



ESRF

Experiment title:

Thermochromic Transition in Thin
Layers of the Conducting Polymers
Poly(alkyl)thiophenes

Experiment

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Report:

Poly(alkyl)thiophenes are examples of coloured organic materials that owe their semiconductive (and optical) properties to the fact that they have alternating single and double bonds along the chain ('conjugated' polymers, or 'conducting polymers' when doped). Optical absorption spectra obtained on *thin, spin-cast layers* on glass substrates, show a band gap at about 2.0 eV, giving the materials their red colour. This gap increases as temperature is raised to more than 130°C, leading to a corresponding change of colour to yellow ('thermochromism').

Diffraction studies on *bulk* materials show that they are partially crystalline at ambient temperatures, and that the crystal peaks disappear at temperatures where the colour changes take place, indicating a 'melting' transition. Preliminary studies using synchrotron X-rays at grazing incidence [1] showed that poly(hexyl)thiophene (PHT) and poly(octyl)thiophene (POT) are partially crystalline also as thin submicron spin-cast layers, and the *absence* of reflection of the type *010* was tentatively interpreted as a possible indication of a strong orientation effect by the substrate. *This point, as well as the temperature behaviour was the subject of the present investigation using BL D5.*

As it turned out BL D5, equipped with the sagittally focussing monochromator, is marginally just of sufficient intensity for this kind of experiments, when the polymer layers are not *too* thin. A vertical beam height of 0.2 mm and an angle of vertical incidence of 0.2° were used. **D5** is equipped with a scintillation detector with slit collimation, able to be scanned only in the horizontal plane. An option to scan vertically ought to be made available.

Two samples of POT different thicknesses were studied (estimated thickness ratio *Of five*). These scans revealed that for the *thick* sample, both *h00* (100, 200 and 300) and *010* were observed, whereas for a *thin* sample the *010* was not seen, confirming the preliminary results [1]. Diffuse scattering is also seen. See Fig. 1.

For a convincing proof of **preferred orientation**, however, also detection in the *vertical* direction is needed. We were lucky to be able to apply a ("D-camera, kindly made available at the Detector Group, and is shown in Fig.2 this provided the ultimate evidence: Whereas for the thick layer

sample the 100 - reflection is distributed evenly in all directions, the thin layer is not only of a preferred orientation; its a -axis is confined to the substrate surface to within $1 - 2^\circ$! (The direct beam hits at the lower left corner of Fig. 2).

The much weaker 010 -relection was not discernable from the CCD-camera exposure. But the fact it was absent in the (horizontal) scintillation detector scan tells us that for thin layers the polymer strands *are oriented with both their main chain (c - axis) and their octyl side chains (a -axis) flat on the substrate surface.* This finding is of great importance to understand the optical properties of deposited thin layers of polythiophenes. it remains to investigate the role of various substrate materials, for instance single crystal surfaces.

This strong orientational effect by the substrate of the poly(octylthiophene) sample could be confronted with an opposite effect found for **poly(dioctyl-bithiophene) (PDOT)**. Whereas the former has its octyl side chains attached to the main chain in essentially the same manner- along the polymer, the latter has an alternating attachment on the right or the left corner of the thiophene monomers ('head-to-head' versus 'head-to-tail' and tail-to-head' configurations). Unlike **POT**, **PDOT** is yellow at all temperatures, and shows no thermochromic 'behaviour'[2]. The diffraction pattern that was observed from the thin layer of PDOT₂ show-ed the presence of both 100 and 010 --reflections.

Temperature studies were performed on the two types of POT deposits. The glass slides were placed horizontally on top of a 25 watt heat plate, and the temperature was measured in a slit cut into the edge of the slides. Care had to be exerted against radiation damages when the temperature was raised. The behaviour of both films were grossly the same as that of bulk POT : the crystallinity disappeared at about 130°C , which coincides with the temperature of the colour change. For the thin layer sample the 010 - region was monitored both during heating and cooling. No indication was found that the substrate anchoring was affected during heating, before the 'melting' takes place. On the other hand the preferred orientation is not reestablished upon retooling, as clearly seen by the presence of the 010 - reflection after a heating cycle to above 130°C . This finding indicates strongly that the orientational effect is not of a thermodynamic, but rather of a kinematic origin, probably being related to the rapidity of the removal of the solvent during the spin casting process. This conclusion corroborates well with the finding that the thin layers are affected by the substrate, but the thick ones not.

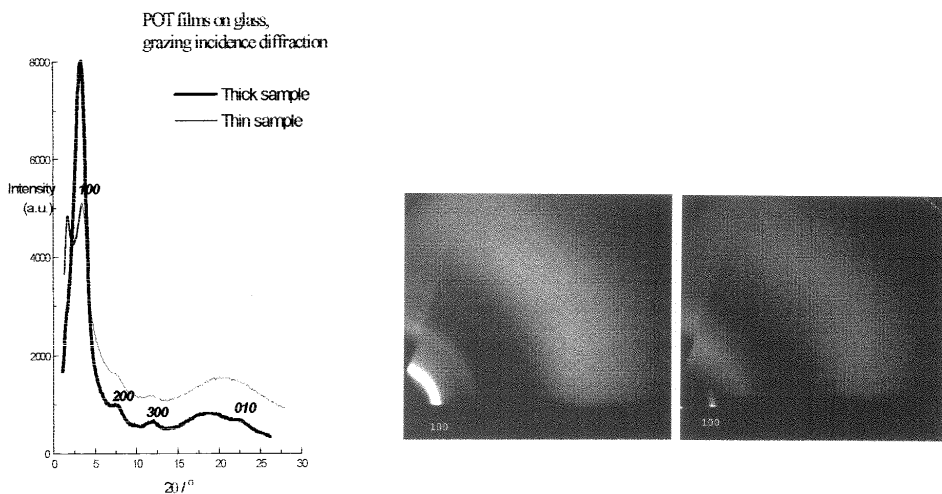


Fig. 1. Diffraction of POT films on glass Fig.2. CCD-patterns. Left:Thick film.Right:Thin film.

[1] H.J.Fell, E.J. Samuelsen, J.Als-Nielsen, G. Gräbel and J.Mårdalen *Solid State Commun.* **94** 843-6 (1995)
 [2] H.J.Fell, E.J.Samuelsen, J.Mårdalen, E.Bakken and P.H.J. Carlsen *Synth. Metals* **69** 301-2 (1995)