ESRF	**Experiment title:** Early stages of polymer crystallisation	**Experiment number**: SC1127
Beamline: BM26	**Date of experiment**: from: 26/11/03 to: 29/11/03	**Date of report**: 25/02/2004
Shifts: 9	**Local contact(s)**: Wim Bras, Igor Dolbnya	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. E. L. Heeley

Mr A. I. Norman

Mrs A. C. Morgovan

Prof. A. J. Ryan

Dr J. P. A. Fairclough

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

Report:

During processing, crystallisation is the essential step that determines the quality of the final product (i.e. toughness, smooth surface, elasticity, etc). Thus, in order to develop more useful, "job specific" materials, the crystallisation process has to be controlled. To do this, model compounds with well-defined architectures are required. They can facilitate the understanding and prediction of the relationships between polymer properties and their structure.

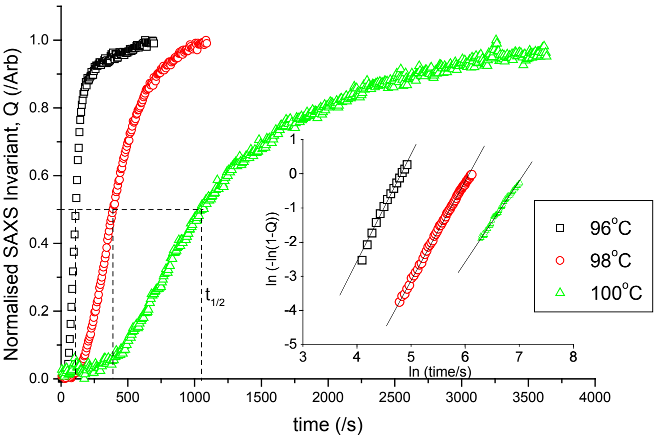
A series of polyethylene-like materials from hydrogenated polybutadienes with well-controlled molecular architecture (pure combs, pure linears and blends of combs and linears), a range of molecular weights and very narrow polydispersities, synthesised by high vacuum anionic polymerisation, have been investigated at CRG DUBBLE beamline BM26 of the ESRF, using time-resolved simultaneous SAXS/WAXS/DSC experiments. Small- and Wide- Angle X-ray Scattering (SAXS/WAXS) are excellent tools to look at the macrostructure development or long range ordering (lamellae stacking) (SAXS) and the microstructure development or crystalline atomic ordering (WAXS).

Quiescent crystallisation experiments were performed, which allowed the kinetics of crystallisation to be analysed (using the Avrami[1] equation) and the morphological parameters of the samples to be determined (using the correlation function[2] analysis).

Adding small percents (typically 5-10%) of comb architecture into a linear material has dramatic effects upon the crystallisation. The long chain branches in the combs slow crystallisation, as it is more difficult to re-organise into regular arrays, to separate and crystallise. Also, the numerous branch points cannot be incorporated into a crystal, thus providing bigger dimensions for the crystallites formed (larger amorphous regions). All these effects are beneficial in industrial processes such as film blowing, where a more amorphous film can be stretched further and orientated, resulting in extensional hardening.

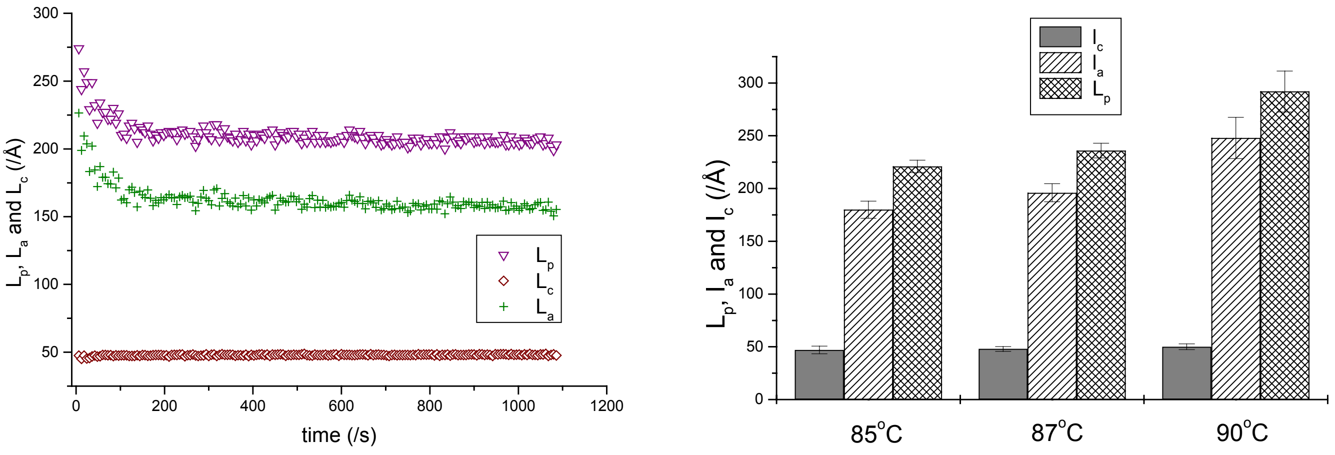
(a) Avrami analysis on the SAXS invariants for Sample D (blend of 90% linear hPBD 112K and 10% comb 8, where Comb 8 has 3.4 branches of M_w=22,700g/mol and a backbone of M_w=118,500g/mol). The inset shows the double log plot of the invariants, Q , with Avrami exponents (obtained from the gradient) of ~3, indicating a growth mechanism where discs are formed from sporadic nuclei.

(a)



(b) Variation with time of long period, L_p (where long period is sum of crystalline and amorphous layer thicknesses, L_p=L_c+L_a) , amorphous, L_a and crystalline, L_c layer thickness for Comb 9 (7.7 branches of M_w=20,100 and backbone of M_w=81,800) at 90°C. L_p and L_a show an early decrease, while L_c is seen to remain constant.

(c) Final values for long period, L_p, amorphous, L_a and crystalline, L_c layer thickness for Comb 11 (8.2 branches of M_w=5,750g/mol and a backbone of M_w=62,700g/mol at three different temperatures. L_p and L_a increase with increasing temperature, while L_c is seen to remain the same.



Due to their chemistry, all samples have a random distribution of poly(ethylene) and poly(ethylethylene) repeat units with 18 ethyl branches per 1000 backbone carbon atoms. This short-chain branching affects the morphology and properties and dictates the crystalline lamellar thickness, L_c=50±10Å, which is constant for all samples, regardless the crystallisation temperature[3]. The early decrease of L_p and L_a in Figure (b) can be explained in terms of an insertion mechanism with constant lamellar thickness. In the beginning, lamellar stacks are formed and they all have the same crystalline thickness, dictated, as mentioned, by the short-chain branches. At later stages, as crystallisation proceeds further, new lamellae are formed or are inserted within the existing stacks, however they have the same crystalline thickness as the initial lamellae.

1. Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103.
2. Strobl, G. R.; Schneider, M. J. *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 1343.
3. Hamley, I. W.; Fairclough, J. P. A.; Bates, F. S.; Ryan, A. J. *Polymer* **1998**, *39*, 1429.