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The effect of pressure pulses on isotactic polypropylene crystallization

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ABSTRACT

High hydrostatic pressure pulses, up to 80 MPa, have been imposed for different time and at various temperatures on molten iPP during cooling. The absence of any effect on the crystallization behavior after pressure release and further cooling demonstrates either that no nucleation precursor is produced by this thermo-mechanical history or that the lifetime of pressure-induced precursors is extremely short, as if no crystallization occurs during pressurization. Even when crystals develop during the pressurized stage, when high pressure is released, subsequent crystallization takes place in the same temperature range in which the polymer crystallizes at atmospheric pressure.

Structure and morphology of samples partially crystallized under pressure were investigated. WAXD show that, as expected, the fraction of γ-crystallinity firstly increases with increasing the time under pressure up to impinging of γ-spherulites and then levels off at a constant value. Morphological investigation performed on microtomed samples reveals that the γ-spherulites formed under high pressure exhibit positive birefringence and that their skeleton continues to grow during cooling when pressure is released. On heating, these spherulites melted first, but incompletely: the radial lamellar texture is still present up to relatively high temperature. These features seem to be consistent with the spherulitic architecture described by Lotz: infilling γ-lamellae grow by epitaxy on a skeleton of α-lamellae. Under the adopted experimental conditions, pre-imposed pressure pulses do not promote formation of extra nuclei, while they largely affect the crystal structure and the morphology of melt crystallized isotactic polypropylene.

1. Introduction

Hydrostatic pressure affects polymer crystallization, both in terms of kinetics and structural features. First of all, high pressure shifts both equilibrium melting and glass transition temperatures to higher values. Consequently, the whole crystallization window is shifted to higher temperatures [1–3]. The pressure shift factor of polyolefines was reported to be of the order of 30 °C/100 MPa [4]. For what concerns the kinetics aspects, it has been reported that, at a given temperature, high pressure accelerates the crystallization process and reduces the Avrami exponent [4]. However, when the crystallization kinetics are compared at a constant undercooling, it has been observed that high pressure slows down the rate of

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crystallization [5], as one should expect as a consequence of the reduced mobility associated to the decrease of free volume. Moreover, Angelloz et al. [6] investigated the nucleation density under different high pressures and found that this characteristic is dictated by the actual undercooling and is independent of the applied pressure. In addition to the influence on the kinetics of development of crystalline order, high hydrostatic pressure has been shown to have a strong effect also on structural and morphological features of the ordered state. For example, under high pressure, HDPE develops a hexagonal phase with extended chain morphology instead of the more stable lamellar orthorhombic modification [7–9]. On the other hand, high pressure crystallization of i-PP leads to formation of the orthorhombic γ-form instead of the most usual α-monoclinic structure [10,11]. Extended-chain morphologies similar to those of HDPE were also found in PET and PA6 crystallized under elevated pressure [12–16].

Due to its important role in the plastic industry, i-PP has been thoroughly investigated, both from scientific and applied point of view, and its rich polymorphism has attracted wide interest since the days it was firstly synthesized. At least four different crystalline structures, namely the α-, β-, γ- and δ-forms, and one mesomorphic phase have been reported for i-PP [17–22]. Under the effect of high pressure, α-, γ- and meso-phase can be obtained, depending on the pressure value, compression rate and cooling rates [8,23–25]. Mostly, i-PP crystalizes in α- and/or γ-phase under high hydrostatic pressure, the higher the pressure, the larger is the fraction of γ-phase. van Drongelen [25] has reported that pressure shifts the development of both α- and γ-polymorphs to a high temperature range, but to a greater extent for the later structure.

Owing to its technological relevance, i-PP is one of the polymers whose crystallization under high pressures has drawn more attention in the past couple of decades. Fulchiron's group [6,26,27] focused on the kinetics aspects by performing crystallization experiments at high pressure under various cooling conditions to simulate polymer solidification and to predict crystallinity development during processing. Rather than to kinetic issues, Phillips et al. [10,11,28,29] tackled the problem of high pressure crystallization from the thermodynamic, structural and morphological point of views. They reported that, for high molecular weight i-PP, the γ-phase starts to form, together with the α-structure, at a pressure of about 50 MPa; and that it becomes dominant at *ca.* 200 MPa [7]. In another publication [8], they attempted to clarify the reason why the γ-phase is favored at the elevated pressure. According to their results, the γ structure develops at high pressure and low undercooling because of thermodynamic reasons since, in these conditions, its free energy is slightly smaller than that of the α-form. In addition, by performing an in-depth morphological characterization of pure γ-form spherulites obtained under the pressure of 20 MPa and different undercoolings [29], they observed peculiar feather-like spherulites, and ascribed this feature to a self-epitaxy growth mechanism of γ-lamellae.

Our experiments of pressure-induced crystallization stem from the above experimental evidences and tackle a problem which has not been considered in the past. Since, during actual processing (*e.g.*, in injection molding), the molten polymer usually experiences high pressure pulses of short duration, our target is to understand if these pressure pulses have an effect on the kinetics of subsequent crystallization when temperature is decreased below the equilibrium melting point.

In analogy to what it has been ascertained for the polymer crystallization behavior during and after imposition of deviatoric stresses (shear or tension), our aim is to establish if pulses of the hydrostatic stresses lead to formation of nucleation precursors which accelerate subsequent crystallization during cooling. In other terms, we performed experiments aiming at understanding if squeezing the system by high pressure favors the formation of bundles of locally parallel chain segments arranged in a quasi-crystallographic register, *i.e.* of precursors of crystallization nuclei.

2. Experimental part

2.1. Materials

A commercial highly stereoregular ZN-i-PP homopolymer (Borealis HD601CF) was used. It has a weight average molecular weight (M_w) of 365 kg/mol and a polydispersity index (M_w/M_n) of 5.4. The nominal melting point (DSC at 10 °C/min) is 163.8 °C.

2.2. P-V-T apparatus

A unique dilatometer (IME Technologies) was used; detailed information on this apparatus, that was originally developed in our group, have already been described elsewhere [23,25,41,42]. The actual imposed cooling conditions are expressed in terms of the average cooling rate experienced by the samples in the temperature range in which the polymer solidifies, *i.e.*, between 195 and 130 °C.

The PVT samples are pre-produced with a mini-injection molding machine (Babyplast) in the form of rings with inner and outer diameter of 21 and 22 mm, respectively. For i-PP, this corresponds to a mass of about 76 mg, wall thickness of 0.5 mm and height of 2.5 mm. PVT experiments were carried out according to the procedure schematically shown in Fig. 1.

The sample is initially heated to 220 °C and kept at this temperature for 10 min to erase previous thermal history. During this period the pressure is defined by the weight of the lid (approximately 5 MPa). In the next step, the melt is brought to the target temperature at which the high pressure is imposed (hereafter T_p) and then, after 5 min, required to stabilize the temperature, a high pressure (80 MPa) is applied and held for different times (t_p). Pressure differences are typically realized within 2–5 s. Finally, the pressure is released to 10 MPa and isobaric cooling to room temperature is obtained by blowing