ESRF	**Experiment title:** Early stages of polymer crystallization: evidence of spinodal crystallization in isotactic polypropylene	**Experiment number**: SC777
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Report:

The classical picture of polymer crystallization involves the creation of a stable nucleus from the entangled polymer melt and then the growth of the crystalline region into the lamellar structures and beyond. In the past, the kinetics involved with the formation of a stable nucleus have been difficult to follow experimentally thus, few theories were developed which describe this process well. However, recently investigations into the early stages of polymer crystallization X-ray scattering techniques have allowed theories to be developed which describe the process in terms of a 'liquid-liquid' phase separation system[1]. The early stages of the crystallization are thought to follow an ordering of the molecules through a mesophase, which continues to evolve through a process of phase separation into crystalline and amorphous regions. The development of a mesophase in the phase separation process can be described theoretically with the kinetics of spinodal decomposition[2]. Here, a continuous transformation of a partially ordered phase (polymer chains with the correct conformation) develops towards more ordered states leading to nucleation of crystallites and growth.

Following the early stages of crystallization kinetics has been successfully reported recently on a range of semi-crystalline polymer samples such as polyethylene terephthalate (PET), isotactic polypropylene (iPP), polyethylene (PE) and polyether ketone ketone (PEKK)[3]. These investigations have observed spinodal like kinetics during the early stages of crystallization. Further investigations into the crystallization of commercial iPP samples have been preformed, using time resolved Small- and Wide- Angle X-ray Scattering experiments on the Dubble BM26b beamline. Particular attention has been paid to the early stages of the crystallization and relating this to the spinodal decomposition kinetics described.

From the scattering data obtained during crystallization, SAXS develops showing long range ordering (stacking of lamellae) or the macrostructure, along with WAXS giving details on the atomic unit cell or microstructure development, Figure 1(a) and 1(b) show SAXS/WAXS development of iPP at 130^{o}C. If the kinetics follow classical nucleation and growth theories then the SAXS and WAXS should, develop together after an induction period, τ_i. However, if the SAXS is seen to emerge before any WAXS is detected during this induction period then the development of some long range ordering must be occurring before any crystalline structure arises, this is shown in Figure 2 (a) for iPP at 142^{o}C. This is identified as the spinodal region during the pre-nucleation stages of crystallization. As the SAXS intensity grows in this period, the kinetics of the crystallization can be fitted to the Cahn-Hilliard (CH) linearized growth model[4] for spinodal decomposition, Figure 2(b). This describes the time evolution of the scattering intensity following an exponential growth from

the increased amplification of density fluctuations. The fitting of the CH theory to the SAXS data at each quench temperature, gives an extrapolated value for the spinodal temperature, T_s, below this temperature the polymer is said to spontaneously separate into two phases. Figure 3, gives the T_s value for iPP to be 416K, calculated from CH plots at several temperatures.

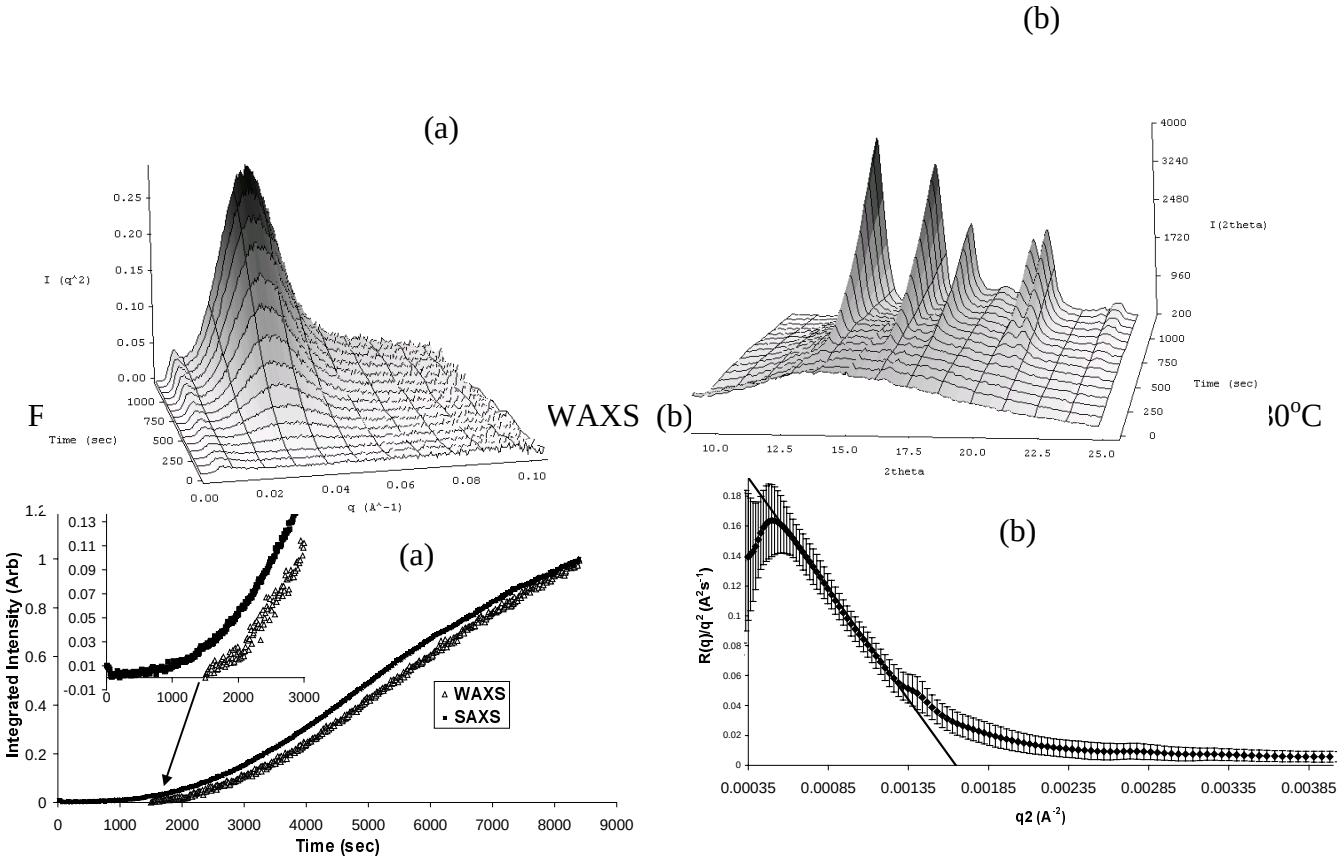

Figure 2, (a) SAXS/WAXS development of iPP and corresponding CH plot 142^{o}C

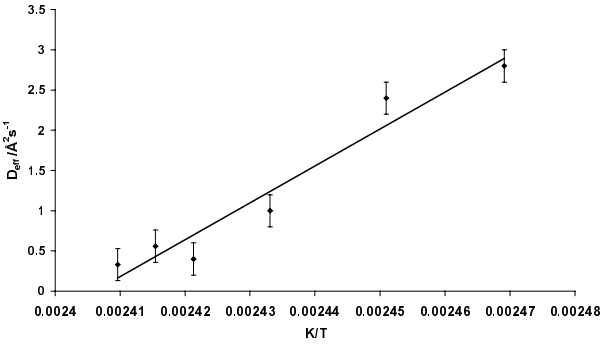

Figure 3, calculation of T_s for iPP

The crystallization kinetics determined by quiescent SAXS/WAXS experiments of isotacic polypropylene have allowed data to be investigated in terms of spinodal decomposition, indicating that this phase separtaion mechanism to the pre-nucleation stages is a theoretically viable route when analysed using the Cahn-Hilliard theory to obtain a spinodal temperature.

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