Autonomous discovery of emergent morphologies in directed self-assembly of block copolymer blends

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The directed self-assembly (DSA) of block copolymers (BCPs) is a powerful approach to fabricate complex nanostructure arrays, but discovering new morphologies that emerge with changes in polymer architecture, composition, or assembly constraints remains daunting due to the increased dimensionality of the DSA design space. Here, we demonstrate machine-guided discovery of emergent morphologies from a cylinder/lamellae BCP blend directed by a chemical grating template, conducted without human intervention on a synchrotron X-ray scattering beamline. This approach maps the morphology-template phase space in a fraction of the time required by manual characterization and highlights regions deserving more detailed investigation. These studies reveal localized, template-directed partitioning of coexisting lamellae- and cylinder-like subdomains at the template period length scale, manifesting as new morphologies such as aligned alternating subdomains, bilayers, or a novel "ladder" morphology. This work underscores the pivotal role autonomous characterization can play in advancing the paradigm of DSA.

We have characterized complex three-dimensional morphologies that emerge via self-assembly of a BCP blend thin films in response to underlying chemical pattern templates. By autonomously mapping a combinatorial sample using synchrotron X-ray scattering, we have significantly expanded the explorable parameter space compared to previous experiments, while simultaneously providing multifaceted morphology descriptors — all without immediate human intervention. The autonomously derived results guided subsequent electron microscopy characterization, enabling the judiciously targeted selection of regions to image for interpreting the assembly behavior. This investigation revealed the emergence of new morphologies such as a bilayer structure, alternating gratings, and a novel "ladder" morphology; it also helped to distill the general principle of subdomain partitioning that can be used to predict, interpret, and design patterns by the DSA of block copolymer blends, thereby adding a valuable mechanism to engineer hierarchical self-assembled morphologies with precise registry control. While our results are germane to selective DSA using BCP blends, the general approach to autonomously characterizing large parameter spaces demonstrated here provides a wealth of crucial information to understand complex assembly behavior while freeing up human experimenters to focus on interpretation and hypothesis formulation.

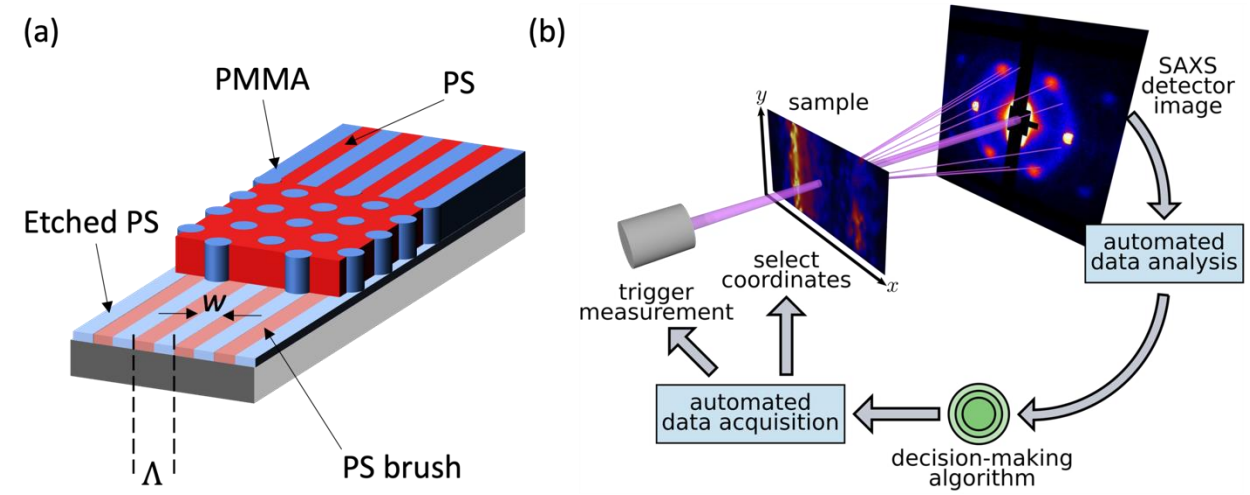

Fig. 1. Schematics of the experimental approach. (a) Directed self-assembly of a 1:1 blend of cylindrical and lamellar PS-*b*-PMMA BCPs is achieved using a grating chemical surface pattern with hydrophilic stripes of width w on a pitch Λ, etched into a surface-grafted PS brush. (b) Autonomous small-angle X-ray scattering (SAXS) measurement schematic. A motion system allows the instrument to select any (x, y) coordinate on the surface of the combinatorial sample for measurement. The SAXS pattern at each position is fed into a data analysis pipeline. A decision-making algorithm based on Gaussian Process methods then selects the next coordinate for measurement.

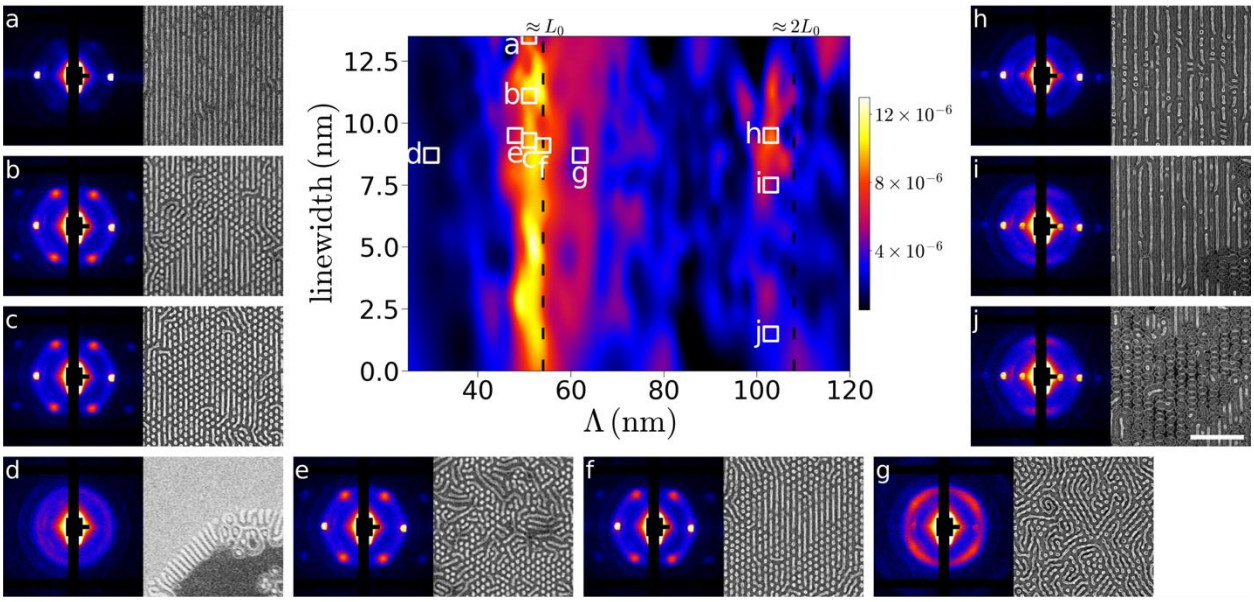

Fig. 2. Emergent morphologies within the DSA design space. At center is a map of scattering prefactor intensity (p) as a function of Λ and w. Exemplar SAXS patterns, accompanied by corresponding scanning electron micrographs (SEMs), indicate regions of the design space dominated by self-assembled line (a), hexagonal or line (b, c, e, f), isotropic (d), and alternating cylinders and lamellae or ladder (h-j) patterns. These pattern types are described in more detail in the main text. The white scale bar denoting 500 nm in (j) applies to all SEMs.