Spherulitic crystallization and structure

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In a quiescent melt, isotactic polypropylene (iPP) crystallizes into spherulitic structures [1, 2]. Spherulite is a spheriform aggregate of chain-folded fibrillar or lamellar primary crystallites. According to a simplified model, crystallites start from a central, pin-point type nucleus and grow uniformly in all spatial directions radially, with noncrystallographic small angle branching in between. The branching of growing crystallites provides complete space filling. The phenomenological theory of spherulitic crystallization of polymers was developed and later partially revised by Keith and Padden [3] and Vaughan [4]. According to this theory, the contaminating components (e.g. fractions with low, if any, tendency to crystallize) segregated from the melt in the vicinity of the growing crystal surface are responsible for the branching of the fibrils and so for the space filling. Based on transmission electron microscopic (TEM) studies on spherulites Vaughan [4] drew attention to some contradictions in the phenomenological theory and proposed a ‘dominant/subsidiary growth model’ for the morphology development in semicrystalline polymers.

Morphological features, kinetics of growth, formation of structure and melting behavior of iPP spherulites were discovered [1, 2 and references therein]. During the crystallization of iPP, being a polymorphic material with several modifications [5], different types of spherulites may develop, which imply crystallites of the α-, β- and γ-modification [1, 2, 5–7]. All these polymorphs consist of right- and/or left-handed three-fold helices with 0.65 nm chain axis repeat distance. The molecular
aspects of crystal structure and morphology of different iPP polymorphs were recently reviewed by Lotz et al. [7]. The types and structural features of spherulites formed are markedly influenced by the thermal conditions of crystallization, by the thermal prehistory of melt, by the mechanical load applied to the crystallizing melt (pressure, shear or tensile stresses), and by the presence of extraneous materials (α- and β-nucleating agents, additives, etc.) [1, 2]. The spherulitic crystallization and structure of iPP may be readily visualized by polarized light microscopy (PLM). Their constituent elements, the primary crystallites, may be usually observed by electron and atomic force microscopy (AFM) [4]. Following two-dimensional crystallization (apart from its very early stage) in a thin film of the melt, PLM reveals the development of birefringent disc-like objects on randomly formed nuclei, radially growing at a constant rate (linear growth rate) under isothermal conditions. Due to the impingement of growing spherulitic fronts, the texture formed will consist of polygonal formations confined by straight or curved lines after the complete crystallization. The possible types of boundary lines developed between two adjacent spherulites and their mathematical description were analyzed by Varga [1, 2]. The average size of spherulites might be reduced by elevating the density of nuclei by adding different nucleating agents or by decreasing the crystallization temperature (Tc) [1].

α-SPHERULITE

During the crystallization of commercial iPP grades, essentially the α-modification is formed, sometimes accompanied by a lower or higher amount of β-modification. The α-modification of iPP (α-iPP) seems to be the thermodynamically stable form (but, see a critical analysis about the types of iPP polymorphism in [1]). The crystal cell of α-iPP is monoclinic with parameters \(a = 0.665 \text{ nm}, b = 2.096 \text{ nm}, c = 0.65 \text{ nm} \) and \( \beta = 99° 80' \), which consists of alternating right- and left-handed helices [5, 7].

Three different types of α-spherulites might grow from the melt depending on the Tc: positive radial (\( \alpha_I \)) below \( \approx 134^° \text{C} \), negative radial (\( \alpha_{II} \)) above \( \approx 138^° \text{C} \), and mixed-type spherulites (\( \alpha_m \)) in the intermediate temperature range [2]. The last have no inevitable birefringence and show no Maltese cross in the optical micrographs. Figure 1 shows SEM micrograph of an \( \alpha_{II} \)-type spherulite. It can be seen that the radial spherulite has a compact crystal array and contains straight lamellae. The formation of α-spherulites has a lower threshold temperature. At high supercooling (i.e. at \( T_c < \approx 90^° \text{C} \)) a mesomorphic (smectic) structure forms instead of a crystalline (spherulitic) one [5]. According to the structural model of spherulites based on the radial growth and small-angle branching of primary crystals, polymers are expected to produce