ESRF	**Experiment title:** On-line commercial blown film extrusion: a SAXS/WAXS/SALS study of orientation and structure development in polyolefins.	**Experiment number**: ME-1121
Beamline: Bm26b	**Date of experiment**: from: 22/06/05 to: 25/06/05	**Date of report**: 10/08/05
Shifts: 9	**Local contact(s)**: F. Meneau	*Received at ESRF:*

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Experimental:

It is industrially important to be able to follow the crystallization in polymers during real-time processing[1]. With this in mind this report uses a recently commissioned ram extruder acting as an analogue to an injection moulder[2-4] to investigate the crystallization kinetics of commercial polymers under very high shear rates. The instrumentation used is shown in figure 1. The polymer is fired into the sample cell at a range of temperatures and pressures and the crystallization is then followed using SAXS and WAXS (both 1D and 2D. A sample of commercial polypropylene has been used here to investigate the dependence of crystallization rates and structure development on changes in pressure and temperature.

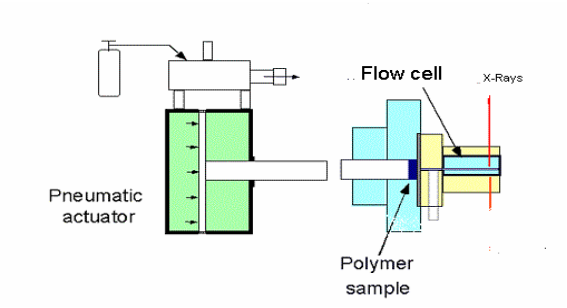

Figure 1. Ram extruder

Results and discussion:

Some initial results of the crystallisation of a commercial polypropylene provided by BP, at 145°C sheared at a pressure of 80psi for 1.5 seconds are shown in figure 2. Here the final frames of SAXS and WAXS are shown. It is clear that there is high orientation in the final structure of the polypropylene. The SAXS shows well defined lobes on the meridian (indicating lamellar stacking) and the WAXS shows oriented points on several Bragg reflections over the angular range obtained. Figure 3, shows the same sample but the development of the SAXS from the integrated meridional scattering and 1D WAXS when sheared at a piston pressure of 65psi, 1.5sec and 151°C.

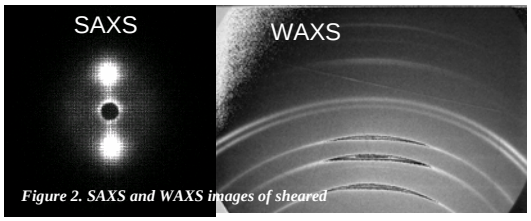

Figure 2. SAXS and WAXS images of sheared

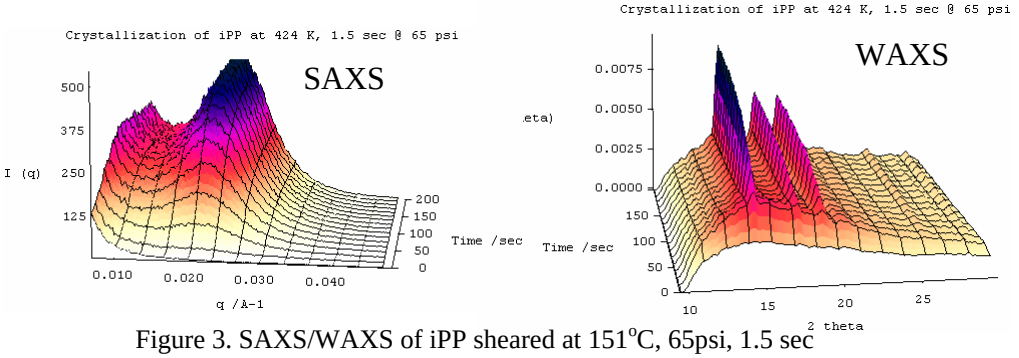

Figure 3. SAXS/WAXS of iPP sheared at 151°C, 65psi, 1.5 sec

The crystallization kinetics at several temperatures and pressures are obtained from the integrated invariant of the 1D SAXS curves as in figure 3. In figure 4, these kinetics are shown with respect to changing temperature and pressure. The first graph gives the crystallization rates when

sheared at a piston pressure of 65psi for 1.5 sec for three temperatures. Clearly an increase in crystallization temperature decreases the rate of crystallization. In the second graph the crystallization kinetics at several temperatures with the piston pressure at 80 psi for 1.5 sec. Again, an increase in temperature decreases the crystallization rate. The final graph shows the crystallization rate at 430 K at various piston pressures. Here, increasing the shear pressure increases the crystallization rate. This is shown in figure 5, where the crystallization half time ($t_{½}$) is plotted against the pressure at 430 K to provide a near linear relationship with crystallization rate and pressure.

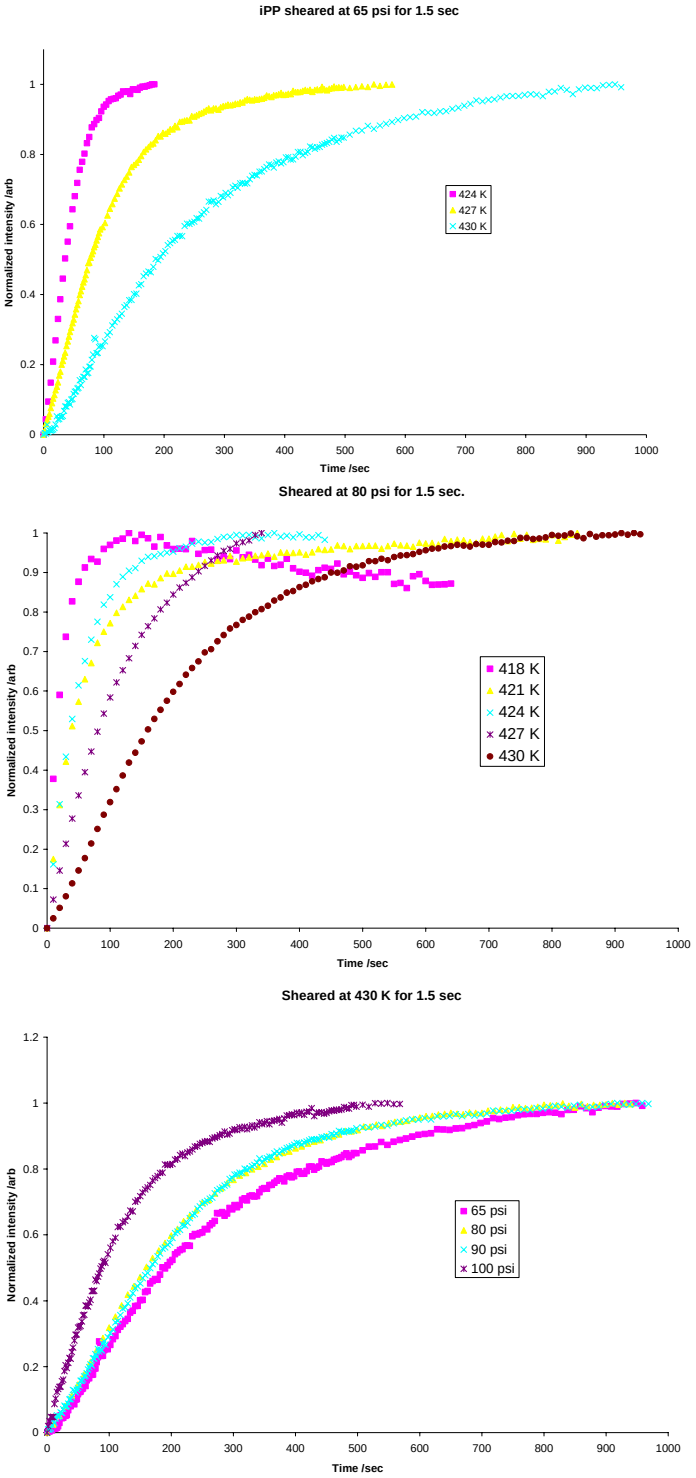

Figure 4. Crystallization kinetics for iPP with respect to temperature and shear pressure.

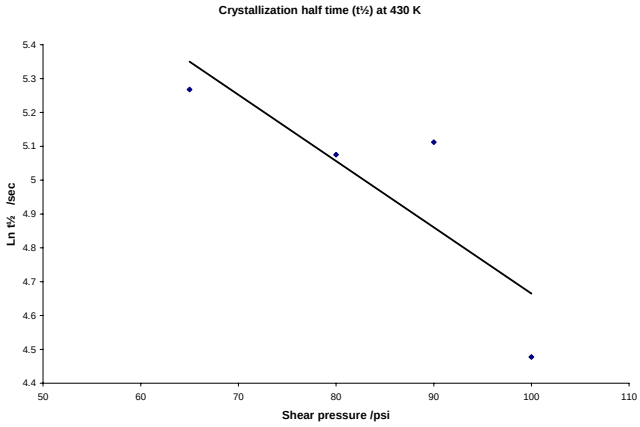

Figure 5. Change in crystallization half time ($t_{½}$) 430 K with shear pressure.

These initial experiments have shown that the crystallization kinetics are sensitive to shear pressure and temperature. Shearing also produces significant orientation over the range of shear pressures investigated here, of the lamellae perpendicular to the shear direction, as seen in the 2D SAXS. The WAXS also indicates the developing orientation and crystallinity. It is expected that the shearing of the sample at the crystallization temperature increases the kinetics drastically compared to that for quiescent crystallization conditions. However, there will be a critical shear pressure which will induce increased kinetics and orientation in the system. This is to be studied in the future by reducing the shear pressure until little if any orientation is seen and the kinetics are similar to those for quiescent conditions.

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2) G. Kumaraswamy, R.K. Verma, J.A. Kornfield. *Rev. Sci. Instrum*. **1999**, 70, 2097.
3) S. Liedauer, G. Eder, H. Janeschitz-Kriegl, P. Jerschow, W. Geymayer, E. Ingolic. *Inter. Polym. Proc.* **1993**, 8, 236.
4) G. Kumaraswamy, J.A. Kornfield, F. Yeh, B.S. Hsiao. *Macromols*. **2002**, 35, 1762.