



	<b>Experiment title:</b> "Supramolecular organization in oligo- and polythiophene thin films for the development of organic thin film transistors (OTFT)"	<b>Experiment number:</b> Sc-852
<b>Beamline:</b> BM01	<b>Date of experiment:</b> from: 28/01/02 to: 1/02/02	<b>Date of report:</b> 28/02/03
<b>Shifts: 9</b>	<b>Local contact(s):</b> Silvia Capelli	<i>Received at ESRF:</i>
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## Report:

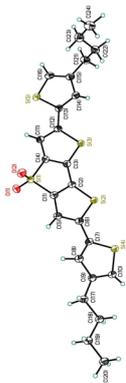
### Introduction

The use of new polymeric materials in the development of Organic Thin Film Transistors (OTFT) aims at devices of wide surface area and high flexibility to be produced at lower costs than those based on inorganic semiconductors. The key parameter to improve the performance of OTFT devices is the carrier mobility in the material to be used as active layer. This property is characteristic of the material itself but also depends on features of the molecular packing, especially for thin films. Amorphous systems show a much lower carrier mobility than ordered films of the same molecules. In macroscopically oriented samples the carrier mobility can become anisotropic.

The aim of our experiment was the study of the structural organization of thin films as compared to bulk of the following two class of systems:

1. Quater-, sexithiophenes and other oligomeric systems carrying various alkyl and alkoxy substituents, grown by Organic Molecular Beam Deposition (OMBD) on silicon and graphite.
2. Thin films obtained by spin coating, casting and ink jet printing techniques, of new poly(alkoxy)- and poly(alkyl)thiophenes with regioregular substitution patterns. Recording of high quality data for the investigation of the crystal structures of the same systems in bulk or as powders.

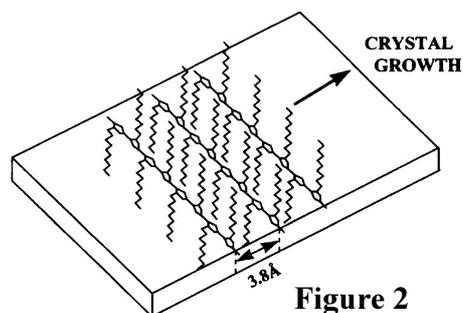
The beamtime allocated on station A of BM1, allowed operation only in transmission mode therefore Part 1. of the the study, which required grazing angle incidence geometry, was not carried out. However 4 hours of beamtime was devoted to the single crystal study of the oxidised alkylated dithienothiophene system P3BDTT (bis(3-butyl-2-thienyl)-dithieno[3,2-b:2',3'-d]thiophene-4,4-dioxide). This molecule is a precursor of the oligomeric thiophenes grown by OMBD and consequently it is a good model systems for studying the interactions of the sidechains in the solid state. The molecular structure of P3BDTT is shown in Figure 1. Note that the two sidechains display different conformations: furthermore in the packing, as in some other  $\alpha$ ,  $\omega$ -alkylsubstitued systems, substantial sidechain interdigitation and tight stacking of the conjugated system is apparent.



**Figure 1**

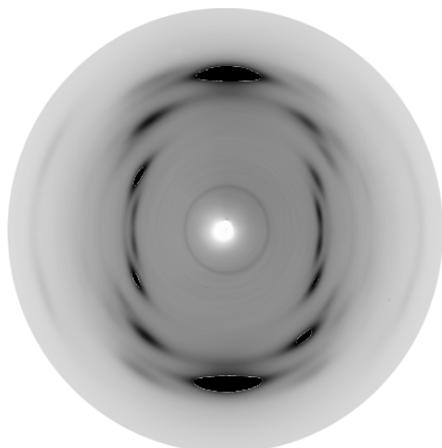
by spin coating we were unable to get results due to excessive background noise. This limited our investigation to solution cast films and bulk samples. The main systems investigated are shown in Scheme 1.

In the case of P3HT and P3HT3 examination of the diffraction data indicates significant preferred orientation consistent with already reported data for P3HT and other polyalkylthiophenes with respect to other substrates. The usual form I crystal modification is obtained and the chains are oriented with respect to the substrate edge on with the



**Figure 2**

of the film. The above results are consistent with literature data of various polyalkylthiophenes and appear to suggest that these orientation effect hardly depend upon specific interactions with the substrate.

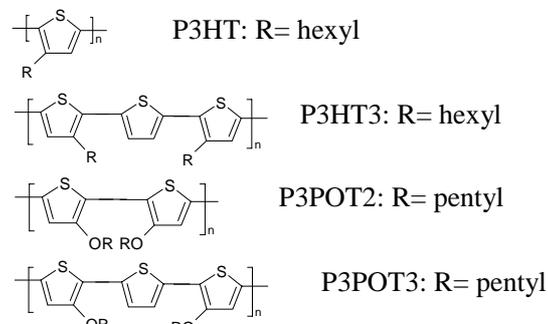


**Figure 4**

P3OPT3 the sharpest in the diffraction pattern. These observations may well relate to the strong propensity to planar conformations of polyalkoxythiophenes and to their low solubility.

For the second part of the project scattering from the air represented a substantial limitation. Significant time was spent attempting to minimize it. We were able to reduce it by a factor of ten, bringing the beamstop close to the sample, albeit at the expense of some information at lower angle. With the setup used we were able to get significant signal for polyalkyl- and polyalkoxythiophene (PAT) film thickness down to about 1 μm deposited by solution casting on 6 μm thick polyethyleneterphalate (PET).

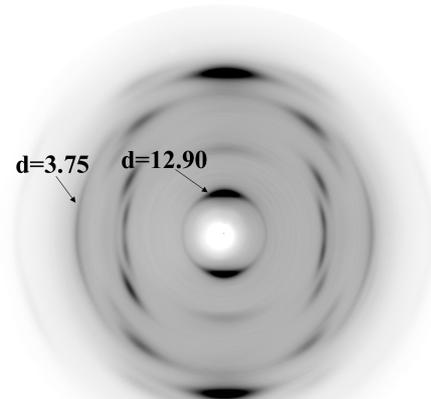
PET was chosen as substrate because it represents one of the possible substrates for “all polymer” OTFT’s. For thinner PAT films, like those prepared



**Scheme 1**

16.5 Å *a*-axis perpendicular to the substrate. A similar orientation of

the lamellar axis is apparent the diffraction patterns of P3HT3 (Figure 3) as the 12.9 Å reflection and its second and third order are clearly orthogonal to the film surface, while the 3.75 Å stacking reflection shows preferential orientation roughly in the plane



**Figure 3**

No preferred orientation effects on PET are on the other hand apparent for both P3POT2 and P3OPT3, the two alkoxy derivatives investigated. P3OPT2 shows (Figure 4) an isotropic orientation of the 12.0 Å lamellar reflection. Similar observation apply to the only strong and sharp reflection of P3OPT3 observed at 3.75 Å. This different behaviour may depends on the morphology of PAT crystals. This interpretation could be corroborated by SAXS investigations. Preliminary experiments in our laboratory yield up to the present moment results that are unclear, probably due to the limited intensity available.

The diffraction data collected for the three new systems in Scheme 1 are being presently analysed in order to determine lattice constants and a plausible packing. At present it is possible to note that at variance with polyalkylthiophenes, alkoxy derivatives show relatively weaker lamellar reflections whereas the interchain stacking reflection at 3.75 Å, is for