

# Guided Self-Assembly of Block-Copolymer Nanostructures

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## ABSTRACT

Block copolymers are an important class of soft-materials with significant potential for a variety of potential applications ranging from high-density data storage devices to nanowires and photonics. These potential applications rely on the ability to not only manipulate and control their structure at the nanoscale, but also to accurately measure the structure and morphology of the film in all dimensions. As is well known, diblock copolymer molecules are comprised of two dissimilar polymers covalently bonded at one end. Typically, the individual blocks are thermodynamically incompatible and the system will microphase separate upon heating. It is also desirable to control order, orientation and defects over large areas in most thin film applications of these materials.<sup>1-5</sup> This paper focuses on the dynamics of directed self-assembly of block copolymers in confining geometries such as thin films modulated by processing parameters such as applied fields which can be surface chemical or thermal gradient. We illustrate the surface chemical gradient approach below. The presentation will discuss some of the "tomographic" neutron scattering measurement methods being developed to investigate the structure and morphology of block copolymer thin films in 3-dimensions as a result of such gradient fields and simulation methods to capture aspects of kinetics and dynamics involved in the evolution of thin film structure.

**Keywords:** block-copolymer, thin-film, directed self-assembly, surface chemical control, scattering, zone annealing

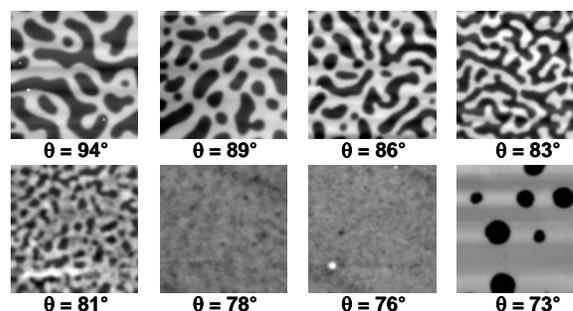
## EXPERIMENTAL<sup>6</sup>

Chemical modification of the substrates is obtained using chlorosilane chemistry for covalent self-assembled monolayers (SAM) on silicon wafers followed by ultra-violet ozonolysis (UVO) to generate stable gradient energy test substrates. The substrate is thoroughly washed with toluene and dried. The resulting SAM was then exposed to a gradient of UVO using a modulated UVO exposure device.<sup>7</sup> The graded oxidative process results in surface chemical modification by the generation of a gradient in surface chemical moieties primarily carboxyl functionalities across the sample. This gradient was characterized using water contact angle measurements. Thin films of the

poly(styrene-block-methylmethacrylate) or PS-b-PMMA block copolymer were cast on these gradient wettability substrates and annealed above their glass transition temperature and characterized by atomic force microscopy, neutron reflectivity and small angle neutron scattering.

## RESULTS

After the block copolymer film (library) was been formed, it was be characterized with atomic force microscopy (AFM), a high resolution technique. An example of this morphology change is shown in Figure 1 where AFM micrographs of an M = 51 k PS-b-PMMA film acquired at h = 75 nm are presented. We observe a progression of surface topography from labyrinthine pattern to smooth surface to islands to co-continuous regions to holes as a function of changing substrate surface contact angle. Essentially, the morphology is observed to change from symmetric to asymmetric wetting of block component on the substrate surface as illustrated in cartoon Figure 2. The nature of the surface patterns formed depended on local film thickness as well as expected due to the quantized nature of the block copolymer films. The evolution dynamics of these film structures offers much insights into the mechanisms behind the ordering processes in these films.



**Figure 1.** 10x10  $\mu\text{m}$  AFM images indicating the progression from holes through a smooth region and back to holes. Substrate water contact angle on the corresponding position are indicated.

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**Figure 2.** Illustration of the effect of surface energy on block copolymer thin films for hydrophobic, neutral, and hydrophilic surface energies.

Neutron Reflectivity (NR) as well as Small Angle Neutron Scattering (SANS) were employed to investigate the ordering kinetics and orientation within deuterated thin films of the block-copolymer. Currently tomographic SANS is being developed to investigate the degree of orientation within these films by collecting scattering data at varying incident angles.

## CONCLUSIONS

The morphology of block copolymer thin films as a function of film thickness and substrate surface energy has been characterized using gradient combinatorial mapping techniques. A switch from symmetric to asymmetric film morphology was observed as a function of substrate surface energy variation. At the center of this surface energy range is a “neutral” surface region that can be exploited to obtain vertically oriented lamellae or cylindrical morphology in thin films. Simulations involving self-consistent field theory (SCFT) invoking ordering dynamics with a mobility gradient are being developed to understand some of the observed phenomena.

## REFERENCES

- [1] Black, C. T.; Guarini, K. W.; Russell, T. P.; Tuominen, M. T. *Appl. Phys. Lett.* 2001, 79, 409.
- [2] Cheng, J.Y.; Ross, C.A.; Smith, H.I.; Thomas, E.L., *Adv. Mater.* 2006, 18, 2505.
- [3] Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* 2003, 15, 226
- [4] Bodycomb, J.; Funaki, Y.; Kimishima, K.; Hashimoto, T. *Macromolecules* 1999, 32 (6), 2075-2077.
- [5] Berry, B.C.; Bosse, A.W.; Douglas, J.F.; Jones, R.L.; Karim, A. *Nanoletters* 2007, 7 (9), 2789.
- [6] Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.
- [7] Berry, B.C.; Stafford, C.M.; Pandya, M.; Lucas, L.; Karim, A.; Fasolka, M.J. *Rev. Sci. Instrum.* 2007, 78(7), 072202.