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Low Dose 4D Scanning Transmission Electron Microscopy of Block Copolymers and Homopolymers at 30 keV in an SEM

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Nanoparticles are of broad interest due to their unique properties and potential applications. In particular, nanostructures based on soft matter formed from homopolymer and block copolymer self-assembly are of interest for applications in optoelectronics, liquid crystals, and medical applications [1]. Self-assembled block copolymers are known to form diverse shapes including worm-like cylinders, lamellar sheets, and branched structures offering further tailoring capabilities. However, details of the crystallization-driven seeded growth mechanism still remain elusive [2]. These low-atomic number materials are challenging to study via transmission electron microscopy (TEM) due to their low-contrast and high sensitivity to beam damage [3]. Scanning Electron Microscopy (SEM) in conjunction with segmented scanning transmission electron microscopy (STEM) detectors can overcome these challenges as they operate at lower voltages (5-30 keV), which improves contrast, and greatly reduces knock-on damage [3]. Four-dimensional (4D) STEM extends upon this through using a fast pixelated detector to acquire diffraction patterns at every scanned position in the image.

In this work we applied 4D-STEM on a 30 kV Scanning Electron Microscope (Hitachi, SU-9000) using a pixelated hybrid direct electron detector (Dectris, Quadro), to study one- and two-dimensional (1 and 2D) structures formed from the self-assembly of block copolymers and homopolymers respectively. The diffraction information obtained was crucial in understanding growth mechanisms of the crystallizable polyferrocenylsilane (PFS) segments within these materials. Here, great convenience was seen in using 4D-STEM on the SU-9000 SEM/STEM instrument, including the ability to rapidly survey large fields view (upto ~20 × 20 μm) from which we obtained 10,000 (512 by 512 pixel) diffraction patterns with exposure times of around ~10 ms, to give a total sample dose of 25 e-/Å^2 or less. This low electron dose proved essential for successful observation of crystalline diffraction. Using Azorus software (from Hitachi High Technologies Canada, Inc.), allowed us to acquire and rapidly visually review the collected data with dynamic and responsive gamma adjustment at the microscope side, thus accelerating our understanding of these materials.

A high angle annular dark-field (HAADF) 30 keV STEM image of a 2D branched copolymer structure (Fig. 1a) and the associated diffraction patterns (DPs) acquired from the 4D-STEM data acquisition (Fig. 1b, c), taken at an average electron dose of 17 e-/Å^2, allows hexagonal diffraction patterns to be easily identified. This demonstrates the heteroepitaxial growth of the α-branch (marked α in Fig 1 (a), with DP in Fig 1(b)). The DP from the β-branch (highlighted in cyan Fig 1(c)) shows a rotation of approximately 7 degrees with the respect to the α-branch DP (yellow, Fig. 1(b,c)) indicating an additional nucleation site at the center of the copolymer. The 110 Miller index indicates the thermodynamic favorable growth direction.

Similar data on homopolymer structures (Fig. 2), shows DPs acquired from an initial 4D-STEM scan with a total dose of ~19 e-/Å^2 (Fig 2(b)), and then from a subsequent scan with an additional dose of 17 e-/Å^2 , to give a total dose of 36 e-/Å^2. Plots of the intensity through the diffraction peaks of these DPs (Fig. 2(d))) shows a diffraction peak intensity reduction of approximately 75% for both peaks in the second 4D-STEM pass. This highlights the high electron dose sensitivity of these homopolymers. Nonetheless we can gain this valuable and sensitive information conveniently in a relatively low kV, and high throughput, SEM type instrument. This technique is set to accelerate discoveries and understanding on this important class of inorganic materials.

Acknowledgements

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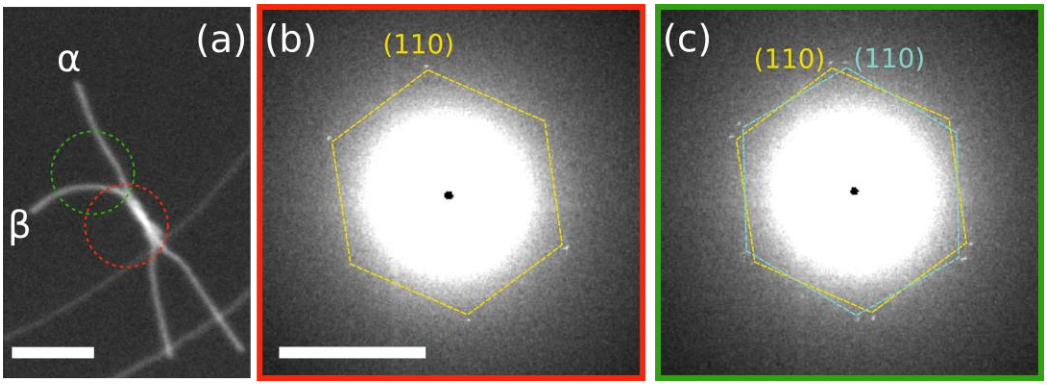

Figure 1. Figure 1. (a) High-angle annular dark field (HAADF) STEM image of a typical branched 2D block copolymer structure. The upper two branches are labelled as α and β and the red and green circles correspond to two regions from which the electron diffraction patterns (b and c) were collected. Yellow and cyan hexagons (inset to b, c) aid the identification of the diffraction pattern and emphasize their rotation. Scale bars are (a) 1 μm and (b, c has the same scale) 2 nm-1.

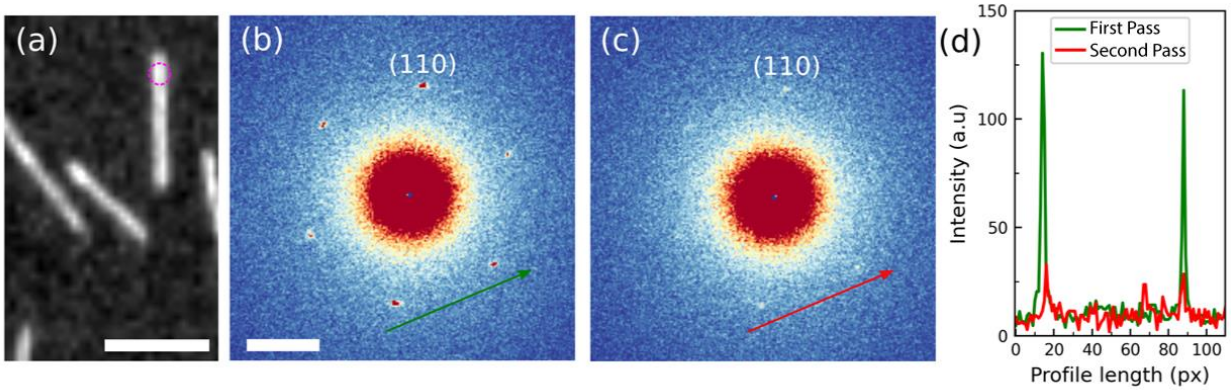

Figure 2. Figure 2. (a) High-angle annular dark field (HAADF) image of a homopolymer specimen. Diffraction patterns taken from the region encircled in (a) from the (b) first and (c) second 4D-STEM acquisition. (d) Intensity versus profile length plot taken in the directions indicated by the arrows in (b) and (c). [Note: the arrows are shifted down to avoid obscuring the diffraction spots]. Scale bars are (a) 1 μm and (b, c has the same scale) 2 nm-1.

References

[1] X. Zhuang, Y. Mai, D.Wu, F. Zhang, and X. Feng, Adv. Mater. 27 (2015)
[2] C. K. Wong, X. Qiang, A. H. E. Müller, and A. H. Gröschel, Prog. Polym. Sci. 102 (2020)
[3] C. Sun, E. Müller, M. Meffert, and D. Gerthsen, Microsc. Microanal. 24 (2018)

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