

Visualizing 3-D Directed Assembly of Block-Copolymer Thin Films on Nanoparticle Substrates using Neutron Scattering

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Research Achievement

Self assembly of block-copolymers (BCPs) is one of the most promising of the emerging technologies for nanofabrication and photovoltaic applications such as polymer solar cells. BCP's can form ordered domains at the 10's of nanometer scale due to incompatibility between the two polymer blocks leading to a rich variety of structures such as cylinders, lamellae, bicontinuous and gyroids. Controlling and measuring the orientational order in 3-D in thin films is important for potential applications of these materials. In thin BCP films, the lamellae or cylinders orient parallel to the substrate interface as one of the blocks exhibits an energetic preference for the substrate, aided by the geometric constraint of the flat substrate. However, the effect of nanoscale roughness on BCP orientation has only been minimally investigated, yet most practical surfaces can be expected to exhibit such roughness.

We investigate the self-assembly of BCPs on nanoparticle roughened substrates as a novel strategy to obtain vertically oriented BCP lamellae. This approach relies on the premise that the interfacial bending energy of BCP lamellae oriented parallel to substrate is unfavorably high by conforming to the nanoscale topology and the system re-orientates to a vertical assembly to minimize it. By using UV tunable modified silica nanoparticles, we additionally bias the self-assembly to form a surface neutral BCP condition to assist the vertical assembly. The nanoparticles have been modified with a propyl ligand, an organic coating that can be easily oxidized by exposure to UV. By controlling the exposure time, the surface energy of the nanoparticles can be controlled in a simple yet precise manner.

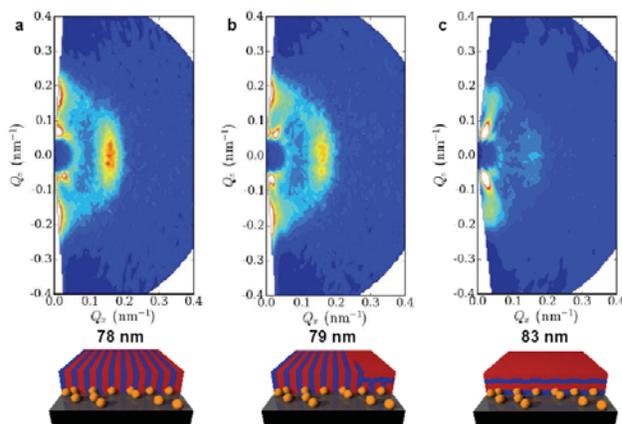


Fig. 1: Small-angle neutron scattering (SANS) data of dPS-PMMA block-copolymer films assembled on nanoparticle surfaces. The reciprocal-space maps were reconstructed by accumulating SANS data as a function of sample rotation angle. A schematic of the inferred lamellae orientation is provided beneath each map. **a,** A 78 nm film, which exhibits the vertical morphology by AFM, generates an intense peak at $Q_x = 0.16 \text{ nm}^{-1}$, indicative of vertical order. **b,** A 79 nm film exhibits a slightly weaker vertical peak. **c,** The 83 nm film has effectively no peak in the SANS data, consistent with the horizontal morphology observed by AFM.

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Using a combinatorial approach for modifying the surface energy and BCP film thickness, in the case of lamellar films, we observed that a theoretically-predicted, but previously unobserved, oscillation between horizontal and vertical orientations achieved in a single sample [1]. The fingerprint patterns observed by AFM can only confirm the surface orientation, *but in conjunction with rotational SANS enables us to set a bound on the orientation in 3-D as shown in Fig. 1.*

Although coating BCP on a non-periodic rough substrate seems to be an attractive and cheaper option, there

is a paucity of knowledge about the mechanism and optimal surface features of a rough

substrate to obtain the vertical lamellae, and more detailed understanding of its dependence on the BCP thickness (L_0) and chemistry of the blocks.

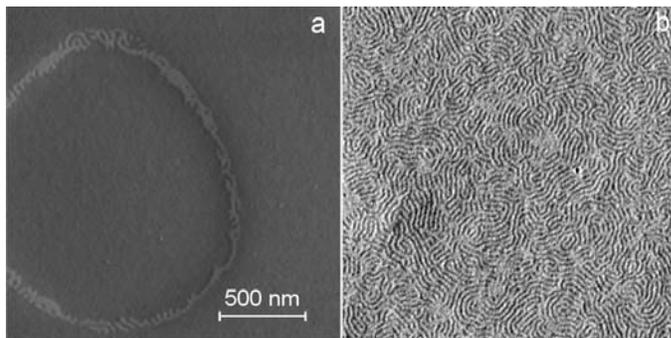


Figure 2. AFM phase images of surface of micro-phase separated lamellar dPS-PMMA BCP film (~65 nm thick) coated on (a) Xero-0.2M7m ($D_f=2.4$) and (b) SNP80 ($D_f=2.5$) substrates. The water contact angle for both the substrates was $\sim 65^\circ$

By developing a new sol-gel based xerogel substrates we have prepared fractally rough substrates to better understand factors controlling BCP orientation. Preliminary results indicate that the fractal dimension (D_f), which is a quantifiable measure of any rough substrate, irrespective of its periodic or non-periodic nature may be a critical determining factor in controlling the orientation

of the BCP lamellae. As seen from Fig. 2, even though the roughness amplitude ($R_{RMS}=30.4\text{nm}$) for the xerogel substrate is much higher than the nanoparticle ($R_{RMS}=5.2$) substrate, vertically oriented lamellae were obtained over a large area for the slightly higher D_f value (~ 2.5) of the nanoparticles rather than xerogel substrate. Xerogels with D_f around 2.5 are able to vertically orient BCP as well, so fractal dimension of roughness rather than amplitude of roughness seems to be the controlling parameter. Finally, besides topography and surface energy, residual solvent effects are shown to produce interesting surface morphology maps as an added control variable [2].

Future Work: In addition to silica xerogels, we will also explore the possibility of using resorcinol-formaldehyde (RF) based xerogels for preparing fractally rough substrates. The advantage of using RF-gel based substrates is that it can be converted to a conducting carbon substrate by pyrolysis, while preserving the fractal nanotopology needed for orientation control. This would be especially useful for solar cell applications, as the carbonized substrate can also work as a base electrode for conducting the holes/electrons through an external circuit for device testing. Due to the difference between the dense carbon-rich FPS phase and the hydrogen-rich P3HT phase, we expect a high contrast in neutron scattering with a scattering length density (SLD) of the order of $4.46 \times 10^{-6} \text{ \AA}^{-2}$. Neutron scattering would be a very useful tool to determine internal structure of these films. Recently we also submitted a proposal to CNMS for studying the directed self-assembly (orientation distribution, defects, long-range order, kinetics of ordering) of CNMS synthesized block copolymers with a [(polymer) – (semi-conducting NP)] or P-SNP architecture in thin films. One of the polymer phases incorporating percolating nanoparticles (PCBM) would act as an acceptor layer while the other polymeric phase (e.g. P3HT) as donor layer.

Publications

- [1] K. G. Yager, B. C. Berry, K. Page, D. Patton, A. Karim, E. J. Amis, *Soft Matter* **2009**, 5, 622.
- [2] Zhang X, Berry B.C., Yager K.G., Kim S., Jones R.L., Satija S., Pickel D. L., Douglas J.F., Karim A., *ACS Nano*, **2008**, 2, 2331. (*Using CNMS synthesized BCP*)