



	Experiment title: Investigation of morphology and kinetics of crystallization under 2D confinement in nanostructured homopolymer thin films.	Experiment number: SC- 2378
Beamline: ID01	Date of experiment: from: 23/07/2008 to: 27/07/2008	Date of report: 26/06/2009
Shifts: 12	Local contact(s): Oier Bikondoa	<i>Received at ESRF:</i>

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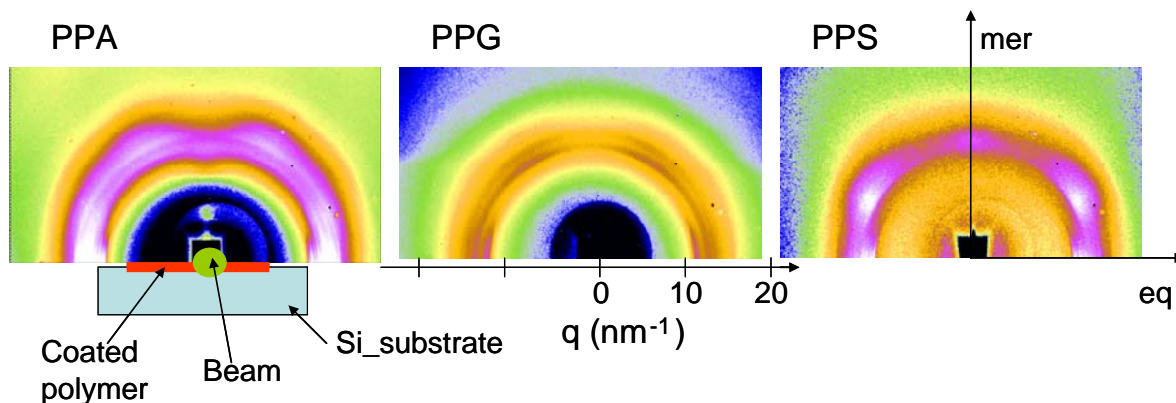
Report:

Note: Unfortunately, our scheduled experiments at ID01 were only partially performed (50%) because of problems with the electronics for the front end which could not be solved during the weekend. Consequently, the spin-coated samples from aromatic polyesters were not investigated as well as experiments planed in situ, at high temperature, using the furnace set-up were not performed.

In the frame of our interest for polymer thin films [1] we have prepared by means of spin coating new samples concerning to a series of aliphatic polyesters: $\left[\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_Y-\text{CO} \right]_n$ made of propanediol and a di-acid unit of different length where $Y = 2, 3, \text{ and } 4$. Then, for simplicity these polyesters (3, Y) can be referred to as PPS, PPG, and PPA, respectively where PP denotes “poly-propylen” and S is for *succinate*, G for *glutarate*, and A for *adipate* taking into account the common name given to these aliphatic di-acids. Polymer-Chloroform (Cl_3CH) solution (40gL^{-1} or 200 mg / 5 mL) was used as mother solution for preparing others more dilute in order to cover a large range of polymer coating thicknesses (400 down to 10 nm) on the Si-substrates [1].

We are reporting here now our GIWAXS experiments carried out last summer at the ID01 beamline of the ESRF. A beam energy of 10 keV ($\lambda = 0.124$ nm) and a Princeton CCD detector (1339 x 1299 pixels) were used. Sample plane is conveniently aligned horizontally and placed at the proper height to cut half of the intensity of the direct beam. Then, the sample is slightly rotated around its axis perpendicular to the beam direction in order to define the desired grazing incidence angle, α_i . GIWAXS patterns from all samples comprising a Si substrate were recorded, in air, at different α_i values: $0.36^\circ, 0.31^\circ, 0.26^\circ, 0.21^\circ, 0.16^\circ, 0.12^\circ, 0.09^\circ, 0.06^\circ$. Detector plane is maintained tilted of 15° from vertical position and located about 67 mm out of the sample center. Calibration was done by using a standard of Alumine, Al_2O_3 and also checked by using a sample of Lupolen. GIWAXS images were properly corrected at ID01 [2] and given to us for further analysis.

Fig. 1 shows a representative GIWAXS pattern for the thickest sample of each of the three polyesters (3, Y) investigated. They correspond to a selected area of the image which is the difference between the images from the sample and the Si-substrate both two recorded under the same α_i value. A correction factor for the different intensity observed, at the meridian and close to the beam stop, was also applied. These patterns clearly indicate the crystalline nature of coating polymers and some chain orientation. Similar patterns were observed for all the different α_i used. Coatings of the next lower thickness (≈ 200 nm) also gave GIWAXS patterns essentially similar to those of Fig. 1. Nevertheless, thinner samples did not exhibit any signal of crystallinity. This could be related to the observed dewetting by AFM for thinner coated samples or to the critical thickness itself which prevents the crystallization of droplets [3].



The azimuth integration of these patterns revealed a multiplicity of peaks and spreading in q range what makes difficult their comparison with those peaks of X-ray diffractograms from bulk polymers. In addition, the present lack of crystallographic data for these three polyesters renders difficult to determine the chain orientation in these polymer coatings. Therefore, an effort has been devoted along this year to determine the crystal chain packing after preparing partially oriented samples of these polymers. Now we can anticipate that polymer chains lie parallel to the substrate.

References.

- [1] D.R. Rueda, A. Nogales, et al., *Langmuir* 23, 12677 (2007)
- [2] V. Urban, P. Panine, C. Ponchut, P. Boesecke, T. Narayan, *J. Appl. Cryst.* 36, 809 (2003)
- [3] Y. Ma, W. Hu and G. Reiter, *Macromolecules* 39, 5159 (2006).