NANO HIGHLIGHT
Thrust 1/Seed: Post-Fabrication Placement of Arbitrary Chemical Functionality on Microphase-Separated Thin Films of Amine-Reactive Block Copolymers

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During the seed grant period, we developed a modular approach to the post-fabrication placement of secondary chemical functionality on microphase-separated block copolymer thin films by exploiting the physicochemical properties of amine-reactive diblock copolymers. Our approach makes use of an azlactone-containing block copolymer [poly(styrene-*block*-4,4-dimethylazlactone), (Fig. 1A)] that microphase separates into domains of perpendicularly-oriented lamellae when spin-coated and thermally annealed as a thin film (Fig. 1B). These thin films present nanoscale patterns of amine-reactive azlactone groups (reactive "stripes") that serve as handles for the subsequent immobilization of primary amine-containing functionality (Fig. 1C). We have demonstrated that arbitrary chemical functionality can be installed on the surfaces of these reactive microphase-separated films by treatment with aqueous solutions of amines under mild conditions (using amine-functionalized fluorophores and small hydrophilic and hydrophobic amines to demonstrate proof of concept). Importantly, this approach can be used to introduce new functionality or modify film interfacial properties (e.g., wetting behaviour) without perturbing the underlying microphase-separated patterns dictated by the structure of the parent reactive block copolymer (Fig. 1D). This post-fabrication approach provides a basis for the development of modular approaches to the design of microphase separated block copolymer thin films and access to polymer-based coatings with tailored interfacial properties or patterned domains that would be difficult or impossible to prepare by the direct processing of functionally complex block copolymers.

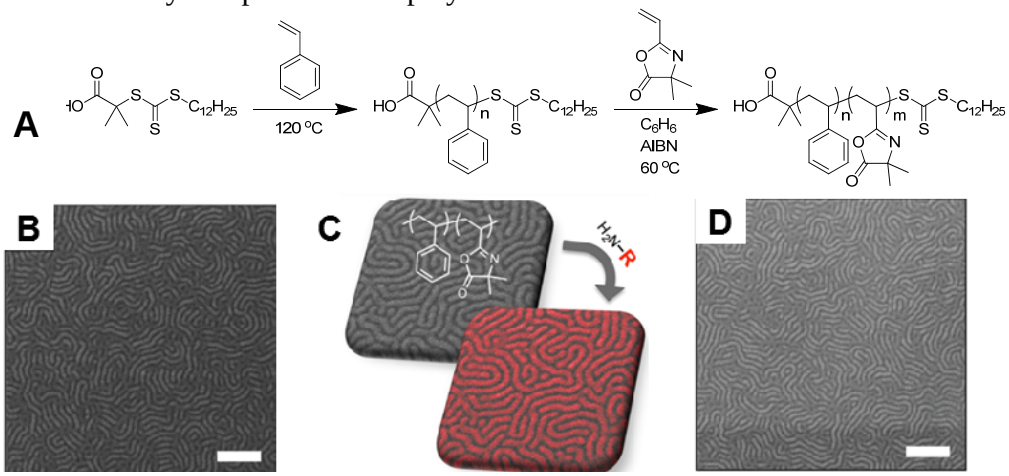

Figure 1: A) Polymerization of reactive poly(styrene-*block*-4,4-dimethylazlactone) block copolymers. B) SEM image of an amine-reactive lamellar block copolymer film. C) Cartoon illustrating the placement of an amine-functionalized molecule on a microphase-separated thin film D) SEM image of the same film as in B) after functionalization with an amine-bearing fluorophore.

References:

1) For further information about this project go to UW NSEC (www.nsec.wisc.edu) or email Padma Gopalan (pgopalan@engr.wisc.edu)
2) Speetjens, F.W., II.; Carter, M. C. D.; Kim, M.; Gopalan, P.; Mahanthappa, M.K.; Lynn, D. M. *ACS Macro Letters* **2014**, *3*, 1178-1182.