



Experiment title: Surface X-Ray Diffraction studies of ordering at poly(ethylene terephthalate) surfaces		Experiment number: 28-01-3
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Report:

The properties of polymeric surfaces and interfaces are central to many technologies: paints and coatings, adhesives, biocompatible materials, membranes etc. In contrast to the extensive data available for semiconductors and other inorganic materials, indicating pronounced differences in the state of order between surfaces and bulk, very little information is available for polymer surfaces. This project is aimed at using grazing incidence x-ray diffraction (GIXRD) to probe chain conformation and ordering in the surface region to either support or refute the ideas developed by theory and simulations.

We used the XMaS beamline to perform GIXRD studies of 1000Å-thick film samples of polyethylene terephthalate (PET) deposited onto silicon substrates and annealed at a range of temperatures up to 180°C. The structure of the surface region (top 50Å) was compared with that of the bulk of the polymer by comparison of 2θ scans with an angle of incidence of 0.15°, just below the critical angle for total reflection (0.18°), with those performed using a steeper angle of incidence of 1.0° (fig. 1). We found that the topmost 50Å starts to crystallise at about 90-95°C whereas the bulk of the film starts to order at about 105°C. This opens the possibility of forming a crystalline surface on an amorphous bulk by simple thermal treatment. A surprising feature of the results was that the scans in Q_{\perp} and Q_{\parallel} showed different subsets of the crystalline PET Bragg peaks. This indicates a preferential ordering in the surface region. The peak intensities are consistent with the benzene rings lying parallel to the surface. Fig. 2 shows scans for a sample annealed at 150°C where the surface and bulk have both crystallised. The bulk-sensitive scans show the same preferential ordering as observed at the surface. This indicates that the surface-induced molecular ordering is now extended throughout the film (fig. 2). This surprising result implies that strong inter-chain ordering occurs in order to transmit the surface-induced ordering throughout the bulk of the film. This result may well have significant implications for understanding the crystallisation process in PET, for which a mechanism involving spinodal decomposition has been proposed. Further investigations are underway in Cardiff using Atomic Force Microscopy.

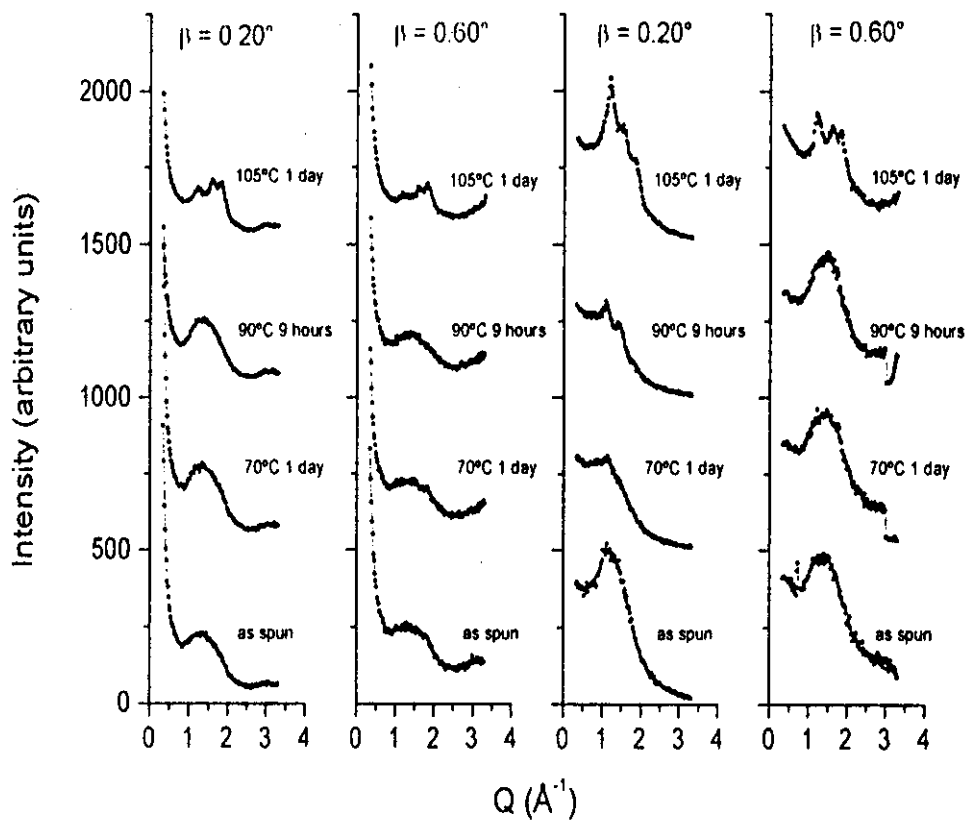


Fig 1: Surface and bulk-sensitive scans for both geometries at various temperatures.
 (a) scanning Q , surface sensitive (b) scanning Q , penetrating the bulk
 (c) scanning Q , surface sensitive (d) scanning Q , penetrating the bulk

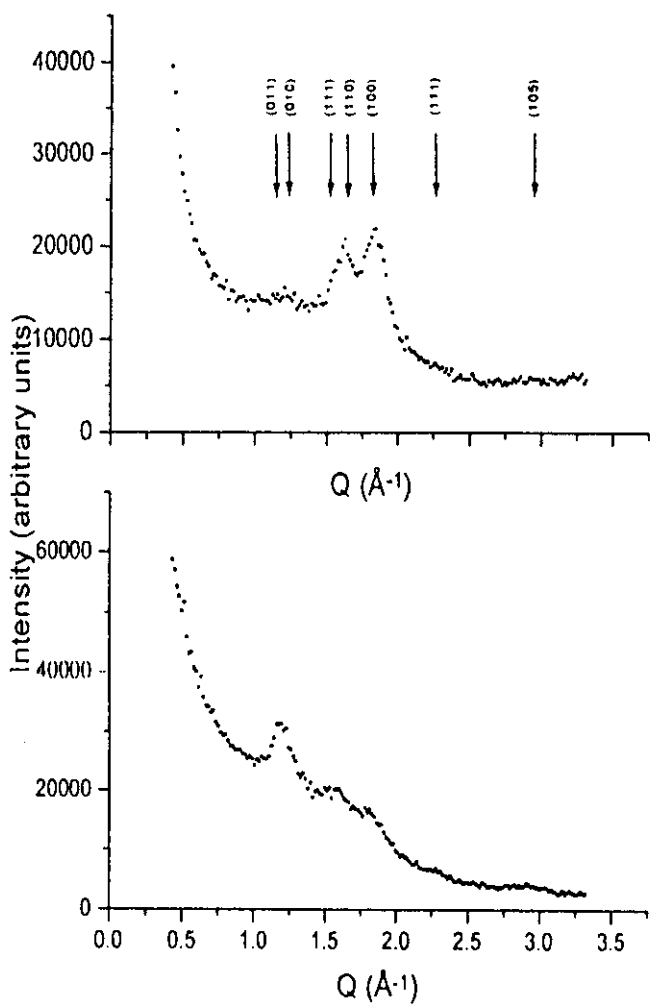


Fig 2: GIXRD scans at an angle of incidence of 1° in (a) Q_x and (b) Q_y , showing preferred orientation of the PET polymer film due to interactions between the benzene ring and the surface