

Microstructural Study of Organic Mixed Ionic-Electronic Conductor Thin Films Using 4D-STEM and HRTEM

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Organic mixed ionic-electronic conductors (OMIECs) are a growing class of soft, dynamic, and functional materials with coupled mixed ionic and electronic conductivity. These materials are promising active elements in thin film electronic devices used for diverse applications such as energy storage and bioelectronics [1]. While new promising families of materials have emerged in this space, little is known about their microstructure. A complete understanding of the microstructure at multiple length scales is needed for building structure–property relationships for this family of materials.

In this study, we investigated the microstructure of synthetically designed polymeric OMIECs thin films using two complementary electron microscopy techniques: HRTEM and 4D-STEM. Both the dried and hydrated states were studied. Using the 4D-STEM technique we acquired microstructural data of our model polymer, a thin film of p(g3T2), over large fields of view in its dry state, and successfully captured its three crystalline characteristic spacings: lamellar stacking, backbone and π - π stacking; spanning dimensions from ~ 3.4 Å to ~ 20 Å (Fig. 1A-D). Using the py4DSTEM software package [2] and additional python algorithms we derived the film's orientation-map, mapping edge-on and face-on orientations in a flow line presentation (Fig. 1E) [3]. The map reveals mixed orientation with significantly more edge-on orientation in agreement with GIWAXS measurements. Furthermore, autocorrelation analysis of these planes reveals different levels of rigidity of the polymer chains along the two packing directions. In the edge-on orientation (along the π - π stacking) the relative grain orientation can reach up to 35° , in the face-on orientation along the lamellar direction 10° is the limit.

HRTEM imaging provided complementary information from the strong lamellar stacking signal, including from disordered and isotropic areas (Figure 2). Hydrated samples were also prepared as vitrified cryogenic samples and measured in HRTEM revealing a clear expansion of the lamellar stacking, rising to ~ 30 Å.

We believe this work yields new insights into the microstructure of OMIECs and contributes to the understanding of their structure-function relationships. These insights are essential for the development of more efficient low-cost organic-based functional devices and may contribute to the development of structural characterization techniques for soft-matter.

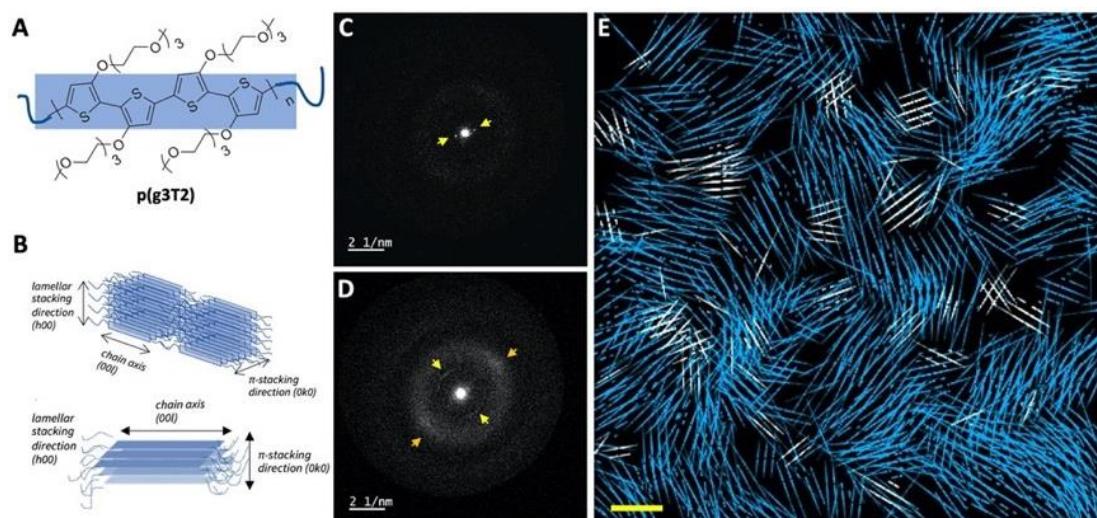


Figure 1. A) Chemical Structure of p(g3T2). B) Schematic of lamellar packing in semicrystalline polymers in edge-on (top) and face-on (bottom) orientations. C) and D) are diffraction patterns acquired in 4D-STEM, detecting both the lamellar stacking (~ 18.5 Å) in C, the backbone and π - π stacking peaks (~ 7.5 Å and ~ 3.6 Å correspondingly) in D. E) Orientation-map of dry film of p(g3T2) derived from 4D-STEM using py4DSTEM [2]. The lines represent the polymer chains. The blue lines are derived from π - π stacking peak whereas the white lines are derived from the lamellar stacking. The scale bar is 200 nm.

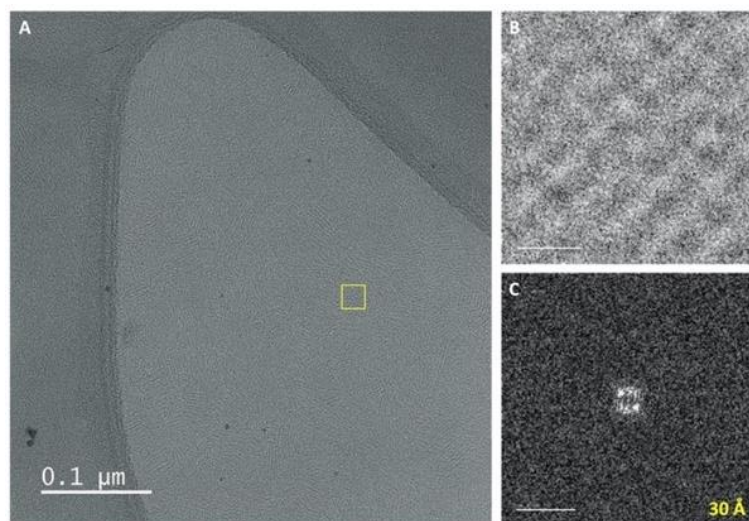


Figure 2. A) HRTEM image of hydrated pg3T2 film. B) Higher magnification of the area marked in A. C) FFT of the B, displaying a spacing of 30 Å.

References:

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