



	<b>Experiment title:</b> <b>In-situ solution crystallization of strictly uniform ultra-long alkanes</b>	<b>Experiment number:</b> SC-905
<b>Beamline:</b>	<b>Date of experiment:</b> from: 10 November 2001 to: 12 November 2001	<b>Date of report:</b>
<b>Shifts: 8</b>	<b>Local contact(s):</b> Ann Terry	<i>Received at ESRF:</i>
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### Report:

The aim of the experiment was to monitor the crystallization from dilute solution of ultra-long uniform alkanes as a function of temperature, chain length and concentration. This was the first attempt to use X-rays to monitor synthetic polymer crystallization from dilute solution. The use of the model, alkane system would provide a firm footing for this new area of research.

The experiment was very successful. Two alkanes,  $C_{162}H_{326}$  and  $C_{294}H_{590}$  were studied (as only seven sessions were awarded, the number of alkanes studied had to be reduced by half) each at three different concentrations. It was possible to detect crystallinity even at concentrations as low as 0.1%, allowing meaningful crystallization rate data to be obtained from a 0.7%w/w solution.

In both of the samples studied a clear minimum in growth rate was observed at the transition in primary crystallization between different integer folded forms. In the case of  $C_{162}H_{326}$  this was a transition from once-folded (1F) to extended chain growth, while in  $C_{294}H_{590}$  the transition was from twice-folded (2F) to once-folded chain growth – see figure 1. This is in agreement with our previous experiments by an indirect method, and convincingly confirms the existence of this phenomenon in solution crystallization.

At each crystallization temperature it was possible to monitor the variation in d-spacing of the principal reflections both during initial 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, two exciting new findings have already been made. Firstly, in all cases there is a gradual contraction of the crystal lattice with time after primary crystallization is complete, which cannot be associated with thickening of the crystals. This is particularly striking as these chains are essentially perfect, and the relatively slow rates obtained during solution crystallization might be expected to lead to very high levels of initial register during primary crystallization. The slow increase in order that this implies is in agreement with recent computer simulations of polymer crystallization, but in contradiction to many existing theories.

Secondly, when crystallization occurs above the minimum in growth rate, the initially crystallized material has a significantly expanded lattice, which then contracts leading to a near doubling in the scattered intensity – see fig. 2. We tentatively associate this behaviour with the formation of an initially cilliated structure which then transforms by a realling in mechanism into a more highly ordered structure. In other words, chains in the initially formed crystals are not entirely in the crystals but have ends dangling out which are gradually incorporated over time. This is similar to the behaviour observed when the alkanes are crystallized from the melt, but it was expected that the slower kinetics and fewer entanglements that occur during crystallization from solution would preclude such behaviour.

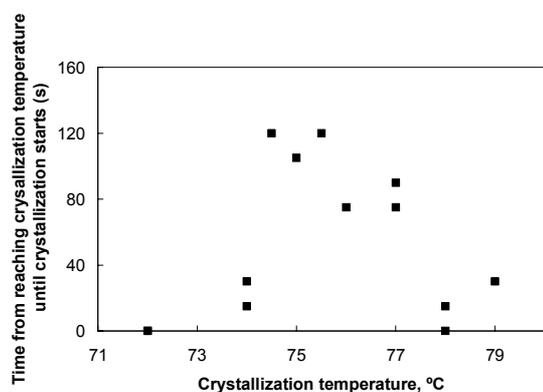


Fig. 1

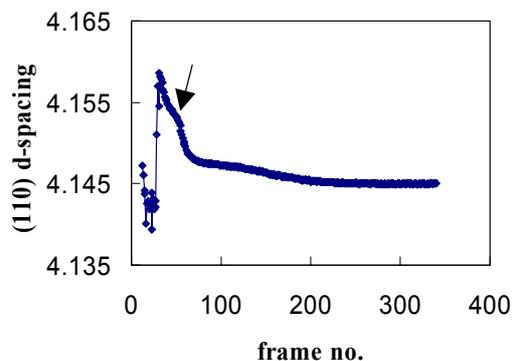


Fig. 2a

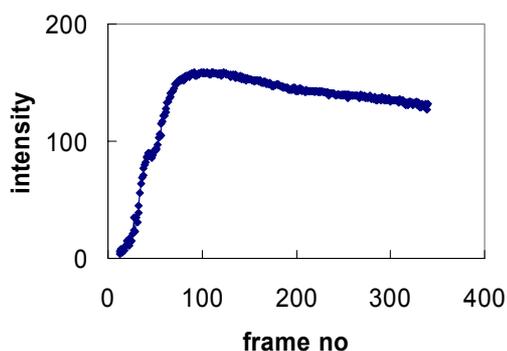


Figure 1 shows the variation in the time until crystallization begins with temperature for a 0.7% solution of  $C_{162}H_{326}$  – related to the reciprocal of nucleation rate. A clear minimum in nucleation rate in the region  $74.5^{\circ}C$  to  $75.5^{\circ}C$  can be seen. This corresponds to the temperature where primary crystallization changes from extended to once folded.

Figure 2a shows the variation in the 110 d-spacing with time for  $C_{294}H_{590}$  crystallized at  $87^{\circ}C$ .

Figure 2b shows the corresponding variation in intensity. The second increase in intensity after approx. 50 frames corresponds to the beginning of the rapid contraction of the lattice arrowed in 2a.