ESRF	**Experiment title:** A real time dynamic temperature modulated study of crystal re-organisation processes in ultra-long alkanes and polyethylene	**Experiment number**: SC993
Beamline: ID11	**Date of experiment**: from: 1/5/02 to: 5/5/02	**Date of report**: 30/8/02
Shifts: 15	**Local contact(s)**: Ann Terry	*Received at ESRF:*

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Report:

A temperature modulated, high resolution WAXS study of the crystal perfectioning and thickening of ultra-long alkanes - a model polymer system – was performed. Long chain alkanes crystallize into different integer folded forms, all of which are unstable with respect to the extended chain crystal. The re-organisation that accompanies thickening from one folded form to another results in a contraction of the crystal lattice - crystals with different numbers of folds have a subtly different structure. Prior to this contraction there is an increase in disorder, revealed by an increase in the peak width.

Wide angle X-ray diffraction patterns of ultra-long alkanes whilst subjected to a temperature modulated DSC-style cycle, were collected on ID11 using a Bruker CCD in high resolution mode. 2k x 2k patterns with a pixel size of 70μm were collected for 2 seconds, but there was a read-out/dead time of 10 seconds. The sample detector distance was such that only the (110) and (200) reflections were collected for this experiment so as to have the maximum resolution for the peak positions. The experiment was performed at 25keV with a 300 x 300μm beam. The alkane samples were sealed in 0.5mm lindemann tubes and mounted in a specially designed holder on the front face of a Linkam heater. The holder ensured that the sample detector distance was maintained as accurately as possible between sample changes so that individual samples did not have to be internally calibrated. The linkam heater was controlled via a serial line through a Labview interface with SPEC, and could be synchronised with the data collection as the Bruker CCD was controlled via the same SPEC session. Andy Götz from the Bliss group wrote the command routines so that a sinuosoidal signal could be overlaid to a standard linear temperature ramp within the Linkam. Without this support this experiment would not have been possible. The first 5 shifts were used for beamline alignment

and to set-up the experiment, synchronise the data collection with the Linkam and to tune the parameters for driving the Linkam.

The diffraction patterns were corrected for spatial distortions prior to integrating to give intensity against 2theta. Using a fitting routine written by Gavin Vaughan, ID11, the (110) and (200) reflections were fitted with a pseudo-voigt function to give the peak position, FWHM and intensity in every pattern.

The experiment showed the feasibility of adding a sinusoidally varying temperature profile to a standard linear ramp (see fig. 1). Only one alkane, $C_{294}H_{590}$, could be studied in depth in the time permitting. Several observations were made. These included: a reduction in expansivity with crystal thickness providing evidence, on top of the previously observed lattice contraction [1,2], that in these monodisperse systems each crystal thickness can be regarded as a different polymorph; a fully temperature reversible change in line width which changes from being in phase to being out of phase with temperature as the crystal transforms from being twice folded to once folded; an apparently reversing crystallization and melting behaviour during the early stages of crystal growth, showing the slow crystal perfectioning that it has been argued is an inherent part of polymer crystal growth. This initial study has shown the strength of the newly developed technique, providing not only proof of concept, but also new insights into the behaviour of $C_{294}H_{590}$.

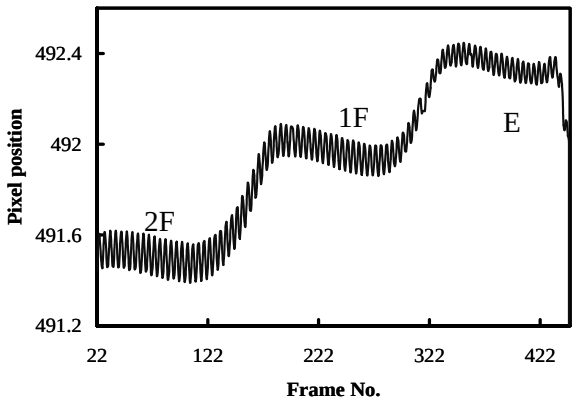

Fig.1. The variation in position of the 110 peak of $C_{294}H_{590}$ during heating from 116°C to 134°C at 0.2°C/min. with an additional sinusoidal temperature variation, amplitude 2°C, period 60 seconds. A clear contraction of the lattice can be seen as the crystals transform between different integer folded forms (twice-folded, 2F, to once-folded, 1F, to extended, E), as well as the difference in expansivity, clearly seen by the amplitude of the response to the temperature modulation.

This work is being presented orally at the Synchrotron Radiation in Polymer Science II Conference (Sheffield, UK, 4-6 September 2002).

1. Terry A., Hobbs J.K., Phillips T.J., Hanna S., submitted to Science
2. Terry A., Phillips T.J., Hobbs J.K., in preparation