ESRF	**Experiment title:** **Anomalous X-Ray Reflectivity and GIXD Studies of Metal Cation – Polyconjugated Langmuir Film Interactions at the Gas-Liquid Interface**	**Experiment number**: SI-1393
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Our previous GIXD studies on polydiacetylene (PDA) Langmuir films (LF) were focused on (a) Study of the crystal structure of each of the existing phases of the PDA LFs while carefully monitoring the phase transition dynamics. (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. (c) Investigation of the anomalous effect of divalent lead ions under PDA LFs, in which the strong interaction between the lead cations and the negatively charged carboxyl headgroups was probed.

The main objective of the current anomalous x-ray studies was to investigate the role of the metal cations in the PDA LF / Zn^{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 Zn^{2+} ions and studied *in-situ* using three different energies 8.087keV, 9.59keV and 9.6658keV (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 Zn^{2+} ions. (ii.) Zn^{2+} and Pb^{2+} ions were introduced to the subphase under PDA LF that was initially polymerized on a different

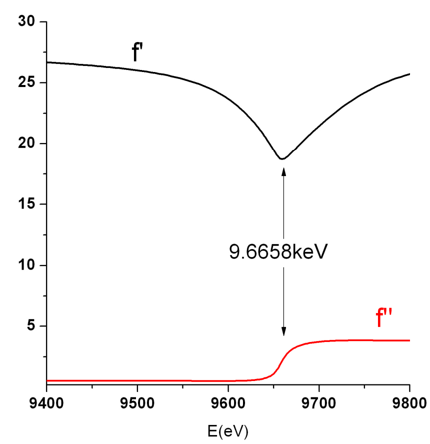
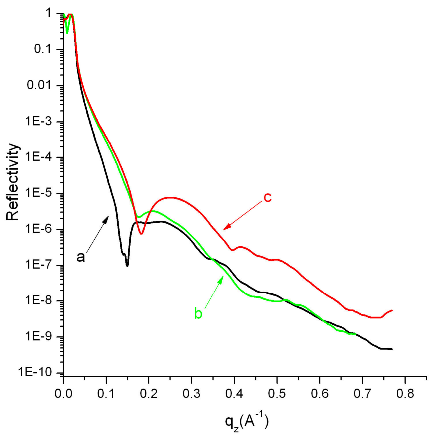


Figure 1: *Anomalous dispersion factors, f' and f'', of zinc.*

subphase. Figures 2 and 3 show the XRR and GIXD results of a PDA film produced on a 5mM $ZnCl_2$ solution. It can be noted that both the in-plane and out-of-plane structure of the film are affected due to the UV irradiation and the subphase exchange to a Pb^{2+} containing solution. The vertical structural information on the PDA film due to those perturbations is summarized in Table 1. It could be seen that while polymerization stretches the film and renders it flatter, solution exchange barely affects the morphological properties of the films.



	film thickness	roughness
a	24.94 Å	13.169 Å
b	26.58 Å	5.619 Å
c	27.14Å	5.121 Å

Figure 2: *Specular Reflectivity of a PCDA monolayer compressed on 5 mM of $ZnCl_2$ solution **a)** before UV polymerization, **b)** after UV polymerization and **c)** after the subphase substitution by 1 mM of $PbCl_2$. The data analysis results are summarized in Table 1 above.*

After UV irradiation some of the reflections which existed in the unpolymerized stage disappeared, while the reflection at q_{xy}=1.38Å^{-1} remained dominant. The subphase substitution by 1mM of $PbCl_2$ caused the PDA film become more ordered and uniform, manifested by the second order of the q_{xy}=1.38Å^{-1} reflections obtained at q_{xy}=2.76Å^{-1}, and the second order of the polymer backbone distance (5.23Å) obtained at q_{xy}=2.4Å^{-1}. In each stage of the experiment the structure of PDA LF compressed and polymerized on Zn^{2+} ions was different from that obtained on pure water.

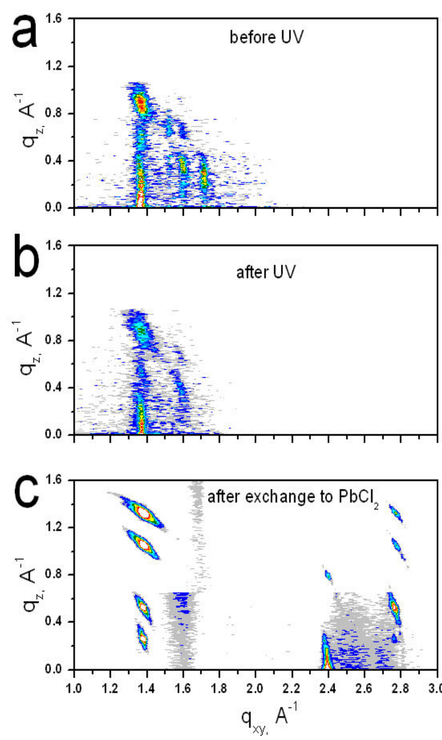


Figure 3: *GIXD reciprocal space maps of PCDA monolayer compressed on 5 mM of $ZnCl_2$ solution **a)** before UV polymerization, **b)** after UV polymerization and **c)** after the subphase substitution by 1 mM of $PbCl_2$.*

Summary:

We report here about the anomalous XR and GIXD experiments obtained on the PDA LFs-system modified by divalent zinc cations from solution. Two main conclusions were drawn: 1. The crystal structure of the PDA film compressed and polymerized on solution containing metal ions is different from that of films produced on pure water. 2. The polymerization stage is critical in the crystal formation of PDA LF. Subphase exchange taking place after polymerization barely changes the structure of the films, yet it may affect the film morphology.

These conclusions are confirmed by our in-house XPS, AFM and optical spectroscopy (Raman and absorbance) studies. It was determined that the presence of zinc cations in the subphase *prior* to polymerization results in distinct optical and chemical properties compared to films obtained on pure water. Nevertheless, introduction of metal ions to the sub-phase *after* polymerization barely changes any of the spectral properties.

Substitution of weakly bound zinc ions with lead drives the PDA-LF into a new, highly crystalline structure that has never been observed before. This ordered PDA phase is very well ordered both laterally and vertically. We presently index this new phase on the basis of previously solved PDA structures.