ESRF	**Experiment title:** In-situ study of structural evolution during photo-isomerization in photosensitive comb-like liquid-crystalline polymers for applications as actuators	**Experiment number**: MA-2824
Beamline: ID10	**Date of experiment**: from: 28.08.2015 to: 01.09.2015	**Date of report**:
Shifts: 9	**Local contact(s)**: Giovanni calogero Li destri nicosia	*Received at ESRF:*

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Report:

According to the polarizing optical microscopy and DSC data, both polymers form two LC phases. At high temperatures the textures of both polymers reveal a cholesteric mesophase, which is characterized by focal conics or planar textures with oily streaks and possesses a selective light reflection in the near-IR spectral range. At less temperature values of λ_{max} of both polymers have tendency to increase demonstrating helix untwisting due to the formation of smectic order fluctuations. The low-temperature phase of **PMAzo-6** has an unspecific texture, whereas **PMAzo-10** forms a fan-shaped texture after prolonged annealing.

Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) was employed to explore the mesophase structure. Figure 1 displays a 2D GIWAXS diffraction pattern measured on a thin polymer film prepared by spin-coating and subsequently annealed at 150^{o}C overnight. The diffraction pattern contains information on two different molecular organization levels: a series of peaks in the small-angle region reflect the layer-like organization of the mesogens at a large scale, whereas the broad peak (halo) at wide angles (4.4 Å) corresponds to the mesogen local organization in the direction perpendicular to the mesogen long axes, similarly to liquid-like order.

For the **PMAzo-6** polymer a group of diffraction peaks in the small-angle region infers the formation of a particular layer-like structure (Fig. 1a). We speculate that the layers have a wavy interface, which gives

rise to splitting of the 110 and 210 reflexes about the meridional direction of the pattern. Comparing these results with the literature data allows one to conclude that this phase has a structure similar to the so-called Sm$\hat{C}$ mesophase [N. Boiko, V. Shibaev, B. Ostrovskii, S. Sulyanov, D. Wolff, J. Springer, Frustrated Behavior of a Side-Chain Liquid Crystalline Polyacrylate, Macromol. Chem. Phys. 2001, 202, 297–303]. In this rather exotic phase, the mesogens are organized in undulated smectic layers with a liquid-like order within the layers.

The cell parameters of **PMAzo-6** are the following: a=43.3 Å, b=26.9 Å, γ=78^o. In Table 1, the calculated and experimental d-spacings are presented. As can be seen, the experimental are in good agreement with the calculated values, which were obtained using the lattice parameters extracted from the fits to experimental data. Figure 2 schematically shows the corresponding molecular arrangement. It is noteworthy that the mesogen length is close to one half of the corresponding unit cell parameter (i.e., the a-parameter). Therefore, it is likely that this polymer forms a bilayer structure. One of the reasons for this can be due to the presence of chiral groups in the side-chain structure. Similar molecular arrangements were described in literature in the past. [Junji Watanabe, Yasukazu Nakata, Kazuya Simizu. Frustrated bilayer smectic phase in main-chain polymers with two different spacers. Journal de Physique II, EDP Sciences, 1994, 4 (4), pp.581-588.] The number of mesogens per layer was calculated from the macroscopic density measured by flotation method (1.13 g/cm^3) and was found to be equal to six.

In an attempt to analyze in more depth the molecular arrangement of **PMAzo-6**, it can be noted that the mesogen-length together with the fully extended linker is slightly bigger than half of the a-parameter. This fact can in principle bring about inclination of the mesogen with respect to the layer normal in order to accommodate the molecule within the smectic structure. To get additional information as to the possible tilt of the mesogen, X-ray measurements have been performed on uniaxially-oriented samples (i.e., fibers). A 2D diffractogram obtanied on x-ray laboratory machine clearly exhibits azimuthal splitting of the halo at 4.4 Å by about 20 degrees, as also illustrated by the azimuthal intensity profile. Given that the smectic layers are running along the fiber axis, the value of the angular split of the amorphous halo about the meridional direction corresponds to the inclination of the mesogen. Therefore, it is logical to assume that the mesogens are tilted about the normal to the smectic layers.

Table 1. Calculated and experimental d-spacings for the 2D unit cell of **PMAzo-6**.

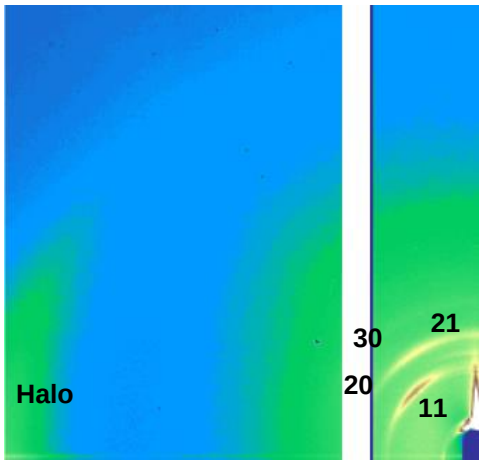
Miller indices		d, Å (experimental value)	d, Å (calculated value)
h	k		
1	1	24.8	24.8
2	0	21.1	21.1
3	0	14.1	14.1
2	1	18.5	18.5

PMAzo-10 also forms a bilayered structure, which however can be considered as being conventional. This can be confirmed by observation of several orders of the smectic peak (cf. Fig. 1b) with the fundamental distance of 85.2 Å. This fundamental peak cannot be observed on X-ray pattern due to the insufficient resolution and can be obtained by extrapolation of the observed experimental orders. The diffraction peak positions are given in Table 2, and the phase structure is schematically shown in Fig. 2b.

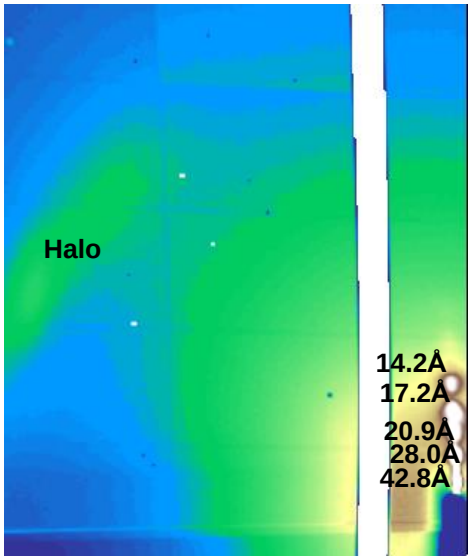
Table 2. Calculated and experimental interlayer distances for **PMAzo-10**.

Order number	1	2	3	4	5	6	Diffuse halo, Å
d, exp., Å, **SmX(1)***	-	42.8	28.0	20.9	17.2	14.2	4.5
d, calc., Å, **SmX(1)***	85.2	42.6	28.4	21.3	17.0	14.2	-
d, exp., Å, **SmX(2)***	-	-	28.0	-	-	14.2	4.5
d, calc., Å, **SmX(2)***	83.2	41.8	28.0	21.1	17.0	14.2	

The temperature-dependent GIWAXS patterns correlate well with the DSC data. The phase transitions at high temperatures (N-I) are not observed on the integrated X-ray patterns due to absence of the halo peak within the measurement range. The two smectic phases observed below the transition to the N-phase were designed as **SmX(1)*** and **SmX(2)*** The **SmX(1)*- SmX(2)*** transition at 138°C visible on the corresponding DSC trace, gives rise to a substantial modification of the X-ray diffractogram. Thus, the first, second, fourth and fifth order of the fundamental smectic peak disappear from the patterns. Since the positions of the remaining diffraction peaks did not change, this modification reflects the internal layer reorganization, which may be induced by enhanced mobility of the alkyl chains. Therefore, the observed structural evolution may consist in modification of the relative thickness of the sublayers pertinent to the mesogen and alkyl regions of the system, without changing the total smectic layer thickness.



a



b

Fig. 1. 2D grazing-incidence X-ray patterns corresponding to room-temperature measurements of spin-coated and subsequently annealed films of **PMAzo-6** (the Miller indexes are indicated) (a) and **PMAzo-10 (b)** (several orders of the main smectic peak are shown).

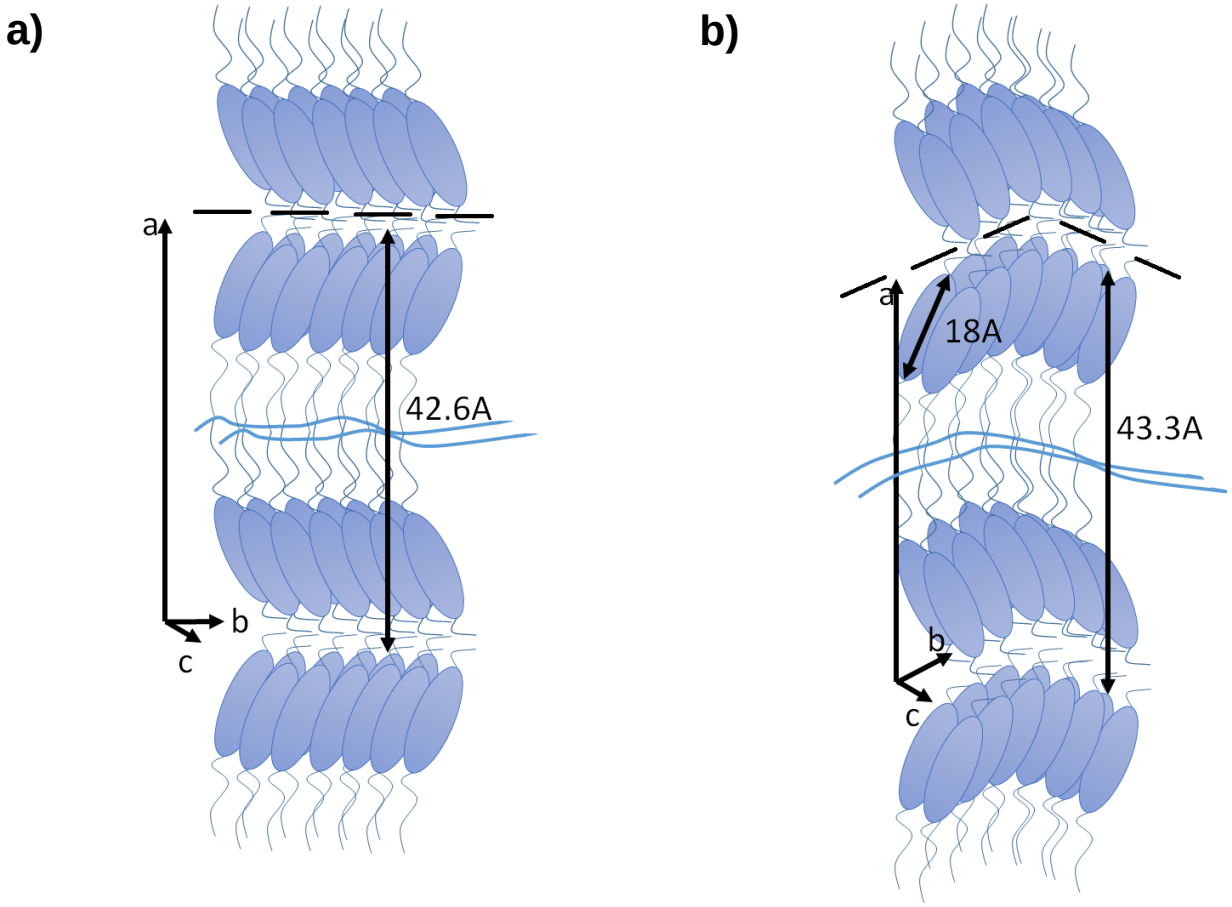


Fig. 2. Schematic representation of a possible mesogen packing in Sm$\hat{C}^*$ phase of **PMAzo-6** (a) and SmX(1,2)* phases of **PMAzo-10** (b). By dashed lines the layer borders are presented.