



	Experiment title: Shear induced crystallization of novel synthesised monodisperse polymer blends	Experiment number: SC-1781
Beamline: Bm26b	Date of experiment: from: 25/06/05 to: 28/06/05	Date of report: 10/08/05
Shifts: 9	Local contact(s): F. Meneau	<i>Received at ESRF:</i>

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Experimental:

The mechanism of primary nucleation in polymer crystallization is still a highly debated area¹⁻³, with continuing investigations experimentally and theoretically being performed. Here, we report on several experiments which investigate the isothermal and shear-induced crystallization kinetics of novel polyethylene systems¹. The polymers to be studied have been specially synthesized in the Sheffield University Chemistry Department and are collectively described as model hydrogenated polybutadienes⁴, having novel molecular architectures. The model polymers are monodisperse systems given in the table below, which have been blended with similar monodisperse ‘comb’ systems which have varying degrees of long chain branching (LCB). These blends have been mixed at levels of 5% and 10%, equal to and above the C* entanglement weight of the comb additive system.

Sample	Backbone (g/mol)	Arm (g/mol)	Number of arms	M _w /M _n
Comb 10	53,800	14,800	8.0	1.02
Linear 50k	52,800	-	-	1.00
Linear 15k	15,600	-	-	1.03

Blended samples used
Blend A 90% 15k 10% Comb10
Blend C 90% 50k 10% Comb10
Blend E 95% 50k 5% Comb10
Blend F 95% 15k 5% Comb10

The samples were subjected to a pulse of shear for 5 seconds at 100 s⁻¹ at the chosen crystallization temperature in the Linkham shear cell. The crystallization was then followed by using SAXS. The crystallization kinetics were compared to those which occur at similar temperatures under quiescent conditions.

Results:

Figure 1, shows the crystallization rates in the graph (B) from integrating the SAXS data in (A) with respect to time and comparing with quiescent crystallization at similar temperatures for the pure comb10 sample. Here, it is clear that the crystallization kinetics are massively increased by the shear pulse compared with quiescent conditions and there is clear evidence that there is orientation in the SAXS patterns. In figure 2, the SAXS data and similar crystallization curves are given for Blend C. Again the pulse of shear increases the crystallization time dramatically and some orientation is seen. The orientation in the SAXS patterns is an indication of the ordered stacking of lamellae in perpendicular to the direction of the shear. Some of the SAXS indicated that orientation was not present (Blends A, E & F) even after shear, however the crystallization kinetics were still greatly increased compared to the same quiescent conditions. In figure 3, the crystallization times at t_{1/2} (crystallization half-time) are plotted with respect to temperature for the complete set of blends under sheared and quiescent experimental conditions.

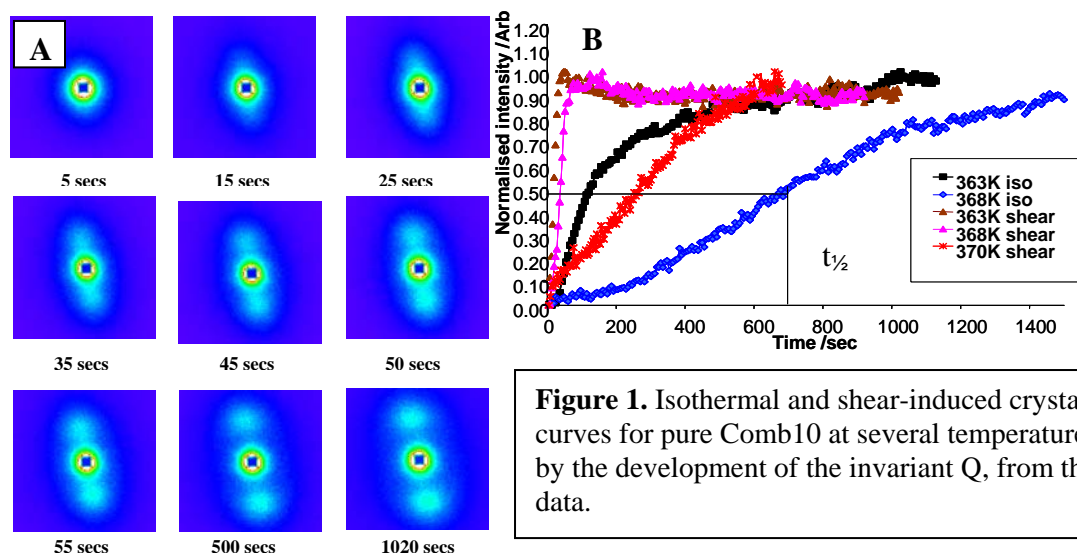


Figure 1. Isothermal and shear-induced crystallization curves for pure Comb10 at several temperatures shown by the development of the invariant Q, from the SAXS data.

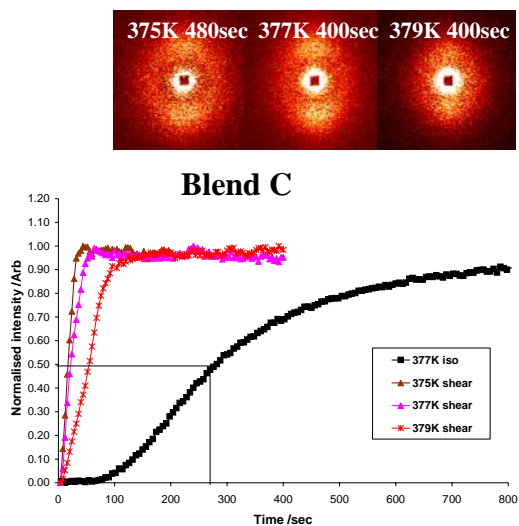


Figure 2. Crystallization curves and SAXS for blend C.

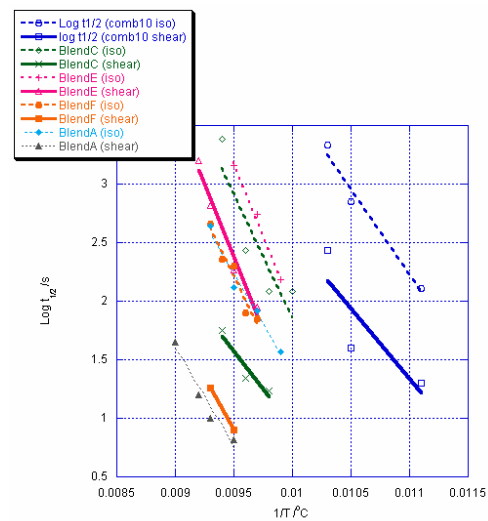


Figure 3. Crystallization rate half-times for all blends and pure comb samples.

Conclusions:

From the crystallization data obtained it is clear that the addition of just a few % long chain branched material into a linear matrix will increase the crystallization rate significantly under sheared conditions compared to that of quiescent crystallization. Also, orientation of the lamellae formed during crystallization does occur in some of the samples, however even if orientation is not seen in the SAXS the kinetics are still increased. The doubling of the comb additive causes a doubling in crystallization kinetics as shown in figure 3. The long chain branched additive is seen to act as nucleation sites during shear, increasing the kinetics and possible orienting of the lamellae. This is due to the long relaxation times compared to the similar linear matrix molecules of the comb material once it has been stretched during the shear motion.

- 1) 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) 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) 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.
- 4) Fernyhough, C. M.; Young, R. N.; Poche, D.; Degroot, A. W.; Bosscher, F. *Macromols* **2001**, 34, 7034-7041