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Unusual crystallization behavior of isotactic polypropylene and propene/1-alkene copolymers at large undercoolings

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During the investigation of the crystallization of metallocene isotactic polypropylene and copolymers with low amount of 1-butene and 1-hexene at large undercoolings, an unexpected behavior has been found. Random copolymers crystallize faster than the homopolymer between 80 and 40 °C, while at high temperatures the overall crystallization rates follow the expected trend. On the basis of structural and morphological evidences we suggest that the overall structuring kinetics of the homopolymer is slowed down by the concomitant formation of mesophase and monoclinic structures. This effect is absent in the copolymers because the branched counits retard the development of mesophase.

1. Introduction

By quenching a semicrystalline polymer to very low temperatures, a high amount of compositional and configurational defective repeating units, as well as of conformational and packing defects, may remain trapped in the developing ordered phases, thus generating a “mesomorphic form” or a “solid mesophase”, i.e., a structure with features intermediate between those of the crystalline and amorphous states.

Because of its industrial and scientific relevance, the mesophase of isotactic polypropylene (i-PP) has been extensively investigated [1–14]. The suggested structure is characterized by small bundles of parallel chains in 3/1 helical conformation with short range lateral order [3], with a density laying between those of the amorphous state and of the monoclinic structure (the common α-phase). Piccarolo et al. [5,8,9] demonstrated that a competition between formation of crystalline and mesomorphic order sets in on increasing cooling rate and, eventually, the latter prevails above *ca.* 100 °C/s. Profound changes in the morphology, and thus in the physical properties of the material, are linked to the development of the mesomorphic form. The typical cross-hatched lamellae of the α-form spherulites are replaced in semi-mesomorphic samples by nanometric nodular morphologies lacking lamellar superstructure. [9,12,13]

The kinetics of mesophase formation has been investigated mainly by Schick and coworkers employing ultrafast chip-calorimetry. De Santis et al. [15] performed isothermal crystallization experiments revealing that two bell-shaped curves, which intersect at *ca.* 45 °C, are required to describe the temperature dependence of the overall crystallization rate. The one at low temperature was attributed to the formation of the mesophase which, at room temperature, goes to completion in fractions of a second. The existence of two distinct kinetic processes, both in i-PP homopolymers and in random copolymers, was independently confirmed by us through a Continuous-Cooling-Curves (CCC) approach [16].

However, the exact mechanism of formation, and thus the correct interpretation of the kinetic curves obtained by chip-calorimetry, is still under debate. Schick et al. suggested that the low temperature region of the plot reciprocal half-crystallization time vs. temperature should be ascribed to homogeneous nucleation [15,17]. On the basis of in-situ optical microscopy and fast time-resolved X-ray diffraction, Nishida et al. proposed that mesophase formation resembles a spinodal decomposition process, i.e., it is preceded by nano-scale density fluctuations throughout the sample [18]. De Rosa et al. investigated low isotacticity polypropylene samples by quenching the molten polymers to 0 °C and observed a decrease of structuring kinetics with increasing defect content [19]. The data were interpreted at the light of the classical

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nucleation and growth model. Similarly, Alamo et al. proposed a diffusion controlled growth of mesophase in propene/1-hexene copolymers crystallized at low temperatures. [20]

In this work the kinetics of isothermal crystallization of metallocenic i-PP at large undercoolings is quantitatively compared with that of narrowly distributed copolymers containing matching low contents of 1-butene or 1-hexene co-units. The kinetic curves recorded by chip-calorimetry are unexpected and suggest a re-interpretation based on competing growth of mesophase and monoclinic structures.

2. Materials and methods

The i-PP homopolymer (i-PP), the propene/1-butene (PB3.4) and propene/1-hexene (PH3.5) copolymers under investigation are experimental samples synthesized with a metallocene catalyst and kindly provided by ExxonMobil. The copolymers were received as powders and are free of additives. The homopolymer had been pelletized and hence, contains ~0.05 wt% antioxidants (Irganox and Irgafos), as confirmed by FTIR. Detailed molecular characterization of the samples was already reported [21,22]. We recall that they have similar molecular weight and polydispersity (around 200 kg/mol and 1.8, respectively) and that the copolymers feature around 1.7 mol% of comonomer and a total defect content of about 3.4 mol %. The intra-chain distribution of the comonomer is random and the single site nature of the catalyst ensures a narrow inter-chain distribution of the comonomer content. The homopolymer contains stereo- and regio-defects for a total content of 1.7 mol %.

Isothermal crystallization experiments at large undercoolings were carried out by means of a Mettler-Toledo power-compensation Flash DSC1. Details on calibration and sample preparation procedure can be found elsewhere [23,24]. The samples were first heated at 210 °C and kept at the melt temperature for 0.1 s, a time sufficient to erase any memory of previous thermal history. After the melt annealing step, the polymer was quickly brought to the chosen crystallization temperature, at a rate of 2000 °C/s, in order to avoid crystallization during cooling. Finally the heat flow released during isothermal crystallization was monitored as a function of time during 5 s. Crystallization temperatures between 90 and −10 °C were explored. Thermograms were also recorded during cooling at rates between 20 and 500 °C/s.

Structural characterization was performed by means of Wide Angle X-ray Diffraction (WAXD) on 200 μm thick polymer films crystallized by rapid quenching in a thermal bath at the chosen temperature (between 60 and 10 °C). Data were acquired at the beamline DUBBLE of the European Synchrotron Radiation Facility [25], using a wavelength of 1.033 Å and a Pilatus 300 K detector about 200 mm distant from the sample.

Free surface films suitable for AFM imaging were prepared by re-melting a melt pressed film (~50 μm) placed on a microscope coverslip in a hot plate at 200 °C for 3 min. The molten film was ballistically dropped into a bath of de-ionized water set at a controlled temperature (0, 23, 60 or 80 °C) and kept for 15–20 min. The samples were further transferred to room temperature and dried under vacuum at room temperature for 2 h prior scanning. AFM images were acquired in tapping mode in air under ambient conditions using either a Multimode 8 or a Dimension Icon atomic force microscope with NanoScope V Controllers, all commercialized by Bruker. The samples were scanned using a J scanner and Bruker silicon probes (FESPA) with a tip radius of less than 12 nm, nominal resonant frequency of 75 kHz, and nominal spring constant of 2.8 N/m. Height, phase and amplitude images were recorded simultaneously at a resolution of 512 × 512 pixels and a scanning rate of 0.5 Hz.

3. Results and discussion

Fig. 1 displays selected examples of exotherms recorded at cooling rates from 20 to 500 °C/s for the homopolymer and the two copolymers. The homopolymer displays the two structural ordering processes observed in prior work for i-PP and i-PP random copolymers [15–17,25–27]. The two exotherms have been previously associated with the formation of monoclinic crystals in the 60–80 °C range, and with the formation of mesomorphic bundles at lower temperatures (25–30 °C).

While the behavior of the homopolymer conforms to literature results, the behavior of PB3.4 and PH3.5 copolymers analyzed here (Fig. 1) is significantly different, as only one exotherm is observed on cooling. The temperature range of the exothermic transition (50–70 °C) is consistent with the formation of the α-phase. Interestingly, mesophase does not develop on cooling, even at cooling rates greater than 20 °C/s, that have been shown to favor its formation in previously studied i-PP copolymers [26–29]. It is apparent from the experimental dynamic cooling data that the development of the mesophase in the investigated copolymers is a slow process, since it is not observed in the explored range of cooling rates.

The range of cooling rates for the formation of α-crystals or mesophase is shown in Fig. 2, where the exothermic peak temperatures detected on cooling are plotted vs. cooling rate. Clearly, only i-PP develops the mesophase at cooling rates greater than 30 °C/s. Ordering of any type in the homopolymer and copolymers is suppressed at cooling rates greater than ~300 °C/s. To better elucidate differences between the homopolymer and the copolymers in crystallization kinetics at high undercoolings, the structuring process from the molten state was also studied isothermally in a temperature (T_c) range between −5 and 90 °C. The amorphous state at T_c was obtained by cooling the molten polymer from 210 °C to T_c at 2000 °C/s.

Examples of Flash DSC traces during isothermal crystallization of the homopolymer and the propene/1-butene copolymer at different temperatures are reported in Fig. 3a–d. Similar results

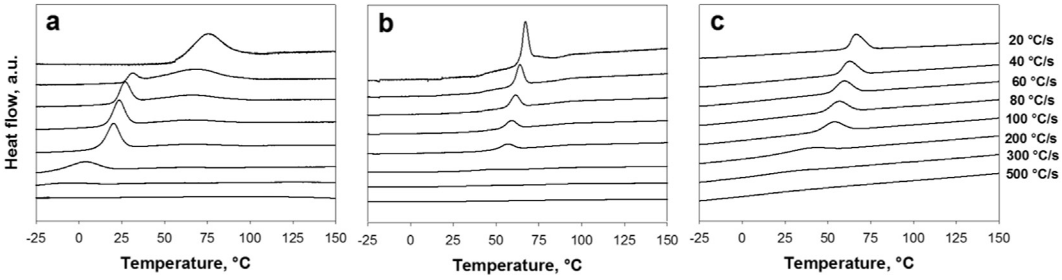

Fig. 1. Heat flow as a function of temperature acquired on cooling at the indicated cooling rates: i-PP homopolymer (a), propene/1-butene (b) and propene/1-hexene (c) copolymers.