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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Analysis in situ of Laser Induced Periodic Surface Structures (LIPSS) Formation on Spin-coated Polymer Films	**Experiment number**: **SC-3748**
Beamline:	**Date of experiment**: from: 21 nov 2013 to: 25 nov 2013	**Date of report**: 21/02/2014
Shifts:	**Local contact(s)**: Giuseppe Portale (email: portale@esrf.fr)	*Received at ESRF:*

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Report:

Report Summary:
The aim of the project was the “in situ” monitoring of Laser Induced Periodic Surface Structures (LIPSS) formation by means of Grazing Incidence Small Angle X-ray Scattering (GISAXS) on spin-coated films of a selection of model polymers.

Scientific background:
The controlled structuring of polymer surfaces at length scales ranging from micrometers to nanometers has appeared as a promising approach to create functional substrates or to mimic some interesting properties present in natural surfaces. Different processes are currently being investigated in order to produce superficial nanostructures on polymers, most of them based on lithographic techniques. Alternative non-lithographic procedures are also attracting a lot of interest aiming to avoid the necessity of demanding experimental conditions like clean rooms, high vacuum or complex mask fabrication. Laser induced patterning of polymer surfaces is a versatile strategy in order to obtain gratings structures in functional polymer materials. Irradiation of solid surfaces by intense laser pulses may induce the appearance of Laser Induced Periodic Surface Structures (LIPSS) with periodicities closely related to the laser wavelength [1]. To assess order in LIPSS on thin polymer films we have proposed the use of GISAXS that in combination with real space monitoring by atomic force microscopy, provides a novel assessment method of the structures[1,2]. However, no “in-situ” technique was implemented so far to monitor LIPSS formation, despite the fact that the assessment of the evolution of the structures as laser irradiation progresses will be crucial to understand the mechanisms involved.

Experimental:
We carried out X-ray scattering experiments on polymer thin films in grazing incidence geometry in the beamline BM26B at ESRF. For GISAXS experiments, incidence angles 0.2°<α_i<0.4° were chosen depending on the nature of the formed nanostructure. Polymer samples were irradiated “in situ” at normal

incidence with the 4th harmonic of a Nd:YAG laser at a wavelength of 266 nm employing different fluences (F = 4-15 mJ/cm^2). In every experiment pulses of 8 ns were sent to the sample at a selected repetion rate ranging from 1 to 10 Hz. The laser beam was directed with the necessary optical elements towards the sample surface with a polarization direction parallel to that of the incident X-ray beam. Simultaneously GISAXS detection was accomplished using an X-ray wavelength λ= 0.124 nm (10 KeV), with a beam size (HxV) of 5x1 mm^2. Scattered intensity was recorded by a PILATUS detector of 981x1043 pixels with a resolution of 172.0 µm per pixel, and a sample-to-detector distance of 3.948 m. Acquisition times were optimized in order to get maximum number of counts avoiding saturation of the detector. In the present case, typical acquisition times of 5 to 30 s were used. A scheme of the experimental set-up is shown in Fig.1a.

Results and Discussion:

Several model polymers were investigated including: poly(ethylene terephthalate) (PET), poly(tri-methylene terephthalate) (PTT), and poly(bisphenol A carbonate) (PBAC). Samples were prepared as thin films of ≈ 150 nm thick by spin-coating on silicon wafer sustrates (Fig.1b).

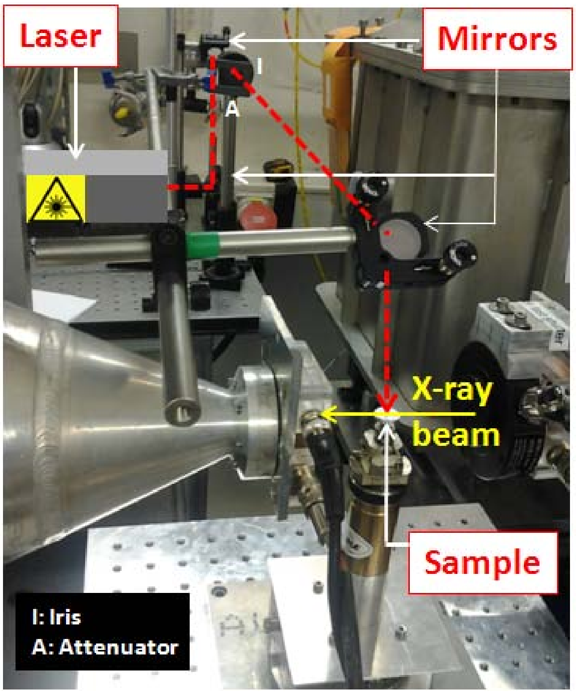

Fig. 1a. Scheme of the experimental set-up. The laser beam is directed to impinge on the sample perpendicularly by means of three mirrors. An attenuator (A) is inserted in the optical path in other to control the laser power on the sample. The laser beam size is controlled by an iris (I).

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Fig.1b. Detail of the sample and sample holder.

For every experiment GISAXS patterns were collected as a function of the number of pulses. As an example Fig.2 shows a typical series of GISAXS patterns taken during “in situ” laser irradiation of a PTT sample with a fluence of 7 mJ/cm^2. The GISAXS pattern of a grating formed by LIPPS is characterized by the appearance of elongated vertical rods along the q_y axis which are also consecutive orders of a first one whose spacing is the reciprocal value of the grating pitch [1,2]. LIPSS formation starts after irradiation with some tens of pulses using a repetition rate of 10 Hz. In Fig.2 one sees that for 90 pulses the presence of LIPSS is already evidenced. This result implies that only few seconds are needed in order to generate the structures. Optimal LIPSS are obtained for around 600 pulses, i.e. after 60 seconds. Results for all the investigated polymers are being analyzed in order to gain knowledge about the formation mechanisms. Preliminary analyses indicate that “in situ” studies by means of GISAXS can be useful in order to understand the kinetics of LIPSS formation. Fig. 3 shows the evolution with the number of pulses of the intensity of the first correlation maximum, appearing at the lowest q_y value, for experiments performed at different repetition rates. It is clear that the irradiation repetition rates plays an important role on LIPSS development. The experiment was successful using the under development GISAXS at DUBBLE. These results are promising for the use of DUBBLE for high quality and competitive GISAXS. t is worth emphasizing that results shown on Fig.3 would have taken a probably unaffordable amount of time if performed “ex situ”.

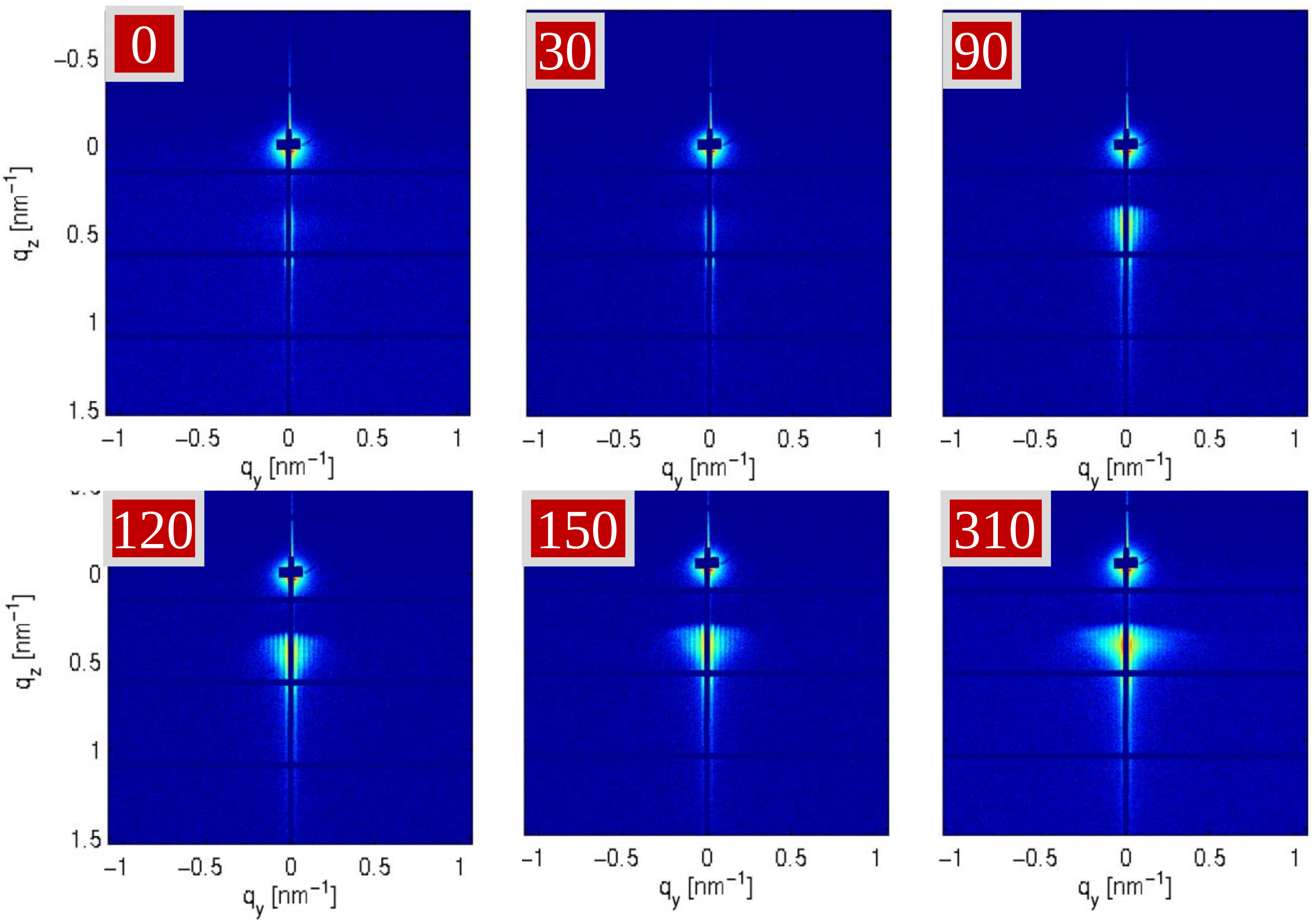

Fig. 2. GISAXS patterns collected as a function of the number of pulses at 10 Hz (labeled on the upper left corner) during "in situ" laser irradiation of poly(trimethylene terephthalate) (PTT) at a fluence of 7 mJ/cm^2.

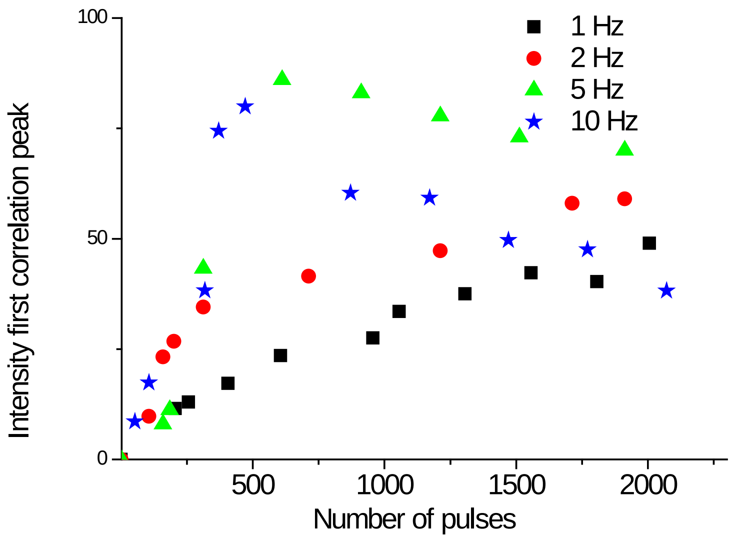

Fig. 3. Evolution with the number of pulses of the intensity of the first correlation maximum, appearing at the lowest q_y value, for experiments performed at different repetition rates on a PTT sample irradiated with 7 mJ/cm^2.

[1] E. Rebollar, S. Pérez, J.J. Hérnandez, I. Martín-Fabiani, D.R. Rueda, T.A. Ezquerra, M. Castillejo, Assessment and Formation Mechanism of Laser Induced Periodic Surface Structures on Polymer Spin-coated Films in Real and Reciprocal Space, Langmuir 27, 5596, 2011.

[2] I. Martín-Fabiani, E. Rebollar, S. Pérez, D.R. Rueda, M.C. García-Gutiérrez, A. Szymczyk,Z. Roslaniec, M. Castillejo, T.A. Ezquerra. Laser Induced Periodic Surface Structures Nanofabricated on Poly(trimethylene terephthalate) Spin-coated Films, Langmuir 28(20), 7938 (2012). 26.