ESRF	**Experiment title:** *Vapour induced Poly(p-phenylene oxide) crystallization in selective photonic crystals sensors.*	**Experiment number**: MA-3272
Beamline: BM26B	**Date of experiment**: from:12/11/2016 to: 14/11/2016	**Date of report**: 16/01/2017
Shifts: 6	**Local contact(s)**: Daniel Hermida-Merino	*Received at ESRF:*

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Report:

In this experiments we probed the crystallization of thin multilayer polymer films upon exposition ot solvent vapors. The aim is to correlate the crystallization behavior of the poly(phenyleneoxide) to the UV-VIS spectroscopic variation in the peak of reflectivity during the absorption of air pollutants. The experimetns were carried out by means of a custom made cell, whose design is reported in Figure 1. he apparatus consists in a small cylindrical sample cell where the polymer film supported on a mica sheet is inserted. two sides of the cell have observation windows made of mica to allow X-ray transmission and collection of WAXD pattern. At a right angle, the other two sides of the cell have an inlet and outlet for optical fibers, connected to the spectrometer to acquire absorption spectra. At the bottom of the box, a small well for liquid is found (approximate volume 3-4 ml). This well communicates with a glass solvent reservoir (volume approx. 5 ml) trough a teflon piep. Finally, the solvent reservoir is separated by an electrically driven valve from a second reservoir which contains air with a slight overpressure (i.e. 5 mbar).

The custom-made cell has been tested in real operation condition during the beamtime, and proved to be efficeint and successful.

Some preliminary tests were made on PPO/CA multilayers (see proposal), however the small thickness limited our sensitivity. Therefore, we moved to bulk-like films of the sole PPO polymer, with thickness of approximately 70 microns. The PPO films were exposed to toluene vapors with different partial pressure (obtained by using a mixture of tolune/oleic acid in different ratios) and WAXd patterns collected in time during the exposure. An example of time evolution of the WAXD patterns is provided in Figure 2.

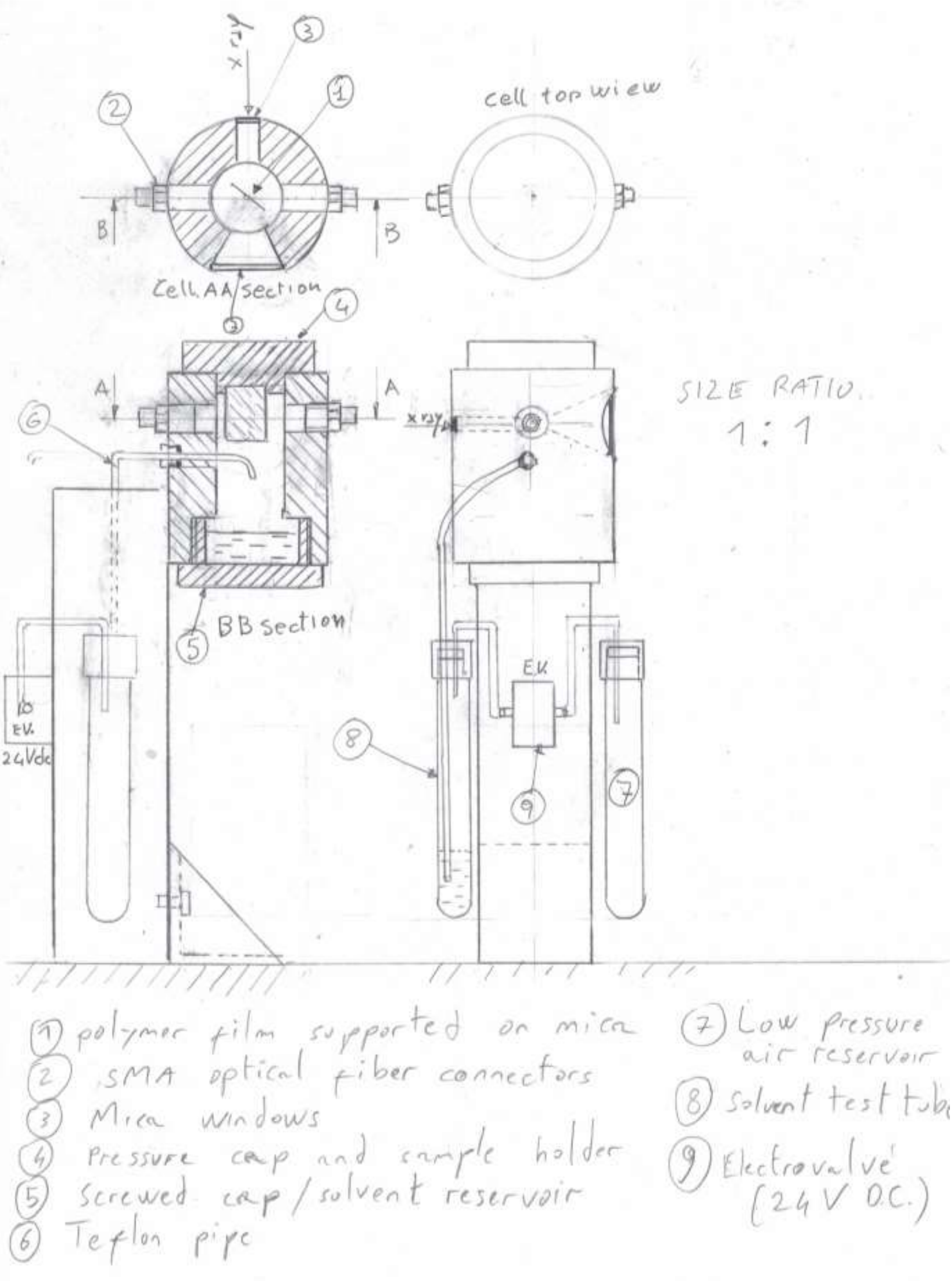

Figure 1: Scheme of the sample cell, which allows simultanenous WAXD and UV-VIS measurement during exposure to solvent vapors.

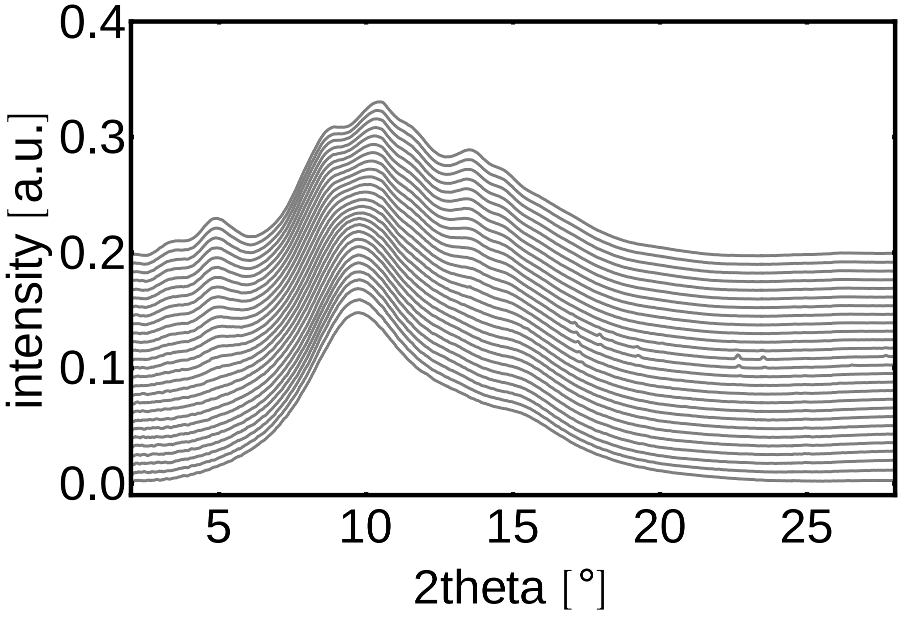

Figure 2: Time evolution of PPO WAXD pattern during exposure to toluene vapors.

In figure 2, the time increases form the bottom to the top curve. PPO is initially in the amorphous state, and a small raise of small diffraction peaks with time can be observed, together with a menaingful shift of the amorphous halo towards larger diffraction angles.

The data of Figure 2 are analyzed to derive a value of crystallinity index and of position of the maximum of the amorphous scattering. These two values are reported as a function of exposure time in Figure 3.

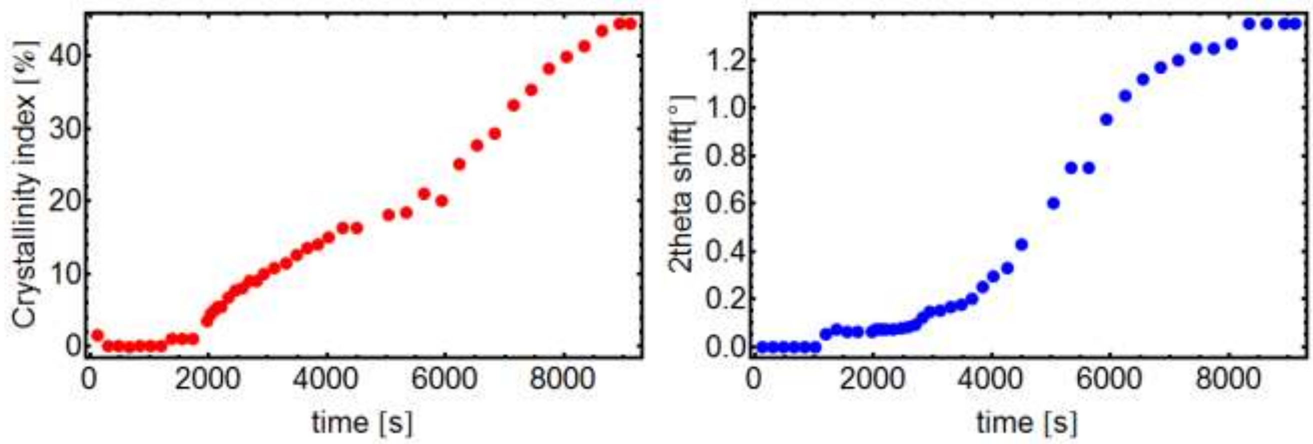

Figure 2: Time evolution of PPO crystallinity index and shift in the 2theta value of amorphous peak during exposure to toluene vapors.

It can be seen that the kinetics of solvent-induced crystallization can be efficiently captured. The trend in crystallinity can be analyzed to reveal a role of diffusion of the guest molecule. Intriguingly, it seems that the amorphous phase gets a more dense packing with the formation of PPO-toluene co-crystal.

Further analysis of data obtained with different concentration of toluene are in progress. The obtained set of data will be helpful for planning future experiemtns with GIWAXD setup, aimed at measuring the multilayer films relevant for sensing applications.