



	Experiment title: <i>In situ</i> doping of conducting polymers	Experiment number: SI - 393
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Report: «*Conjugated polymers*» are organic semiconductors, whose conductive and spectroscopic properties are modified upon *doping*. This makes the materials challenging subjects for scientific studies, and opens for many fields of applications, among them the use as LED. The doping can be performed chemically or electrochemically.

In-situ doping/dedoping

Poly(ethylenedioxy-thiophene) (PEDOT) is particularly interesting because of its very high stability. Its band gap is 1.5 eV in the undoped state, giving it a bluish colour, but it turns essentially colourless upon doping. Structural studies of the doped material were recently performed both on bulk samples and on thin, deposited layers by means of grazing incidence X-ray diffraction with synchrotron radiation.

In the present project in-situ electrochemical doping/dedoping studies were attempted in combination with diffraction.

Two PEDOT films of thickness 200 nm on a glass substrate were separated by a 1 mm opening. In *a first attempt* a solid state polymer electrolyte covered the gap, and voltages of 1-2 V were applied between the two parts. A colour change was observed upon reversing the voltage, and attempts were made to monitor the changes by diffraction very close to the electrolyte edges. However these attempts were not successful.

In *a second attempt* water was used as an electrolyte. Also this time a colour change was observed upon switching. After each switch the water was removed and the sample allowed to dry under a weak nitrogen flow (introduced in order to prevent oxygen to react with the undoped PEDOT). In this case clear diffraction effects could be detected between the doped (colourless) and the dedoped (blue) sides of the PEDOT film. In Fig. 1. We show the intensity level observed at a scattering angle of 4.7 degrees (with wavelength 1.218 angström) as the sample is scanned sidewise in the beam. An intensity jump is seen as the gap region is passed, and, furthermore, the effect is reversed when the voltage is reversed.

However, the diffraction pattern is not altered in any essential way by the doping/dedoping process, only the intensity level as well as the peak widths are considerably changed. This finding lead us to the conclusion that by the doping/dedoping process using water as the electrolyte the *range of the (para-)crystalline regions*

is lowered upon dedoping from about 4.2 nm (doped) to about 3.7 nm (dedoped state). Since otherwise no pronounced structural changes are seen, it must be concluded that the electronic transitions associated with the colour changes can take place without a gross rearrangement of the polymer and dopant molecular structures.

Preferred orientation of various conjugated polymers

Although the work with the in-situ doping/dedoping required quite much time for trying-and-error, the allotted beamtime allowed also a few auxiliary surface diffraction problems to be elucidated in the realm of preferred orientation:

Poly(octyl-thiophene) (POT) solution cast from various solvents: Solutioncasting always gave rise to a strongly preferential orientation with the polymer main chains parallel to and side chains normal to the glass substrate.

Stereoregular poly(hexyl-thiophene) (PHT): Spincast stereoregular PHT exhibited a mixed preferred orientation, always with main chains parallel with the substrate, but with side-chains both parallel and perpendicular to the substrate. Solutioncast PHT behaves like solutioncast POT.

Poly(dioctyl-bithiophene) (PDOT₂), a stereoregular variety of POT: The material did not show appreciable preferred orientation in its spincast form, in good agreement with its assumed twisted chain structure.

Structure, and effects of treatment

Polypyridine (PPyr) is a new conjugated polymer, recently synthesised at the University of Durham. A 100 nm layer on glass was found to exhibit very anisotropic diffraction that could be indexed, and a structural model could be proposed. The structure is monoclinic, with the polymer chains parallel to, and the molecular plane essentially normal to the substrate. Reflectivity studies were performed to determine the actual layer thickness.

The polymer **poly(phenylene-vinylene)** substituted with methoxy-(ethyl-hexyl-oxy) (MEHPPV) and doped with fullerene (C₆₀): The studies revealed that heat treatment of the material has an appreciable effect on the location and sharpness of the diffraction patterns.

Poly(dioctyl-phenyl-thiophene (PDOPT) also showed a pronounced anisotropy, a fact which has been of considerable importance for the modelling of its crystalline structure. The studies also aimed at looking for eventual storage-dependent ordering of the material. Indeed the ordering was observed to develop considerably from freshly made to nine hours later.

