ESRF

	Experiment title: Probing the nucleation and growth of inorganic crystals at polymer monolayers at the air-solution interface	**Experiment number**: SI-785
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Report:

Preliminary report on experiment SI-785

The focus of this session was on the cooperative structural relationship between template monolayer and CdS crystallites during crystal nucleation and growth. As mentioned in the original proposal, the process bears relevance to biomineralization, where crystal nucleation and control of growth also take place at the organic –inorganic interface.
Two experimental setups were examined. The template film used was a Langmuir monolayer of polydiactylene. The monomer units, 10,12 pentacosadiynoic acid (PDA) were spread on the air-water interface and UV polymerized. Subsequently, $CdCl_2$ were added to the subphase, thus forming structural transition due to salt bridges formation. Small and controlled amount of H_2S gas were infused into the Langmuir trough chamber, causing CdS to precipitate. In the first setup, grazing incidence diffraction (GID) scans of the film were performed at each step and during and after the crystallites precipitation. In a second setup, a preformed similar assembly (CdS/PDA) was transferred onto a solid support (Si(111)) and was examined with high angle x-ray diffraction in a conventional configuration and in GID.

These two diffraction configurations are complementary in that the GID probes ‘in plane’ diffraction vectors, while in the high angle configuration only diffraction vectors that are normal to the plane are probed. A $\theta/2\theta$ scan of the solid supported film resulted in one prominent broad reflection, corresponding to (10.1) of CdS hexagonal structure (Greenockite), overlapping with the (11.1) sharp reflection of the silicon substrate. The GID setup yielded reflections of the type (10.0), (11.0), (20.0) and possibly the (11.2). However, reflection (10.1) that was observed as normal to the surface in the high angle configuration was absent (figure 1). This suggests that preferential orientation of the crystallites is taking place with (10.1) normal to the substrate plane and the other at near parallel orientation. (A difficulty is raised here, as the reflections that were observed as lying parallel to the surface are not orthogonal to the one that is normal to the surface. The "out of plane" orientation of these reflections will be examined in detail in the 2-D maps, of which data was collected but not yet analyzed).

Simultaneously with the development of the inorganic phase, the template monolayer phase was explored. The different interfacial environments (water/$CdCl_2$/CdS) induced changes in the organization of the monolayer film. It was observed that the PDA film on water give rise to several prominent reflections, which upon substitution of the subphase to $CdCl_2$ are either unchanged, shifted to different position or disappear. Based on the available data that is presently at hand, it is premature to assign these reflections to specific structural features of the polymer film. However, it is plausible that the unchanged reflection at $2\theta=20.6^\circ$ (d=4.35Å) arises from the rigid, covalently bonded polymer backbone. The reflection at $2\theta=19.8^\circ$ (d=4.53Å) may be assigned to the inter-chain distance, which upon replacement of water with cadmium ions at the subphase came closer together due to formation of salt bridges. Other reflections at $2\theta=18.3$ and $2\theta=22.5$ has shifted in the out-of-plane direction. This may represent increased tilt of the alkyl side chains that result from the different environment.

Figure 1.