Epitaxial crystallization of isotactic and syndiotactic polypropylene

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Epitaxy is defined as the growth of one crystalline phase (the guest crystal, here the polymer) on the surface of a crystal of another phase (the host crystal, here the substrate) in one or more strictly defined crystallographic orientations. The interactions imply a structural analogy between the two species in their contact planes, either in two, or sometimes only one direction. The details of the molecular interactions may be difficult to reach, and, as a consequence, the epitaxy is often defined in terms of a geometrical concordance of matching unit-cell dimensions: the disregistries should remain < 10%.

Polymer/substrate epitaxial interactions are of interest in order [1]:

1. to produce well-oriented polymer thin films well adapted for morphology and structural analyses by electron microscopy and electron diffraction;
2. to produce well-defined exposed crystalline surfaces highly appropriate for combined electron diffraction-atomic force microscopy (AFM) molecular modelling studies;
3. to understand the mechanisms of action and the efficiency of nucleating agents for polymers, and therefore establish guidelines for the search and design of new, or more effective, nucleating additives.

A major problem in the processing of crystalline polymers is indeed to achieve high concentration of crystalline nuclei which initiate crystal
growth, and thus to reduce molding cycles while improving properties (mechanical, optical). The number of ‘spontaneous’ nuclei in isotactic and syndiotactic polypropylenes (iPP and sPP) is, under normal conditions, in the range of \(10^6/\text{cm}^3\), giving rise to spherulites of \(\approx 100 \mu\text{m}\) diameter. Processing constraints would make it desirable to increase this number, sometimes up to \(>10^{12}/\text{cm}^3\) (spherulite size \(<\approx 1 \mu\text{m}\)), i.e. a size for which spherulites barely scatter light, and samples become less hazy. To this end, nucleating agents are added to the polymer. As a rule, they are minerals or low molecular weight organic materials, sometimes other polymers, which are crystalline at the crystallization temperature of the polymer; they act as a crystalline substrate for the crystallization of the polymer. Their overall activity depends on their degree of dispersion and the ‘quality’ of the interactions between the substrate and the polymer.

Although a number of nucleating agents are used for ‘simple’ polymers, such as polyethylene (PE), and for iPP and sPP, the real nature of the interactions has been worked out only in the last ten years or so. These interactions are essentially of epitaxial character, i.e. do not involve chemical reactions. For polymers with a ‘linear’ envelope (such as PE), the epitaxial relationship involves, as a rule, the chains lying ‘flat’ on the substrate (with the helix axis parallel to the substrate). The major dimensional match involves the interchain distance in the contact plane; the latter may differ for different substrates. As a consequence, the polymer lamellae stand ‘edge on’ on the substrate [1].

**EPITAXY OF ISOTACTIC POLYPROPYLENE**

The structural correspondence between iPP (in its stable \(\alpha\) phase) and the substrate is more complex than for linear chains. Indeed, iPP crystallizes in a three-fold helix in which the helical path rather than the helix axis (which is not materialized) interacts with the substrate when the chain lies on the substrate. Since this helical path is at a significant angle to the helix axis, and has opposite tilts for right- and left-handed helices, two orientations of the chains (and therefore the lamellae) are generated [1]; these are illustrated in Figure 1. They are very reminiscent of the so-called ‘cross-hatched’ morphology of iPP in its \(\alpha\) phase [2]. Technically, the \(ac\) face of the iPP unit-cell is in contact with the substrate (in this case, benzoic acid, used as a model for the well-known nucleating additive sodium benzoate). The major dimensional match involves the \(\alpha i\)PP interstrand distance (distance between two successive helical turns) of \(\approx 0.5 \text{ nm}\), and a substrate near \(0.5 \text{ nm}\) periodicity. Note that this \(\approx 0.5 \text{ nm}\) distance corresponds also to a standard interchain distance in PE. This feature explains that sodium benzoate is a nucleating agent for both \(\alpha i\)PP