

**Experiment title:**

Isothermal Phase Reversal In a Semi-crystalline
Polymer : polyethylene

**Experiment
number:
SC-125**

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Report:

Solid phases may exist in a wide variety of forms such as polymorphs, solvates, liquid, crystals and ampholytes. For a given set of experimental conditions such as temperature, pressure and composition only one solid phase will be consistent with a minimum free energy of the system. This will then be the most stable solid phase available and all other phases will be metastable with respect to this phase. However, the fact that these solids are metastable does not preclude their existence for long time periods. An extreme example of this is diamond which is metastable with respect to graphite at room temperature and pressure. The appearance of polymorphs from a supersaturated and/or supercooled mother phase is, however, not only determined by the drive to minimise the free energy but also by the need for the system to do this by the kinetic route with the lowest activation energy. It is the balance between two processes -thermodynamic and kinetic that forms the basis of this experimentation.

Polyethylene is a semicrystalline polymer, it crystallizes in the orthorhombic phase from the melt, but when crystallized at the elevated pressures and temperatures usual orthorhombic phase gives way to the hexagonal phase before it melts. Within hexagonal phase mobility of chains increases, instead of usual folded chain morphology extended chain crystals are obtained. With the help of high pressure DTA and conventional X-ray experiments it has been shown that the hexagonal phase is accessible only beyond 3.6kbar before melting. In-situ observations made by polarised optical microscopy predicts the incoming of hexagonal phase below 3.6kbar in the thermodynamically stable orthorhombic regime.

In the present set of experiments which were feasible due to the high flux available at ESRF we will show the in-situ X-ray evidences for the transient nature of the hexagonal phase at much lower pressures. To perform these set of experiments we have prepared Solution Casted Ultra High Molecular Weight Polyethylene films (SCUHMWPE), having regular lamellae thickness of 120Å. Transmission Electron Microscopy and SAXS patterns show the regular stacking of crystals when viewed along the preferred direction.

Fig. 1 shows the in-situ WAXS pattern of a SCUHMWPE sample placed in between two diamonds at the fixed pressure of 2.4kbar. To overcome the X-ray absorption by diamond windows X-ray wavelength of 1 Å was used. For the present purpose we have made use of own built piston cylinder pressure cell. in the existing setup of the cell the temperature could be raised upto 300°C and the pressure to 5kbar. On heating the sample at 2.4kbar, the (1 00) reflection of hexagonal phase appears alongwith the (1 10) and (200) reflections of the orthorhombic phase of polyethylene, Fig. 1 a. When the sample is left to anneal at a fixed temperature, the (1 00) reflection of the hexagonal phase gradually diminishes, Fig. 1 b-d. On heating further at 2°C/min. the (100) reflection reappears and intensifies before it melts, whereas (1 10) and (200) reflections loose intensity. On cooling from the melt recrystallization occurs directly in the orthorhombic phase. Since on annealing usually polymer crystals thicken, the transient nature of the hexagonal phase in the thermodynamically stable orthorhombic region will be dependent on the crystal thickness. Results here show that isothermal phase reversal occurs on annealing at the fixed pressure and temperature i.e. the initially thermodynamically stable hexagonal phase is no longer stable once lamellae thicken- i.e. stability of a phase is dependent on crystal size, which in polymers will be influenced because of the kinetic reasons too. The importance of kinetics was recognised by Ostwald and is summarised in his 'Law of Stages' which simply states that when a system moves from an unstable to a stable state it does so by transformations to intermediate metastable states. Similar effects can be demonstrated in range of polymers where mobile phase is accessible like poly di alkyl siloxanes, poly di alkyl silanes, poly chloro tetrafluoro ethylene, poly phosphazenes et.al.

Figure 1 SCUHMWPE

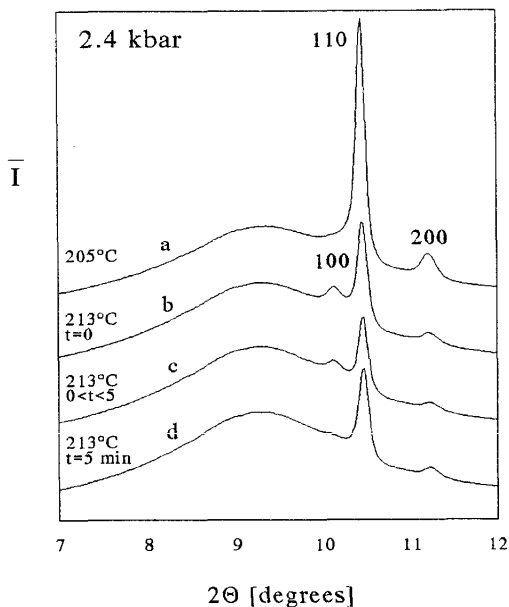


Figure 1 Individual curve is the integrated 2D X-ray pattern as recorded by Princeton CCD detector. Integration has been performed using Fit2d program of Hammersley