

High Resolution TEM Imaging of Polymer Crystals using Low Dose Techniques

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The imaging of soft matter with electron beam-based microscopes is difficult due to the interaction mechanisms of the electrons with the material. In biological and organic samples, radiolysis processes that change the molecular structure of the material under investigation predominate. For imaging by electron microscopy, the change in the morphological appearance of the sample during the examination is more serious than the molecular change. Although there are different strategies to reduce the sensitivity of soft matter to radiation, such as cryo-conditions, exceeding a "lethal" electron dose ultimately leads to irreversible damage of the sample. This mechanism of radiolysis cannot be avoided and occurs in any material with covalent C-C bonds.

The strategy for imaging such radiation-sensitive samples is therefore mainly to reduce the local dose load. With the introduction of direct detection cameras, the total electron dose for image acquisition could actually be reduced. This led to a revolution especially in cryo-EM and structural biology. However, material science issues also benefit from this new camera technology. Thus, extremely beam-sensitive metal-organic frameworks could be displayed in high resolution in TEM [1].

Polymers, especially their crystals, are a comparable radiation-sensitive material family. Up to now, it has only been possible to produce high-resolution of polymer crystals with a great deal of effort [2,3].

In this article we show how high-resolution investigations of polymer crystals can be performed with the help of direct detection cameras. Although the structure of crystalline polymers has already been sufficiently researched, some questions are still challenging. The example of precision polymers, which are defined by equidistantly distributed defects in the chain, shows how these defects are arranged in the crystal. Furthermore, we show how the structure of orientation-induced polymer crystals can be represented by means of high resolution TEM examination. These orientation induced crystals form from a highly oriented melt which results in the formation of needle-like polymer crystals. We will show first results on their crystal structure and compare these results with the models proposed.

[1] D Zhang et al., *Science* **359**, 675-679 (2018)

[2] CJG Plummer, R Gensler and H.H. Kausch, *Colloid Polym. Sci.* **275** (1997) p. 1068 [3] LF Drummy, I Voigt-Martin and DC Martin, *Macromolecules* **34** (2001) p. 7416

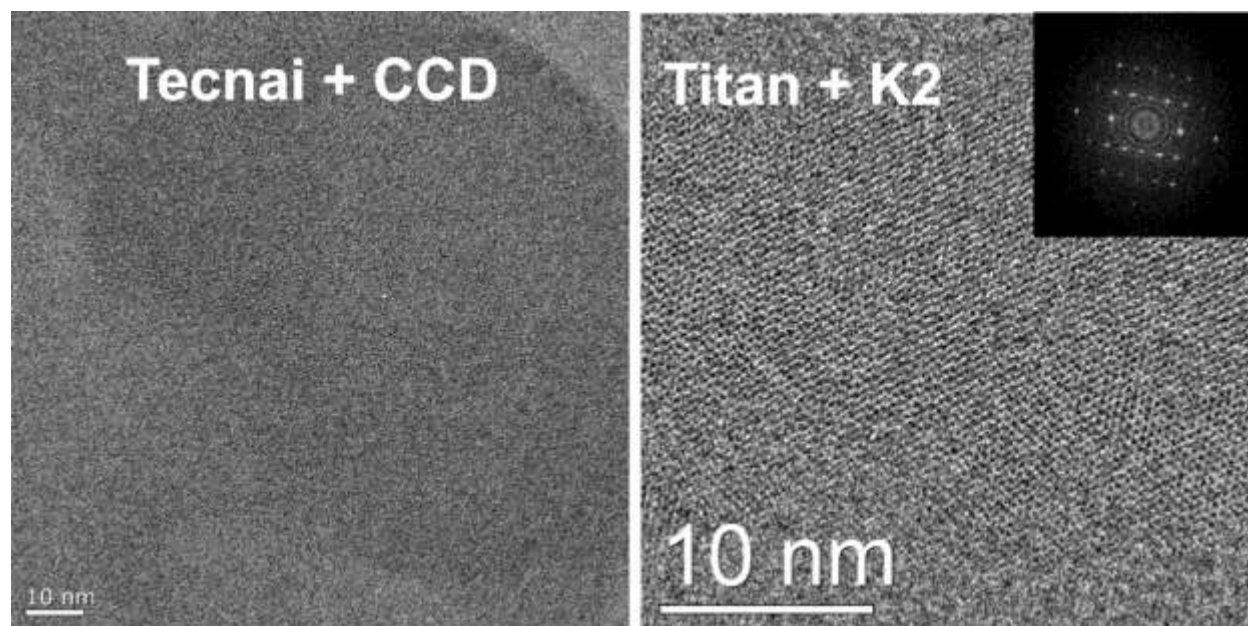


Figure 1. TEM micrographs of a solution crystallized precision polyethylene, having a propyl branch at every 38th position in the main chain. Using the same electron dose for acquisition of a TEM bright field micrograph, the CCD Camera does not collect enough electrons, to display the lattice pattern before the lethal dose is accumulated (left). With a direct detection camera less than the lethal dose is sufficient to achieve the lattice pattern (right).