



	Experiment title: GIXD Studies of Oriented Nucleation of Semiconductor Nanoparticles on Polyconjugated Monolayers at the Air-Solution Interface	Experiment number: SI-1016
Beamline: ID-10B	Date of experiment: From: 26/02/2004 to: 03/03/2004	Date of report: 22/09/2004
Shifts: 18	Local contact(s): Dr. Oleg Konovalov	Received at ESRF:
Names and affiliations of applicants (* indicates experimentalists): Dr. Yuval Golan*, Nataly Belman*, Yevgeniy Lifshitz*, Dept. of Materials Engineering, Dr. Amir Berman*, Dept. of Biotechnology Engineering Ben-Gurion University of the Negev, Beer-Sheva 84105, ISRAEL		

1. Radiation induced phase transition in Polydiacetylene (PDA) Langmuir Film (LF)

The investigation of PDA LF was done at the air-water interface by GIXD technique. PDA LF exist in two chromatic phases (blue and red) which differ by their color and subsequent absorption maxima¹. TEM² and AFM¹ were used to determine the crystal structure of PDA for both phases. The transition from blue to red can be activated chemically, thermally, mechanically and by high radiation dose¹. The blue to red transition is accompanied by shortening the average conjugated length in the polymer direction and is coincident with the reorganization of the molecular side chains.

The aim of the first experiment was to use *in-situ* GIXD in order to monitor the phase transition of PDA LF at the air-water interface. The same film was exposed to different radiation doses by controlling the dose of UV radiation or of synchrotron light. With increasing radiation dose, prominent changes in the structure of the PDA LF were observed, which indicate a structural phase transition from the blue phase to the red one. This transition, shown in Figure 1, seems to be discontinuous (discrete) and dependent on the radiation dose applied to the film. When the applied dose is not sufficient for the blue-to-red transition, the film remains in the blue phase. On the other hand, when the radiation dose exceeds a certain threshold, the entire film is found exclusively in the red phase. This is manifested in a change in the q_{xy} and q_z position of the two Bragg peaks obtained from the centered rectangular structure to higher q_{xy} values (see Figure 1). Note the shift in position of the peak at $q_{xy}=1.18$ and $q_z=1.1$ [\AA^{-1}] along the same arc

(radius corresponding to the same q_{total}) to circa $q_{xy}=1.60 \text{ [\AA}^{-1}]$ and q_z close to zero from Figure 1a to Figure 1d.

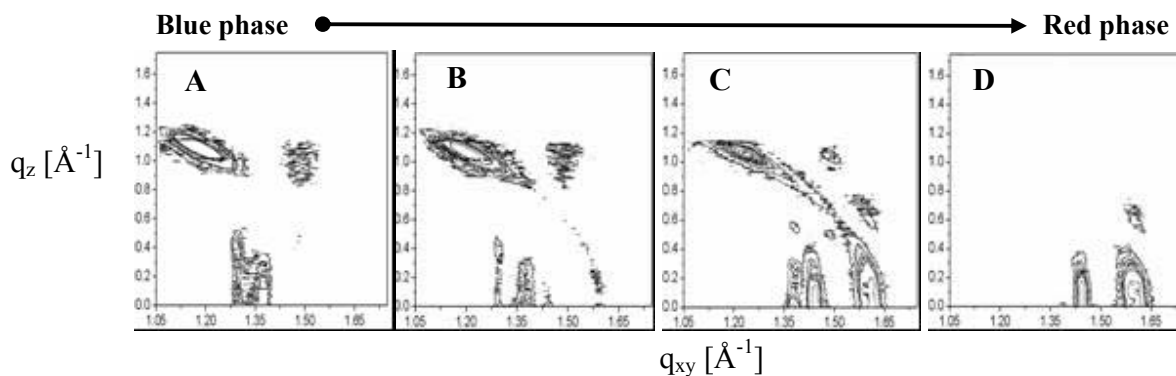


Figure 1: Radiation induced chromatic transition of PDA LF. A-D The q -space reciprocal maps represent GIXD scans with different radiation dose applied to the films (from A – the lowest dose to D – high radiation dose). B, C – represent two intermediate stages in which the two chromatic phases are present³.

Between these two extremes, coexisting forms of both chromatic phases are observed (Figure 1b,c)³. Based on these GIXD results, a model describing the long range molecular arrangement corresponding to each phase is presented in Figure 2.

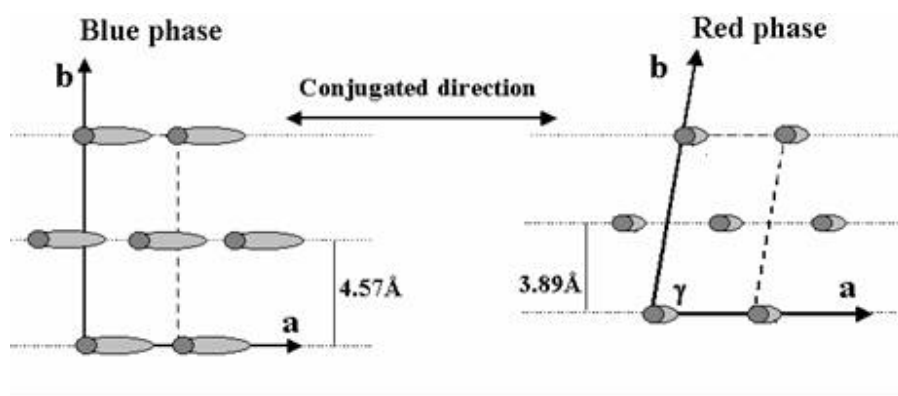


Figure 2: Schematic representation of horizontal crystalline alignment of PDA in two chromatic phases. Blue phase is centered rectangular with $a_b=4.84 \text{ \AA}$ and $b_b=9.14 \text{ \AA}$. The red cell is oblique ($a_r=4.89 \text{ \AA}$, $b_r=7.86 \text{ \AA}$, $\gamma_r=82.6^\circ$). In both phases the molecular tilt is parallel to the conjugated direction. (Ellipses indicate the projection of the alkyl chains onto the surface). The blue to red transition is accompanied by a decrease in molecular tilt from 35° from the surface normal to a nearly vertical position and simultaneous decrease of the distance between conjugated strands to the van der Waals distance.³ This is in agreement with FTIR measurements of similar PDA structural transition.⁴

Comparing these unit cells to previous reports on *ex-situ* measurements (electron diffraction in the TEM², AFM¹) clearly shows that the structure of solid-supported PDA LF at the air-water interface is different from that observed after transfer onto solid supports. This observation will be studied in subsequent GIXD experiments.

The second goal of this experiment was to determine the structure of the trilayer PDA LF in the vertical direction, and to compare the structure of the first layer (in contact with the

aqueous subphase) with that of the two other layers. Interestingly, our attempts to polymerize PDA LF compressed to area per molecule values corresponding to a single layer resulted in clear cut evidence for spontaneous transition of the films to the trilayer form. Stabilization of the monolayer structure was possible only with cations such as Cd^{2+} present in the subphase at sufficiently high concentration, but this could not allow direct comparison with the trilayer structure on pure water. The data is not shown here due to the limited scope of this report.

2. The influence of divalent ions in the subphase on the structure of PDA

In our previous experiments, the effect of the presence of several divalent metal ions (Pb^{2+} , Cd^{2+} , Zn^{2+}) in the subphase solution on the PDA structure was established and found to be correlated with the ionic radius³. In the current experiment the influence of two additional ions was investigated (Ba^{2+} , Ag^+). The former was chosen due to its significantly larger ionic size, and the latter was a monovalent rather than a divalent cation. The results are shown in Figure 3 below. The monovalent Ag^+ ions barely affected the PDA structure, while the addition of Ba^{2+} ions lead to the stabilization of blue phase of PDA. The mechanism in which these ions influence the PDA LF is not completely understood and will be carefully investigated in future experiments using anomalous x-ray scattering.

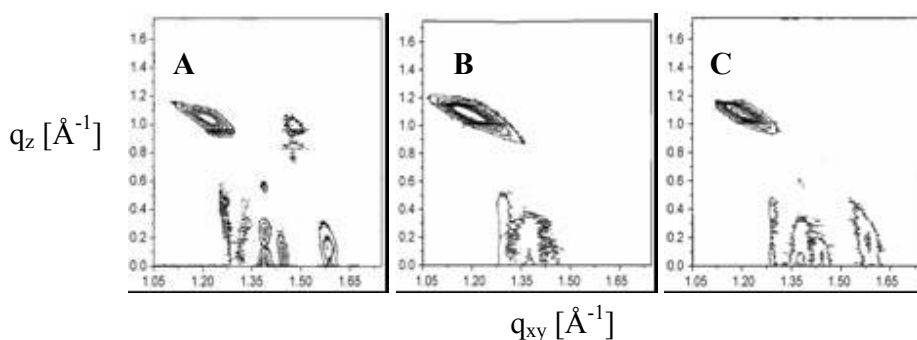


Figure 3: Cation influence on PDA LF crystal structure. GIXD q-space reciprocal maps of PDA LF on **A** – water subphase, **B** – 5mM BaCl_2 and **C** – 1mM AgNO_3 subphases.

3. References

1. Carpick R.W., Sasaki D.Y., Marcus M.S., Eriksson M.A., Burns A.R., *Journal of Physics: Condensed Matter* **16** **2004** R679.
2. Kuriyama K., Kikuchi H., Kajiyama T., *Langmuir* **14** **1998** 1130.
3. Lifshitz Y., Konovalov O., Berman A., Golan Y., **2004 paper in preparation**.
4. Ahn D-J., Berman A., Charych D., *J. Phys. Chem.* **100** (30) **1996** 12455.