



In-situ self-assembly of organic semiconductors under nano-confinement

Experiment number:
MA-1174

Beamline: BM-26	Date of experiment: from: 06.12.2010 to: 10.12.2010	Date of report: 28.08.2011
Shifts: 9	Local contact(s): Giuseppe Portale (email: portale@esrf.fr)	<i>Received at ESRF:</i> <i>Yaroslav Odarchenko</i> <i>Martin Rosenthal</i> <i>Dimitri Ivanov</i>
Names and affiliations of applicants (* indicates experimentalists): Ya.I. Odarchenko, M. Rosenthal, D.A. Ivanov Institut de Science des Matériaux de Mulhouse, LRC CNRS 7228, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse CEDEX, France.		

Report:

Highly-oriented materials with hierarchical multiscale organization obtained through self-assembly hold promise for a variety of practical applications. In particular, controlling the structure of thin films and surfaces at spatial scales ranging from Angstroms to centimeters is found crucial for sensors,¹ light emitting diodes,² photovoltaic cells³ and field-effect transistors.⁴ The control of morphology and alignment in the course of crystallization is, however, not simple due to high free energy change associated to this phase transition. To this end, liquid-crystalline (LC) materials combining order and mobility at molecular and supramolecular levels can be employed.

In the present work the orientation of poly(di-*n*-alkylsiloxanes) family polymers containing side groups with two to six carbon atoms embedded in nanoporous templates was studied by Micro-focus X-ray Scattering. By confining the LC polymers in nanoporous templates one can expect to induce orientation due to the geometrical constraints imposed by the pore walls. To explore this effect, we performed an X-ray microfocus scan across the membrane with 200 nm pores impregnated with poly(diethylsiloxane) (PDES), as shown in Fig. C. The extent of filling of the membrane pores with the polymer can be appreciated by comparing the SAXS signal originating from the AAO template and 10 reflection from the hexagonal mesophase of PDES. The 2D microfocus X-ray patterns corresponding to the overplayed PDES film (i.e. the one on the top of the membrane) and to PDES located inside the pores are exemplified on Fig. A-B. Fig. A shows the 10 reflection

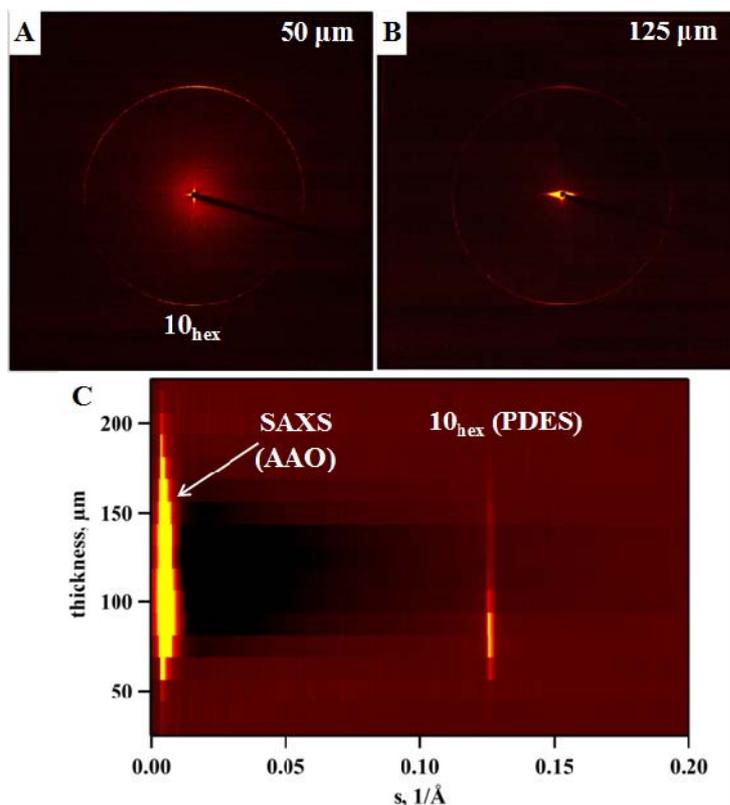


Fig. 1. 2D Microfocus X-ray patterns measured on a PDES thin film close to the surface (A) and in the nanoporous template with 200 nm pore size (B). Pore axis is vertical. 1D-reduced intensity measured during the microfocus scan across the polymer-impregnated template (C).

Fig. A shows the 10 reflection

corresponding to the intercolumnar distance of 9.3 \AA with two clear maxima situated on the meridian. Such orientation is similar to the one reported for thin films on rubbed PTFE surface and can be viewed as a layer-like packing of the backbone siloxane chains with $\mathbf{10}_{\text{hex}}$ vector normal to the substrate (**Figure A**).⁵ Importantly, for PDES embedded inside the pores the diffraction pattern does not change (cf. **Fig. B**). It can be assumed that the layers in the pore are preferentially parallel to the surface of the AAO membrane due to the epitaxy with the polymer chains on the top surface as illustrated in **Figure A-B**. The alike behaviour is observed for all the studied polysiloxanes such as poly(dipropylsiloxane) (PDPS), poly(dibutylsiloxane) (PDBS), poly(dipentylsiloxane) (PDPenS) and poly(dihexylsiloxane) PDHS that exhibit the columnar diameters comprised between 11.2 and 14.6 \AA . When the pore size is decreased to 35 nm one observes a six-spot pattern with the diffraction peaks situated at 60° with respect to each other starting from the equatorial direction. A typical 2D diffractogram corresponding to the PDES film is shown on **Figure A**. In the case of the template-impregnated PDES, the well-oriented pattern with unusually-oriented distinct 10 siloxane reflections (cf. **Figure**) prompts us suggesting that the grapho-epitaxy with the pore walls takes place. Thus, one would expect the mesoscopic lamellae growing strictly along the pores direction, i.e. with one of the $\mathbf{10}_{\text{hex}}$ vectors of the columnar phase oriented perpendicular to the pore axis (see **Figure B-C**). We speculate that this change in orientation is due to geometrical constraint imposed by the pores with a small diameter. Thus, the pore curvature guides mesoscopic lamellae to grow exclusively in the direction of pore length, which can be considered as infinite as compared to the perimeter of the pore wall. Noteworthy, the same result was also obtained for other polymers of the poly(di-*n*-siloxane) family, i.e. for PDPS, PDBS, PDPenS and PDHS.

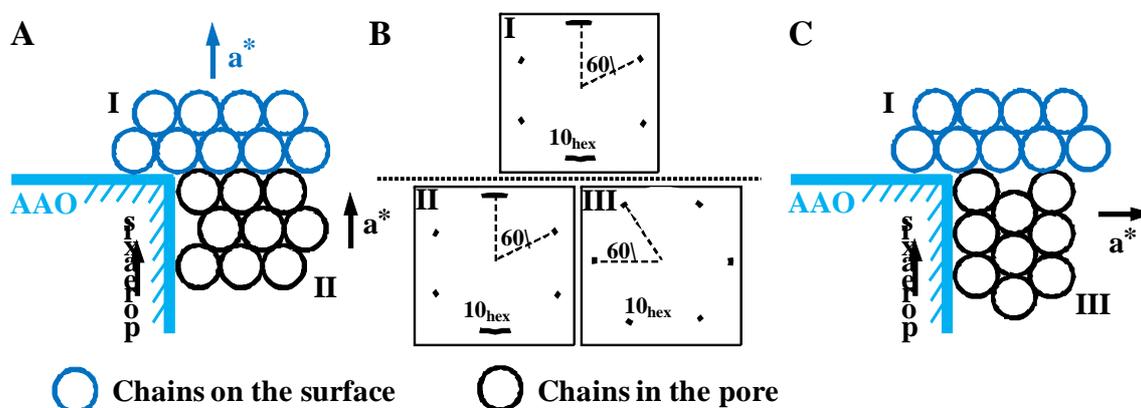


Figure 2. Cartoon showing two different orientations of the poly(di-*n*-alkylsiloxanes) LC lattice. The layers formed by the polysiloxane chains in the 200 nm pores are perpendicular (A) and in the 35 nm pores are parallel (C) to the pore axis. (B) Schematic 2D diffraction patterns from the LC columnar phase on the surface of the membrane (I) and inside the 200 nm (II) and 35 nm (III) pores.

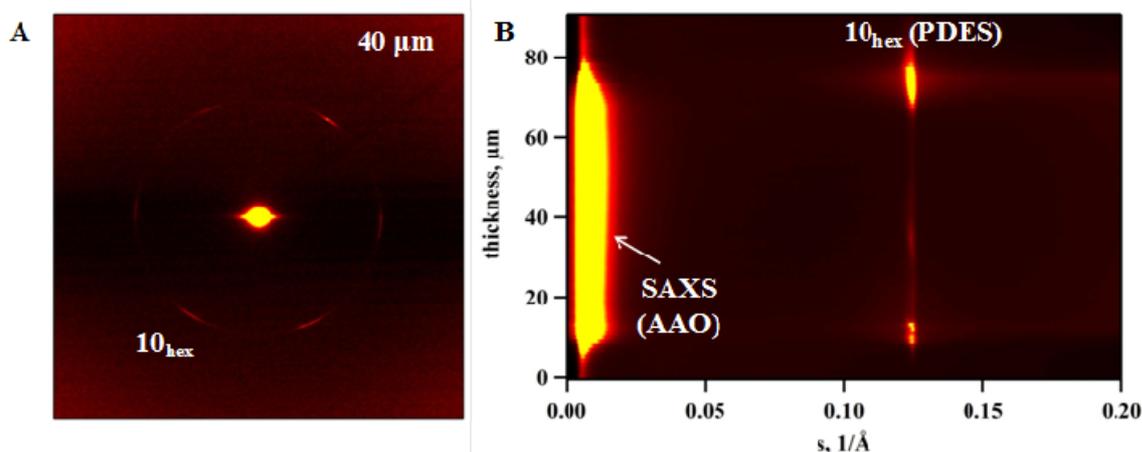


Figure 3. 2D Microfocus X-ray patterns measured on a PDES-impregnated nanoporous template with 35 nm pore size (A). Pore axis is vertical. 1D-reduced intensity measured during the microfocus scan across the polymer-impregnated template (B).

In summary, the microfocus X-ray Scattering allow us to get insights about the mechanisms of the liquid-crystalline orientation under 1D confinement. The grapho-epitaxy was found to take place in nanoporous templates with the pore diameter of 35 nm owing to geometrical confinement imposed by the pore curvature. In contrast to the thin film, which can be regarded as infinite in 2D, the perimeter of the pore walls is very small, which precludes all lamellar orientations except the one with the growth direction parallel to the pore axis.

References:

- (1) Bearzotti, A.; Bertolo, J. M.; Innocenzi, P.; Falcaro, P.; Traversa, E. *Journal of the European Ceramic Society* **2004**, *24*, 1969–1972.
- (2) Tang, C. W.; VanSlyke, S. A. *Applied Physics Letters* **1987**, *51*, 913.
- (3) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science (New York, N.Y.)* **2001**, *293*, 1119–22.
- (4) Dimitrakopoulos, B. C. D.; Malenfant, P. R. L. **2002**, 99–117.
- (5) Defaux, M.; Vidal, L.; Möller, M.; Gearba, R. I.; Dimasi, E.; Ivanov, D. A. *Macromolecules* **2009**, *42*, 3500–3509.