ESRF	**Experiment title:** In-situ study of structure evolution in thin films of photovoltaic transistor bilayers based on spiropyranes.	**Experiment number**: SC 4326
Beamline: ID10	**Date of experiment**: ID10 26/04/2016 - 03/05/2016	**Date of report**:
Shifts: 9	**Local contact(s)**: Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Dimitri Ivanov Moscow State University Laboratory of Soft Matter

Dr. Denis Anokhin Moscow State University Laboratory of Soft Matter

Alexey Piryazev Moscow State University Laboratory of Soft Matter

Report:

Photosensitive organic materials are widely known for their pronounced correlations between morphology and physical properties. For example, the derivatives of spiropyran are well-known systems for different practical applications because of their photosensitive properties and ability to change morphology under irradiation.[1] Using spiropyran as 1st layer of bilayer film and second layer with photosensitive liquid-crystalline polymer molecules was able us to produce perspective photosensitive materials with different controlable properties. As part of the study of photosensitive LC block copolymers, the phase behavior of PMHA molecules with different ratios of flexible decoupling lengths and end groups (PMHA6-6, PMHA6-10, PMHA10-6, PMHA10-10, respectively) was studied. By DSC, we obtained phase behaviour of samples during the heating. We also combined this data with in-situ x-ray studies. According to small-angle X-ray diffraction data, all samples except PMHA 10-6 form a smectic phase, which is characterized by the presence of a meridional peak. For the PMHA10-6 sample, three peaks of the hexagonal phase are observed.

Peak parameters corresponding to smectic interlayer distances for samples: PMHA 6-6 - 30A, PMHA 6-10 - 42A, PMHA 10-10 34.6A. The peak parameter of the hexagonal phase for sample 10-6 is 36A. Based on the estimation of the length sizes of mesogens and flexible blocks, comparing their sizes with the layer thickness, we can conclude that the mesogen block is inclined relative to the plane of the substrate. For a more detailed identification of the phases of samples PMHA 6-10 and PMHA 10-6, measurements of the structure were performed at large diffraction angles. The results are shown in Figure 1.

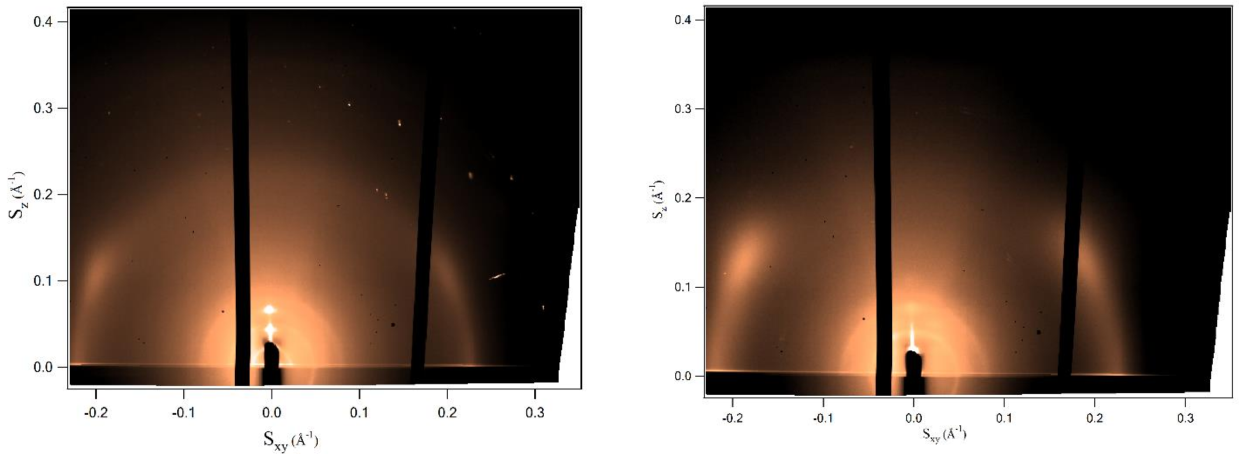

Figure 1 - Two-dimensional diffraction patterns obtained at large diffraction angles. PMHA 6-10 (left), PMHA 10-6 (right).

Based on the assessment of the position of the peaks in the region of 4.5A, we can conclude that confirms the assumption of the inclination of mesogenic blocks. For the PMHA6-10 sample, the second and third order of the peak at 42.5A (21.7A and 14.5A, respectively) are visible in the two-dimensional diffractogram, which is in good agreement with the diffraction data at small angles. Peaks corresponding to large distances are not visible due to the bimstop. A low degree of orientation of the nematic peak may indicate the presence of a nematic phase in the film. The slope of the mesogenic block calculated from the maximum of the nematic peak is 61 °. Such packaging of molecules is known in the literature as SmF. [2] For the PMHA 10-6 sample, the maximum of the nematic peak is at 56 °, which is extremely close to 60 °.

For samples PMHA10-6 and PMHA6-10, diffraction patterns were obtained during heating and cooling. The dependence of the intensity of the meridional reflex on temperature during cooling is shown in Figure 5. The data are in good agreement with the DSC data, and it can be seen that no destruction of the smectic structure is observed up to the temperature of the third transition. Based on these data, it can be assumed that the peaks on the DSC are at lower temperatures can correspond to the glass transition and local rearrangement of mesogenic groups associated with an increase in the mobility of alkyl fragments.

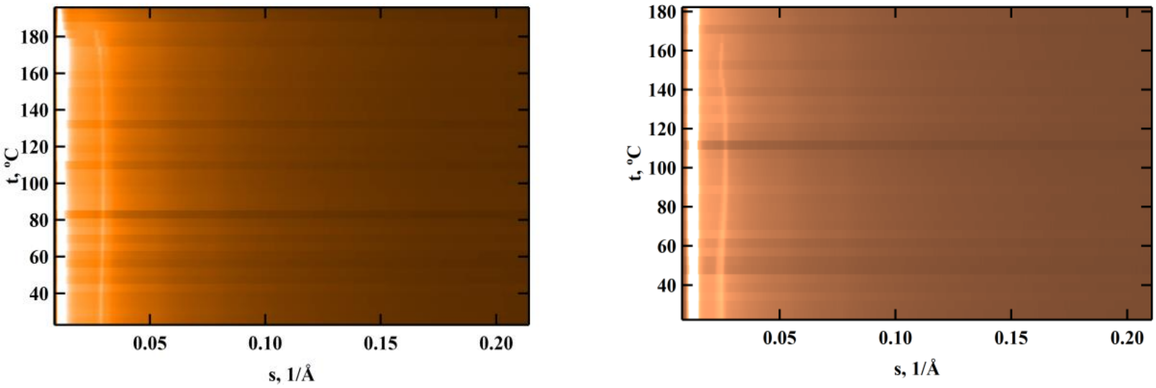

Figure 2 – temperature profiles obtained at large diffraction angles. PMHA 10-6 (left), PMHA 6-10 (right).

1. Lukyanov, B. S.; Lukyanova, M. B. (2005). "Spiropyrans: Synthesis, Properties, and Application. A review". Chemistry of Heterocyclic Compounds 41 (3): 281–311
2. Ya. S. Freidzon, R. V. Talroze, N. I. Boiko, S. G. Kostromin, V. P. Shibaev & N. A. Platé (1988) Thermotropic liquid-crystalline polymers XXIII. Peculiarities of uniaxial orientation of comb-like liquid-crystalline polymers under mechanical stress, Liquid Crystals, 3:1, 127-132,