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ESRF

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
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- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** "Resolving Kinetics of Early Structure Formation During Shear-induced Crystallization of Polypropylene"	**Experiment number**: ME-964
Beamline: BM26B	**Date of experiment**: from: 10-Feb-2005 to: 14-Feb-2005	**Date of report**: 25-Feb-2005
Shifts: 12	**Local contact(s)**: Dr. Florian Meneau	*Received at ESRF:*

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Report:

During our recent beamtime allocation at BM26b (10-14 Feb, 2005), we successful commissioned a new instrument specially designed to probe shear-induced crystallization at this beamline. Thanks to the detector capabilities at the beamline BM26b, we were able to reduce by an order of magnitude the required WAXD acquisition times for resolution of early structure formation in sheared iPP from our previous 5 s to 500 ms. Also, the capability of simultaneous SAXS and WAXD allowed us to compare the time that structure emerges on the nanoscale and unit-cell scale.

This work is part of a broader program to discover the molecular basis of the dramatic effects of flow on the early stages of flow-induced crystallization in semicrystalline polymers [1-3]. The presence of oriented precursors prior to crystallization has attracted scientific consideration in the last few years [4], and its impact on development of semicrystalline morphology during and after flow is of enormous commercial interest. Processing can accelerate crystallization kinetics by orders of magnitude. Indeed, for isotactic polypropylene (iPP), the time necessary for the appearance of wide angle X-ray diffraction (WAXD) crystallinity can be 100 times faster after cessation of short–term shearing than for quiescent conditions at temperatures in the vicinity of 145 ºC [1].

Previous synchrotron work provided valuable information regarding the influence of shear stress, shearing duration and crystallization temperature on the nanostructure (lamellar thickness, crystallinity, orientation, etc.) of iPP subjected to shearing [1]. However, the initial stages of crystallization could not be resolved due to the limited time resolution detection capabilities (the fastest acquisition time was 5 s). In addition, the set up only allowed measurement of either WAXD or SAXS patterns. The goal of the present work was to find evidence on the precursor structures of shear-induced crystallization of iPP, using rapid time resolution detectors for simultaneous SAXS and WAXD measurements, which are available at BM26b. Our shear equipment was designed specifically to be mounted on BM26b. The apparatus consists of three primary parts: a reservoir for holding and heating the sample, a pneumatic actuator for driving the flow and a flow cell with diamond windows that permit in situ x-ray measurements.

Simultaneous SAXS and WAXD measurements were carried out using 2-D detectors. The 2-D multiwire gas-filled SAXS detector was placed 4.1 m away from the sample. WAXD data were acquired using a CCD camera placed 25 cm from the sample such that the equatorial region of the crystalline reflections could be observed. In the experiments performed, the flow cell was initially held at 215 ºC (above $T_{m,o}$ = 208°C) and filled with polymer melt from the reservoir. The cell was then cooled down to the crystallization temperature, 145 ºC, and held isothermally thereafter. Then, a short-term high shear pulse was applied to the melt, and the diffraction patterns were recorded during and after the shear pulse. After being subjected to a wall shear stress of 0.12 MPa for 3 s, a strongly oriented population of crystallites forms (Figure 1). Prior studies have shown that the oriented growth occurs in the regions of high shear stress, and the non-oriented crystallites form where the stress is lower.

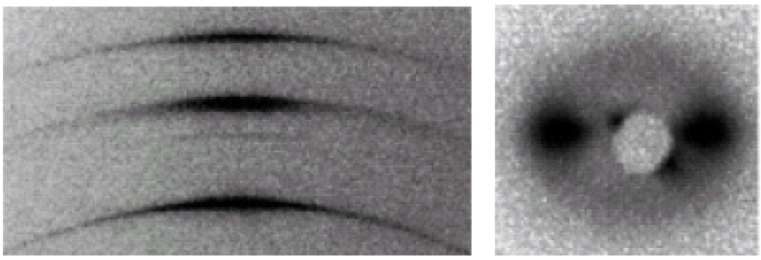

Figure 1. The flow direction is horizontal. Left: WAXD pattern showing the equatorial maxima of the (110), (040) and (130) peaks of α phase of iPP. Right: SAXS pattern exhibiting two diffraction maxima on the meridian, associated to well developed oriented lamellar stacks. Patterns acquired 25 min after shear.

To detect the peaks corresponding to dilute oriented structures at very early times after shear, the 2-D patterns were subjected to the following analysis. For each 2θ diffraction angle of the 2-D SAXS and WAXD patterns, an azimuthal integration over 80º - 100º for SAXS (i.e., ± 10º away from the meridian), and 82º - 98º for WAXD was carried out. With time after cessation of flow (3 s, 0.12 MPa, 145 °C), WAXD peaks are evident at approximately 5 s and SAXS maxima already appear at 2 s (Figure 2). The acquisition time for WAXD and SAXS was 500 ms and 1 s respectively. The time labeled in Figure 2 corresponds to the time after cessation of shear. Under our prior time resolution (5 s), both were evident in the very first frame; now we can see that they are separated in time.

Analogous experiments carried out using a shearing time of 6 s yield similar results, WAXD maxima appearing later than SAXS. The acquisition time of 500 ms was determined to be the limit for acceptable resolution for WAXD patterns. Thus, we have improved our WAXD time resolution from 5 s to approximately 500 ms. We intend to improve our WAXD time resolution capabilites in subsequent runs by incorporating the 1-D MicroStrip Gas Chamber detector developed in BM26b beamline.

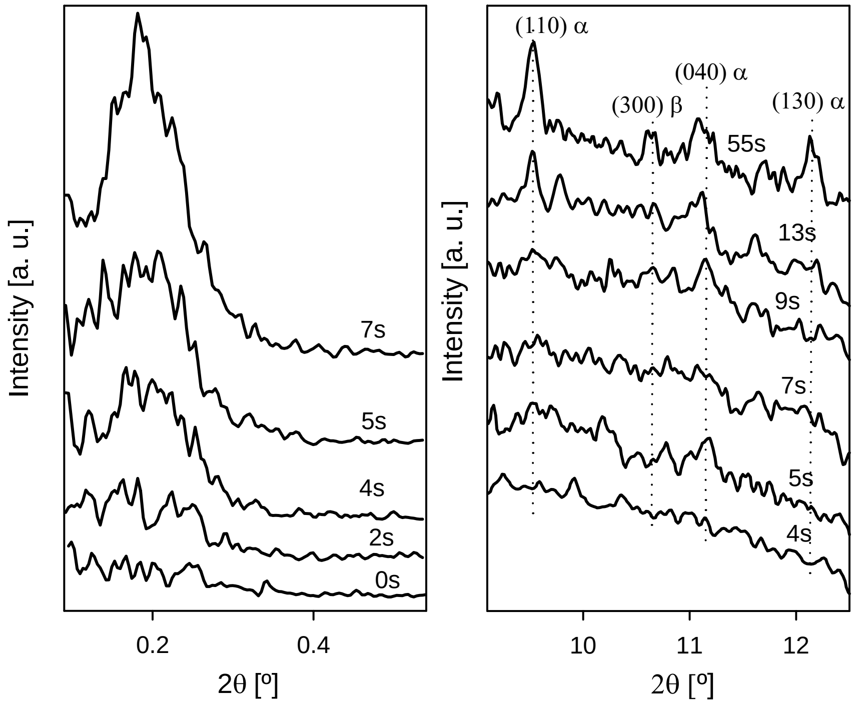

Figure 2. Diffraction intensity as a function of 2θ, for SAXS (left) and WAXD (right) at different times of the crystallization process after cessation of the shear. The acquisition time was of 500 ms and 1 s for WAXD and SAXS respectively. The shear was applied for 3 s at 145 ºC.

ACKNOWLEDGEMENTS

Thanks are due to the ESRF for the facilities provided, and to Drs. G. Heunen and F. Meneau for their valuable technical support. We also acknowledge Dr. W. Bras for stimulating discussions.

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