X-ray Linear Dichroism Microscopy of Crystalline Short Chain Alkanes and Semi-crystalline Polyethylene Thin Films

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Scanning transmission x-ray microscopy (STXM) has been used to determine the two Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra of *n*-tetracontane ($C_{40}H_{82}$) crystallites corresponding to the ***a*** and ***b*** directions of the orthorhombic unit cell of crystalline polyethylene. The two anisotropic lateral crystalline axis ***a*** and ***b***, *i.e.* <100> and <010> directions, respectively, can be distinguished by intensity changes in the spectral doublet near 287.5 eV. Prior NEXAFS dichroism data of PE and alkanes integrated over the <100> and <010> directions and only the dichroisms between the C-C chain along the ***c***-axis and the average for the C-H bonds has been known [1]. The spectra of *n*-tetracontane crystals can only be explained by a “further breakdown” of the building block model [2] and interactions between individual molecules.

This new information allows us to understand details of the growth orientation of polyethylene (PE) in ultrathin films. Overall, the same average spectra are found for PE thin film as in the bulk for PE of the same density [3, 4], clearly indicating that PE thin films are just as crystalline in thin films as they are in the bulk. In linear low density PE films, STXM shows large dichroic signals between various sample features for photon energies of ~287.4 eV and ~294 eV, irrespective of film thickness. This suggests that in these thin films, the average C-C bonds are in the plane of the thin film with predominantly edge-on lamellae orientation. In very thin films, the averaged NEXAFS spectrum switches from a slight dominance of ***b***-axis signal to one of slight ***a***-axis signal dominance. This suggests that the interfacial constraints alter the average orientations of crystallites. Linear medium density PE thin films showed a transition from edge-on to flat-on lamellae (C-C backbone parallel to the surface normal) in films thinner than 30 nm.

References:

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