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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Possible surface-induced ordering in isotactic-polystyrene	**Experiment number**: SC 1137
Beamline: ID01	**Date of experiment**: from: 23 April 2003 to: 29 April 2003	**Date of report**: 23/11/03
Shifts: 18	**Local contact(s)**: Dr. Peter Boesecke	*Received at ESRF:*

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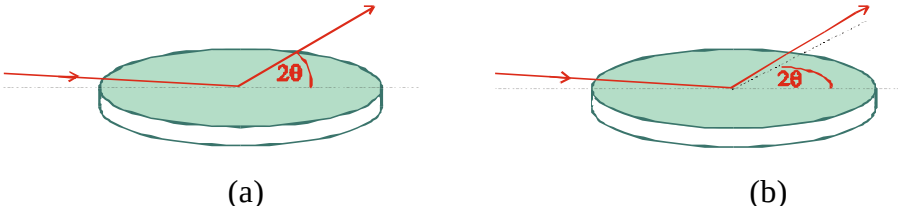
Report:

Polymer surfaces and interfaces play a vital role in applications such as adhesion, barrier coatings, polymer electronic devices and yet there is a severe shortage of experimental information and techniques on chain structure at interfaces. Grazing incidence x-ray diffraction (GIXRD) studies is one of the few suitable techniques: we have developed GIXRD studies of the polymer surface which we can now perform during *in-situ* processing. To date, we have focussed on the important commodity polymer poly(ethylene terephthalate) (PET), in which we have demonstrated that the surface crystallises at a lower temperature than the bulk of the film [1]. In this experiment, we extended these measurements to isotactic-polystyrene, i-PS, in order to investigate whether some or all of the effects observed in PET occur at other semi-crystalline polymer surfaces. This is the first experiment on ID1 studying polymer surfaces with GIXRD, in which we explored the use of a linear detector for rapid data acquisition to enable good time-resolution during *in-situ* annealing.

i-PS films of thickness about 1000 Å were deposited by spin-coating onto Si(001) substrates. Angles of incidence α of 0.18° and 0.60° were used to probe the surface and the bulk of the film respectively, the critical angle being 0.22°. Scans were performed in two geometries with photons of energy 8.0 keV in order to probe correlations in the plane of the surface and normal to the surface (fig. 1). It was found that the surface scattering was swamped by the background scattering from the beryllium dome when using a 120° linear detector. It is clear that polymer surface scattering with an area detector will require an evacuated beam path with no windows visible to the detector – a mode which will be useable in future on ID1 by virtue of the evacuated diffractometer chamber. In this experiment, due to time pressures, we needed to resort to the Braun short linear detector oriented normal to the surface with collimation slits scanned mechanically using the diffractometer.



(a) (b)

Fig. 1 Scattering geometries employed (a) Grazing incidence asymmetric Bragg scattering (GIABS) geometry, in which **Q** has a large component (≈Qcosθ) normal to the surface (b) Grazing incidence surface plane scattering (GISPS) geometry, in which the **Q** is in the plane of the surface for $\alpha \approx \alpha_c$.

A i-PS film pre-annealed at 150°C, prior to the experiment, was investigated in both the GISPS and GIABS geometries for surface and bulk-sensitive scans. The scans show a pronounced anisotropy (fig. 2): the scattering in the plane of the surface (fig 2a) is very different from that normal to the surface (fig 2b).

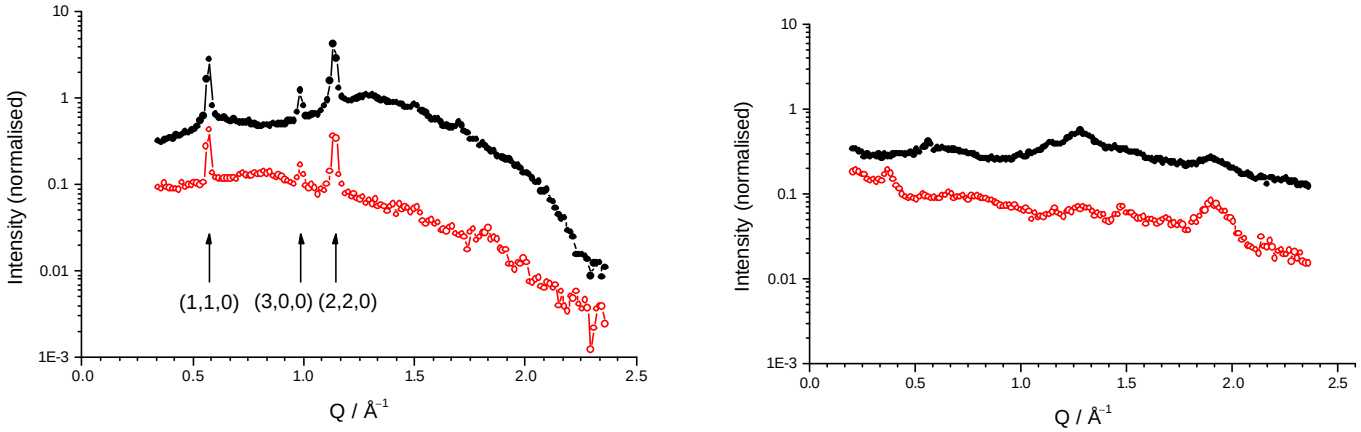


Fig. 2 GIXRD scans from i-PS film in the (a) GISPS (b) GIABS geometry, sensitive to in-plane and out-of plane correlations respectively.

The in-plane scattering is dominated by three sharp peaks, which can be indexed according to the hexagonal unit cell, which is conventionally used to describe the rhombohedral primitive unit cell, as the (1,1,0), (3,0,0) and (2,2,0) Bragg peaks. These are the l=0 Bragg peaks in this Q-range and hence it establishes that there is a dominant ordering in which the α-helices of the i-PS crystalline structure, lying parallel to the c-axis, are oriented normal to the surface (fig. 3). The narrow peak widths correspond to a domain size of 180 Å.

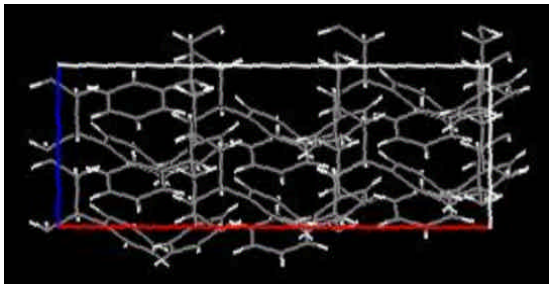


Fig. 3 The crystalline structure of bulk i-PS viewed along the (010) direction.

These crystalline peaks appear similarly in both the surface scattering and the bulk scattering, possibly indicating that the orientation of the α-helices is primarily caused by the buried interface with the Si substrate. However, the more diffuse scattering displays significant structural differences between the surface and bulk:

1. the peak in the amorphous scattering at the surface occurs at about 0.8 Å in the GISPS geometry whereas the corresponding peak for the bulk of the film lies around 1.3 Å (fig. 2a).
2. the peak positions in the GIABS geometry differ significantly between bulk and surface scattering (fig. 2b).

The cause of these two differences between the surface and bulk structure is currently unclear and under investigation. A series of in-situ GIXRD scans during annealing at 85°C showed little difference between the kinetics of surface and bulk ordering in stark contrast to PET. It appears that the ordering in i-PS is dominated by the buried interface whereas the ordering in PET is driven from the surface. However, in i-PS, the amorphous structure at the surface is significantly different from the bulk of the film, requiring further investigation.

References

[1] The role of surface-induced ordering in the crystallisation of PET films, M Durrell, J E Macdonald, D Trolley, A Wehrum, P Jukes, R A L Jones, C J Walker and S Brown, Europhysics Letters 58 (2002) 844-850