ESRF	**Experiment title:** Influence of pressure on hydrogen bonded polymers; polyamides and biopolymers	**Experiment number**: SC-1279
Beamline: ID02	**Date of experiment**: from: 09th Dec 2004 to: 13th Dec 2004	**Date of report**: 14th January 2005
Shifts: 12	**Local contact(s)**: Peter Boesecke	*Received at ESRF:*

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Report:

Combined SAXS/WAXD studies were performed in combination with our novel rheometer in order to study the influence of flow and thermal history on the crystallization behaviour of polymers. A commercial isotactic polypropylene, HD120M0 from Borealis (Mw=365.000 g/mol, Mw/Mn=5.4) was investigated.

The experimental protocol adopted is the so called "pre-shear" test where the sample, annealed for 10 min at 220ºC, is cooled down from the melt and then held at a constant temperature (test temperature) below its equilibrium melting temperature, thus causing crystallization. Moreover as soon as the test temperature is reached, a shear flow is applied. See *Figure1*. Flow induced primary nuclei formed during the shearing enhance the kinetics of nucleation (upturn of the storage modulus) whereas the growth rate stays the same (slope of the profile). Some of the results obtained, in terms of storage modulus vs time, are summarized in the *Figure2*:

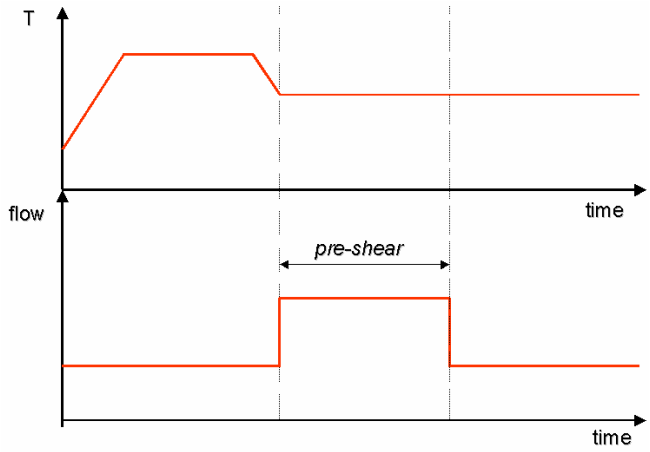


Figure 1: Step shear protocol

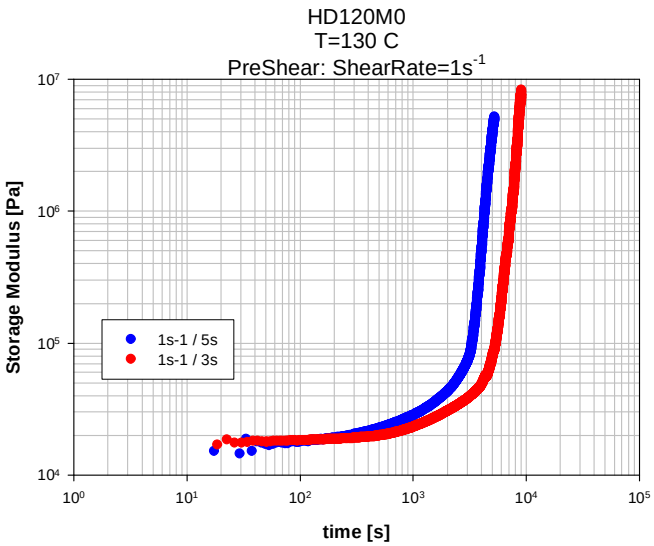


Figure 2: Storage modulus build up for two experiments varying only the shear time

The effects of both temperature and step stress amplitude on the crystallization were studied by performing several tests, varying only one of the parameters each time.

The high brilliance available at ID02 provided the opportunity to run time-resolved x-ray experiments with a time-resolution good enough to follow the onset of the crystallization in this material. Similar experiments previously done by us on other ESRF beamlines (BM26, ID11) suggested that the SAXS detector may show the onset of the crystallization before the WAXD. The opportunity to use both detectors (2D SAXS/WAXD)

at the same time made it possible to prove and strengthen this hypothesis. Crystallinity was always detected first by the SAXS detector. An example is given in the sequence of SAXS and WAXD patterns shown below:

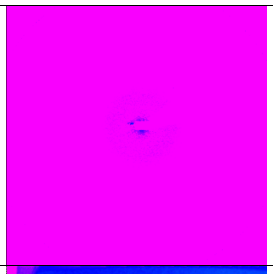
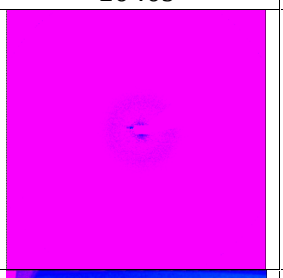
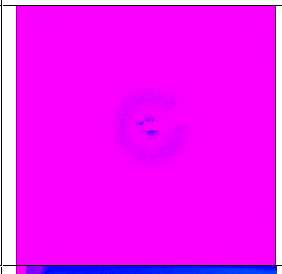
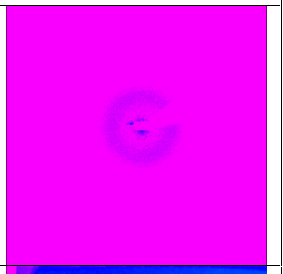
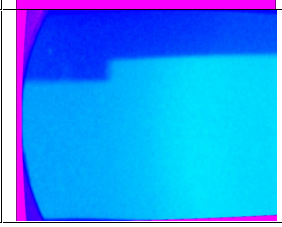
	960s	1040s	1120s	1200s
SAXS				
WAXD				

Table1: SAXS and WAXD patterns taken during the nucleation of a pre-sheared melt (T=130C, shear rate=1s^{-1}, shear time=5s). The correspondant rheological data are given by the blue curve in Figure2. Flow direction is horizontal.

When the flow strength overcomes a certain critic value we have observed that the SAXS pattern shows the presence of anisotropic structures while, at the same time, in the WAXD pattern scattering coming from isotropic structures is still detected. Indeed, for the flow regimes investigated by us, it was not possible to observe arcing in the WAXD patterns. This is a major point requiring further investigation.

Furthermore a few preliminary experiments were done investigating the crystallization behaviour of polypropylenes with a bimodal molecular weight distribution (mixture of two different polypropylenes having very different molecular weights). In this case, the flow conditions applied were not so extreme to determine a relevant difference in the nucleation kinetics. From the sequence of patterns shown below an important difference in the crystallization behaviour appears. In fact the material modified with a high molecular weight tail shows (weak) anisotropy in the SAXS, this was not the case for WAXD:

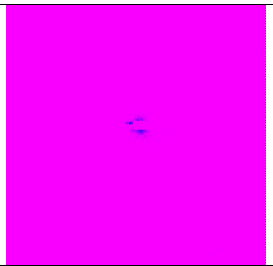
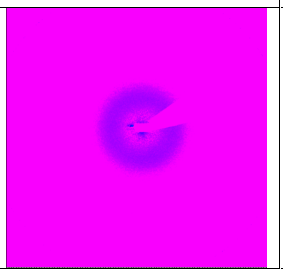
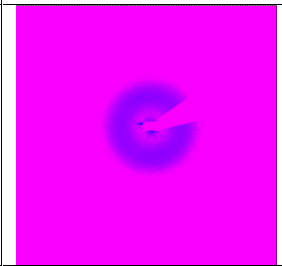
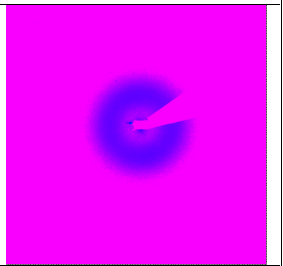
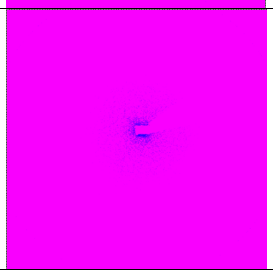
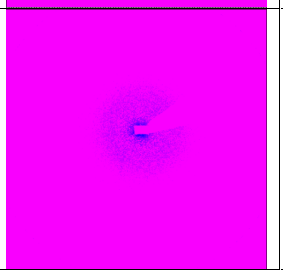
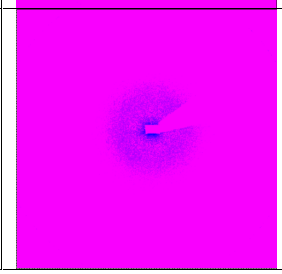
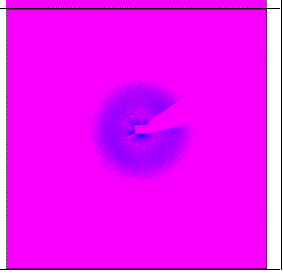
	784s	1584s	1784s	2384s
HD120M0				
HD120M0 Modified with HMW tail				

Table2: Time resolved SAXS patterns taken during the nucleation of presheared polypropylene melts. Flow direction is horizontal. From the second pattern further, the different intensity recorded in the two series of data is due to a change in the exposure time that was necessary during the experiment.

Tilting of the reflections, compared to the flow direction, denotes the weakness of the flow, capable to induced oriented nuclei but not to orient them properly.
Summarizing shear flow influences to a high degree the crystal nucleation. It changes not only the number but also the type of nulcei. Adjusting the molecular weight distribution it is possible to develop a new generation of polymers where the formation of oriented structures is “easier” and can be tuned in the desired way.