	Experiment title:	Experiment number:
	Unravelling polymorphic crystallization of metallocenic isotactic poly(1-butene)	MA-2809
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Shifts: 6	**Local contact(s)**: Daniel Hermida	

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Report:

Isotactic poly(1-butene) (i-PB) is a semicrystalline polymer exhibiting an intriguing polymorphic behavior: three crystalline structures, characterized by different chain conformations and packing modes have been identified, and addressed as Form I, II and III. In commercial samples, made by heterogeneous catalysts, melt crystallization invariantly leads to the formation of the tetragonal structure, Form II. However, Form II is metastable and evolves toward the ultimately stable trigonal Form I upon storage at room temperature. The orthorhombic Form III is obtained instead from diluted or semi-diluted solutions only.

The development of homogeneous, single-site, metallocene catalysts enabled a true engineering of polymer chain defects, providing a wide tunability of defects type and content. As a consequence, the final polymer properties can be tailored directly from the synthesis step, affording for instance the preparation of stiff or soft materials starting from the very same monomer. Among the various common chain defects in stereoregular polyolefins, constitutional (i.e. comonomer units) and configurational (i.e. stereodefects) defects can be mentioned. Obviously these defects, which interrupt the chain regularity, have a large impact on polymer crystallization. The case of metallocene-made isotactic poly(1-butene) is relevant to the present proposal. It has been shown that the presence of stereodefects in otherwise regular isotactic poly(1-butene) has surprising effects on its polymorphic crystallization.4 Indeed, for defects content (quantified as the value of [rr] triads) above about 2 mol%, the usual tetragonal Form II is replaced by the trigonal Form I. Form I, in stereodefective samples, develops directly from the melt, bypassing the commonly observed Form II-to-Form I phase transformation.

Moreover, the polymorphism of these samples also shows a remarkable supercooling dependence.

Indeed, samples containing more than about 2 mol % of [rr] triads develop either the trigonal Form I, when cooled from the melt at about 10 °C/min; or the orthorhombic modification (Form III), for slightly faster cooling conditions. It is worth to underline that Form III melt-crystallization has never been observed in commercial samples.

The present proposal aimed at a deeper understanding of melt crystallization of i-PB, including the effect of microstructure and cooling conditions, in order to generate new knowledge and eventually lead to the control over i-PB polymorphism. In particular, the conditions of formation of the different polymorphs in

metallocene i-PB with various stereodefects content have been explored with temperature-resolved WAXD aiming at gaining a deeper understanding on the role of chain defects and crystallization conditions on i-PB polymorphic behavior by melt crystallization.

i-PBu homopolymers containing two different percentages % of [rr] defects have been first characterized for their non-isothermal crystallization behavior at cooling rates between 5 and 40 °C/min. Both samples developed only Form II on cooling (crystallization around room temperature) or on cold crystallization during subsequent heating (@ 10°C/min). Therefore we focus on isothermal crystallization at lower undercoolings. Only the sample containing higher %mol [rr] defects developed both structures in the explored crystallization temperature range.
It is clearly assessed that in this polymer Form I (or I') and Form II grow concomitantly from the melt in the temperature range ≈45-60 °C. An example is shown in Figure 1 below, for a crystallization temperature of 55 °C.

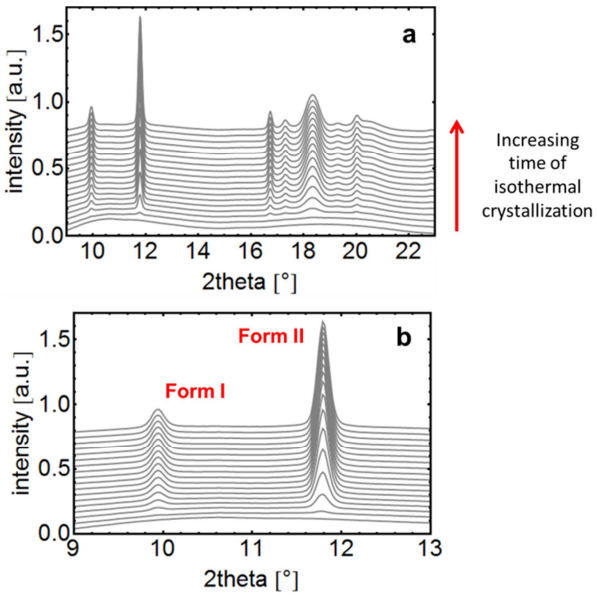

Figure 1. Time resolved WAXd patterns of L02_186 sample (3 mol% [rr] defects) crystalized at 55°C. Full angular range (a) and detail of the diagnostic peaks (b) of the two polymorphs.

At lower temperatures (i.e. ≤ 40 °C) only Form II develops, while at higher (≈65 °C) the sole Form I is observed (in traces, since we did not allow a sufficient time for complete crystallization).
The relative amount of the two structures depends on their respective crystallization rates.
The observed trend determining the final polymorphic content at a given crystallization temperature, can be schematically described with the following plot.

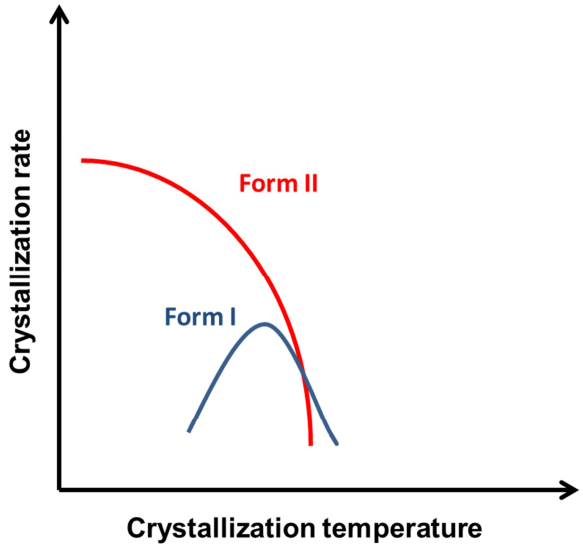

Figure 2. Schematic trend of the temperature dependence of crystallization rate of the two polymorphs.

In the next figure, the intensities of the (110)I and (200)II peaks of the two polymorphs are reported as a function of time for the various crystallization temperatures. The crystallization rate of Form I (or I') reaches its maximum value at 50 °C, and thus decreases for lower or higher temperature values. On the other hand Form II crystallization is the fastest at 40 °C, and then gets slower and slower with decreasing undercooling up to 60 °C.

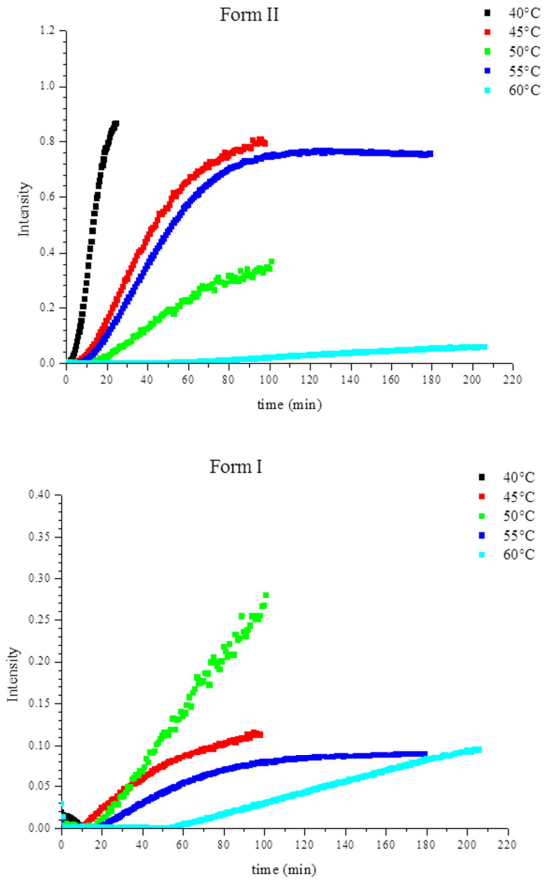

Figure 3. Intensity of the diagnostic Form II (above) and Form I(below) diffraction peaks as a function of crystallization time for different temperatures.

The results obtained in this synchrotron study of the crystallization behavior of different i-PBs containing different [rr] defects, allow further understanding of the relationship between the molecular architecture and the complicated kinetics of the crystallization of the melt, in particular at conditions relevant in polymer processing, that is, on fast cooling and high supercooling, respectively.
Further studies are in progress to clarify still opened issues.