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Conformationally disordered crystals and their influence on material properties: The cases of isotactic polypropylene, isotactic poly(1-butene), and poly(L-lactic acid)

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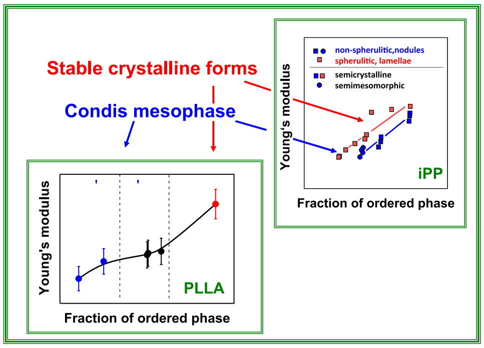
HIGHLIGHTS

- iPP, iPB-1 and PLLA can develop conformationally disordered (condis) structures.
- The condis phases of these three polymers are metastable.
- Transition to the stable crystalline structure is linked to chain mobility.
- The influence of the condis modifications on materials properties is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

This article provides a comprehensive review of the physical properties of the conformationally disordered (condis) structures of isotactic polypropylene (iPP), isotactic poly(1-butene) (iPB-1) and poly(L-lactic acid) (PLLA), in comparison with the respective more stable crystalline forms. The aim of this review is to define the influence of the condis modifications on the thermal and mechanical properties of these materials. The condis structures of the three polymers are metastable and spontaneously transform into the more stable crystalline structures upon annealing above a critical temperature. The transition from the mesophase to the more stable crystalline structure becomes possible when the chains have sufficient mobility to allow rearrangements of chain conformations. A rigid amorphous fraction develops during solidification of iPP, iPB-1 and PLLA. Crystallization of iPB-1 and PLLA into the more stable forms leads to a larger coupling of the amorphous and crystalline chain segments, compared to the conformationally disordered arrangements, which results in a higher fraction of rigid amorphous chain segments. The difference in chain packing, together with the varied mobility of the coupled amorphous chain portions, affects both the initial resistance to the tensile strain and the large strain properties. All the three stable crystalline forms have a higher Young's modulus compared to the condis mesophases, and can sustain lower deformation under mechanical stimuli.

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1. Introduction

The subject of polymer crystallization has received great interest over several decades and still provides fruitful area of research. Nevertheless, a general and complete understanding of polymer crystallization has not been achieved yet [1]. In recent years new concepts describing polymer crystallization were developed. Some of them take into account not only the needed polymer chain regularity and the ordered parts, but also the mobility of the amorphous phase, as it changes with the progress of the phase transition [1–3]. The ordered phase is surrounded by amorphous molecule segments, and the covalent linkages between the crystals and the surrounding amorphous phase can lead to the formation of a rigid amorphous fraction (RAF), which exhibits different properties than the bulk amorphous phase. The RAF remains glassy at temperatures higher than the glass transition temperature of the bulk amorphous phase, T_g, and can significantly affect the property profile.

Moreover, in several semicrystalline polymers the ordered phase can adopt different structures and morphologies, depending on the conditions of crystallization, which can largely affect materials properties. It is well known, in fact, that a wide range of physical properties such as thermal, mechanical, and electrical properties are influenced by the crystal modifications of polymorphic polymers. Therefore, studies on the relationship between crystal structure and crystallization conditions are of fundamental importance because they allow the tuning of physical performances of the polymeric materials by controlling their processing conditions.

Additional complication arises from the various degrees of order that the flexible, linear macromolecules can attain upon solidification. Among the different modifications of a given polymer, only one polymorph is thermodynamically stable at a specific temperature and pressure, other less stable modifications are metastable in the same conditions [1,4].

The main difference between the liquid and solid phases is the presence/absence of three types of large-amplitude motion (translation, rotation, and conformational motion). For a number of semicrystalline polymers, under a given thermo-mechanical history, not all the large amplitude motions are frozen in the ordered phase. In such case, the resulting condensed phase is a mesophase.

In synthetic polymers, various types of mesophases have been identified, which differ in the degree of order: Liquid crystals (liquid phases with orientational order, based on rigid mesogens of linear, lath-like, or disc-like shape within the molecules), plastic crystals (small molecules, rotatable within the crystal to produce orientational disorder) and condis crystals (conformationally disordered crystals with positional and orientational order) [4]. These mesophases are characterized by an increase of disorder relative to the crystal. Moreover, they have large-amplitude intermolecular or intramolecular mobility, i.e., a glass transition temperature below which they are solids can be detected. Of special interest are the conformationally disordered crystals, which can form upon conventional processing conditions in a number of polymers, as detailed in Ref. [4]. These crystals are often metastable and transform into a more stable crystal modification upon aging or heating, and the transformation is usually accompanied by remarkable variations in materials properties [4].

The aim of this manuscript is to define the influence of condis crystal modifications on material properties, with detailed analyses on three polymorphic polymers of great industrial interest: two polyolefins, isotactic polypropylene (iPP) and isotactic poly(1-butene) (iPB-1), and a biodegradable polyester, poly(L-lactic acid) (PLLA). All these three polymers develop metastable conformationally disordered crystals upon industrial processing, and their properties are highly affected by crystal polymorphism, as detailed below.

2. Isotactic polypropylene

2.1. Polymorphs of isotactic polypropylene

Isotactic polypropylene (iPP) is a crystallizable polymer with a maximum degree of crystallinity of 60–70%. It is a polymorphic polymer and can develop various crystal modifications, called α-, β-, and γ structures, and a mesophase [5–7]. Cooling the relaxed, isotropic melt at low or moderate rates typically leads to the formation of the thermodynamically stable monoclinic α-crystal polymorph [7–9], in which the molecular segments adopt a 2^*3_1 helical conformation, that is, three repeating units, each one containing two backbone carbons, are needed to complete a 360° turn of the chain [7,10]. Similar as in the case of isotactic poly(1-butene) detailed below, the formation of a helix in iPP is caused by the intramolecular steric hindrance between the methyl groups on adoption of a straight molecule segment upon crystallization/ordering. The helices are aligned parallel to the *c*-axis of the unit cell, and left-handed and right-handed helices are arranged such to achieve closest packing as nearest neighbors, by contacting two isochiral helices in addition to three nearest neighbor helices of opposite chirality, ultimately leading to a coordination number of five. The equilibrium melting temperature, enthalpy of melting, and crystal density of the α-structure are 187.5 °C, 8.7 kJ mol^{-1}, and 0.94 g cm^{-1}, respectively [7]. Crystallization of the α-form from the melt occurs by chain folding and spherulitic growth of lamellae [11–13]. Epitaxial branching of mother lamellae during radial growth within the spherulites occurs at the lateral {010} surfaces and leads to tangential growth of daughter lamellae [14,15].

The β-structure of iPP is observed at special crystallization conditions including crystallization in a temperature gradient, or crystallization of the oriented melt [16–20]. The growth rate of β-crystals is higher than that of α-crystals in a wide temperature range between 105 and 141 °C, which is attributed to a lower surface free-energy penalty on addition of molecular stems at the {110} growth face, that is, to presence of favorable secondary nucleation sites [21–23]. Since the primary nucleation rate of the β-phase is lower than that of α-crystals, iPP containing β-crystals typically is obtained only with the use of specific heterogeneous β-phase nucleators [24–26]. The β-phase exhibits a trigonal unit cell, and forms negatively birefringent, radial or banded spherulites on crystallization from the quiescent melt [27,28]. Being controlled by the thermal history, the β-phase may re-crystallize to α-crystals upon heating. iPP containing β-phase is technically important since it shows lower stiffness and yield strength, as well as higher ductility, impact strength and toughness than iPP containing α-crystals, caused by the absence of cross-hatching of lamellae [29–31].

The orthorhombic γ-structure is observed in low molar mass fractions of polydisperse iPP, in random copolymers with shortened isotactic sequences, or on crystallization at elevated pressure [32–38]. Typically it forms in conjunction with the α-phase, mixed within spherulites. Since α- and γ-crystallization leads to simultaneous occurrence of radially and tangentially aligned lamellae within spherulites, the net birefringence of spherulites is lower than that of β-spherulites, which allows straightforward identification of the latter by polarizing optical microscopy [39].

Besides the α-, β-, and γ-crystal polymorphs, a mesophase may form from the isotropic melt at high supercooling. Initially, the mesophase of iPP was considered as a 'smectic' phase in which helical chain segments are positioned parallel, irrespective of their handedness, forming a pseudo-hexagonal structure [8,40,41]. Although isotactic polypropylene forms a helix, this helix is not as rigid to serve as mesogen. Without a mesogen, a liquid crystal structure is unlikely [4]. Later on, it was suggested that the

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