ESRF	**Experiment title:** Shear induced suppression of nucleation and growth of crystals from solution	**Experiment number**: SC-2656
Beamline: BM16	**Date of experiment**: from: 22 July 2009 to: 24 July 2009	**Date of report**: 31 August 2009
Shifts: 6	**Local contact(s)**: Francois Fauth	*Received at ESRF:*

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Report:

The aim of this experiment was to explore a recent discovery that shear flow be used in conjunction with a low molar mass additive to template the nucleation and growth of polymers crystals.

We used dibenzylidene sorbitol (DBS) and a number of dichloro-substituted dibenzylidene sorbitol derivates (namely, para, meta and ortho substituted) as the solute. We have utilised poly(ε-caprolactone) (PCL) (Mw 80K Daltons m.p. ~ 60°C) as the host matrix polymer. PCL at room temperature is semi-crystalline polymer and above 130°C fully dissolves the DBS.

We have used the SAXS/WAXS capability of BM16 coupled with a user supplied shear flow cell specifically designed for the purpose which allowed x-ray scattering data to be measured during shear flow. The design of the shear cell meant that it fitted directly on the beam-line facilitating both the collection of high quality 2-d SAXS data and high resolution WAXS patterns essential for this project; the low molar mass compound generates sharp diffraction peaks commensurate with a high crystalline structure.

We were able to obtain high quality SAXS patterns with a time slice of ~ 9s. We were able to obtain useful WAXS data (parallel to the flow direction) centred around the 110 peak for PCL and peaks for the DBS which enabled us to confirm the presence or otherwise of crystalline order simultaneous with the SAXS collection. The

SAXS and WAXS patterns in Figure 1 show the quality of the data obtained. The horizontal streak arises from the aligned nano fibrils formed by the low molar mass compound. The scattering in the vertical direction arises from the formation of lamellar crystals templated by the DBS fibrils.

We have prepared halogenated derivatives of DBS to enhance the contrast with the sample and lower the detection threshold and the experiments we carried out confirmed our expectation. We were able to examine samples with just 0.2% w/w Cl-DBS.

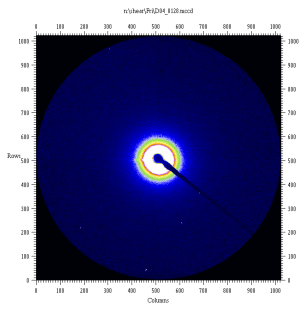	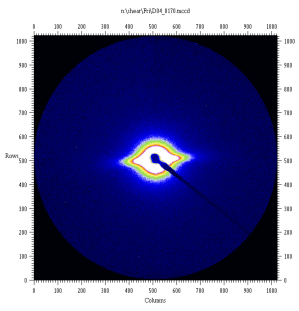	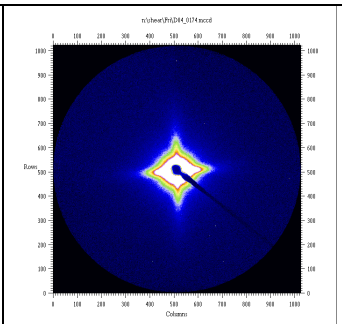
Figure 1a SAXS PCL + 3% o-Cl-DBS 80°C quiescent melt	Figure 1b SAXS 80°C shear rate =$10s^{-1}$ shear strain=1000su	Figure 1c SAXS first stage of Crystallisation at 34°C
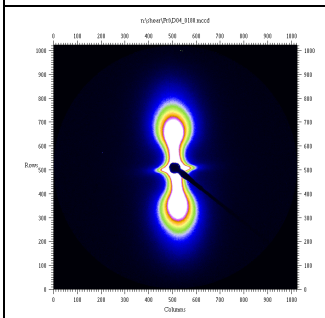	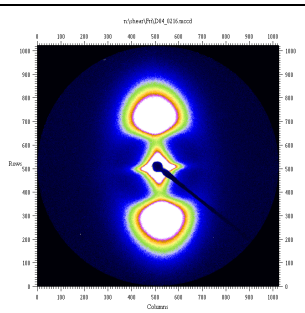	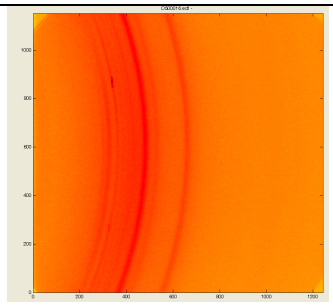
Figure 1d SAXS 1c + 60s	Figure 1e SAXS Room temperature	Figure 1f WAXS Room temperature most intense peak is 110 For PCL crystals, the peaks at lower Q (to the left arise from the o-CL-DBS

Detailed analysis of these data is still underway but we have already established that the ortho and para di-chlorobenzylidene sorbitol are highly effective at templating the crystallisation of the matrix polymer as revealed in Figure 1. We have found that the meta di-chlorobenzylidene sorbitol and the para di-bromo benzylidene sorbitol behave a similar manner to di-benzylidene sorbitol while a related compound xylitol does not template the crystallisation.

The analysis yields quantitative parameters which describe the nature of the DBS fibrils and the levels of orientation of the matrix polymer achieved in relation to the temperature and shear profile

The preliminary results will be presented at the European Congress on Advanced Materials and Processes in Glasgow in September 2009.