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Slice and View SEM Tomography of 3D Periodic Block CoPolymer Tubular Morpholgies

Edwin Thomas[1], Xueyan Feng[2] and Wenpeng Shan[2]

[1]Texas A & M University, Williamsburg, Virginia, United States, [2]Rice University, Houston, Texas, United States

We employ slice and view scanning electron microscopy (SVSEM) to reconstruct the microdomain morphology of tubular network block copolymer morphologies including the double gyroid and double diamond structures over large specimen volumes (1). Materials comprised of tubular networks have many unique and intriguing properties due to the percolated nature of the two networks in all 3 directions (i.e. multicontinuous structures).[2] Such tubular BCPs possess (nano)composite functional property attributes stemming from the nature of each component block and from their small length scale, mutual arrangement and in particular, the 3D continuity of each type of domain. Due to their complex nature and need to view defects over large volumes, SVSEM tomography allows unambiguous characterization of topological defects (2), dislocations and grain boundaries as well as the supra-unit cell structure and especially the sub-unit cell morphology, which for soft matter phases is intrinsically heterogeneous. We find that the lengths and diameters of struts of tubular network phases are relatively soft, and easily accommodate deformation while their angular geometry is stiff, maintaining local correlations even under strong symmetry-breaking distortions (3). The relative malleability of lengths and rigidity of angles between sub-unit cell features is in contrast to hard molecular crystals, where covalent geometry restricts bond lengths but accommodates strain via bond angle distortion. Crucially, unlike TEM tomography, SVSEM tomography can provide significantly larger extent of reconstruction in all three spatial dimensions, facilitating 3D reconstruction of volumes orders of magnitude larger than the typical volumes of the unit cell (4). Selected volume Bragg diffraction and Fourier filtering can be used to average coherent regions to achieve enhanced sub-unit cell feature resolution. The SVSEM milling technique and slice thickness, low voltage SEM image acquisition, image registration, Fourier filtering, definition of the isosurface, selected volume diffraction, domain segmentation and subsequent morphological measurements of block copolymers of polystyrene-polydimethyl siloxane will be discussed. Symmetry breaking in soft crystals is likely ubiquitous, but the intricate rearrangements can be disguised unless examined locally. Such symmetry-breaking distortions and point, line and surface defects are predicted to have critical impacts on charge and mass transport, wave propagation and photonic/phononic band gaps, and battery performance in materials with the tubular microdomain structure.

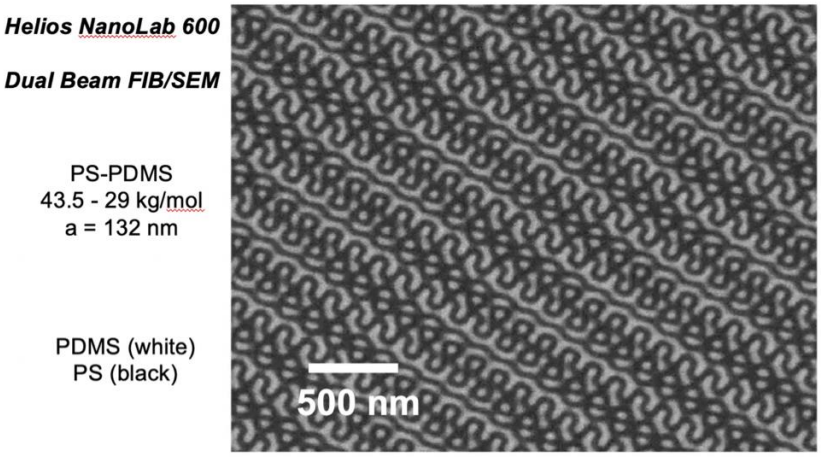

Figure 1. 1 keV SEM image or tubular network phase for a PS-PDMS diblock copolymer showing long range order.

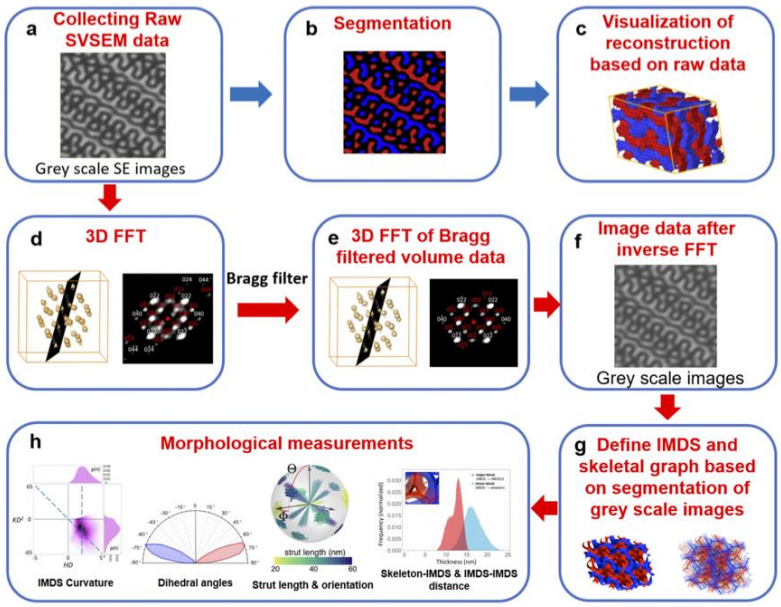

Figure 2. Work flow for SVSEM of tubular microdomain phases.

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