



	<b>Experiment title:</b> Shear induced crystallization of commercial polymers.	<b>Experiment number:</b> SC1127
<b>Beamline:</b> BM26	<b>Date of experiment:</b> from: 16/04/03                      to: 22/04/03	<b>Date of report:</b> 25/02/2004
<b>Shifts:</b> 18	<b>Local contact(s):</b> Wim Bras, Igor Dolbnya	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

**Dr. E.L. Heeley\***

**Ms A. Morgovan\***

**Mr. P. Topham\***

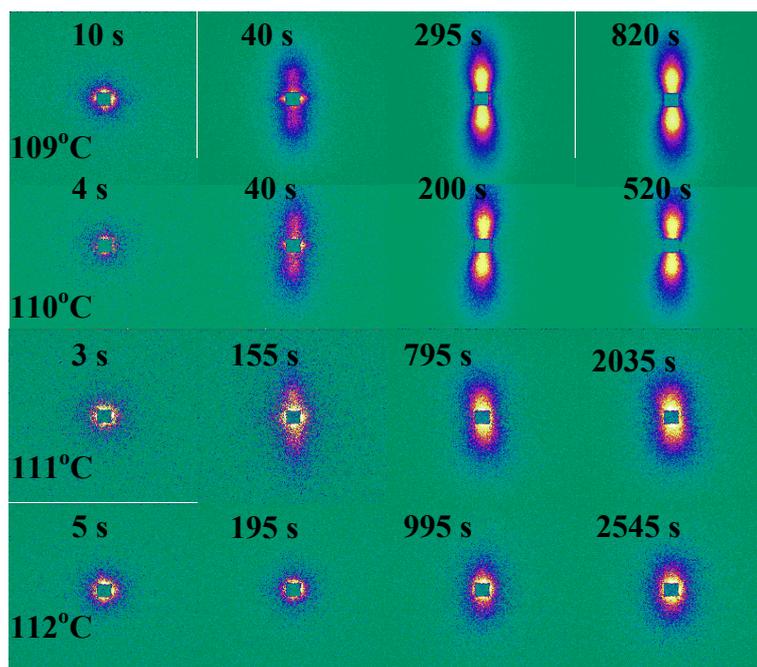
**Prof. A. J. Ryan**

Department of Chemistry, University of Sheffield, Sheffield, U.K, S3 7HF.

It is important in polymer processing to understand the kinetics of how the crystallization of materials controls and produces the macrostructure. The crystallinity of a polymer inevitably controls its mechanical and aesthetic properties in the finished product and thus its usefulness as a material. During processing of a polymer, in molds and dies, some orientation is introduced. The development of this orientation and hence crystallinity is important in the finished product and it is imperative that this is controlled and the mechanisms understood during the processing steps. Here commercial polyethylene has been studied under shear processing conditions and its structure development followed using small angle scattering (SAXS). By using SAXS we can determine the amount of crystallinity, orientation effects and the kinetics of the process.

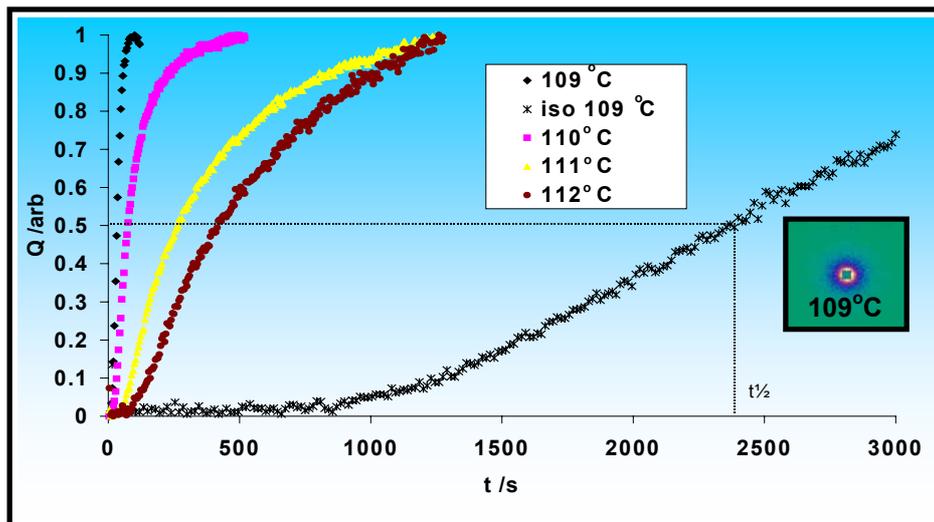
**Experimental.**

Samples of a commercial polyethylene Lupolen 1840H(Basell)  $M_w = 250$  K and a polydispersity of 13.5, was studied using the shear cell system available on the Dubble CRG beamline. Here, a constant shear regime was employed whilst changing the processing temperature to investigate the kinetics of crystallization time and the orientation in the final material. Figure 1 shows SAXS patterns pre-sheared Lupolen PE (5 s at  $100^{-1}$  or 500 shear units) crystallized at several temperatures. The SAXS data shows clearly how the orientation in the sample develops at the crystallization temperature, indicated by the 'tear drop' scattering shape in the meridian direction<sup>1</sup>. This scattering pattern shape is indicative in relating to lamellar and amorphous stacking. The higher temperatures do show some crystallization but some relaxation has occurred with crystallization temperatures being close to the melting point.



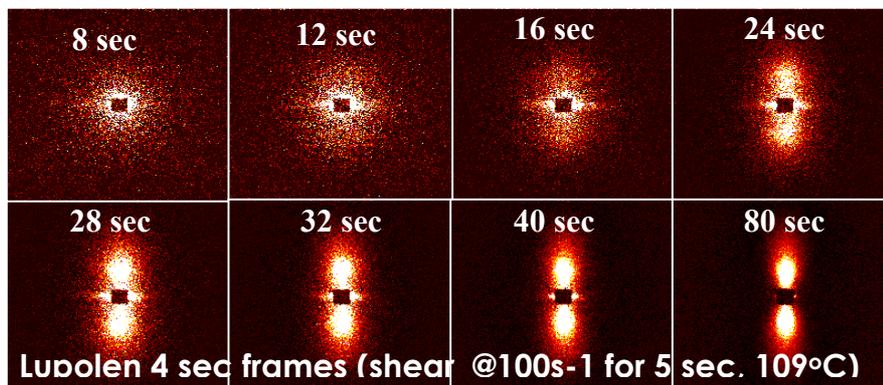
**Figure 1. SAXS of sheared PE at several temperatures**

Figure 2 shows the crystallization kinetics at different temperatures with respect to shear and isothermal processing conditions. The crystallization half times ( $t_{1/2}$  is time for 50% final crystallinity to be reached) is seen to be increased by up to two orders with shear compared with that of isothermal crystallization at the same temperature.



**Figure 2. Shear-induced crystallization of PE (Lupolen sheared for 5 s at  $100\text{s}^{-1}$ ) comparison with isothermal crystallization (integrated SAXS data). The crystallization half times ( $t_{1/2}$ ) is time for 50% final crystallinity to be reached.**

Furthermore, the crystallization rate is still greatly increased even at temperatures close to the melting point than in the isothermal crystallization at lower temperature. The crystallization kinetics are greatly increased during shear processing conditions thus, it has been necessary to try and investigate the mechanisms of the process early on. Other experiments were performed to enable us to investigate these 'early stages'<sup>2,3</sup> and the relevant structure development. The early stages of the crystallization kinetics have been observed by obtaining SAXS data at a high temporal rate. In figure 3, the crystallization of lupolen is followed at a fast frame rate of 4 seconds. Here equatorial 'streaks' can be seen in the SAXS which indicate initial ordering of oriented molecular chains in the shear direction and eventually disappear as the lamellar stacks start to grow perpendicular to the shear direction on these chains.



**Figure 3. SAXS of sheared PE showing equatorial streaks**

Initial experimental work with the shear system on Dubble, has shown that high quality data at fast frame rate is possible. We have been able to obtain good quality data during shear-induced crystallization at frame rates of 0.5 seconds. This gives detailed information on the structure development and eventually the crystallization kinetic and molecular mechanisms of the process. Further experiments have been conducted which investigate more novel PE polymer systems enabling information to be obtained on the influence of molecular architecture on the crystallization process, this having important and significant commercial applications of 'designer polymer materials' in the future.

- 1) Shear induced crystallization of Polyethylene studied by Small- and Wide- angle X-ray Scattering (SAXS/WAXS) techniques. E.L. Heeley, A.C. Morgovan, W. Bras, I.P. Dolbnya, A.J. Gleeson and A.J. Ryan. *Phys.Chem. Comm.* 2002, 5 (23), 158-160.
- 2) Early stages of crystallization in isotactic polypropylene. E.L. Heeley, A.Maidens, P.D. Olmsted, W. Bras, I.P. Dolbnya, J.P.A. Fairclough, N.J. Terrill and A.J. Ryan. *Macromols.* 2003, 36, 3656-3665.
- 3) Are Metastable Pre-crystallisation Density Fluctuations a Universal Phenomenon? E.L.Heeley, C.K. Poh, W.Li, A. Maidens, W. Bras, I.P. Dolbnya, A.J. Gleeson, N.J. Terrill, J. P.A. Fairclough, P.D. Olmsted, R.I. Ristic, M. J. Hounslow & A.J. Ryan, *A.J. Faraday Discuss.* 122 2003, 343-361.