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Pursuing ordered microphase separation in mixed polymer brushes

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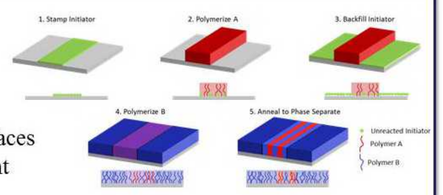
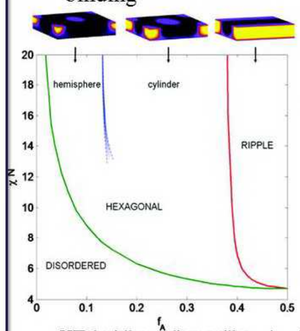
Introduction

Polymer brush lithography

- Can be grown a number of surface geometries
- Diblock copolymers are spin coated which needs planar surfaces
- Physically robust due to covalent binding



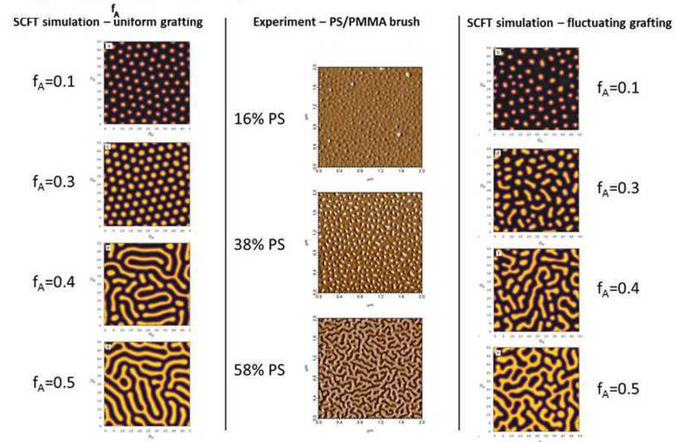


Mixed polymer brushes

- Contains two or more polymers
- Phase separate similar to diblock copolymers[1]

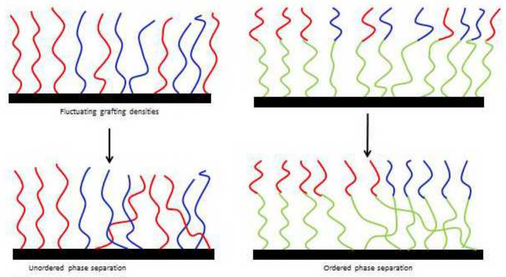
Binary polymer brushes

- Phase diagram calculated using SCFT
- Demonstrates multiple phase behaviors
- Fluctuating grafting density of experiments leads to less ordering than seen in simulations
- Accounting for this in the simulation leads to better correlation with experiment



[1] Price, A.P.; Hur, S.M., Fredrickson, G.H.; Frischknect, A.L.; Huber, D.L.. *Macromolecules.* **2012**, *45*, 510-524
US Patent #8,652,768, Huber and Frischknecht.

Diblock Mixed Polymer Brushes

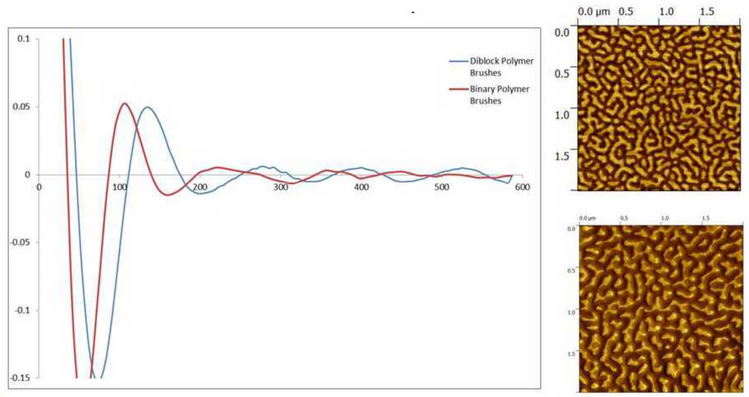


Fluctuating grafting density

- Polymer grafting leads from the surface to a random distribution of polymers, not a uniform one
- Heterogeneity of polymer density means less long range ordering

Solution: increase polymer mobility

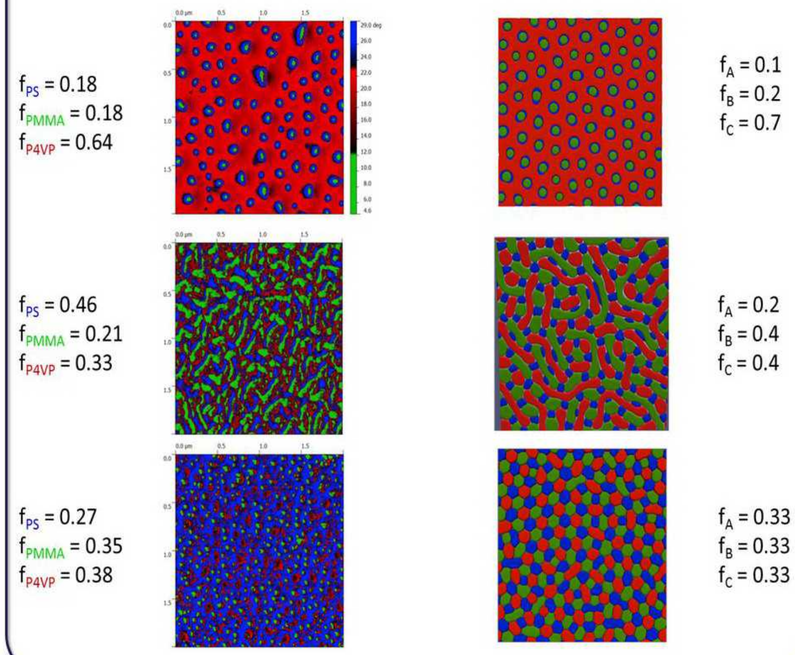
- Add a neutral polymer block attached to the surface before the PS or PMMA
- Allows the homopolymer block to move to areas that are more favorable
- The neutral block is made from a random copolymer of PS and PMMA
- Comparing binary polymer brushes (top AFM image) with diblock polymer brushes (bottom AFM image) demonstrates some longer range ordering in the diblock brush system



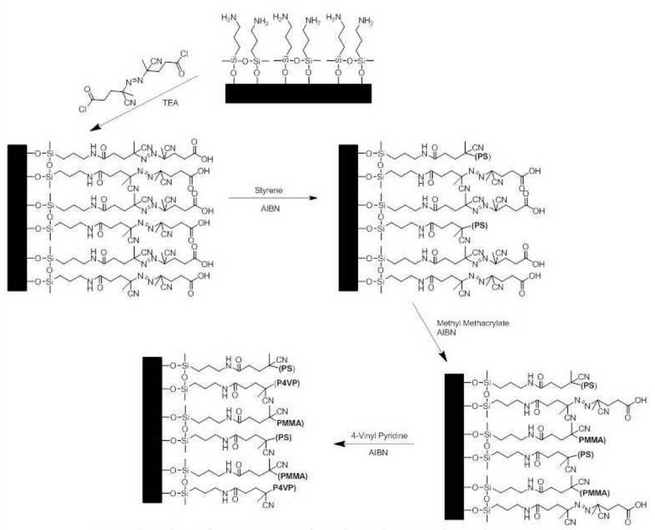
Ternary Mixed Polymer Brushes

Unique ternary brush behavior

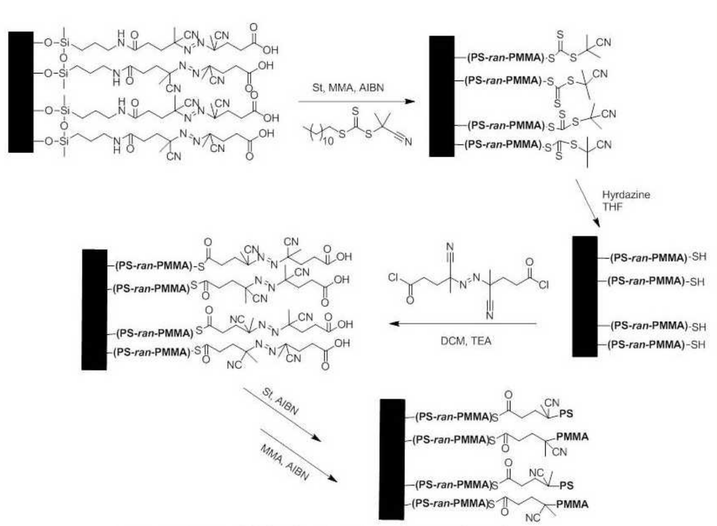
- Contains three polymer; PS, PMMA, and poly(4-vinylpyridine) (P4VP)
- Polymers were selected because they share common solvents and can be polymerized using the same method
- Brushes display unique phase behavior
- AFM phase images (left column) correlate well to the SCFT (right column) of similar polymer fractions
- More work needs to be done to create a phase diagram but already interesting structures have been observed.



Brush Synthesis



Synthesis of ternary mixed polymer brushes



Synthesis of diblock mixed polymer brushes

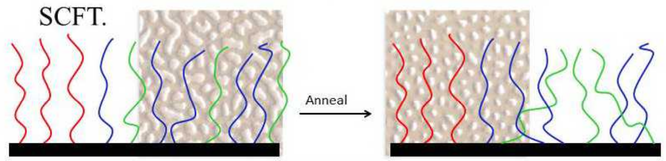
Conclusions

Diblock mixed polymer brushes

- Synthesized polymer brushes consisting of (PS-*ran*-PMMA)-*block*-PS and (PS-*ran*-PMMA)-*block*-PMMA
- These brushes demonstrate more persistent ordering then traditional binary mixed polymer brushes.

Ternary mixed polymer brushes

- Synthesized ternary mixed polymer brushes containing PS, PMMA, and P4VP
- AFM demonstrated unique phase behavior for a variety of polymer fractions
- This phase behavior correlates well with simulations done using SCFT.



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