ESRF	**Experiment title:** Early stages of polymer crystallisation	**Experiment number**: SC777
Beamline: BM26	**Date of experiment**: from: 20/06/01 to: 23/06/01	**Date of report**: 01/03/2002
Shifts: 9	**Local contact(s)**: Wim Bras, Igor Dolbnya	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. E. L. Heeley

Mr A. I. Norman

Miss A. C. Morgovan

Prof. A. J. Ryan

Dr J. P. A. Fairclough

Department of Chemistry, University of Sheffield, Sheffield, U.K, S3 7HF.

Report:

The structure of a range of poly(oxyalkylene) block copolymers in aqueous solution has been investigated using time resolved SAXS/WAXS/DSC techniques on the CRG DUBBLE beamline BM26 of the ESRF.

Three different chain architectures have been explored, poly(oxyethylene)-poly(oxybutylene)-poly(oxyethylene), (EnBmEn), poly(oxybutylene)-poly(oxyethylene)-poly(oxybutylene), (BnEmBn), and poly(isoprene)-poly(oxyethylene), (InEm). The chain architecture affects the way in which these block copolymers behave when diluted in aqueous solution.

Micelles are formed when the polymers are dissolved in water. This micellisation process occurs at a concentration known as the *C.M.C,* critical micelle concentration.

As the concentration of block copolymer is increased these micelles pack together in to various arrays, depending on structure, temperature, and hydrophilic content. The structures formed can be Cubic, (Body-Centered or Face-Centered), Hexagonal, or Lamellae. The structure adopted can be estimated by rheological measurements and the appearance under polarized light microscopy, but SAXS gives us a clearer indication as to the actual structure. This is determined by the positional ratios of the reflections in the scattering pattern.

Cubic: 1:√2:√3:√4

Hexagonal: 1:√3:√4:√7

Lamellae: 1:2:3:4

Block copolymer solutions are placed in a Linkam DSC Stage and heated from 5°C through to 90°C at a ramp rate of 5°C/min. The scattering patterns are observed to the temperature at which the phase transitions occur. Phase diagrams have been previously constructed through similar experiments.

From the phase transition temperatures known, kinetic experiments can be performed. The sample is either heated or cooled to a region in the phase diagram where the structure is known to be stable. Rapid heating or quenching is performed to a temperature just inside the region of another phase and held at that temperature until the structure changes. The SAXS patterns will show a number of reflections due to the structure it adopts. The WAXS observed displays no Bragg peaks because the sample is not crystalline. An amorphous hump is seen.

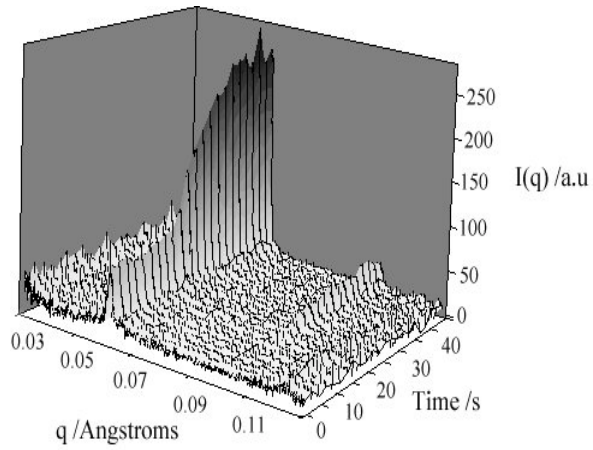

Fig. 1– Evolution of the Hexagonal phase for 45% B11E47B11 on quenching from 70℃ to 56℃.

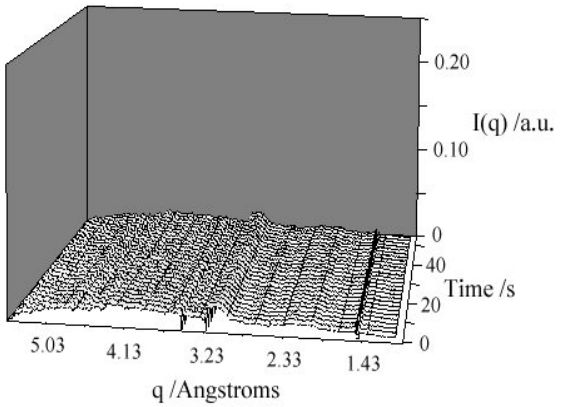

Fig. 2 WAXS pattern for 45wt%B11E47B11 at 56℃.

Integrating between the two pixel values at which the reflections change in intensity monitors the kinetics.

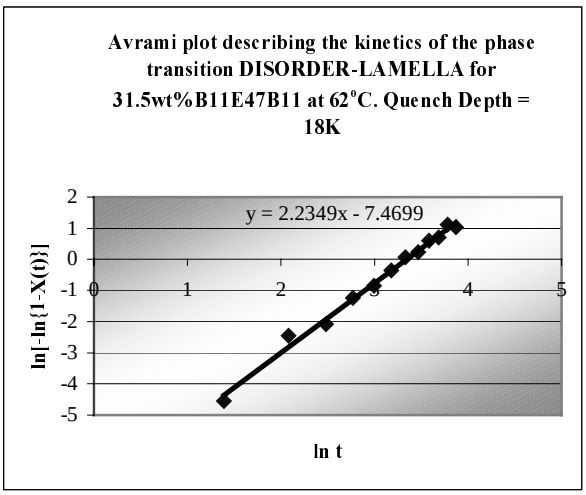

Fig. 4 – Avrami plot for 31.5%B11E47B11. The gradient is indicative of the mechanism of the phase transition. The intercept gives us a value for the rate constant.

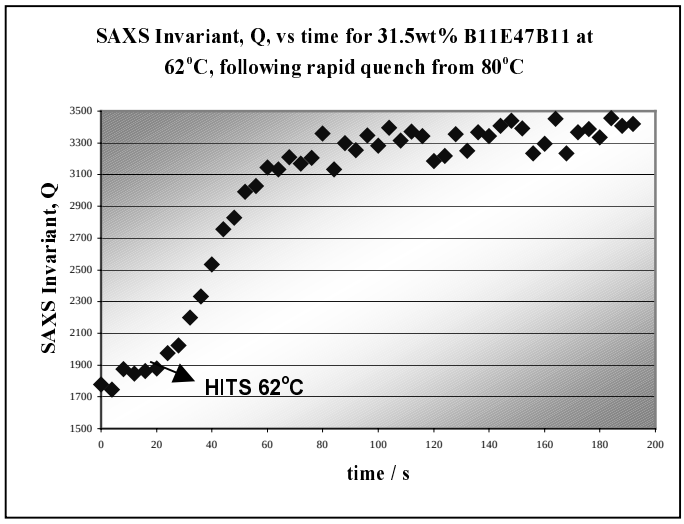

Fig. 5 – Evolution of SAXS intensity monitored with time.