	Experiment title: Anomalous X-Ray Reflectivity and GIXD Studies of Metal Cation – Polyconjugated Langmuir Film Interactions at the Gas-Liquid Interface	Experiment number: SI-1085
Beamline: ID-10B	**Date of experiment**: From: 29/11/2004 to: 06/12/2004	**Date of report**: 30/08/2005 ***Received at ESRF:***
Shifts: 18	**Local contact(s):** Dr. Oleg Konovalov	

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Our previous GIXD studies on polydiacetylene (PDA) Langmuir films (LF) were focused on (a) Study of the molecular structure of the two phases of PDA LF, the meta-stable blue phase and the red phase, and the monitoring of the radiation induced phase transition between them. (b) Study of the mutual structural relationship between the PDA LF templates and metal-sulfide nanocrystals that were deposited onto them by reacting divalent metal cations in the subphase with hydrogen sulfide gas. The main objective of the current experiment was to investigate the role of the metal cations in the PDA LF / Pb^{2+} system using anomalous x-ray scattering. For this purpose, the anomalous dispersion factors f' and f" were experimentally determined using x-ray fluorescence as shown in *Fig. 1*. Subsequently, PDA LF were exposed to controlled amounts of Pb^{2+} ions and studied *in-situ* using three different energies 12keV, 13keV and 13.035keV (below, slightly below and directly at the absorption edge of lead ions, see *Fig. 1*). Two types of experiment were carried out: (i.) PCDA ($CH_3(CH_2)_{11}C \equiv C - C \equiv C(CH_2)_8COOH$) molecules were compressed directly on a subphase containing Pb^{2+} ions. (ii.) Pb^{2+} ions were introduced to the subphase under PDA LF that was initially polymerized on a pure water subphase. For the first type of experiments our in-house studies showed that the Pb^{2+} ions inhibited polymerization of the films. The second type of experiments represents an important system in which doping PDA by metal ions can potentially increase conductivity of the LF by many orders of magnitude. This route

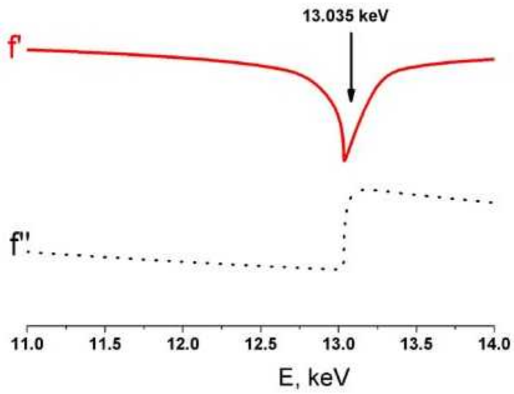

Figure 1: Anomalous dispersion factors, f' and f", of lead.

is an important intermediate stage in the deposition of metal sulfide (MS) nanocrystals on PDA templates (where M is determined by the type of metal ions introduced into the subphase), obtained by exposure to H_2S gas.

X-ray specular reflectivity (XR) results:

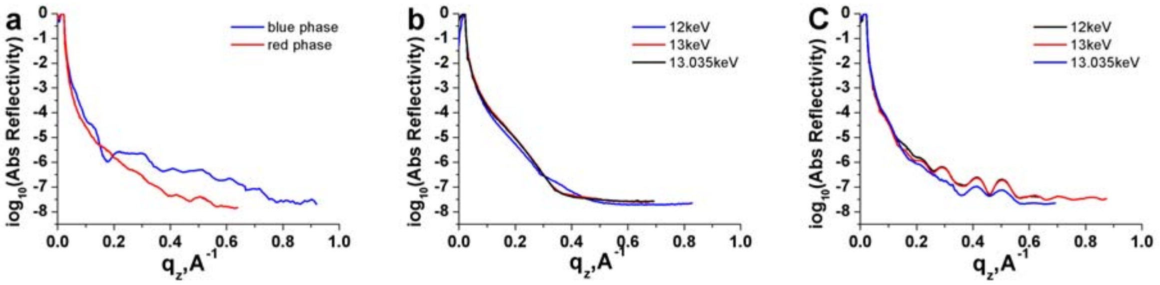

Figure 2: Specular Reflectivity of **a)** Blue and Red phases of PDA LF, **b)** PCDA molecules compressed on 2mM $PbCl_2$ solution (type i) **c)** Red PDA LF produced on pure water subphase that was exchanged to a 2mM $PbCl_2$ solution (type ii).

Figure 2a shows the difference between the blue and the red phases of PDA LF produced on water surface. All the peaks obtained from the blue phase correspond to the same distance of ~60.2Å that is consistent with the height of a trilayer of PDA in which the aliphatic chains are tilted by ~35° in average. The red phase film thickness was found to be 74.53Å, in good agreement with a nearly vertical PDA trilayer (Note that the length of the fully extended PCDA molecule is ~25Å). Both results are in excellent agreement with our previous GIXD results that were recently published in *ESRF Highlights 2004*. It is also observed that, as expected, red phase PDA LF are rougher and more disordered compared to the blue films. *Figure 2b* shows that in *"type i"* experiments the layer obtained is not structured in the vertical direction, in agreement with our in-house studies. In this type of experiment no anomalous effect was found. In *Fig. 2c* a clear anomalous scattering effect is presented. The scans obtained below, and far below, the absorption edge (12 and 13keV) of Pb show a similar behavior; while the scan obtained right at the absorption edge (13.035keV) shows a similar reflectivity profile as the previous scans, but with significantly lower intensity due to enhanced absorption of x-ray photons (f’’) and probably due to a decrease in f’ at the resonance frequency.

Grazing incidence x-ray diffraction (GIXD) results:

GIXD measurements were carried out on the same samples as described above using XR. The scans, taken with three different energies (12, 13 and 13.035keV), are presented in *Fig. 3*. Generally, the effect of introduction of controlled amounts of Pb^{2+} ions to the subphase solution *after polymerization* resulted in a prominent, yet diffuse reflection located right above the PDA

2D characteristic peaks. It corresponds to a structure with interplanar distance centered circa 3.173Å that is tilted at roughly 45º. The enhanced intensity of Bragg Rods from the PDA characteristic peaks hints on a possible structural relationship existing between the lead cations and the carboxylic headgroups in the LF.

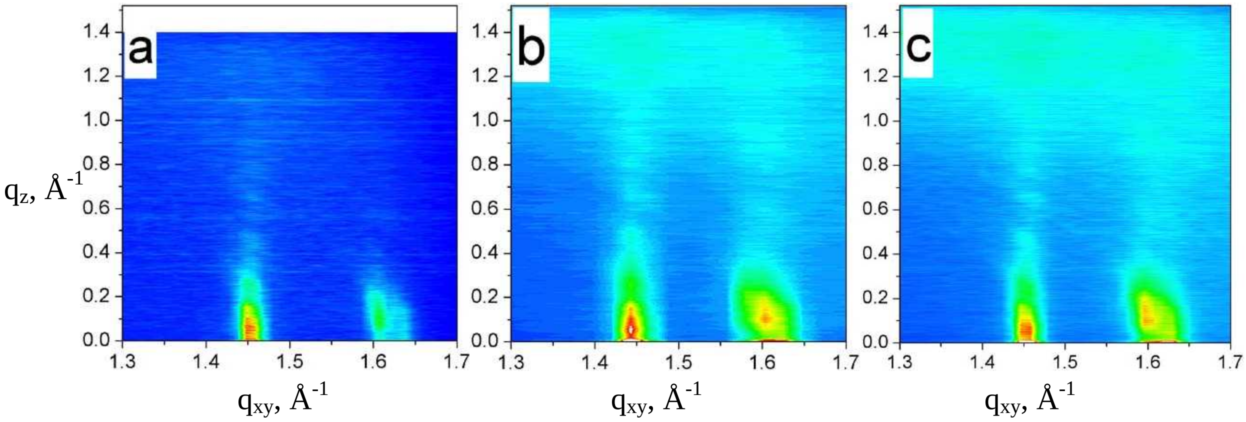

Figure 3: GIXD reciprocal space maps of red phase PDA LF produced on pure water and subsequent exchange to 2mM $PbCl_2$ solution (experiment type ii) for beam energy of **(a)** 12keV, **(b)** 13keV and **(c)** 13.035keV. The q_{xy} position of the two bottom peaks in all three scans confirmed the presence of red phase PDA, as determined in our previous work (see *ESRF Highlights 2004*).

Moreover, the intensity of this reflection increases with Pb^{2+} concentration in the subphase. *Figure 4* shows integrated GIXD spectra on the same PDA layer that was compressed and polymerized on a pure water subphase, which was then exchanged to 2mM (solid line) and 12mM (dashed line) of lead cations (experiment type ii). While the shape and the intensity of PDA peaks remain similar, the additional features obtained from the cations significantly increases.

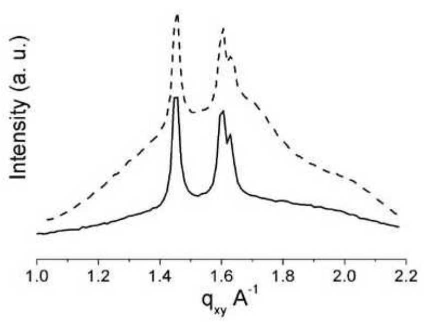

Figure 4: The effect of Pb^{2+} concentration on the integrated GIXD intensity with subphase concentration of 2mM (solid line), 12mM (dashed line).

Summary:

In conclusion, we have hereby reported on the first successful experiment of anomalous XR and GIXD carried out at ESRF at the air-solution interface. The anomalous effect of divalent lead ions under PDA LF was clearly observed for type-ii experiments. This confirms the strong interaction between the lead cations and the negatively charged carboxyl headgroups and suggests the presence of a commensurate structure of lead ions under the polymerized organic template. This intriguing result is under intensive investigation by our group. In type-i experiments, the presence of Pb^{2+} ions was found to inhibit polymerization of the organic layer and thus to prevent the formation of PDA.