

MAR12-2011-007923

Abstract for an Invited Paper
for the MAR12 Meeting of
the American Physical Society

Directed Ordering of Block Copolymer Thin Films with Flexible Interfaces for Functional Materials¹

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Orientation control of block copolymer (BCP) films is important for advanced technological applications. We present studies on directed ordering of block copolymer thin films on rigid substrates such as quartz to elastomeric PDMS and flexible Kapton substrates for tunable orientation of microphase separated poly (styrene) – block -poly (methacrylate) (PS-PMMA) cylinder and lamellae forming BCP films. Although the crosslinked PDMS has low surface energy, its surface energy can be tuned by exposing to UV-Ozone (UVO) that presents an opportunity to change BCP-PDMS interfacial energy to control BCP orientation across full range of orientation and film wettability. On the other hand, Kapton offers a near neutral surface for PS-PMMA without surface modification. Via a modified version of a dynamic thermal processing termed cold zone annealing-sharp (CZA-S), we obtain a wide range of orientations of the block copolymer films in unfilled and nanoparticle filled systems with an interest in photovoltaic systems. With CZA-S, vertical orientation of PS-PMMA can be obtained in films as thick as 1 micron with etchable PMMA domains for membrane applications. GISAXS characterization of these etched BCP membranes reveals up to 5 orders of diffraction indicating hexagonally packed vertical nanopores that extend throughout the film. Under similar thermal gradient, but static conditions, temporally stable vertical cylinders form only within a narrow zone of maximum temperature gradient. Primary CZA-S ordering mechanism thus involves propagating this narrow vertically oriented zone of BCP cylinders created at the maximum thermal gradient section, across the film. An optimal speed is needed since the process competes with preferential surface wetting dynamics that favors parallel orientation. These results are reproduced on large area flexible films on a prototype dynamic R2R assembly platform with incorporated multi-CZA gradient for thin (100 nm) BCP films currently.

¹Acknowledgements: NSF-DMR and DOE-BES