*XMaS the* **X-RAY MAGNETIC SCATTERING**
*and* **HIGH RESOLUTION BEAMLINE** *at the*
**EUROPEAN SYNCHROTRON RADIATION FACILITY**

# Experiment Report Form

**This report form is to be filled in by all users or groups of users who have had access to beam time for measurements at the XMaS Beamline.**

### *Reports accompanying requests for additional beam time*

An experimental report on previous measurements - if necessary, a preliminary report - must be attached to all subsequent requests for beam time. The Peer Review Panel reserves the right to refuse to examine new proposals from groups who have not reported on the use of beam time allocated previously.

### *Instructions for preparing your Report*

- fill in a separate form for each project or series of measurements.
- 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
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as “Times”, 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.

### *Deadlines for submission of Experimental Reports*

- Within 6 months of the experiment and normally before any subsequent submission

***Should you wish to make more general comments on the experiment, please enclose these on a separate sheet, and send both the Report and comments to the XMaS Administrator at the address below.***

### *Published papers*

All users must give proper credit to XMaS staff members and proper mention to XMaS facilities which were essential for the results described in any ensuing publication. This should take the following form:

“This work was performed on the EPSRC-funded XMaS beam line at the ESRF, directed by W.G. Stirling and M.J. Cooper. We are grateful to the beam line team of S.D. Brown, D.F. Paul, A. Stunault and P. Thompson for their invaluable assistance, and to S. Beaufoy and J. Kervin for additional support.”

Further, they are obliged to send to the XMaS Administrator the complete reference and the abstract of all papers appearing in print, and resulting from the use of the XMaS beamline.

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|---|---|---|
| | **Experiment title:**<br>**Structural studies of aligned polyfluorenes** | **Experiment number:**<br>SC-1626 |
| **Beamline:**<br>**BM 28** | **Date of experiment:**<br>from: 28rd Sept to: 5th Oct 2004 | **Date of report:**<br>25th Feb 2005<br>*Received at XMaS:* |
| **Shifts:**<br>18 | **Local contact(s):**<br>L. Bouchenoire | |

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**Report:**

We have performed grazing incidence x-ray diffraction (GIXD) and x-ray reflectivity experiments on a series of thin films of the technologically important polyfluorene PF2/6.. Polymers such as PF2/6 (which is a branched side chain hairy-rod molecule) are some of the most promising class of electroluminescent polymers in thin film applications, such as organic light emitting diodes which are to be used in the displays of digital cameras or mobile phones instead of conventional liquid crystal displays. In order to obtain the desired photophysical properties suitable for device implementation there remain two major issues that need to be addressed: Firstly, a detailed understanding of the relationship between the photophysics and the intermolecular structure within the device environment; and secondly, how this structure is modified on the addition of energy transfer dopants.

As part of our continuing development of the optimisation of the first of these concerns we have undertaken several studies of the alignment of PF2/6 thin films [1]. In bulk the polymer self-assembles into a hexagonal (Hex) structure when the molecular weight, $M_n$, is high. In PF2/6 thin films spun coated onto rubbed polyimide (PI), rigid PF2/6 chains (characterized by **c** axis, parallel to the rigid backbone) align and run parallel to the substrate along the rubbing direction of the PI (**z** axis). The PF2/6 shows two differently oriented coexisting crystalline types. Part of the structure is characterised as having the crystallites with the crystal axis (**a**) perpendicular (**x**) to (type I) and the other aligned parallel (**y**) to (type II) the substrate surface. There is large optical absorption and dispersion (over the spectral range 250-1000 nm) of the refractive index parallel to **x** axis and small absorption and dispersion of the refractive index perpendicular to it. Above a well defined threshold value $M_n$*=$10^4$ g/mol, there is a phase transition from the Hex to the nematic (Nem) phase with increasing temperature. The theoretical phase diagram is illustrated in Fig. 1. Schematics of the crystallite types and molecular structure in aligned hexagonal films are also shown.

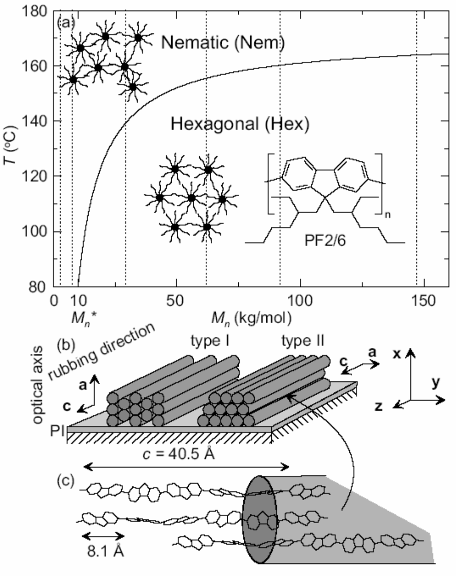

**Fig. 1.** (a) The phase diagram and head-view schematics of Nem and Hex phases of PF2/6 as a function of $M_n$. The dotted lines represent the molar weights of the samples studied. . Adapted from ref.[2].

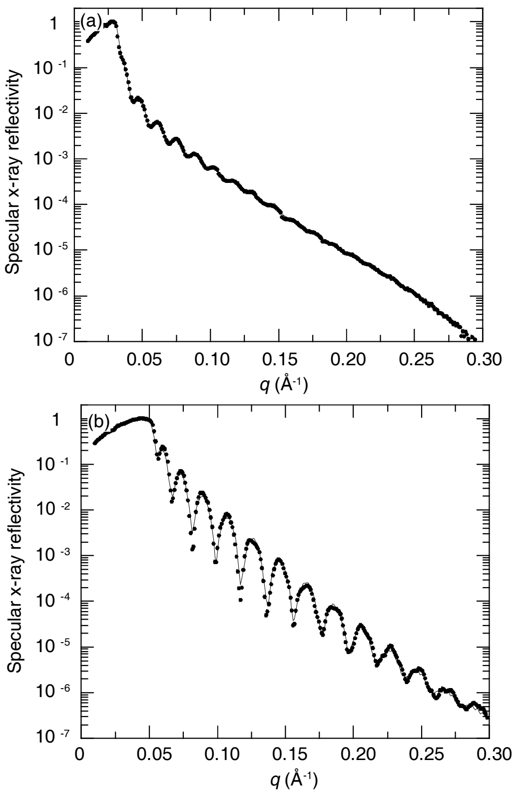

**Fig. 2.** Reflectivity curves of (a) non-aligned film on quartz and (b) aligned film on PI/ITO. The difference in the critical angle is due to the difference in the electron density between quartz and ITO.

Unlike our previous work [1], in this experiment, we concentrated on understanding the relationship between the photophysics and the surface morphology in aligned films [2]. The surface morphology was studied as a function of $M_n$ in the range 3-150 kg/mol. Polarized microscopy, AFM, GIXD (Fig 3 (a)) and x-ray reflectivity (Fig. 2) were employed. In particular, the aim was to highlight the relation between macroscopic-submicron scale morphology to the self-organized intermolecular structure and the uniaxial alignment. At the threshold $M_n$, $M_n$*=$10^4$ g/mol, there is a distinctive transition in morphology from featureless ($M_n$<$M_n$*) to rough ($M_n$>$M_n$*) corresponding to the Nem-Hex phase transition that defines the phase boundary in figure 1. The Hex phase that reveals two coexistent crystallite types in the whole film also shows needle like domains (20-60 nm in size) at the surface but a rigorous microscopic picture on their internal structure cannot be given as yet. The study has enabled us to show that the optimal alignment and surface smoothness is achieved slightly below $M_n$*. The combined optimum of orientational and local order however is achieved slightly above $M_n$* when the roughness is smaller than far above $M_n$*.

Adding suitable dopants is another crucial factor in refining key optical properties such as the fluorescence efficiency, and excited state lifetimes of the dopant/polymer derivative. Porphyrines have shown to be promising dopants for polyfluorene with the amount of spin-orbit coupling exerted to the host by the dopant controlled by the choice of the central metal atom of the porphyrin. Figure 3 shows the grazing incidence diffraction profiles for a pure PF2/6 (a) and Zn doped porphyrin/PF2/6 derivate (b). The dopant has significantly reduced the degree of hexagonal alignment. We were unable to observe any resonant enhancement in the diffraction peaks close to the Zn K edge.

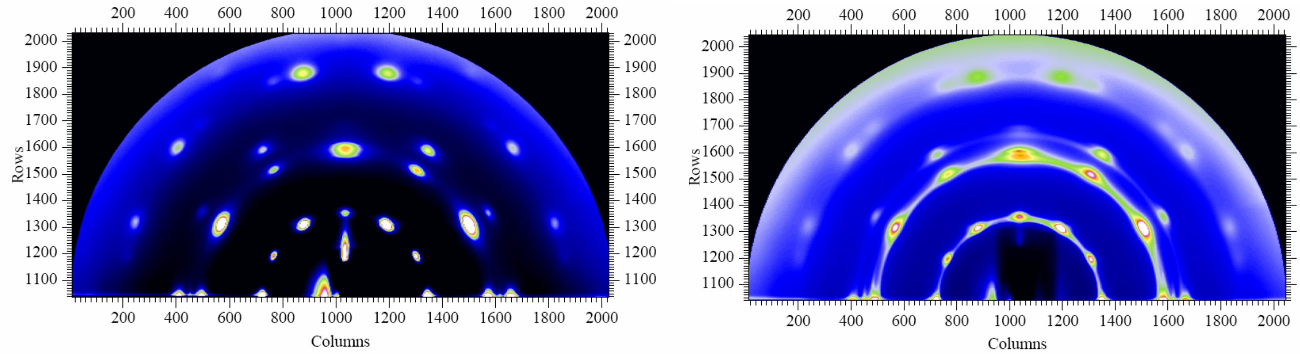

**Fig. 3:** Raw GIXD patterns of aligned PF2/6 spun onto rubbed PI along the ((*ab*0) plane). On the left pure PF2/6 and on the right Zn doped PF2/6. The hexagonal order is clearly observed over several orders for both samples but there is an increase in disorder on addition of the Zn dopant.

[1] M. Knaapila, R. Stepanyan, B. P. Lyons, M. Torkkeli, T.P.A. Hase, R. Serimaa, R. Güntner, O. H. Seeck, U. Scherf, and A.P. Monkman, *The influence of the molecular weight on the thermotropic alignment and self-organized structure formation of branched side chain hairy-rod polyfluorene in thin films*, 2005, Macromolecules, in press.
[2] M. Knaapila, B. P. Lyons, T. P. A. Hase, C. Pearson, M. C. Petty, L. Bouchenoire, P. Thompson, R. Serimaa, M. Torkkeli, A. P. Monkman, *The influence of the molecular weight on the surface morphology of branched side chain polyfluorene,* 2005, Adv. Funct. Mater. Submitted