

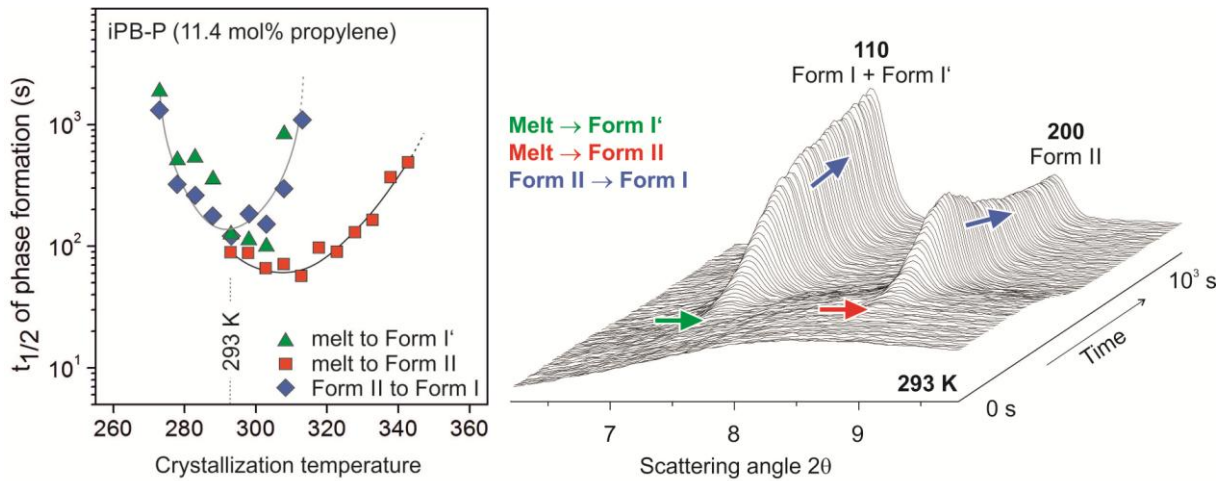


	Experiment title: The effect of molecular features on Ostwald's Rule of Stages in Butene-1/Propene copolymers	Experiment number: MA-2058
Beamline: BM26	Date(s) of experiment: From 23/09/2013 at 08:00 to 27/09/2013	Date of report: 21-02-2014
Shifts: 9	Local contact(s): Giuseppe PORTALE	
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Report:

Isotactic polybutene-1 (iPB-1) is a semicrystalline thermoplastic with a balanced property profile including high heat distortion temperature and low tendency to creep. In industrial applications, iPB-1 is favored for rather specific products; however, the commercial use of this material can further be broadened by random copolymerization of butene-1 with low amount of 1-alkenes as co-units. The modification and tailoring of the semicrystalline morphology and of the crystallization kinetics of iPB-1 based materials results from the disruption of the chain regularity. Despite of enormous industrial importance and extensive past research, the dual-step transition of the melt into Form II mesophase followed by conversion of the mesophase into Form I crystals is still focus of scientific discussions. While in the past in particular the copolymer system butene-1/ethylene has been characterized regarding the crystallization behavior, in this work the copolymer system butene-1/propylene has been investigated. Note that it is assumed that the transition kinetics in these two copolymer systems is expected significantly different due to different tolerance of these co-units to participate on the crystallization process. While ethylene co-units are excluded from crystallization, propylene co-units may isomorphically replace butene-1 units in the ordered phases.

In the current work, we investigated the solidification and crystallization process of random isotactic butene-1/propylene copolymers (iPB-P) by wide-angle X-ray scattering (WAXS) upon rapid cooling of the melt followed by isothermal solidification using a switchable Linkam hot stage. In combination with the use of a Pilatus 300k detector with high data acquisition frequency of 20 Hz, the experiments enabled us to follow the solidification at conditions as are evident in polymer processing. Furthermore, the performed X-ray experiments served for assignment of calorimetrically detected phase transitions, obtained by fast scanning chip calorimetry (FSC) in prior work.



In the left Figure are shown half-times ($t_{1/2}$) of the transition of the melt into Form II mesophase (red symbols), of the melt into Form I' crystals (green symbols) and of the Form II mesophase into Form I crystals (blue symbols) of an iPB-P copolymer with 11.4 mol% propylene as a function of the crystallization temperature, obtained by calorimetry. The data can be read such that at rather high temperature first mesophase develops (red symbols) which then transforms into Form I crystals (blue symbols). Additionally with decreasing transition temperature, there is simultaneously observed direct formation of Form I' crystals (green symbols). Important in the context of the performed synchrotron experiments, an assignment of the different exothermic transitions was possible only with the knowledge of the WAXS patterns collected here. As an example, a representative WAXS data set, illustrating the process of isothermal structure development of the particular iPB-P copolymer with 11.4 mol% propylene at 293 K, is shown with the right Figure, demonstrating the urgent need to combine calorimetry and WAXS as experimental techniques to quantitatively describe the crystallization kinetics and polymorphic behavior of iPB-P copolymers. The plot shows with the front curves the WAXS pattern of the melt which begins to transform after about 80 s almost simultaneously into Form II mesophase and Form I' crystals, as it is indicated with the appearance of the characteristic peaks. The decrease of the intensity of the scattering peak of the Form II mesophase reveals the phase transition of the Form II mesophase into Form I crystals.

In a wider view, it has been shown that addition of propylene into the butene-1 chain leads to a retardation of the phase transition of the melt into Form II mesophase, and an acceleration of the Form II to Form I transition. At high co-unit content, even direct formation of the melt into Form I' crystals may be possible. The results obtained in this synchrotron study of the crystallization behavior of iPB-1 based copolymers allows further understanding of the relationship between the molecular architecture and the complicated kinetics of the solidification of the melt, in particular at conditions relevant in polymer processing, that is, on fast cooling and high supercooling, respectively.