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ESRF

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

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

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:** Kinetics of a buried polymer interface studied with time-resolved surface diffraction	**Experiment number**: SI-657
Beamline:	**Date of experiment**: from: 26 February 2001 to: 7 March 2001	**Date of report**: 27/8/02
Shifts: 21	**Local contact(s)**: Dr Paul Steadman	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The properties of polymeric surfaces and interfaces are important in many commercial applications: paints and coatings, adhesives, polymeric semiconductors, biocompatible materials, membranes etc. The project aims at understanding chain conformation and kinetics at polymer surfaces and interfaces and to compare them with the corresponding properties in the bulk. In recent experiments, we investigated the crystallisation of the archetypal semi-crystalline polymer poly(ethylene terephthalate) (PET) and showed that there are significant differences in the ordering at the surface compared to the bulk. We have also demonstrated the role of the surface in inducing a preferred orientation of the polymer chains on crystallisation [1]. The detailed kinetics can now be followed in real-time using a compact high vacuum chamber for in-situ studies.

Buried polymer interfaces are crucial for structural integrity of multilayers, for adhesion and for semiconducting polymer devices. In this experiment, we aimed to *understand the kinetics of crystallisation at a buried polymer-polymer interface*. Does the kinetics of crystallisation at such an interface proceed at a rate similar to that of the free surface or at a rate typical of the bulk polymer?

In order to investigate the upper interface of a buried polymer layer, we needed a suitable polymer complement having a lower electron density than PET. Polystyrene (PS) was selected for this giving the required refraction effects (fig. 1). However, the difference in the

critical angle for PET and PS is of the order of 0.02° and hence considerable care was required to penetrate the PS while limiting the penetration in the PET film.

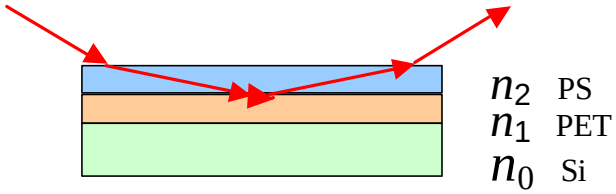

Fig. 1 Refraction at the buried polymer interface

Considerable difficulty was experienced in the first 3 days of the experiment in setting up our compact vacuum chamber on the diffractometer and overcoming initial problems. Samples annealed for 90 minutes at four different temperatures between 90°C and 115°C indicated that crystallisation is more rapid at 95°C than at 90°C. Samples annealed at 100°C and 115°C did not display distinct crystalline peaks. This initially puzzling result has now been resolved by a more recent experiment on BM28 where time-resolved GIXRD and reflectivity scans showed that PET/PS interfaces suffer severe interdiffusion at temperatures of 100°C and higher. The time-series of scans at 95°C showed that crystallisation of the PET occurs during shorter anneal times. For anneal times of several hours, the crystalline peaks disappear – as a result of more gradual inter-diffusion at the interface.

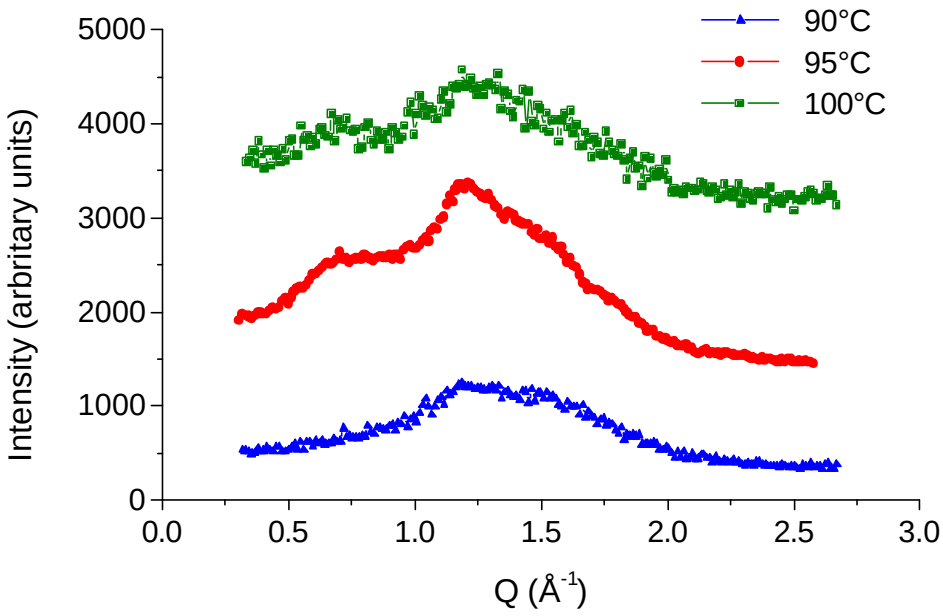

Fig. 2 GIXRD scans of the scattering in the plane of the interface from a PET/PS bilayer annealed at 90°C, 95°C and 100°C for 90 minutes. Distinct but broad crystalline peaks from PET can be observed at 95°C. Annealing at 100°C does not result in crysalline peaks from the interfacial PET. There is a slight inconsitency in the scale factor due to small variations in the angle of incidence around the critical angles of PS and PET.

The reflectivity results are currently being analysed in detail and a publication will be prepared shortly.

[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