



	Experiment title: Molecular length dependence of the pressure-temperature phase diagram in ultra-long alkanes	Experiment number: Sc1310
Beamline: ID02/ID11	Date of experiment: from: 21/02/2004 – 24/02/2004 to: 21/04/2004 – 26/04/2004	Date of report: 28/02/2005
Shifts: 26	Local contact(s): Pierre Panine and Jonathan Wright	<i>Received at ESRF:</i>
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Report:

We carried out two series of experiments, on ID02 and ID11, to map out the pressure-temperature diagram of a series of perfectly monodisperse ultra-long alkanes – model materials for polyethylene and crystallizable polymers. Of particular interest was the effect of pressure on chain folding, the possibility of the formation of the hexagonal phase at high pressures in analogy with polyethylene, and the detailed study of the impact of pressure on lattice parameters.

SAXS on ID02 showed that, despite the very high crystallization temperatures (above 200°C) at high pressure, crystallization still occurs initially in a metastable, folded form. Indeed, a non-integer form, in which there is a well defined fraction of amorphous material between lamellae, was observed as a transient during the early stages of growth, in a similar manner to the same materials at ambient pressure. Figure 1 shows a typical data set taken during cooling from the melt.

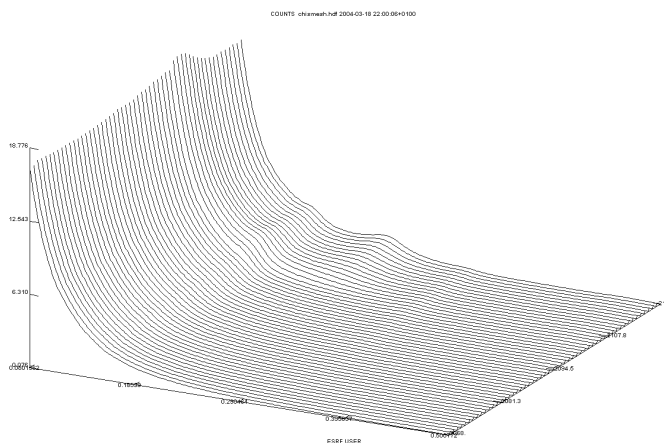


Figure 1 SAXS data collected during cooling $C_{390}H_{782}$ at 3.5kbar

On ID11 the beamline was set up with the WAXD area detector as a partial quadrant, allowing simultaneous collection of SAXS data (although not of the same quality as that collected on ID02, this allowed the unambiguous correlation of behaviours). At least 32 reflections were collected in the WAXD so as to allow a full pattern refinement to be performed – of particular importance here was the collection of the 002 peak as the c axis is expected to be strongly affected by pressure. This refinement is currently underway by Mr Tim Lord, a PhD student based at the ESRF on ID11, and will be published as soon as it is completed as the effect of pressure on lattice parameters in these model materials has not been previously explored.

For most of the materials studied no hexagonal peak was observed. However, this was most probably because sufficient pressure could not be obtained. In $C_{390}H_{782}$ a very brief hexagonal peak was observed at a pressure of 6kbar – the pressure limit of the cell. This is agreement with less direct evidence obtained in [1], and confirms that the hexagonal-orthorhombic-melt triple point moves to higher temperatures with decreasing chain length. Unfortunately this very high pressure made it impossible to collect much data during crystallization into the hexagonal phase. We are currently considering alternative pressure cell designs that will allow such a study to be performed.

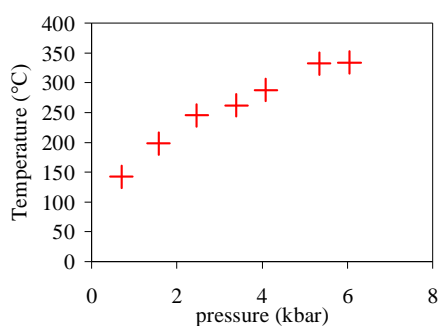


Figure 2. The pressure-temperature phase diagram of $C_{198}H_{398}$.

Full temperature pressure runs were obtained for pressures up to 4kbar with 3 alkanes. Figure 2 shows an example of a typical melting point versus pressure curve (in this case for $C_{198}H_{398}$). In most cases these are phase diagrams, as the crystals were equilibrium extended chain – the exception is $C_{390}H_{782}$ where crystallization always occurred in a metastable folded form (see above). Again, this data is of wide significance, especially with the growth in computer simulation where such reference parameters are vital, and will be published as soon as the analysis is complete.