ESRF	**Experiment title:** Probing the early stages of polymer crystallization by x-ray photon correlation spectroscopy	**Experiment number**: SC-1287
Beamline: ID10A	**Date of experiment**: From: 9-10-2003 to: 12-10-2003	**Date of report**: 5-2-2004
Shifts: 9	**Local contact(s)**: Anders Madsen	*Received at ESRF:*

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Report:

A limited number of shifts had been assigned to assess the feasibility of the full project. The latter involves bringing an extrusion system ('spinline') to the Troika III beamline to perform XPCS on the early SAXS signal associated with the onset of polymer crystallization. Going down along the spinline (which provides continuously fresh material) long-term measurements are possible of the various stages of crystallization. The objective is to determine a possible gel point from the slowing down of the diffusion of the objects/network associated with these early stages. For the test measurements standard polymer samples were used: crystallized high-density polyethylene (HDPE), ordered kraton (triblock copolymer), and isotactic polypropylene (iPP, the relevant substance) at various stages of crystallization. The samples were kept in a standard Linkam oven allowing applying temperature cycles. The pink beam of Troika III was focused on a pinhole of 10 μm providing a stable, partly coherent beam of about 10^{11} photons/s.

The following aspects were investigated.

1. Beam damage. It proved to be possible to work for many tens of minutes on the various samples without appreciable signs of degradation under influence of the small but high-flux beam. Hence using the spinline no problems are expected regarding this point. However, experiments at room temperature of crystallized HDPE showed re-arrangement of the crystals. This is an indication of appreciable heating due the beam at the sample position and creates considerable uncertainty regarding the local temperature.

2. SAXS intensity. Under the high-resolution conditions of XPCS, the SAXS signal of a crystallised polymer sample is considerably reduced because the peaks are intrinsically rather wide. In crystallized HDPE a broad peak could be clearly observed, in crystallized iPP only a weaker 'bump' (see Fig. 1). Hence in principle intensity is a matter of concern. Intensities in the relevant q-range are of the order of 30-100 cts/s at the early stages of crystallisation.

3. Feasibility of XPCS. We investigated any effect of time dependence in the correlation function of iPP melted and kept for 5 min at 200 ^{o}C and subsequently cooled to 142 ^{o}C to crystallize isothermally. In this situation crystallization is expected to take up to 20-40 min with considerable pre-ordering visible in SAXS. Questions are after the possibility of XPCS at low intensities, and the time scale of the possible fluctuations.

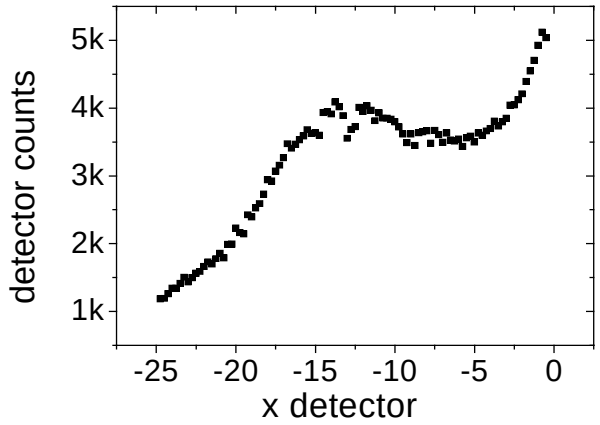

Fig. 1. Crystal peak of iPP at q=0.03 $Å^{-1}$ for 100 ^{o}C.

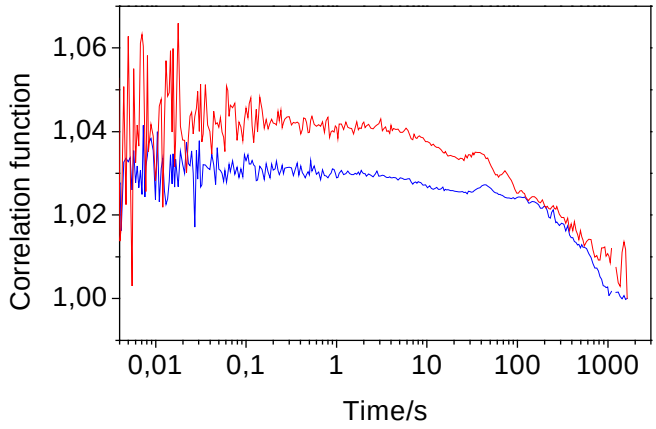

Fig. 2. Correlation function (detector/monitor) of iPP at q=0.02 $Å^{-1}$ during isothermal crystallisation at 142 ^{o}C.

(a) *XPCS at low intensities.* While XPCS at sub-second time scales requires intensities of at least about 1000 cts/s, larger times (that require long acquisition times anyhow) can also measured at much lower intensities.

(b) *Time scales involved.* The question after the relevant timescales is delicate. The nature of the objects/network associated with the density fluctuations or local 'embryo's' at the early stages of crystallisation is the subject of investigation. The time constants associated with their diffusion will vary in time with the progress in approaching and realizing crystallisation. Hence it is difficult to take meaningful XPCS measurements during this process. Only the spinline captures the various stages in time along the line in a quasi-static way and allows investigating them. Figure 2 shows the correlation function (divided by the monitor signal) of crystallizing iPP at 142 ^{o}C from two different positions on the sample. The meaning of the observed fall-off (in the range of minutes) is not clear yet.

(c) *XPCS at long times.* In principle the experiment aims at approaching a gel-point where any time scale involved will go to infinity. It should be realized that timescales above minutes would be difficult to capture with XPCS.

Conclusions

1. Technically the proposed project seems feasible. Especially previous doubts about low intensities and possible beam damage are no objection anymore.
2. Uncertainties remain regarding two points. (a) The nature of the movements and the time scales of the 'embryo's' involved in the early stages of crystallisation. (b) The possibility to capture with XPCS a change from probably already long time scales to arrested motion (even longer ones).

It has been concluded that the proposed experiment is at the borderline of the experimental possibilities. Because of the considerable effort and manpower required to set up the spinline at Troika III, it has been decided not to submit a full proposal.