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| ESRF | **Experiment title:**<br>Structural determination of Langmuir-Blodgett multilayers of poly-azo-acrylates mesogenic polymers. | **Experiment number**:<br>SI-673 |
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| **Shifts:**<br>19 | **Local contact(s)**:<br>Oleg Konovalov | |

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**Report:**

This experiment is part of our research program of characterization of thin film of photosensitive side-chain polymers by means of x-rays reflectivity and GID, ellipsometry, scanning force microscopy (NC-AFM) and vibrational spectroscopies.

The system under study are polyacrylates containing the photosensitive azobenzene group as side chain, the prototype substance being studied (PA4) is shown in fig.1.

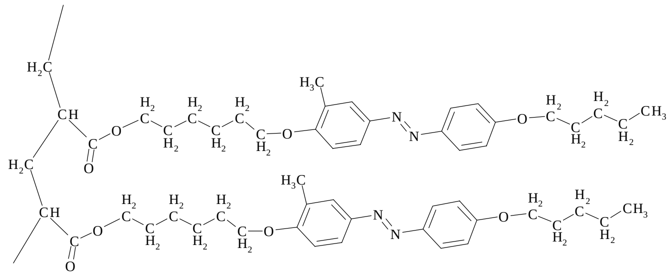

**Fig 1:** sketch of the structure of PA4.

Here we report on an extensive study of the morphology and the related photoinduced changes in Langmuir-Blodgett and Langmuir-Schaefer multilayers of such a polymer deposited onto different substrates: silicon covered by native oxide, silanized (hydrophobic) silicon, metal coated glass, and alkylic-chain-coated surfaces.

We measured the reflectivity signal, the GID and some selected rods at relevant in plane angles. The sample temperature was varied by means of a Peltier cell, the T being independently measured by a high precision Pt-100 sensor (accuracy better than 0.01C). Uv illumination, needed for the photoisomerisation of the azobenzene side-group, was provided by a Hg lamp, a set of suitable filters and polarizers. A typical result of the uv illumination is illustrated in fig. 2, where we report the reflectivity of PA4 multilayers of different thickness deposited onto Si wafers covered by natural oxide (20A) before and after uv illumination. We clearly observe a smoothing effect of uv illumination (also independently quantified by non-contact AFM measurements), together with the disruption of the structure developed

around 0.48A$^{-1}$ in the pristine multilayer. The latter structure presumably originates from features in the first LS layers of the polymer. Investigation is in progress, as we also measured the same multilayers onto hydrophobic (silanized) Si substrates, which in turn show a different, less pronounced, modulation of the reflectivity in the same Q region.
Furthermore we measured the temperature evolution of the GID and of the reflectivity signals from films of different thickness of PA4. A typical result of GID measurement for a thick film (40LS) of PA4 is reported in fig 3; above T=60C we observe a phase transformation from the amorphous glassy state stable at T=RT to a more ordered, presumably smectic-like phase. Such phase is stable up to around T=80C, above this temperature the structure of the film disappears (as also confirmed by reflectivity experiments) as the polymeric liquid crystal reverts to its isotropic phase. These findings are in agreement with the phase diagram well established for bulk PA4, although this is the first direct investigation of the smectic-like phase in such thin films.

Finally we used part of our beam-time for a preliminary investigation of superlattices made of Langmuir-Blodgett fatty acid salt layers alternated with Langmuir-Schaefer polymeric layers, namely [2-LB Ba-Behenate : *n*-LS PA4]$_{12}$. Preliminary results suggest a partial survival of the fatty acid salt periodic building which however is reduced in the samples with higher polymer content '*n*'. Some partial modifications in the reflectivity signal are indeed induced by uv illumination of such super-structures. This latter investigation was only partly completed, as most of the superlattice samples were deposited on top of a film of Cr deposited on glass. This type of substrate proved to be unsuitable for x-ray reflectivity experiments, presumably due to a combination of roughness and insufficient thickness of the Cr film. We plan to extend such investigations in a forthcoming proposal.

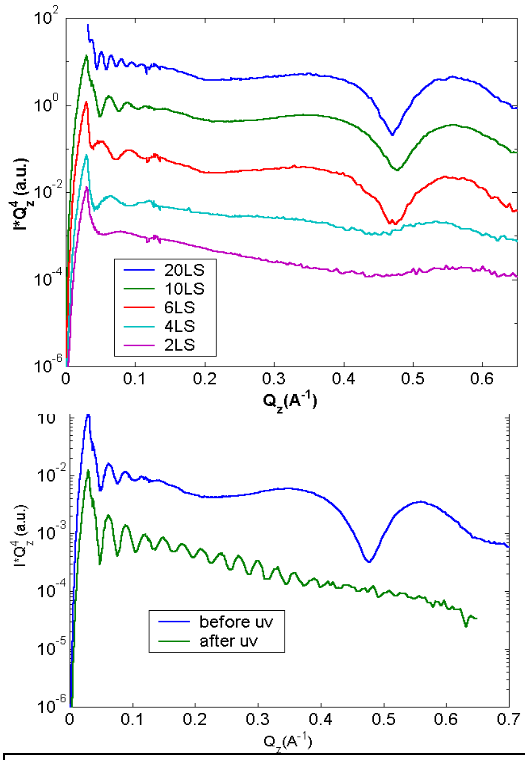

**Fig 2**: top panel: reflectivity from PA4 multilayers of different thickness, bottom panel: effect of uv illumination on a multilayer (10LS) of PA4; the upper curve corresponds to the same film before, the lower after uv exposure.

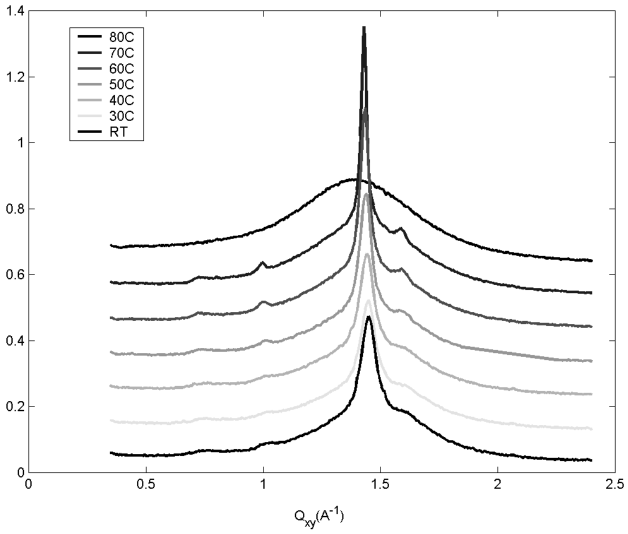

**Fig 3**: GID signal from a sample made by 40 layer of PA4 as a function of T. Curves from the bottom to the top correspond to increasing T as indicated in the caption. Note the transition from the amorphous RT glassy phase, to a more ordered structure which develops around T=60, 70C and disappears above 80C.