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:** Self-organisation in ultra-thin layers of conjugated polymers floating films	**Experiment number**: SC-989
Beamline: ID10B	**Date of experiment**: from: Mar 6th 2002 to: Mar 12th 2002	**Date of report**: 2002-08-23
Shifts: 18	**Local contact(s)**: Bernd Struth, Oleg Konovalov	*Received at ESRF:*

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Report:

Materials: Regio-regular poly(hexylthiophene) (R-PHT) with > 98% head-tail couplings, and $FeCl_3$ polymerised poly(octylthiophene) (POT) with ~80% h-t couplings, were used. Closely analogous results were obtained also for poly(dodecylthiophene) and other poly(thiophene) derivatives.

A few drops of low concentration (~ 1 mg / ml) of the polymer dissolved in chloroform were spread on a clean water surface in a shallow teflon trough. Ultra-thin (down to 10 *nm*), faintly reddish layers were produced by the spreading technique. Efforts to further reduce the film thickness by using more diluted solutions failed, leading to the formation of numerous islands rather than a homogeneous film.

The films were studied at the X-ray beam line ID10B at the ESRF, with *?* = 1.55Å. A 1D position sensitive detector covering a vertical angle *?* of approximately 8º was used for collecting the scattered intensity. The detector could be moved a horizontal angle *d* from the plane of the incident beam and the surface normal. An incidence angle of 0.15º was used.

For *in situ* doping of the floating films, $NOPF_6$ dissolved in acetonitrile was injected into the water sub-phase. Acetonitrile was chosen because it can dissolve $NOPF_6$, and is miscible with water, but does not affect the polymer.

Diffraction results: Using GID, we could observe the *100* and *010* reflections, also for films down to a thickness of 100Å (Fig.1 for *100*). For probing the anisotropy, the detector was scanned in the *d* – direction, thereby effectively mapping the Debye-Scherrer cone. Strong anisotropy was thus revealed: The intensity along the Debye-Scherrer ring of *100* is confined to the region of scattering vector perpendicular to the film plane, with FWHM along the ring as low as ~12º for regio-regular PHT. From previous knowledge of the structure, this implies a preferred orientation of the side chains and the thiophene rings perpendicular to the substrate plane, in fact as reported also for thicker films. Conversely, the *010* reflection could only be observed for scattering vector parallel to the substrate, as a broad peak around *d* = 23.5º± 0.5º. From the width of the *100* diffraction peak, the average dimension of the crystallites could be estimated to about 100Å. This shows

that such ultra-thin films (consisting of only five molecular layers) are in fact *single-domain* in the direction of their thickness (see later for thickness determination); each crystallite protrudes the film.

Doping is known to give rise to some structural changes in PATs, notably a contraction of the *b*-axis and an expansion of the *a*-axis. In Fig. 1 the change of the *a*-axis following *in situ* doping of the floating films with $NOPF_6$ is clearly seen, a remarkable effect. The doping could also be observed visually, as the film changed its colour from being weakly reddish to a hardly visible pale blue. Dedoping takes place; after 2 hours the film is regaining its original colour accompanied by a contraction of the *a*-parameter.

Morphology by reflectometry: Using specular reflectometry on a POT film floating on the water surface, the pattern of Fig. 2 was recorded. The fitted curve is obtained by applying standard matrix formalism from optical theory of stratified media. Both curves are multiplied by Q^4 for increased readability, which also explains the drop in intensity for Q smaller than the critical wave vector of reflection Q_c.

The best fit was obtained using a density profile as shown in the inset of Fig. 2. The refractive indices of water and polymer were determined from tabulated values. The rough air-polymer interface was fit using a Gaussian smearing of the profile with s = 5.3Å. As is seen from the inset, the contrast is quite small between polymer and water. This particular film is seen to have a thickness of about 100Å, corresponding to roughly 5 repetition units along the *a*-axis.

The feature at $Q \sim 0.3$Å^{-1} is a result of the film's internal structure, a Bragg-like signal interfering with the reflections from the interfaces. The best fit was obtained assuming an exponentially damped harmonic variation of the electron density, a model sometimes used for modelling smectic liquid crystals. The periodicity of the fitted modulation was 20.8 Å, i.e. comparable to the *a* - parameter of solid POT, being 20.4 Å. Physically, the model can be interpreted as a well-developed layering near the air-polymer interface, deteriorating into the film. The ordering is least pronounced at the polymer-water interface, in qualitative agreement with the hydrophobicity of the aliphatic side chains. For intermediate depths, the arrangement is a compromise between the polymer's inherent tendency of layering and the reluctance of the side chains to being submerged in water.

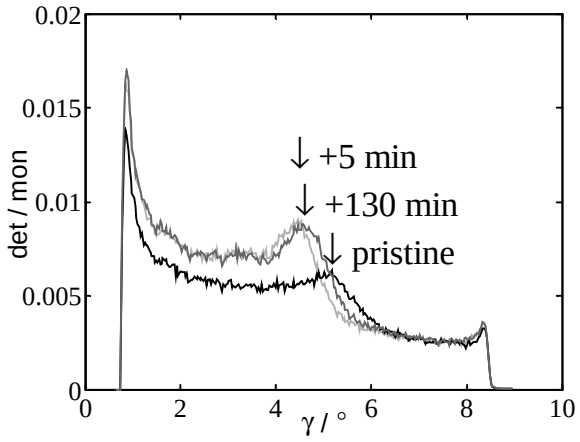

Fig.1 Diffraction signal from a floating R-PHT film before doping, immediately after, and about 2 hours after adding $NOPF_6$ to the subphase. The abscissa axis corresponds to the vertical scattering angle. The horizontal angle *d* was kept at 0.2º. Peaking at both ends of the diffractogram is an artefact of the detector

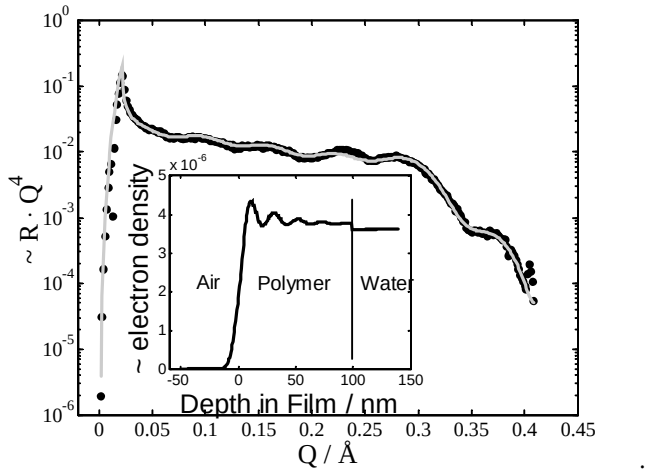

Fig. 2. Reflectometry data (filled circles) as obtained from a thin POT film floating on water. The solid line is the fit. The **inset** shows the fitted variation of the scattering density (the deviation from unity of the real part of *refractive index*) through the floating film, as placed between air and water. The periodic variation corresponds to the crystallographic unit cells (20.8Å), being damped by surface effects.

Other results: Some conjugated polymers films on *Si* or *glass* substrates were also investigated for structure, anisotropy or morphology: R-PHT, POT, PDoDT, $PDOT_3$, PEDOT-PSS, PEDOT1-ClO_4, PEDOT10-ClO_4, the three former obtained by transfer to glass after being formed as floating films on water surfaces.