

# Optimization of Swelling Process in Solvent Vapor Annealed Block Copolymer Thin Films

H. Huang\*, T Chang

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China  
hyhuang@ciac.ac.cn

Long range ordered nanostructures formed by self-assembled block copolymer (BCP) thin films, has been proved to be an excellent candidate for next generation nanolithography over traditional photolithography.<sup>1</sup> In general, thermal or solvent annealing is utilized to promote BCP self-assembly for constructing ordered nanostructures.<sup>2-3</sup> Nevertheless, due to the high intrinsic viscosity of polymers, long annealing time is often required to fabricate well-ordered nanostructures in BCP thin films.

In this work, we developed a facile and effective solvent annealing method to fast assembly of poly(styrene-*block*-2-vinylpyridine) (PS-*b*-P2VP) thin films in 1-3minutes. The well-ordered BCP morphology was obtained by optimizing the annealing process in a high surface-to-volume vessel, which can provides delicate control of solvent vapor pressure corresponding to different swelling ratio (SR). It was found that the type and density of defects were sensitive to equilibrium SR and the optimal SR is limited to a narrow range, in which the long range ordered nanostructure can be produced. When SR much higher than the optimal range, disordered nanostructure appeared as the  $\chi_{\text{eff}}N$  largely decreased. When SR slightly higher than the optimal range, the ordering of BCP morphology was improved significantly, but at the cost of blooming of short-range defects. However, when further reducing SR below optimal range, it may not provide chain enough mobility to cross the energy barrier and enhance the long-range order. We considered that such annealing strategy could be applied to other solvent-based annealing system as well, and contribute to the high quality and cost-effective manufacturing process.

## Acknowledgement

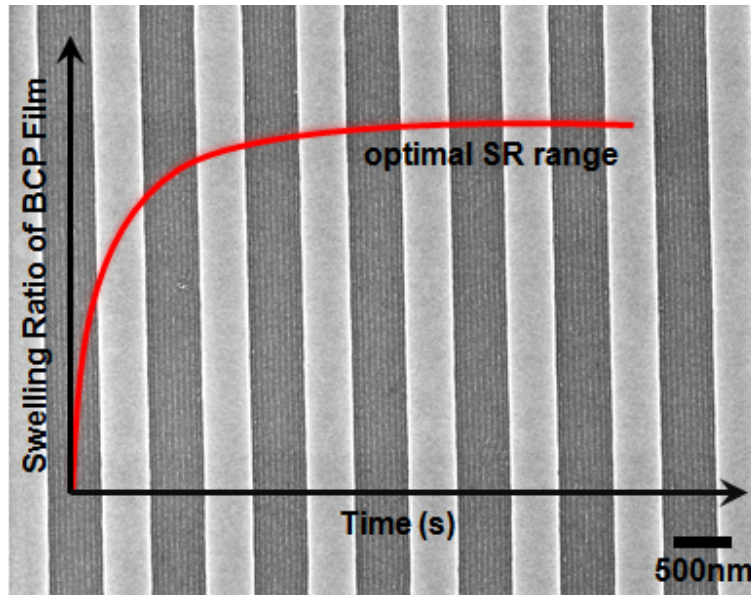
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<sup>1</sup> Bates, C. M.; Maher, M. J.; Janes, D. W.; Ellison, C. J.; Willson, C. G. *Macromolecules* **2014**, 47, 2-12.

<sup>2</sup> Sinturel, C.; Vayer, M.; Morris, M.; Hillmyer, M. A.; *Macromolecules* **2013**, 46, 5399-5415.

<sup>3</sup> Jin, C.; Olsen, B. C.; Lubner, E. J.; Buriak, J. M. *Chem. Mater.* **2017**, 29, 176-188.



*Figure 1: Pt nanowires on the nanopatterned silicon substrate: SEM images of Pt nanowires fabricated from PS<sub>62k</sub>-*b*-P2VP<sub>26k</sub> films after annealing in THF vapor for 180s at the optimal SR condition. The parallel cylinders aligned exclusively along the trench walls. The period of topographically patterned Si substrates is 833nm with mesa width 416.5 nm.*