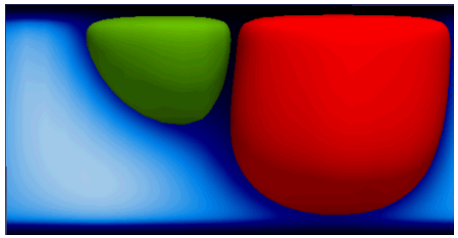
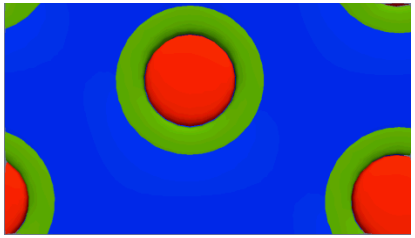
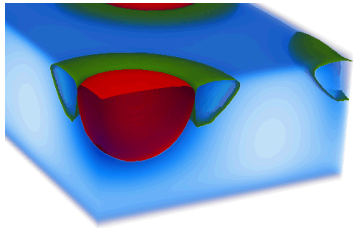


33% PMMA

Checkerboard

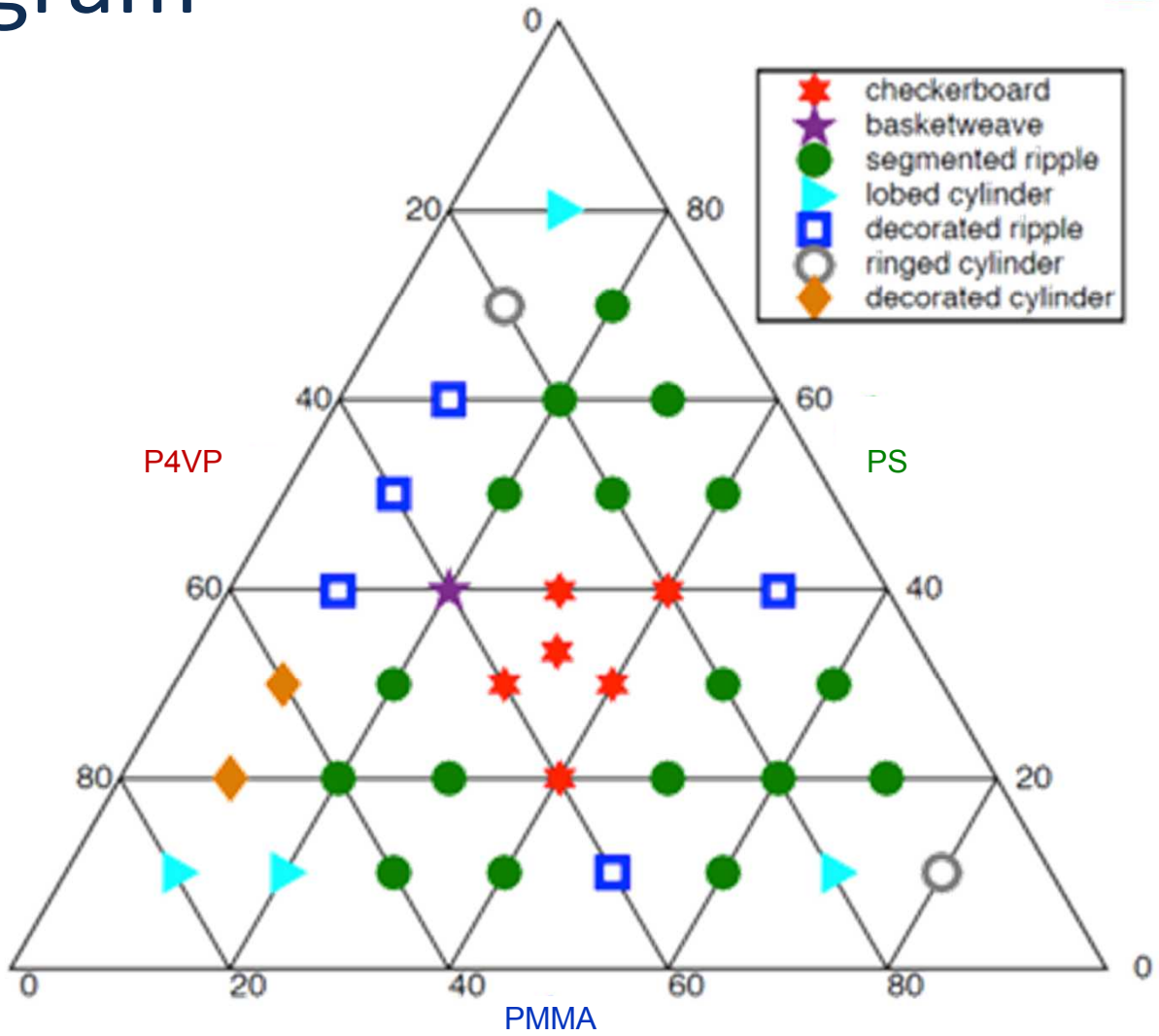
Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Below the Surface

	PMMA	PS	P4VP	
	0.1	0.3	0.6	
	0.1	0.4	0.5	
	0.7	0.1	0.2	
	0.8	0.1	0.1	

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

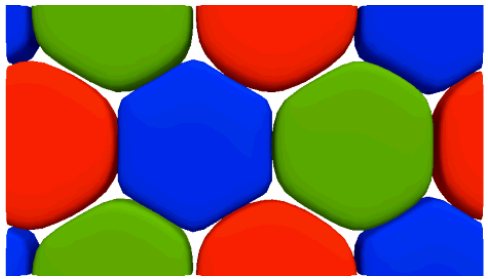
Phase Diagram

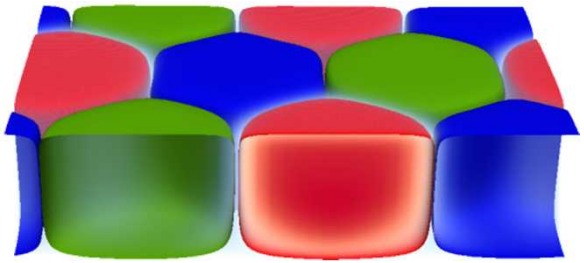


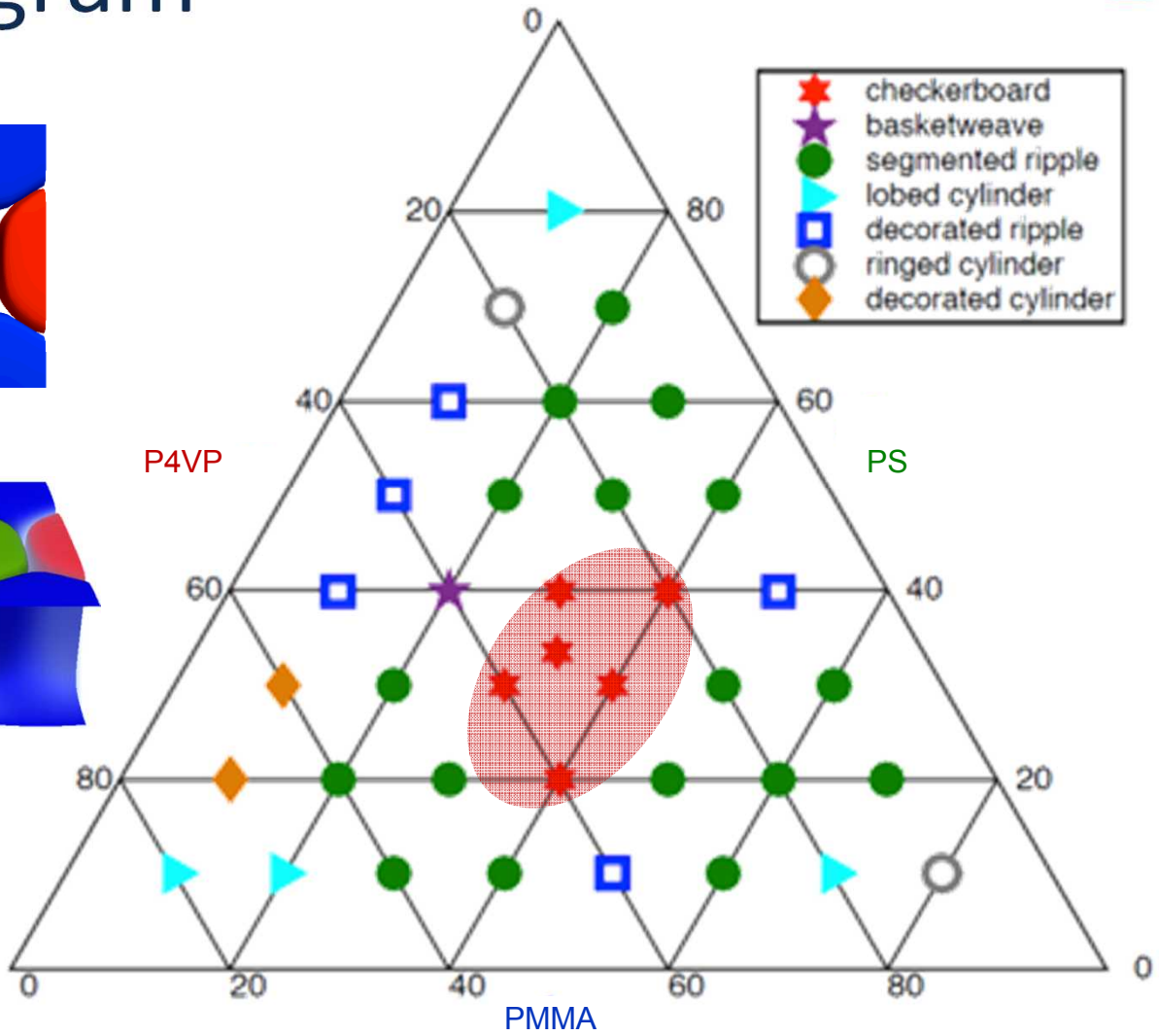
The phase diagram was calculated using SCFT and several phases were observed

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram



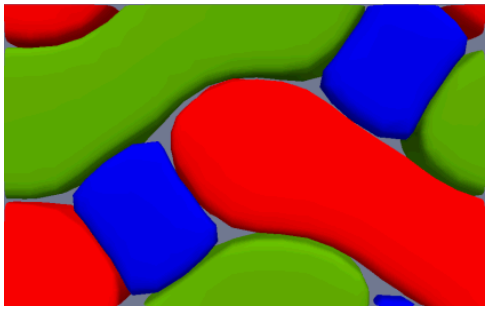


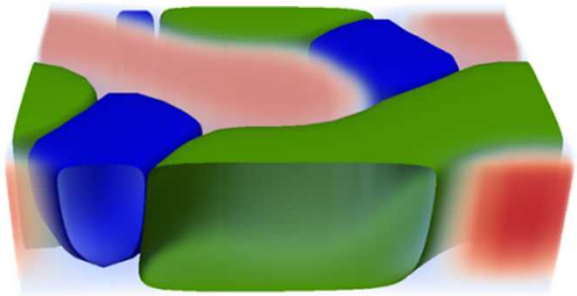


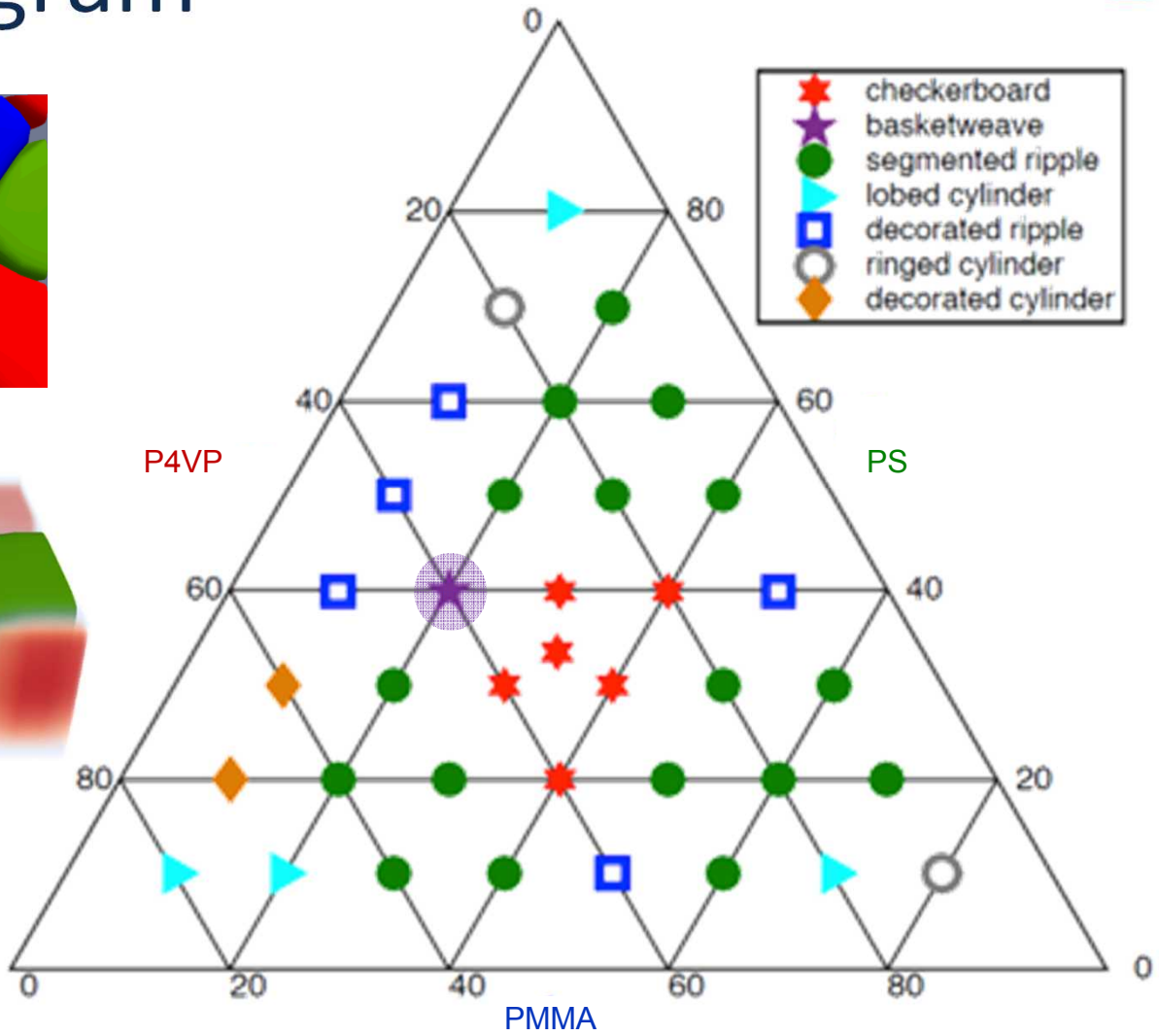
The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram



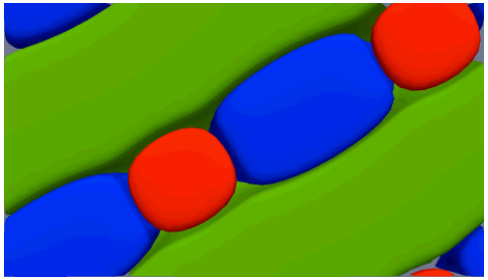


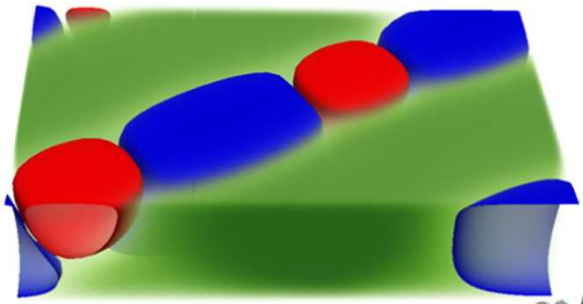


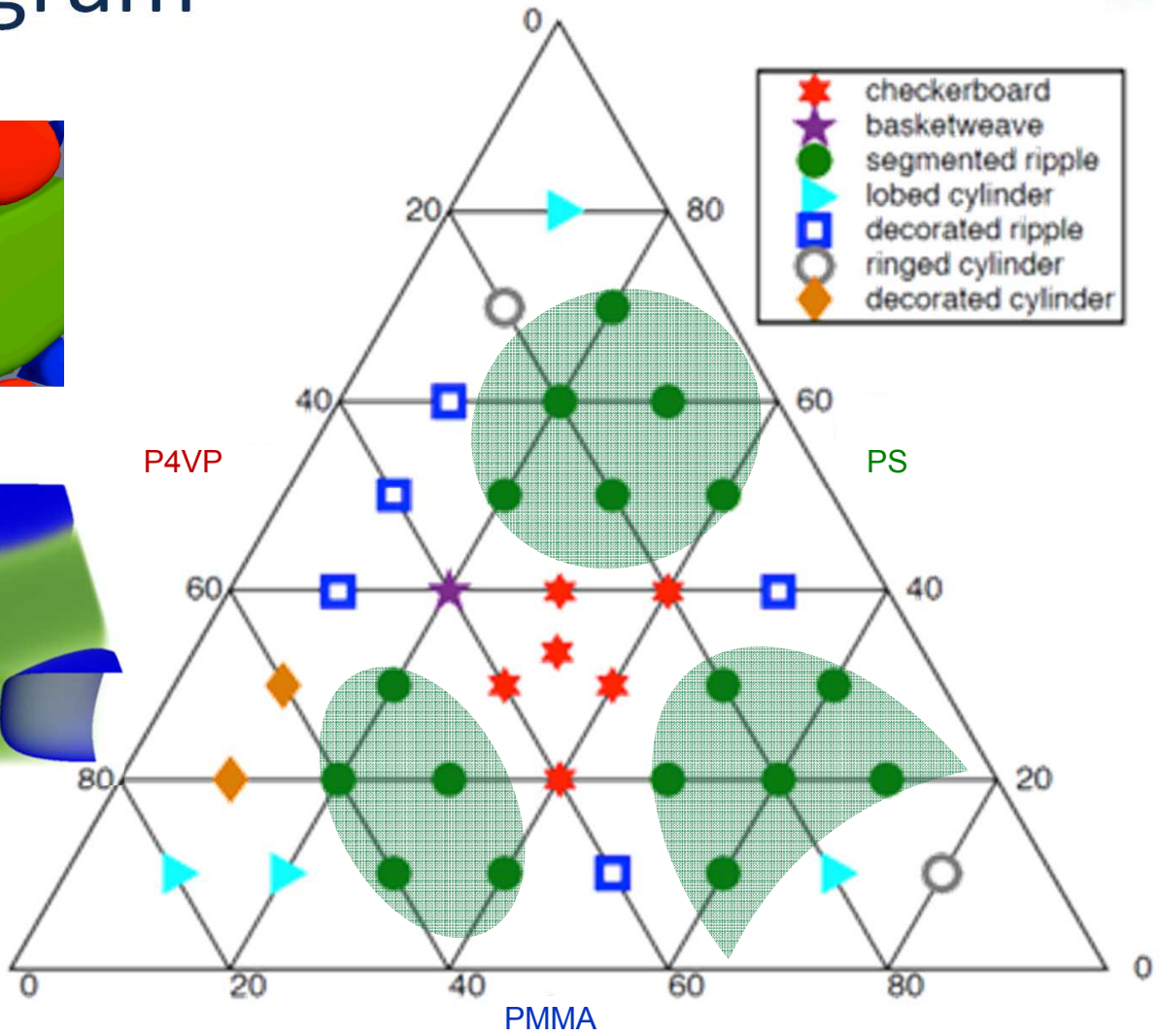
The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram



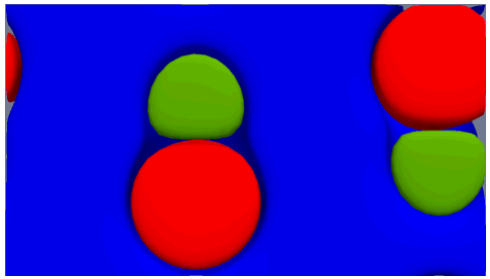


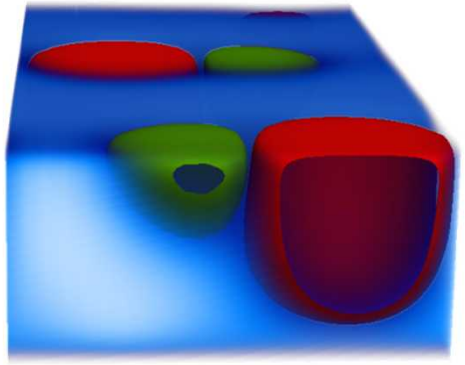


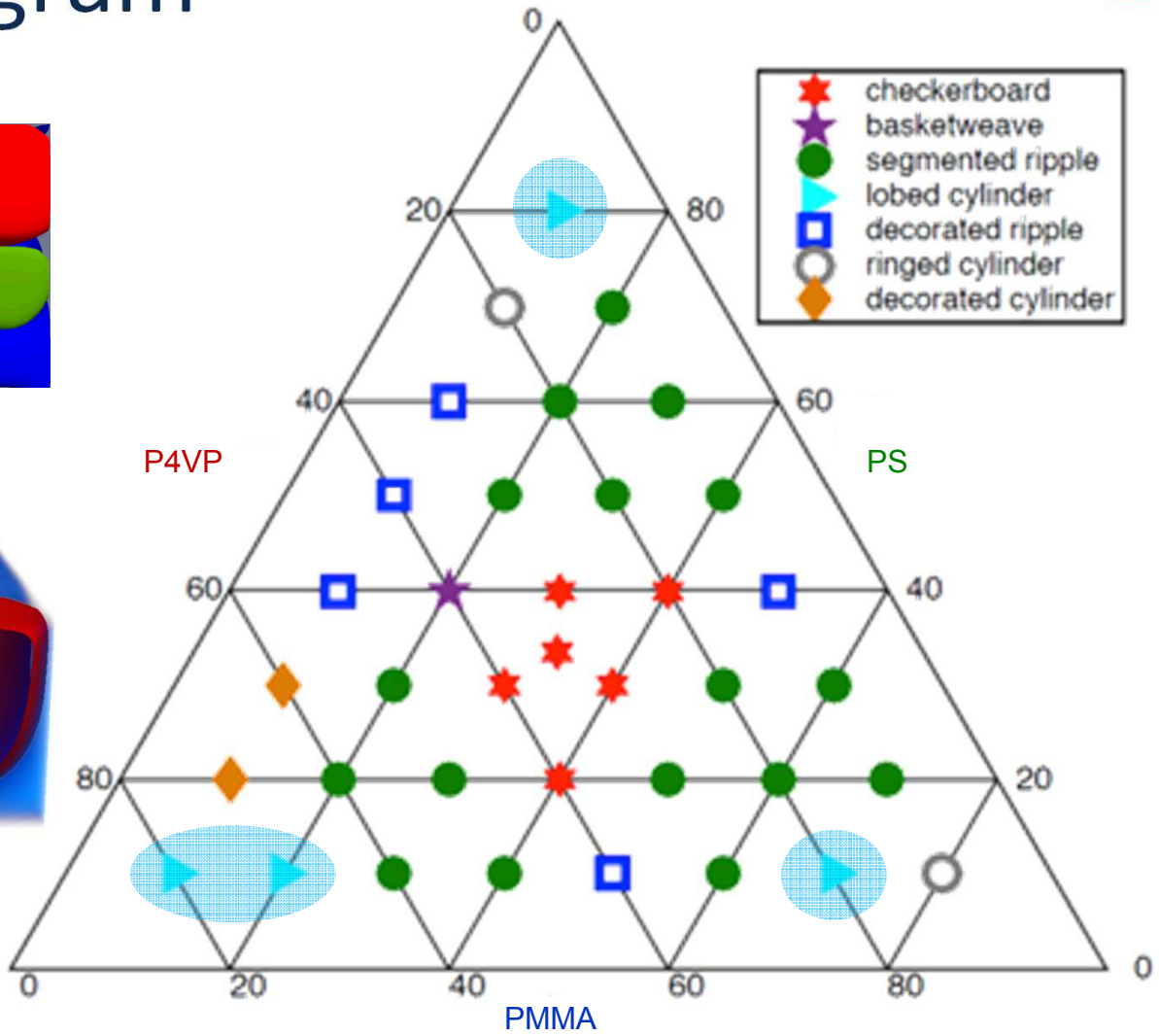
The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram



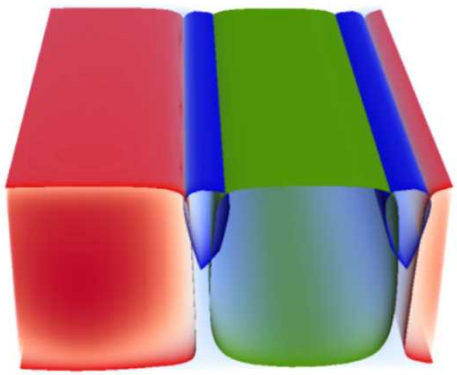


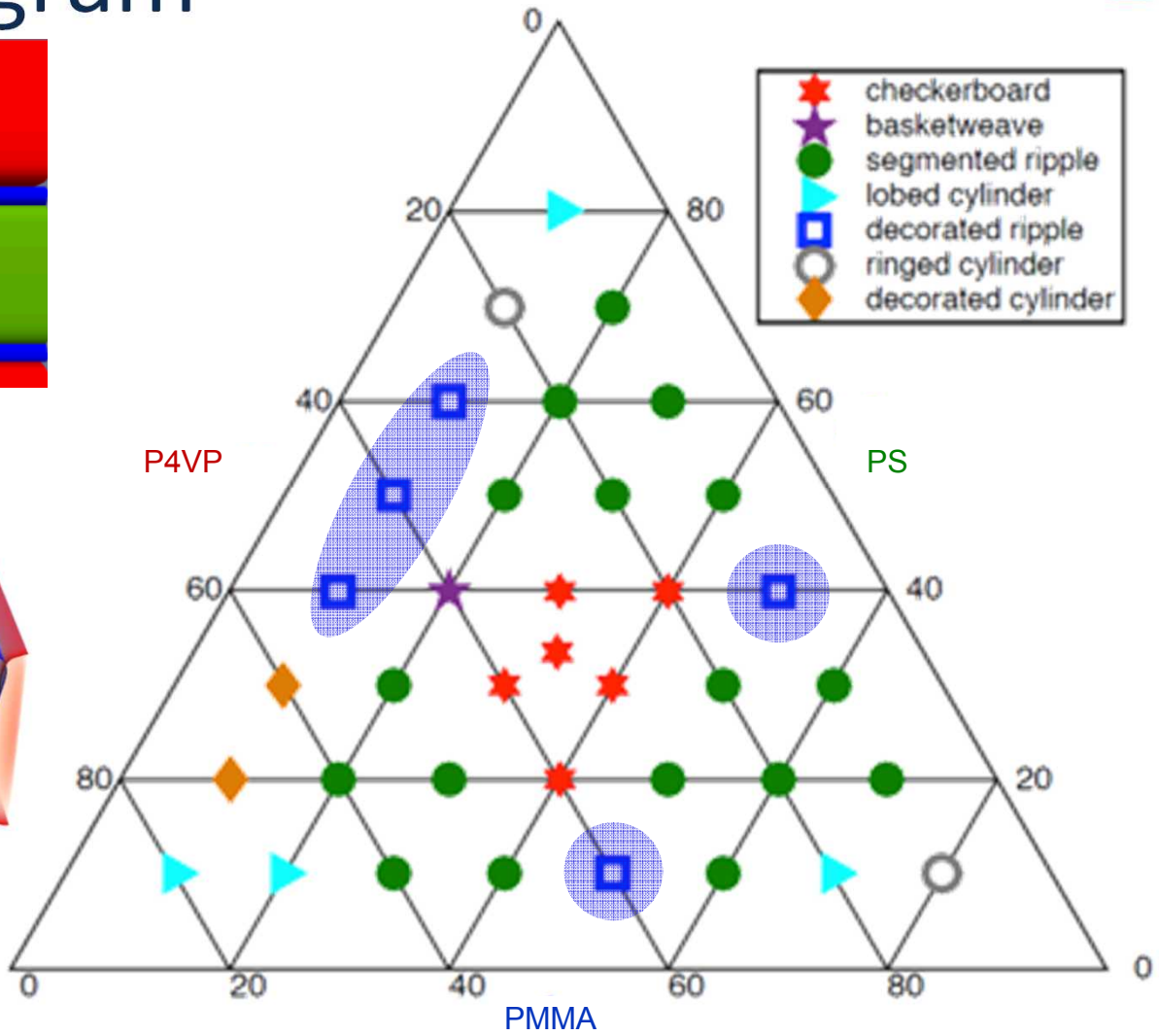


The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram

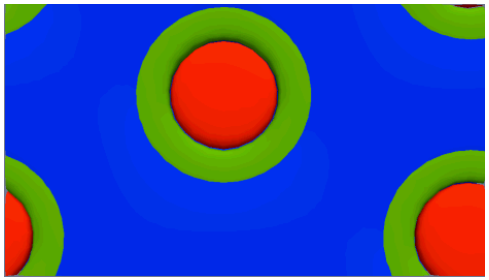


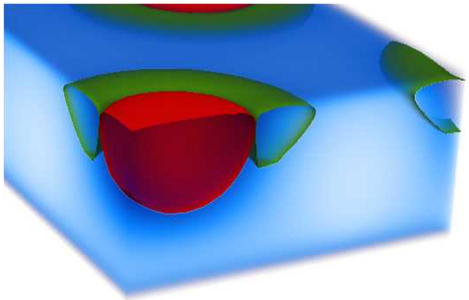


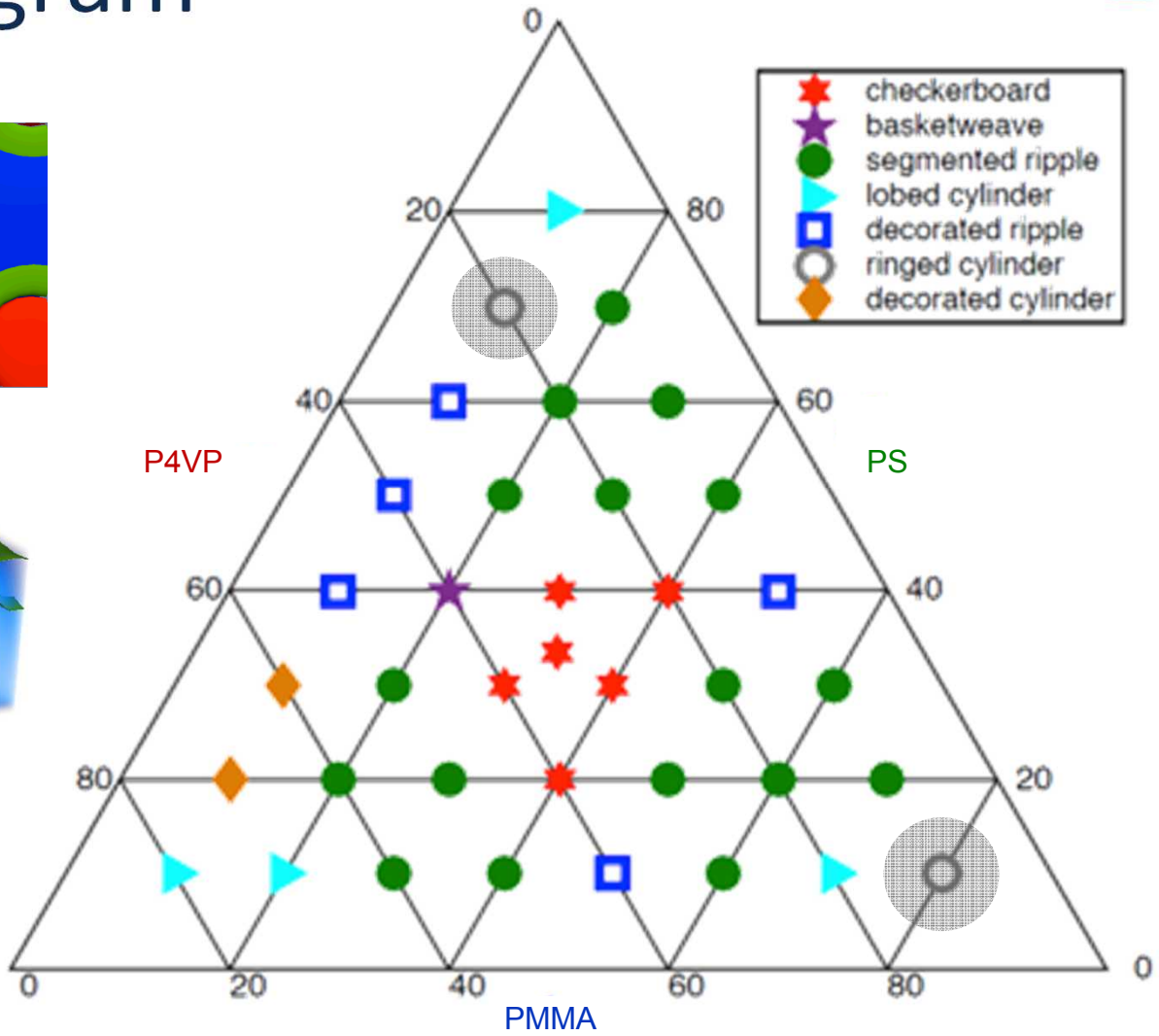
The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram



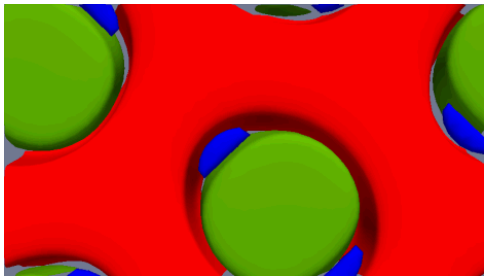


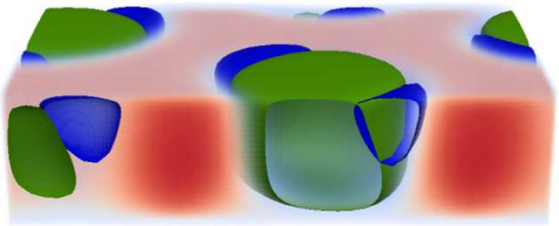


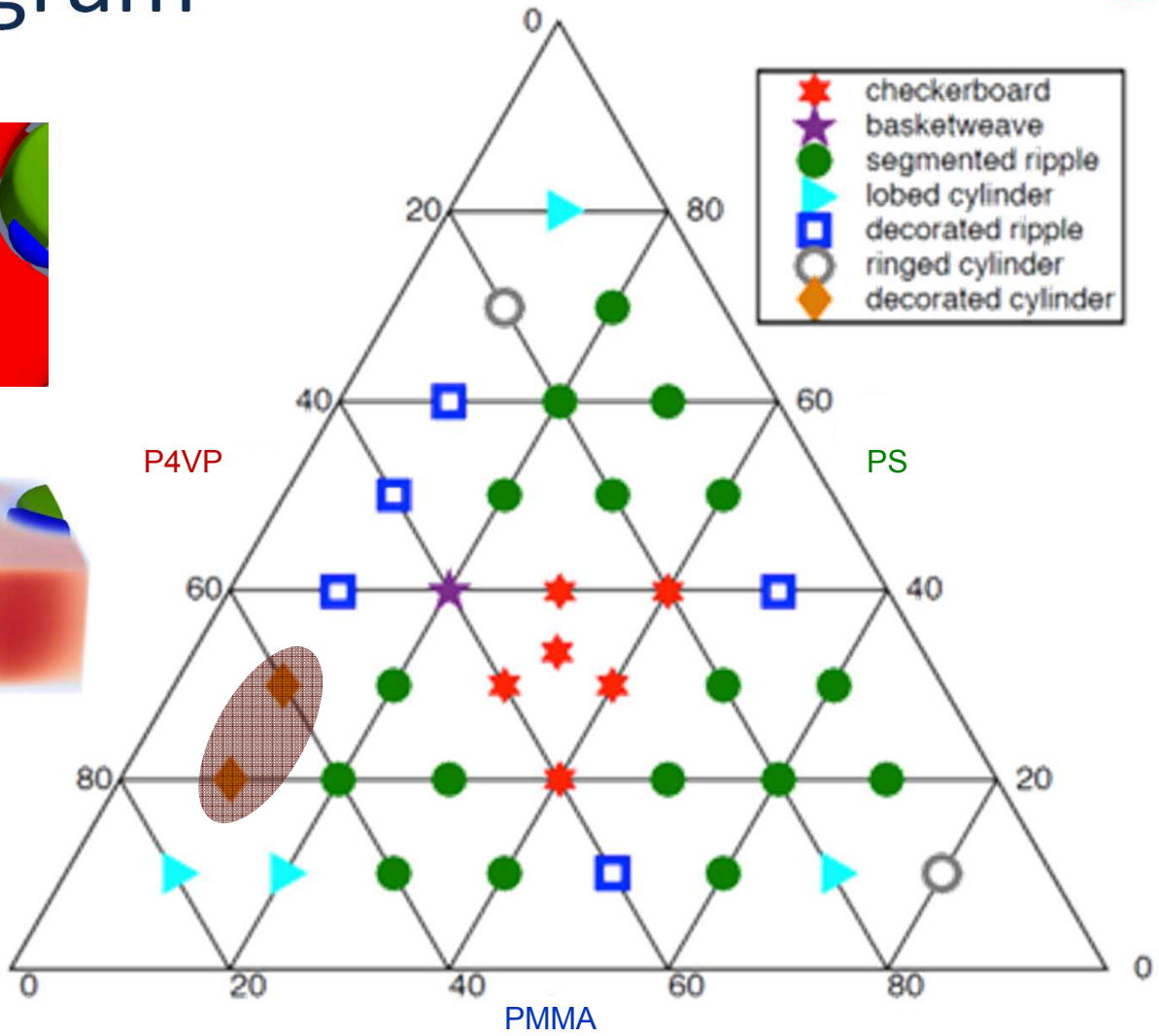
The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Phase Diagram



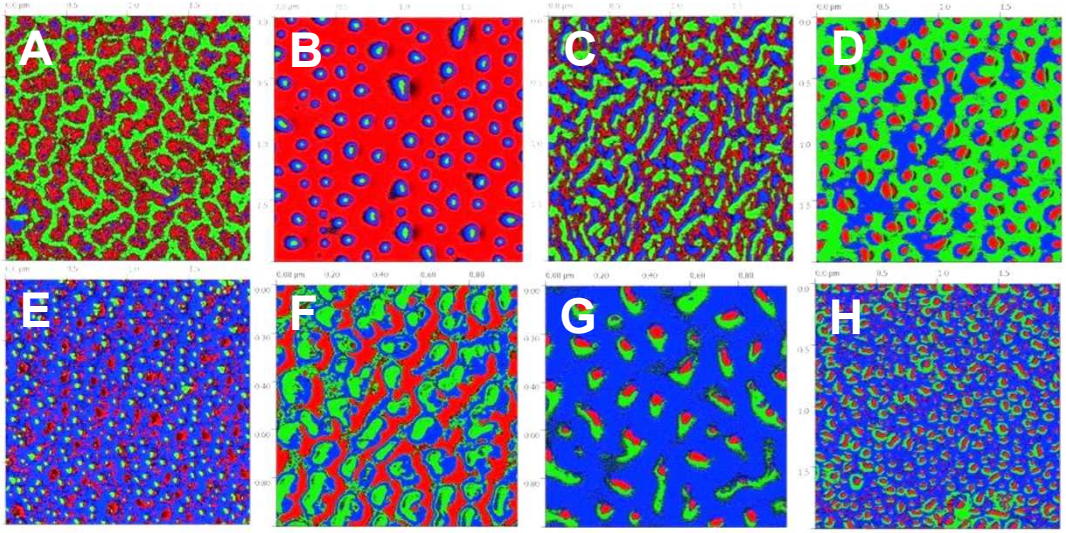


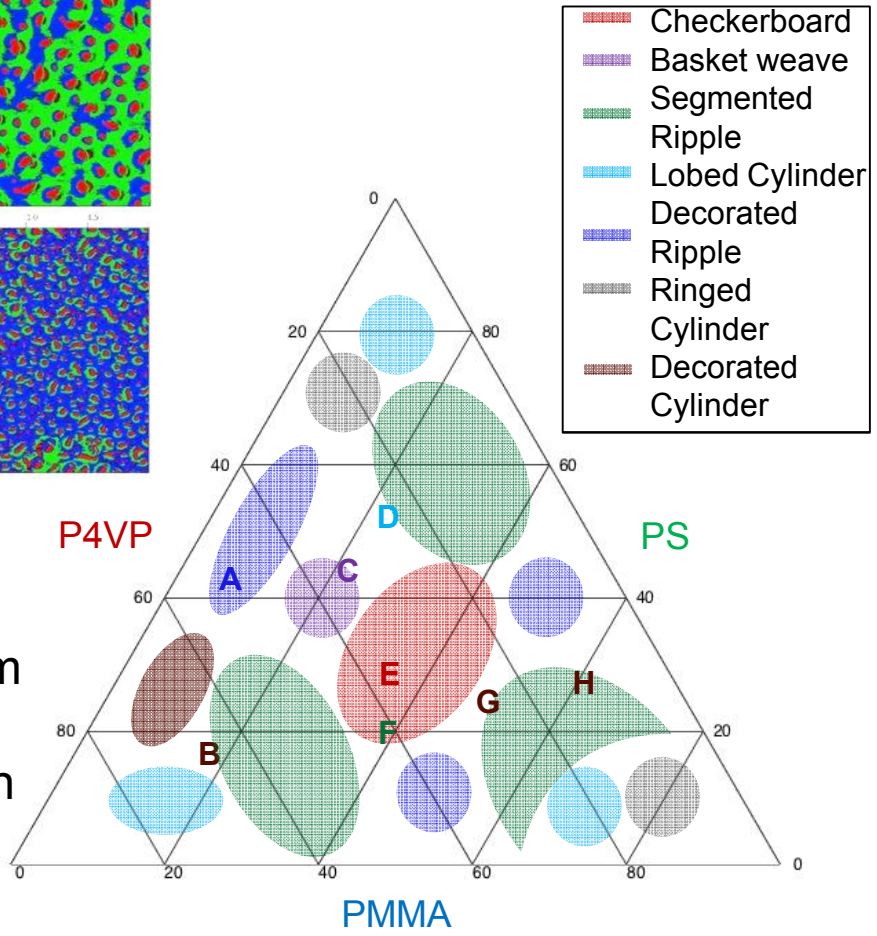


The phase diagram was calculated using SCFT and several phases were observed:

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Matching Experiment to Theory



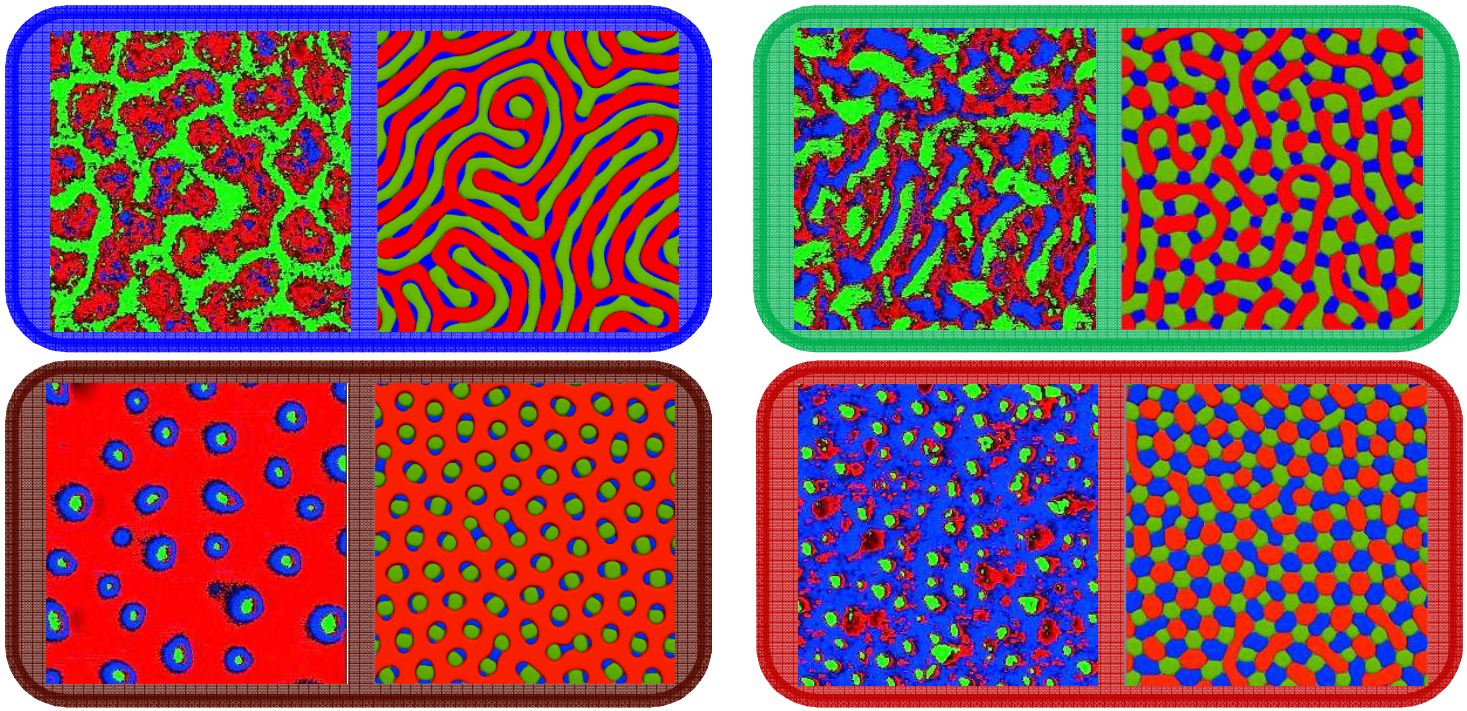


The Phase Diagram

- Experimental phases match well with the simulated phases diagram
- Differences are caused by the difference in the *X* values between the simulations and experiments

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Matching Experiment to Theory



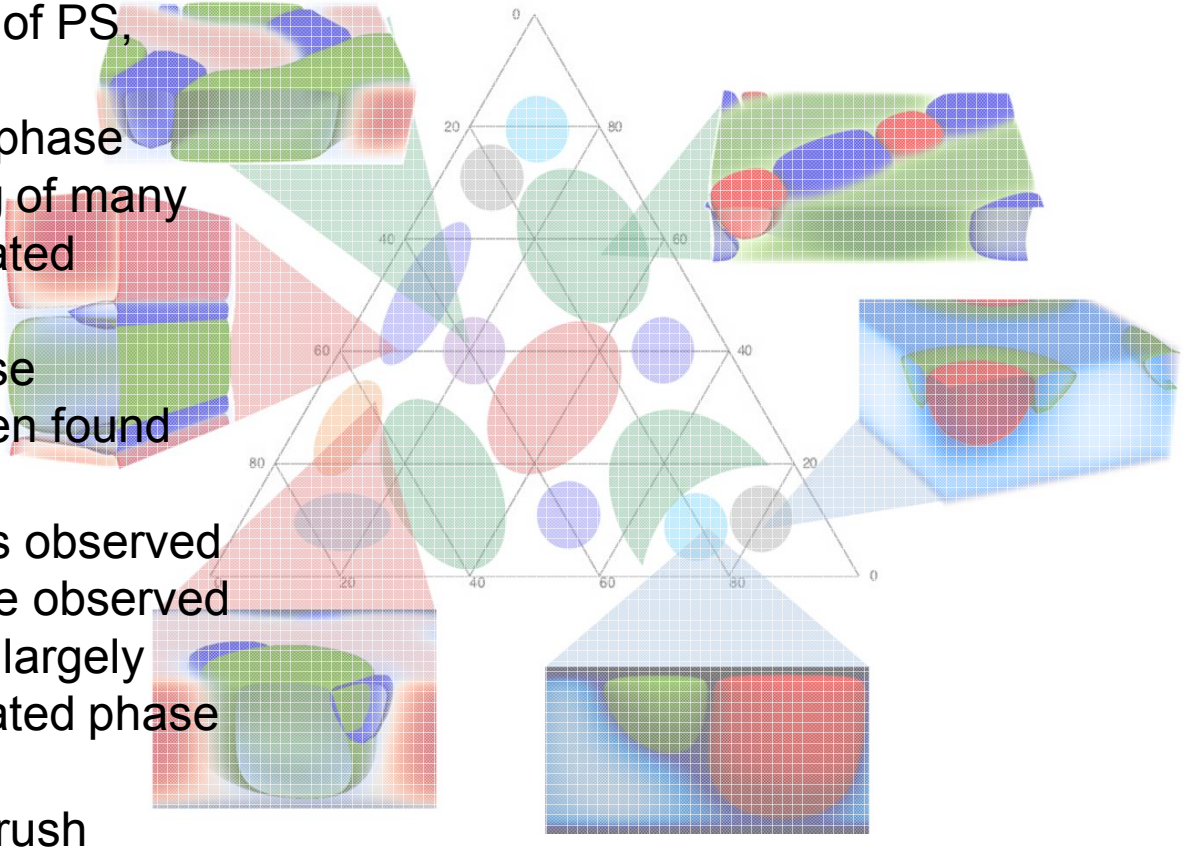
Comparing SCFT to Experiment

- Large scale SCFT simulations match well with experimental results
- The phase areas are determined via SCFT
- The colored match the same color as the phase diagram

Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Conclusions

- Synthesized ternary polymer brushes consisting of PS, PMMA, and P4VP
- Display a range of phase behavior consisting of many horizontally separated patterns
- Seven distinct phase behaviors have been found using SCFT
- All phase behaviors observed experimentally were observed in simulations, and largely match to the simulated phase diagram
- Work on polymer brush lithography is currently ongoing



Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

Acknowledgments

Dr. Dale Huber

(Postdoc Advisor)

The Huber Group

Collaborator:
Dr. Amalie Frischknecht (CINT)

U.S. DEPARTMENT OF ENERGY | Office of Science