

# Electron pair distribution function analysis in the scanning TEM for probing nanoscale heterogeneity in amorphous and crystalline polymers and metal–organic frameworks

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The concept of microstructure is well defined in crystalline materials, encompassing the heterogeneity of crystal phases and the relative orientation, size, and composition of grains, defects, and interfaces. In amorphous materials, quantitative descriptions of local atomic structure often remain lacking. Many metal–organic framework (MOF) and polymer materials of interest in diverse applications from chemical separations and membranes to organic solar cells and organic light emitting diodes (OLEDs), as the result of synthesis or by design, form composites of crystalline as well as amorphous phases. To understand and predict the structure-determined properties in these materials, a local, nanoscale probe of amorphous structure is required. Electron beams offer the spatial resolution needed in the form of transmission electron microscopy, but imaging offers limited prospects for quantifying the structure of amorphous phases. As an alternative approach, spatially resolved electron beam pair distribution function (ePDF) has been developed in the scanning transmission electron microscope (STEM) [1]. Using a nearly parallel beam ( $\sim 1$  mrad convergence semiangle), a two-dimensional diffraction pattern can be recorded for crystalline materials at every beam position in a two-dimensional raster pattern over the sample, denoted 4D-STEM [2]. This dataset is also suited for total scattering analysis and ePDF with spatial resolution approaching the beam diameter ( $< 5$  nm), albeit with compromises in the effective PDF resolution and damping. Moreover, MOFs and polymers also undergo rapid changes in structure under conventionally used electron fluences for both imaging and STEM-ePDF approaches.

This presentation will introduce the development of low-dose STEM-ePDF (fluences  $\sim 10$  e<sup>-</sup> Å<sup>-2</sup>), first for blends of inorganic and MOF glasses [3] and for Fe-BTC [4], a MOF comprising nano-crystalline and amorphous fractions. The spatial resolution in STEM-ePDF enables separating data from distinct amorphous phases or from mixed crystalline and amorphous phases, delivering ePDF analysis of sufficient quality for assessing short- and medium-range order. In Fe-BTC, for example, STEM-ePDF has provided direct insight into the contributions of tetrahedral assemblies of metal clusters and ligands by isolating the ePDF from the amorphous Fe-BTC only. Building on this work, extensions to semi-crystalline polymer semiconductors will be discussed. In the case of blends of poly(9,9-di-n-octylfluoreny-2,7-diyl) denoted F8 and poly(9,9-dicetylfluorene-alt-benzothiadiazole) denoted F8BT, a green OLED material, STEM-ePDF likewise supports speciating signals from crystalline and non-crystalline regions. However, the non-crystalline phase separations and multi-layer model OLED device interfaces are visible in the total scattering data but give nearly identical ePDFs due to the limitations of the STEM-based ePDF and similarity in short-range order. Progress in modelling the contrast visible in angle-resolved STEM total scattering will be discussed as well as opportunities for further improvements in the quality of STEM-ePDFs and next steps in further applications to address questions like interface structure and structural changes during phase transitions.

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