

## Defects in Polyethylene Single Crystals: From Precisely Branched Molecules to Defect Planes in Polyethylene Single Crystals.

Haixin Zhou<sup>1,4</sup>, Bora Inci<sup>2</sup>, Kenneth B. Wagner<sup>3</sup> and Ingo Lieberwirth<sup>4</sup>

1. Beijing University of Chemical Technology, Department of Chemical Engineering, Beijing, China
2. University of Illinois, Beckman Institute, Illinois, USA
3. University of Florida, Department of Chemistry, Gainesville, USA
4. Max Planck Institute for Polymer Research, Mainz, Germany

Polyethylene (PE) single crystals grown from dilute solution are lozenge-shaped lamellae where the molecular chains are oriented normal to the lamellar surface. The molecular chains traverse the lamellar thickness many times by folding back and forth at the basal surfaces of the crystal [1]. The unique feature of polymer crystallization is, that the crystal units, e.g. the covalently bonded monomer units in the polymer chain, need to be arranged sequentially into the crystal taking the monomer sequence of the polymer into account. Defects in the polymer chain like branches, errors in tacticity or hetero-monomers will influence the crystallization process. Some of these can be incorporated into the crystal whereas others, for example large branches, are expelled to the amorphous phase. Due to this feature, it is possible to control crystal properties like degree of crystallization or lamellae thickness already by adjusting the macromolecular architecture during polymerization of the polymer.

Usually, any polymerization process will yield more or less irregularities, which are randomly distributed along the polymer chain. The type and density of defects in the polymer chain then determines e.g. the degree of crystallinity of the polymer as for example in high-(HDPE) and low-density polyethylene (LDPE).

However, in order to examine the influence of chain defects on the crystal structure and defect localization within the polymer crystal a well-defined and characterized system is essential. In our studies we used precisely tailored polyethylene with well-defined defects along the polymer chain. Using acrylic diene metathesis polymerization (ADMET) we were able to synthesize a homologous series of polyethylenes with defects precisely placed at every 39<sup>th</sup> carbon. Here the defects are alkyl groups (methyl, ethyl, and so on) attached at the respective position [2]. For our studies we focused on the polyethylene with a propyl group placed on every 39<sup>th</sup> carbon (PE-39-propyl) because we found by measuring the lamellar thickness that the defects must be incorporated into the crystal.

Single crystals of PE-39-propyl were grown from dilute solution in n-octane and transferred to a carbon coated TEM grid. Since polymer crystals in general, and especially the defect containing PE-39-propyl single crystals, are sensitive to beam damage under electron beam irradiation, special attention was paid to work under extreme low dose conditions during TEM inspection. We used a combination of scanning TEM in order to locate the crystals and nano-area parallel beam electron diffraction. Furthermore, we drastically reduced the intensity of the electron probe so that we were able to obtain electron diffraction (ED) patterns from areas as small as 20 nm in diameter. This gentle approach allowed for recording either a local ED or a dose series of ED. The TEM examinations were carried out at a FEI Tecnai F20 transmission electron microscope, operated at an acceleration voltage of 200 kV. For parallel beam ED measurements a 10  $\mu\text{m}$  C2 condenser aperture was used. ED patterns were acquired with a Gatan US 1000 CCD camera.

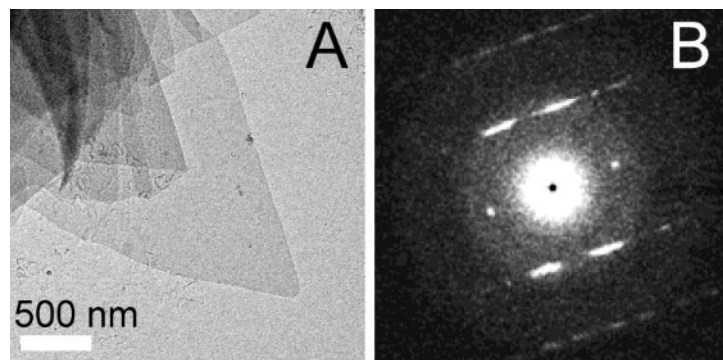
From ED analysis we were able to determine the lattice parameters and the crystal structure of the PE-39-propyl single crystals. Due to the incorporation of the bulky propyl side groups into the crystal the crystal structure changed from orthorhombic (for PE) to monoclinic, including a significant inflation of the lattice in crystalline a-direction. Furthermore, we could observe, that in the case of PE-39-propyl the polymer chains don't traverse the lamellae normal to the surface, but that they were tilted by  $30^\circ$  along the  $[-110]$  axis.

But the most remarkable observation was the presence of streaking at some of the reflections in the ED patterns. These are a clear indication for a defective plane within the crystal. Accordingly, the incorporated defects are aligned forming a layer of defects due to the constraints of the precisely arranged defects along the polymer chain.

Precision polyethylene with well-defined and well-arranged side groups is an ideal model system to study the effect of chain defects on the crystallization of polymers. Especially the examination with electron microscopic methods yields revealing insights to the crystal structure and the localization of defects. The observation of streaking in a polymer single crystal ED is rather unique as it clearly indicates that the defects are not randomly distributed, but arranged on a crystallographic plane within the crystal.

#### References:

- [1] A Keller, *Philosophical Magazine* **2** (1957) p. 1171.
- [2] B Inci *et al*, *Macromolecules* **45** (2012), p. 3367.



**Figure 1.** TEM brightfield micrograph of PE-39-propyl single crystals grown from dilute solution (A). Low dose nano area parallel beam electron diffraction pattern showing distinct streaking of the (110) and (200) reflections.