

Nanostructure and Self-Assembly in Copolymers and Copolymer Films

Chambers, L.¹, Bennett, T.¹, Huang, Y.¹, Blakey, I.^{1,2} and Jack, K.³

¹ Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Australia, ² Centre for Advanced Imaging, The University of Queensland, Australia, ³ Centre for Microscopy and Microanalysis, The University of Queensland, Australia

Block copolymers are ubiquitous materials with a vast range of applications, e.g. in drug delivery, photolithography, chemical sensors, surfactants, and as templates for the production of hard material¹. The properties and self-assembly of these materials, and hence the range of potential applications, can be tuned through a variety of mechanisms including the control of chemical functionalities of the blocks and their placement, addition of low molecular weight diluents, and the use of external stimuli such as chemical patterns or light. Moreover recent advancements in characterisation methods have opened up the possibility to interrogate these materials at the molecular- and nano-scale and to, therefore, better understand structure-property-performance relationships within them and to better control their self-assembly.

This work will focus on recent studies using high-throughput and grazing-incidence SAXS and microscopy to study the nanostructure of a range of bulk and thin-film copolymers. In particular the paper will focus on recent work in controlling the meso-phases and length scales that can be achieved in polystyrene-*b*-poly(methyl methacrylate) block-copolymers through the addition of ionic liquids (IL)². These studies have allowed for fabrication of targeted points on the phase diagram, such as the co-continuous phases, and the finer control over feature sizes. In addition, we present work on the development of long-range order in recently synthesised photo-responsive poly(benzyl methacrylate)-poly(*o*-nitrobenzyl methacrylate) block copolymers and the characterisation of patterned thin films created using a phot mask and selective solvent annealing of the exposed materials. We show that by tuning the feature size and by control of the solvent swelling it is possible to produce hierarchical patterns.

¹Mai, Y.; Eisenberg, A., *Chem. Soc. Rev.* 2012, **41**, 5969

²Bennet, T. M.; Jack K. S.; Thurecht, K. J.; Blakey, I., *Macromolecules* 2016, **49**, 205

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