



Orientation mapping of semicrystalline polymers using scanning electron nanobeam diffraction



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ABSTRACT

We demonstrate a scanning electron nanobeam diffraction technique that can be used for mapping the size and distribution of nanoscale crystalline regions in a polymer blend. In addition, it can map the relative orientation of crystallites and the degree of crystallinity of the material. The model polymer blend is a 50:50 w/w mixture of semicrystalline poly(3-hexylthiophene-2,5-diyl) (P3HT) and amorphous polystyrene (PS). The technique uses a scanning electron beam to raster across the sample and acquires a diffraction image at each probe position. Through image alignment and filtering, the diffraction image dataset enables mapping of the crystalline regions within the scanned area and construction of an orientation map.

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1. Introduction

An outstanding question in the field of semicrystalline polymer characterization is how to directly observe the nanoscale orientation of crystalline domains. While characterization techniques such as electron backscattered scanning diffraction (Randle, 2009) can efficiently map the local grain structure in metals and ceramics at the nanometer scale, the sensitivity of polymer structure to electron bombardment precludes the use of these techniques, which require an extended exposure or a high electron dose. Furthermore, soft materials usually consist of light elements (e.g. C, O, N, and H) and lack contrast across different nanostructures as well as between nanostructures and the matrix. Most importantly, due to their chain folding mechanism, crystalline regions in a polymer are always surrounded by amorphous regions, which leads to local variations in the degree of crystallinity.

A number of characterization techniques have been successful in providing structural information in soft materials: X-ray diffraction (Kadem et al., 2014; Park et al., 2005), small-angle X-ray scattering (Dudenko et al., 2012; Kao et al., 2014; Mårdalen et al., 1992), wide-angle X-ray scattering (Duong et al., 2013; Müller et al., 2008; Perlich et al., 2010; Xiao et al., 2010), differential scanning calorimetry (Chan et al., 2010; da Silva and Mortimer, 1984; Remy et al., 2014), nuclear magnetic resonance imaging (Yazawa et al., 2010), UV-vis spectroscopy (Hammer et al., 2014), and molecular simulation models (Meredig et al., 2009). However, these techniques typically furnish data that is averaged over the bulk of the sample and thus do not provide a map of the dispersion and relative orientation of the crystallites within a local area. A few spatially resolved techniques have shown to be effective in mapping local polymer structure: a high-resolution transmission electron microscopy (TEM) technique has mapped polymer structure by tracing the lattice fringe arrangement visible in bright field (Takacs et al., 2014; Takacs et al., 2013); electron energy-loss spectroscopy spectra have been used in conjunction with scanning transmission electron microscopy (STEM) to differentiate between polymer molecules by their bonding types (Siangchaew et al., 1996); and

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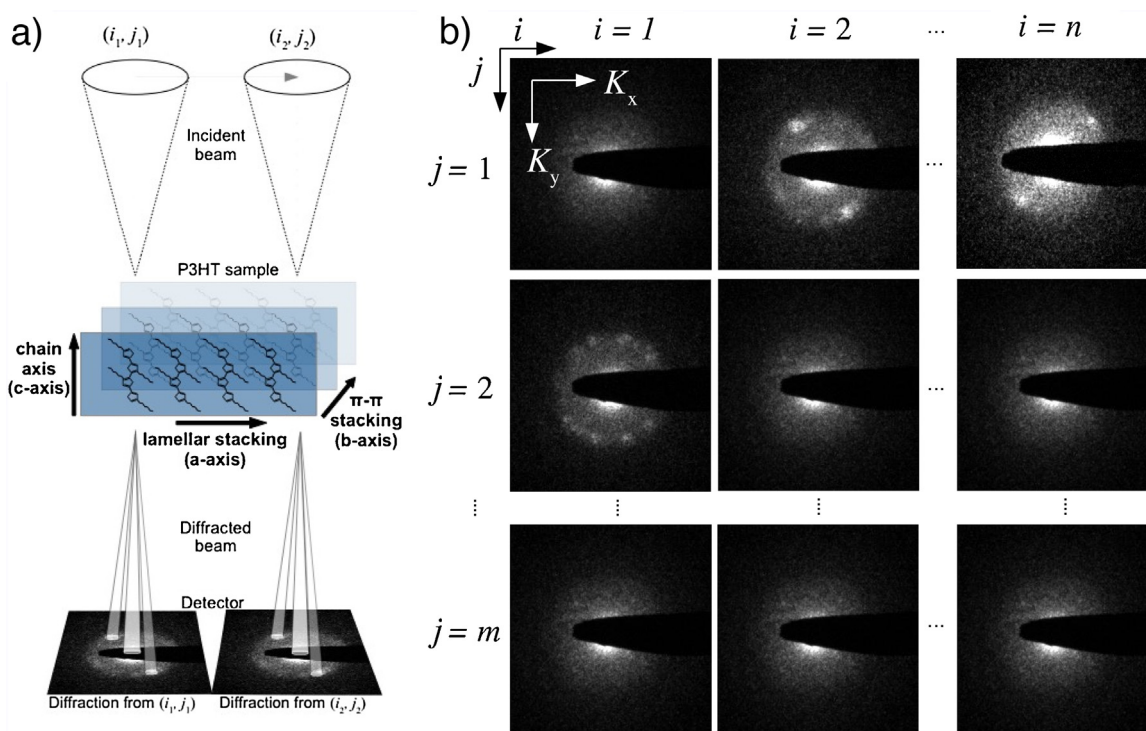


Fig. 1. The 4D-STEM experiment. (a) Convergent beam rasters the beam across the sample (i, j) and captures a full diffraction pattern (K_x, K_y) for each probe location. (b) The data takes the form of a 4-dimensional $n \times m$ set where each pixel in real space (i, j) corresponds to a full diffraction pattern (K_x, K_y) .

cryo-TEM tomography has determined the location of crystalline regions in polymers via diffraction of the encasing ice (Wirix et al., 2014).

The nanoscale orientation of semicrystalline polymers directly affects their electronic properties (Chu et al., 2008; Coropceanu et al., 2007), including their ability to generate excitons (Paquin et al., 2015) or carry charge (McMahon et al., 2011). While they do not yet rival the efficiency of ceramic materials, organic polymers and blends are promising candidates for organic photovoltaic (OPV) applications (Mazzio and Luscombe, 2014) due to their portability, low cost and ease of manufacturing. The preferential crystallization of poly(3-hexylthiophene) (P3HT) (Ludwigs et al., 2014) along its pi–pi bonds (Northrup, 2007) allows electrons and holes to easily move within the crystal bulk (Dag and Wang, 2010), which has a direct effect on device efficiency. P3HT was chosen as the subject of study in this work because its bulk and nanoscale crystalline structures have been examined extensively. In order to study distinct morphologies, the P3HT was blended with polystyrene (PS), which is known to form a phase-separated morphology with distinct phase boundaries that facilitated the validation of our image reconstruction methods. This work addresses the size, distribution, and the local Bragg peak orientation of crystalline domains in P3HT, information that is critical for engineering the improvement of organic photovoltaic materials.

In this study it is our goal to introduce a new technique for imaging semicrystalline polymers on the nanoscale; we apply this technique to the technologically relevant P3HT to produce spatially resolved maps of the crystalline domains.

2. Experimental methods

2.1. Materials and techniques

Regioregular P3HT was synthesized (93% regioregularity), purified, and characterized using the techniques described by Bhatt

et al. (2015). The molecular weights of P3HT and PS used in this work were 9 kg/mol and 10.8 kg/mol, respectively. P3HT and PS were dissolved separately in a solution of chlorobenzene (Motaung et al., 2010; Xie et al., 2009) with a concentration of 10 mg/mL and subsequently filtered with 0.2 μm polytetrafluoroethylene filters. A 50:50 w/w blend of P3HT and PS was made by blending equal weight of P3HT and PS solutions. The mixed solution was spin-coated onto a glass substrate at 3000 rpm for 60 s, resulting in a 30 nm thick film which was then deposited onto a lacey carbon-supported copper grid via lift-off in deionized water. The TEM samples were dried at room temperature in vacuum for 24 h and subsequently annealed for 1 h at 150 °C in an Ar-filled glovebox.

The 4-dimensional scanning electron microscopy (4D-STEM) data was acquired using a FEI Titan TEM operating at 200 and 300 kV (Fig. 1). A custom written Python script directed the STEM acquisition, which used a convergent beam with a convergence half-angle of 0.51 mrad (Fig. 1a) to raster over an $m \times n$ area and collect a stack of diffraction patterns (Fig. 1b). While the convergent probe allowed for STEM rastering, the small convergence angle ensured that the diffraction disks did not overlap in the diffraction patterns (DPs). The probe in this study was not aberration corrected. Initial low-dose low-mag STEM images (dwell time of 1 μs) enabled us to find the regions of interest. Annular dark-field STEM images were collected with a semi-angle of 34 mrad. The rastering was performed with a 20 and 40 nm step size and an exposure of 70 and 50 ms respectively; the time was chosen to optimize the diffracted signal given a chosen probe current. The 20 nm minimum step size was chosen because it was the smallest step size that did not result in a decrease in the Bragg scattered peak intensities. The diffraction images were captured with a Gatan Orius camera, but a more sensitive camera might be able to record similar diffraction intensities with a shorter dwell time and electron dose, effectively increasing the spatial resolution of the technique. The presence of sulfur atoms within P3HT backbone allowed us to map the sulfur K-edge

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