ESRF	**Experiment title:** Crystallization of hydroxybutyrate oligimers from dilute solution	**Experiment number**: SC1082
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Shifts: 12	**Local contact(s)**: Gavin Vaughan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Peter Barham, Polymer Physics Group, University of Bristol
*Jamie Hobbs, Polymer Physics Group, University of Bristol
*Sally Organ, Polymer Physics Group, University of Bristol
*Jun Wei, Polymer Physics Group, University of Bristol
*Tim Lord, Polymer Physics Group, University of Bristol
*Ann Terry, Dept. of Zoology, University of Oxford

Report:

The aim of the experiment was to monitor the crystallization from dilute solution of hydroxybutyrate oligomers as a function of temperature, chain length and concentration.

WAXD patterns were collected using a high resolution Bruker 6500 CCD. The data collection was controlled through SPEC and could be synchronised with the temperature ramp applied using a Linkam TMS600 hotstage also controlled via a serial line. When compared to previous occasions, the data collection device server was more stable though perhaps just due to our own experience in knowing what not to do, and not through any active improvements. It was possible to reduce all of the data at the ESRF.

The experiment was very successful. Two samples were studied each at three different concentrations. It was found that it was possible to detect crystallinity even at concentrations as low as 0.1%, allowing meaningful rate data to be obtained from a 0.7%w/w solution.

At each crystallization temperature it was possible to monitor the variation in lattice parameters both during intial crystallization and on subsequent annealing. Due to the high resolution of the Bruker detector and the high energies used, excellent resolution could be obtained even in these solution samples. Although the detailed analysis of this data is not yet complete, exciting new findings have already been made. There is preliminary evidence of a minimum in the growth rate at the temperature where crystallization in the folded form, rather than the extended form, becomes stable. This is behaviour similar to that previously observed in the ultra-long alkanes (polyethylene oligomers) but has not been observed in this system before. If confirmed through further analysis of the data it will support the generality of this behaviour as crystallization in one metastable state competes with that in another.

Re-heating experiments carried out on material that had been crystallized in solution in a folded form were also successful. From inspection of the data during the experiment, crystal thickening (or unfolding) transitions were observed in the 32mer oligomer, accompanied by changes in the lattice parameters. This

thickening was similar to that we have observed previously for alkanes, where a lattice contraction occurred as the polymer relaxed into the lower energy, thicker crystal. However, in the current experiment, the HB oligomer was seen to go through a step-like expansion of the lattice – a surprising and interesting result, with possible implications for our understanding of the energetics of the crystallography in the high polymer. Further analysis of the whole diffraction pattern is required to understand this more clearly.

The data obtained was new and of a high quality, and we envisage publishing the results as soon as the analysis is complete.