



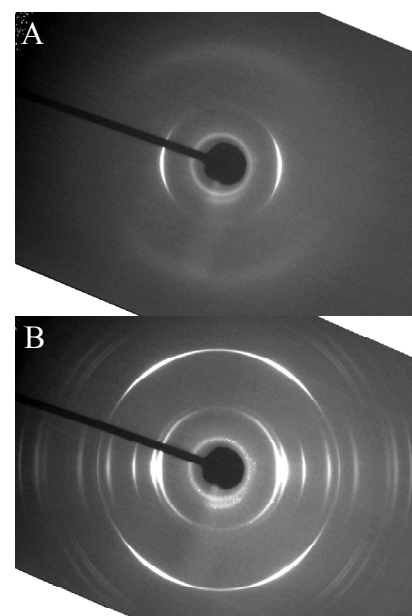
	<b>Experiment title:</b> Templating crystallization of main-chain LC polymers in thin films	<b>Experiment number:</b> SC-2203
<b>Beamline:</b> BM26B	<b>Date of experiment:</b> from:12.03 to:16.03.2007	<b>Date of report:</b> 29.08.2007
<b>Shifts:</b> 9	<b>Local contact(s):</b> Kristina Kvashnina Wim Bras	<i>Received at ESRF:</i> <i>Denis Anokhin</i> <i>Martin Rosenthal</i> <i>Matthieu Defaux</i> <i>Houssam Hamie</i>
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## Report:

In the last years, important efforts were devoted to fabrication of materials organized on multiple scales by means of self-assembly. In particular, controlling the structure of thin films and surfaces at spatial scales ranging from angstroms to centimeters was found crucial [1-4]. The main objective of this project is to spatially control the crystallization process for main-chain liquid crystalline (LC) polymers confined in thin deposited films (thickness < 1.0  $\mu\text{m}$ ). In this case, the LC-phase (hexagonal columnar mesophase) naturally imposes a strong spatial confinement condition on polymer chains: they become squeezed within cylinders of about 1 nm in diameter. Moreover, the chains fully disentangle, with their axes being ordered on a 2D hexagonal lattice. In this project, the stages of the structure formation in thin polymer films such as the isotropic-LC transition and mesophase-assisted crystallization was studied as a function of temperature, film thickness, as well as the nature of the substrate. The object chosen for this study is poly(diethyl siloxane), PDES. The structure of this polymer in bulk was studied in the past [5,6], however, the structure of thin films of PDES was never addressed. We observed by optical microscopy lamellar ribbons of several hundred  $\mu\text{m}$  having the aspect of long needles. Besides the “needles”, we were able to identify new morphological features of the films at room temperature, which is cylindrites with a diameter of several hundred microns.

The studied sample of PDES is characterized by  $M_w$  of 573 Kg/mol, and a polydispersity of 1.46. Oriented samples for X-ray diffraction experiments were obtained by extruding the material in the LC phase with a home-built mini-extruder resulting in 0.7 mm diameter fibers. The measurements were carried out at room temperature (in mesomorphic state) and at  $-25^\circ\text{C}$  (in crystalline state). The thin films were prepared by spin-coating a PDES solution in toluene on glass, silicon wafer or PTFE-rubbed silicon to obtain films with a thickness of several hundred nm.

X-ray fiber diffraction measurements show that PDES is nicely oriented in the mesophase by extrusion (Fig. 1A). The diffraction pattern of the fiber shows a sharp peak on the equator at 8.01  $\text{\AA}$ . A second peak, although very weak, is visible at 4.64  $\text{\AA}$ . The halo usually attributed to disordered alkyl side chains is observed on the meridian at 4.24  $\text{\AA}$ . There are no reflections revealing order along the chain axis. Note that the ring close to the beamstop is due to the Kapton tape used to hold the sample in the beam. The positions of



**Fig.1** X-ray patterns of PDES fibers at room temperature (A) and at  $-25^\circ\text{C}$  (B).

the peaks is similar to those previously reported by Tsvankin et al. for a cross-linked PDES [5,7]. There are no reflections related to the c-axis. The structure can be assigned to a hexagonal or a monoclinic lattice. The 2D X-ray pattern measured at  $-40^{\circ}\text{C}$  corresponding to the crystalline phase is given in Figure 1B. It shows a large number of sharp reflections which can be attributed to two coexisting crystalline polymorphs ( $\alpha_2$  and  $\beta_2$ ) and indexed to the following unit cells: ( $\alpha_2$ )  $\mathbf{a} = 8.15 \text{ \AA}$ ,  $\mathbf{b} = 8.92 \text{ \AA}$ ,  $\mathbf{c} = 4.71 \text{ \AA}$ ,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 62^{\circ}$ ; ( $\beta_2$ )  $\mathbf{a} = 8.25 \text{ \AA}$ ,  $\mathbf{b} = 8.1 \text{ \AA}$ ,  $\mathbf{c} = 4.95 \text{ \AA}$ ,  $\alpha = \gamma = 90^{\circ}$ ,  $\beta = 104^{\circ}$ . The parameters obtained for the monoclinic lattice of the  $\alpha_2$  phase are in good correlation to the one proposed by Tsvankin et al. [6,8] while for the  $\beta_2$ -phase we observed a monoclinic lattice, like Inomata et al. [6].

In thin films, we were able to isolate and orient lamellar ribbons using a PTFE-rubbed glass prepared as described elsewhere [8]. AFM allows observing orientation of lamellar ribbons, which is parallel to the rubbing direction, i.e. parallel to the PTFE chains. Although no diffraction intensity was recorded at normal incidence, nicely oriented diffraction patterns were obtained when the beam was parallel to the plane of the substrate. Since the geometry is in this case similar to that of a grazing incidence setup, only half of the pattern is observable. For example, a clear signature of a hexagonal mesophase is received when the beam is perpendicular to the rubbing direction (Fig 2C): all the observed diffraction spots having the same intensity and are separated by  $60^{\circ}$ . Therefore the polymer chains are lying in the plane of the substrate perpendicular to lamellar axis. When the beam is directed along the lamellar axis, the pattern is identical to that of a PDES fiber rotated by  $90^{\circ}$ .

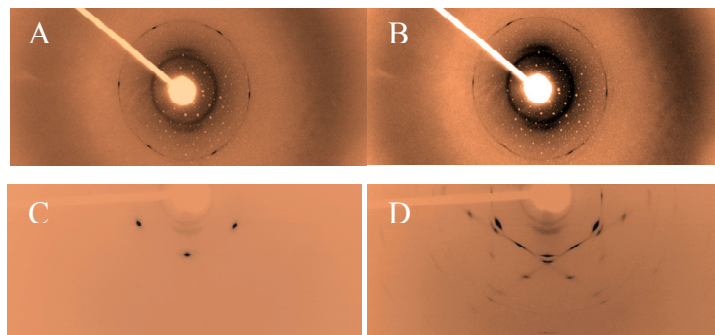
In order to get insights into the structure of cylindrites, we prepared a sample on a glass substrate, in which the needles were almost absent and cylindrites have a diameter comparable to the size of the X-ray beam. A classical pattern of a hexagonal mesophase (six spots pattern with spots of equivalent intensity and separated by  $60^{\circ}$ ) is obtained at normal incidence (Fig 2A), which indicates that the chains have homeotropic alignment, i.e. are standing upright. This conclusion is confirmed by measurements with the X-ray beam parallel to the substrate plane, for which the diffraction pattern exhibits only two broad equatorial peaks. A meridional peak at the same characteristic distance is also observed, and is probably due to the presence of some amount of lamellar ribbons.

Studies of the film crystallization allowed us to observe an interesting behaviour that we identified as epitaxial crystal growth on the mesophase. In the pattern obtained upon crystallization in the direction parallel to the chains (Fig 2D), two different polymorphs can be clearly discriminated. The separation of the peaks is much clearer than in the case of a fiber pattern (cf. Fig1B). The single crystal-like structures pertinent to two polymorphs have different orientations: four orientations for  $\alpha_2$ -phase and two- for the  $\beta_2$ -phase. The appearance of these orientations is directly related to the mechanism of the crystal growth, which proceeds epitaxially on the parent hexagonal mesophase.

In conclusion, PDES thin films present two different morphological features: cylindrites composed of homeotropically-aligned chains and lamellar ribbons containing chains lying in the plane of the substrate and perpendicular to the needle axis. Both features have the same structure identified as a hexagonal mesophase. Upon crystallization of the samples, we observed two crystalline polymorphs previously identified in the case of PDES fibers. Crystallization of lamellar ribbons proceeds via epitaxial growth on the parent mesophase.

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**Fig.2 (A,B)** X-ray diffraction patterns of a PDES cylindrite formed in a thin film. The patterns are recorded at normal incidence at room temperature and  $-25^{\circ}\text{C}$ , respectively. **(C,D)**: the same as (A,B) but on PDES lamellar ribbons in the direction perpendicular to rubbing.