



	Experiment title: A scattering study of shear-induced crystallization kinetics using novel polyethylene systems.	Experiment number: SC1127
Beamline: BM26	Date of experiment: from: 16/04/03 to: 22/04/03	Date of report: 25/02/2004
Shifts: 18	Local contact(s): 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.

The mechanism of primary nucleation in polymer crystallization is still a highly debated area¹⁻³, with continuing investigations experimentally and theoretically being performed. Here, several experiments have been performed which investigate the isothermal and shear-induced crystallization kinetics of novel polyethylene systems¹. The polymers studied have been specially synthesized in the Sheffield University Chemistry Department and are collectively described as model hydrogenated polybutadienes, having novel molecular architectures. The model polymers are monodisperse systems, which have been blended with similar monodisperse ‘comb’ systems which have varying degrees of long chain branching (LCB), the architectures are shown in Figure 1. These blends are mixed at levels below and equal to the C* entanglement weight of the comb additive system. Experimental

We have investigated the long chain branching effects of the blended model polymer systems by performing crystallization experiments having been subjected to flow and comparison isothermal processing conditions. These blends have been subjected to a pulse of constant shear units in a flat plate shear cell system, at the desired crystallization temperature. Generally, the development of crystallization and thus structural morphology in these materials, has been followed using Small Angle X-Ray scattering (SAXS) techniques on BM26b at the ESRF.

The samples investigated are detailed in the table below:

Sample	Backbone (g/mol)	Arm (g/mol)	Number of arms	M _w /M _n
Comb 8	118,500	22,700	3.7	1.07
Comb 10	53,800	14,800	8.0	1.02
Linear 50k	52,800	-	-	1.00
Linear 112k	114,250	-	-	1.04

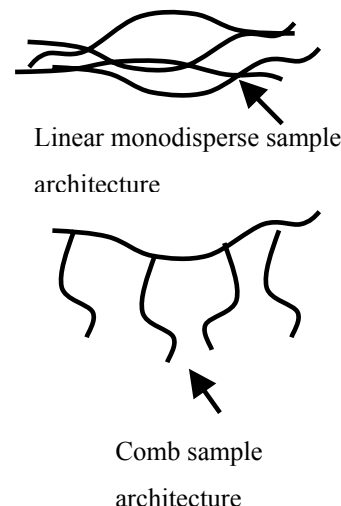


Figure 1. Polymer architecture

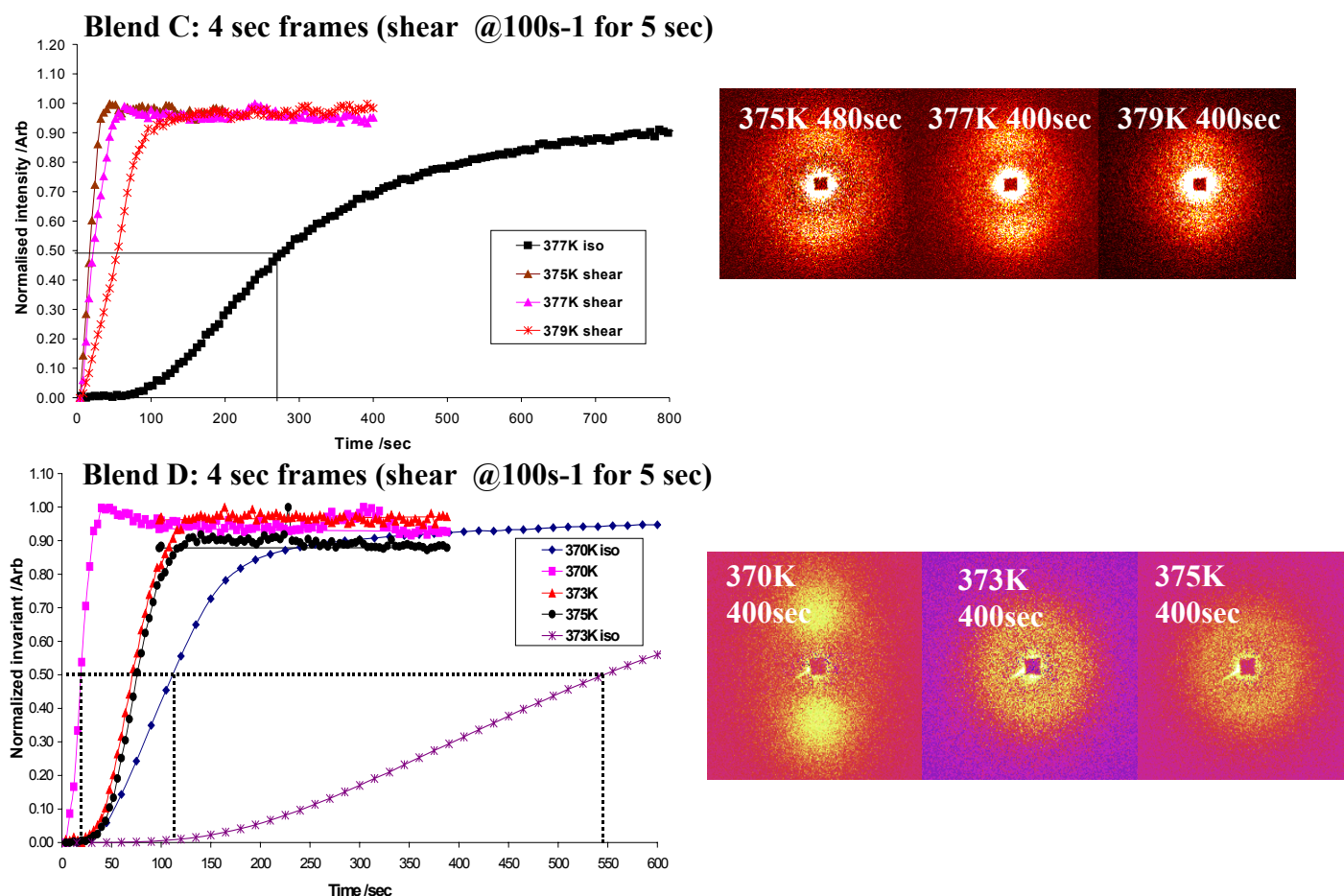


Figure 2. Scattering patterns and integrated SAXS data graphs for time resolved shear-induced crystallization of blended hydrogenated polybutadienes.

Figure 2, shows SAXS patterns and integrated SAXS data with respect to time of the shear-induced crystallization of blended linear samples with 10% of comb samples. Normally the shearing of the linear monodisperse sample will give little orientation as the relaxation times are fast with the molecular weights used here. However, blending with a small amount of comb of similar M_w (backbone) as the linear sample will give increased crystallization rates and some obvious orientation in the SAXS. Crystallization rates are still increased in these blends compared with isothermal crystallization conditions, even if no orientation is seen at higher crystallization temperatures.

From scattering experiments of the model blended systems, it has been seen that during flow the crystallization kinetics are increased greatly compared to that of the isothermal crystallization at the same temperature¹. Shear-induced crystallization in the model systems are seen to give rise to oriented 'shish-kebab' morphologies to varying degrees¹, depending upon the composition of the blend and crystallization temperature. However, the shear-induced crystallization kinetics in the blended systems were still increased (compared to isothermal conditions) even though no 'orientation' was observed in the SAXS data collected, shown in figure 2, with blend D.

These results have led to the development of greater theoretical understanding of crystallization kinetics at the molecular level²⁻³, using these model systems compared with poorly defined polydisperse commercial polymers. The advancement in *in-situ* processing equipment, improved data quality and rapid collection times using synchrotron radiation, has also allowed a deeper insight into the early crystallization mechanisms to be explored.

- 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.