	Experiment title: Structure formation of polymers at rapid cooling: Crystal polymorphism of poly(butylene naphthalate)	Experiment number: 26-02-580
Beamline: BM26	**Date(s) of experiment**: From 31/08/2011 at 08:00 to01/09/2011	**Date of report**: *16-09-2011*
Shifts: 3	**Local contact(s)**: Hermida Merino Daniel	

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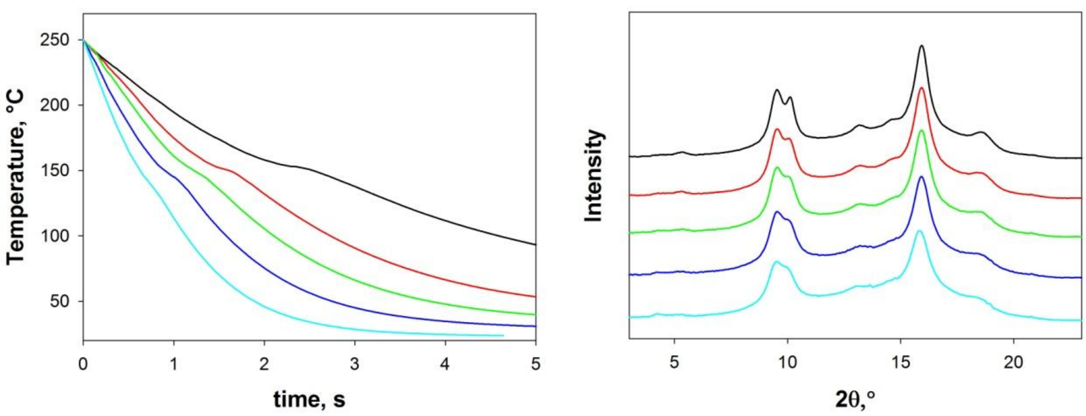
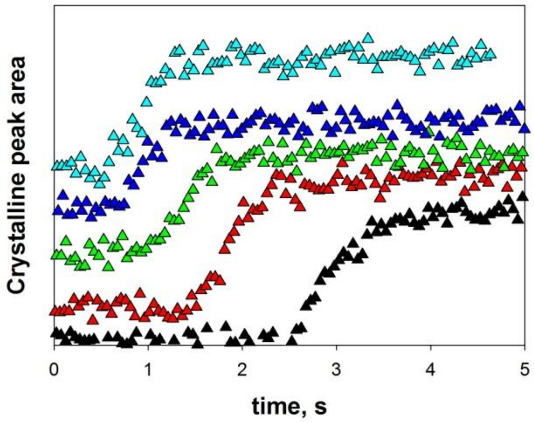
Report:

Poly(butylenes naphthalate) (PBN) is a novel crystallizable polyester with superior thermal stability; the melting and glass transition temperatures are around 240 and 70°C. Despite its commercial use e.g. for fiber or container production, only little is known about structure formation at rapid cooling. Several crystalline polymorphs have been reported, including a mesophase which develop upon quenching. However the conditions required for the formation of this latter lower-order structure, in terms of cooling rate and/or undercooling, are still unknown. Due to the scientific and industrial relevance of this information, the structuring of PBN at high cooling rates has been investigated in this beamtime, by simultaneous acquisition of WAXD pattern and thermal history during rapid cooling from the melt state in an home-built quenching device. The use of a Pilatus 300k detector enabled us to attain an high acquisition frequency (20Hz), suitable to follow structural evolution taking place even in less than one second.

The figure below reports some representative thermal histories, along with the correspondent structure at room temperature.



The crystallization process can be clearly identified by looking at the cooling curves (left). The temperature exhibits a deviation from the expected exponential decay with time, due to the release of crystallization latent heat. It can be noticed that, with increasing cooling rate, the structuring process shifts towards shorter times, while the crystallization temperature is only slightly affected. This is typical of polymers presenting a fast crystallization kinetics.
The structural changes with the applied cooling rate can be appreciated on the right side of the figure, where the colors of the WAXD patterns represent the particular thermal history. In the explored range of cooling rates PBN solidifies in the crystalline α-form. A decrease of crystallite sizes and/or perfection can be deduced by observing the broadening of the crystalline diffraction peaks.
Crystallization kinetics data can be conveniently derived from the real-time WAXD during cooling, for instance by tracking the evolution of the area of a given diffraction peak. Some preliminary results are summarized in the figure below. The colors of the data points refer to the thermal histories of the previous figure, the curves have been shifted vertically for the sake of clarity.



The typical sigmoidal trend of crystallinity vs. time is always observed. Remarkably, the tecnique proved to be efficient even to probe processess occurring in split seconds.

The preliminary results presented in this report will be integrated with further data obtained by off-line structural characterization of quenched samples, as well as with a detailed calorimetric study, to be performed with Flash DSC of Mettler Toledo. The combination of different experimental techniques will allow us to understand - and quantitatively describe - the crystallization and polymorphic behavior of PBN in processing-relevant conditions.