Solvent Vapor Annealing Conditions for Poly(Vinylmethylsiloxane)-*b*-Poly(Styrene) Informed by Solvent Partitioning Software

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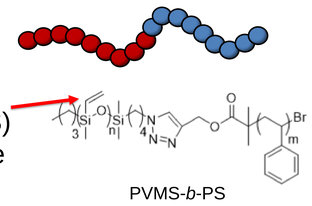
SMART SUMMER MATERIALS RESEARCH @ TULANE

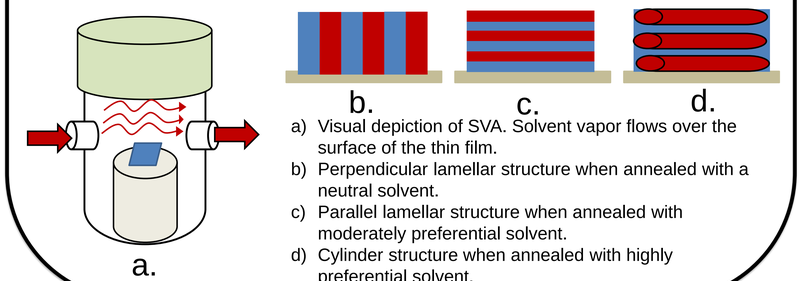
Introduction

- Block copolymers (BCPs) are advantageous materials for nanolithography.
- Poly(vinylmethylsiloxane) (PVMS) is a polymer of interest due to the functionality of its vinyl group.
- Solvent vapor annealing (SVA) is a method to control the self-assembly of thin film BCPs and induce long-range order.
- The surface morphology of thin films can be altered through the selectivity of the solvent and the swell ratio during SVA.



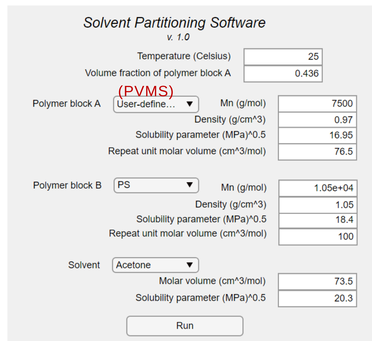
PVMS-*b*-PS

Uddin, M. Tulane University, New Orleans, LA. Presentation on PVMS-b-PS, 2020.

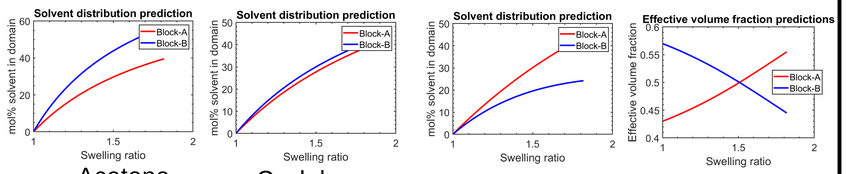


a) Visual depiction of SVA. Solvent vapor flows over the surface of the thin film.
b) Perpendicular lamellar structure when annealed with a neutral solvent.
c) Parallel lamellar structure when annealed with moderately preferential solvent.
d) Cylinder structure when annealed with highly preferential solvent.

Solvent Partitioning Software



- The Solvent Partitioning Software is a novel tool to inform SVA conditions and predict solvent distribution and effective volume fraction.
- The software narrowed down 16 potential solvents to three, and the range of swell ratios from 1-3 to 1.5-2.
- This study used the predictions to select swell ratios at which the PS block would be mobilized (20 mol% solvent in domain).



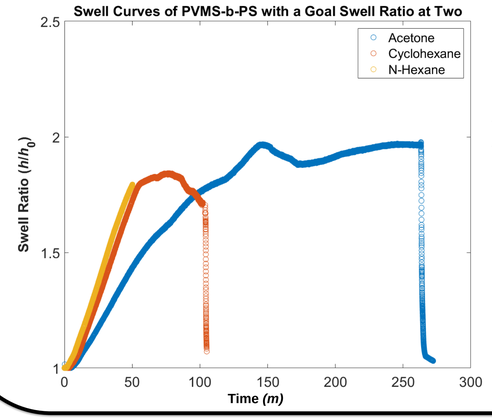
Acetone
PS-preference
Moderately preferential
Solubility Parameter: 20.3 $MPa^{0.5}$

Cyclohexane
Equal block preference
Neutral solvent
16.8 $MPa^{0.5}$

N-Hexane
PVMS-preference
Solubility Parameter
14.9 $MPa^{0.5}$

Behzadinasab, S et al. Tulane University, New Orleans, LA. Manuscript in preparation, 2019.

Solvent Vapor Annealing of As Cast Films



Swell ratio is the relationship between the current thickness (h) and the original thickness of the film (h_0):

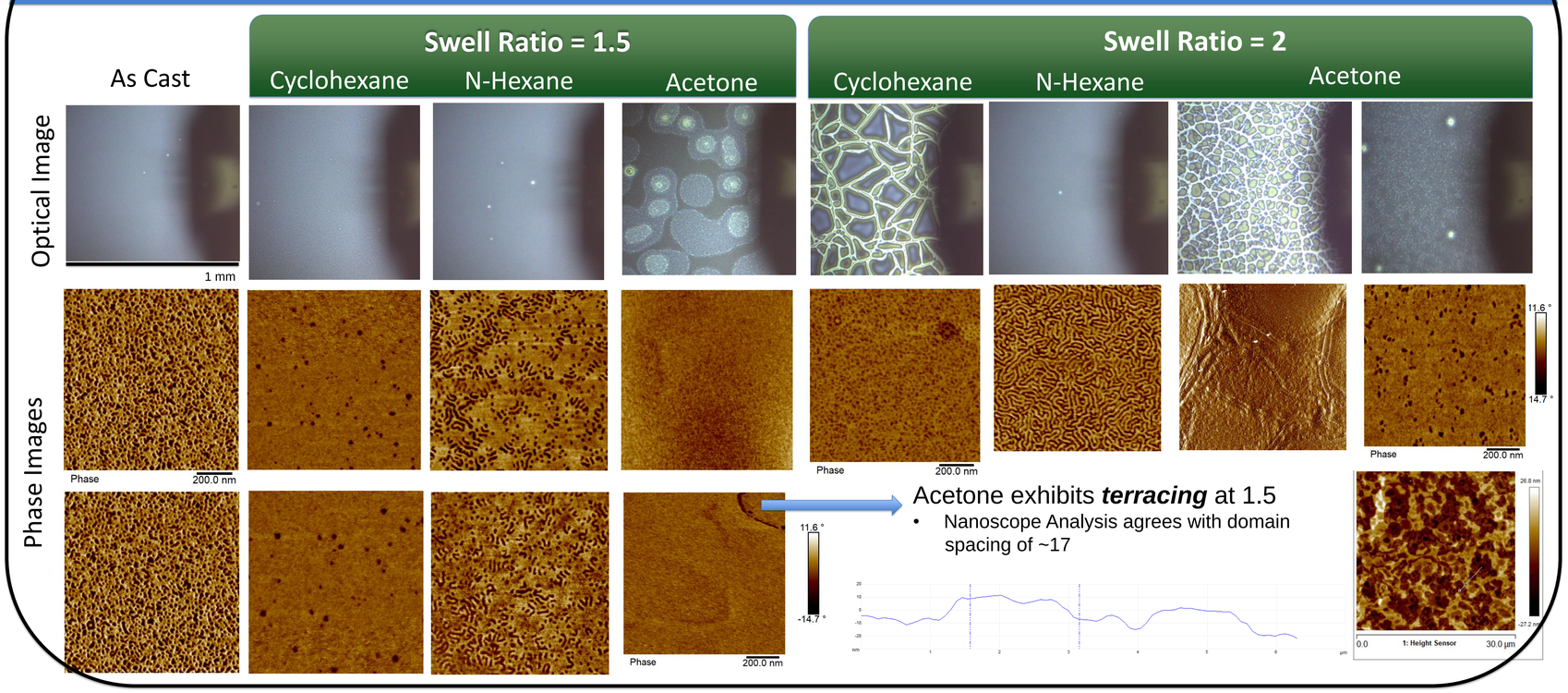
$$\frac{h}{h_0}$$

Note: Data for the 1.5 swell was not successfully recorded.

Conclusion

- The n-hexane annealed film assembled into perpendicular cylinder structure.
- Phase images suggest parallel cylinders formed in the cyclohexane annealed film before dewetting during the SVA with a swell ratio of two.
- Acetone may be too polar of a solvent to induce long range order before dewetting. However, terracing occurred before dewetting during the 1.5 swell ratio SVA.
- The Solvent Partitioning Software can greatly reduce the number of solvent options and swell ratio ranges for the user to choose from.

Atomic Force Microscopy Results



Acetone exhibits ***terracing*** at 1.5

- Nanoscope Analysis agrees with domain spacing of ~17

Future Work

- Replicate the SVA trials with different parameters to prevent dewetting. Such parameters include longer holds at lower swell ratios or choosing solvents with different solubility parameters.
- Investigate the terracing properties of the acetone annealed film.
- Functionalize the vinyl group through a thiolene reaction.
- Use block copolymer in direct application, such as creating a microfluidic device or nanolithographic mask.

Acknowledgements

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