Supporting Information

One Methylene Group in the Side Chain Can Alter by 90 Degrees the Orientation of a Main-Chain Liquid Crystal on an Unidirectional Substrate

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Experimental Section

Materials: The details of the synthesis and characterization of the poly(di-*n*-alkylsiloxanes) with number of C atoms per alkyl side-chain from two to six are described elsewhere.[1] The polymer characteristics are given in Table S.1. The experimental details concerning PTFE rubbing and nanotemplates impregnation are described below.

Atomic Force Microscopy (AFM): AFM experiments were carried out with a Nanoscope IV Multimode AFM (Veeco Metrology Group) in Tapping Mode, which is most suitable for soft materials imaging. Tapping mode Si probes from Nanosensors were used (PPP-NCL, resonant frequency 172-191 kHz, spring constant 33-47 N/m).

Grazing-Incidence X-ray Diffraction (GIXD): The analyzed samples were contained in a chamber with Kapton windows equipped with a computer-controlled heating stage Instec HCS402. The focused beam of 0.25 mm vertical × 0.5 mm horizontal was hitting the film at an incidence angle θ_{inc} of 0.2°. The 2D diffraction patterns were collected using a CCD detector from Princeton Instruments having a 120 mm × 120 mm image area (2084 × 2084 pixels). Each sample was measured in the machine direction (MD), i.e. when the beam is parallel to the rubbing direction, and in the transversal direction (TD), that is perpendicular to the rubbing sense.

Table S1. Molecular weight distribution and thermal characteristics of poly(di-*n*-alkylsiloxanes).

Sample	number of C atoms per side-chain, *n*	M_w, kg/mol	PDI [a]	T_m, °C [b]	T_i, °C [c]
PDES	2	573	1.5	17	50
PDPS	3	461	1.6	70	224
PDBS	4	34	1.5	-19	310
PDPenS	5	325	1.3	-19	330
PDHS [d]	6	681	1.9	14	322

[a] polydispersity, [b] melting temperature, i.e. the transition from the crystal to mesophase, [c] isotropization temperature, [d] copolymer poly(di-pentyl/hexylsiloxane) with the monomer ratio of 10/90

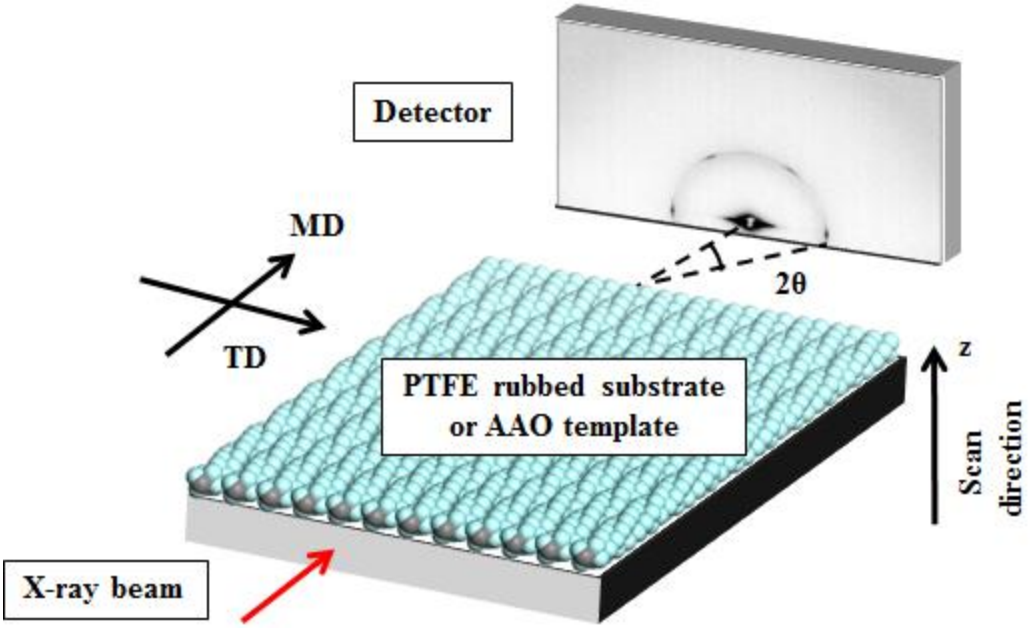

Figure S1. Schematics of the experimental Grazing-Incidence and Microfocus X-ray diffraction setups. Rubbed PTFE substrate and AAO template were used for the GIXD and μXRD experiments, respectively. MD and TD stand for machine and transversal directions with respect to the PTFE-rubbed substrate.

Microfocus X-ray diffraction (μXRD): The measurements were performed in transmission with the pore axis normal to the X-ray beam using crossed-Fresnel optics and wavelength of 1.0 Å. The illustration of the experiment is shown in Figure S.1. The images were recorded with a Frelon fast CCD with a pixel size of 50 microns (not rebinned) and a 16-bit readout. The spot size of the monochromatic X-ray beam at the focus point was about 1.0 micron along both axes. The norm of the scattering vector s ($s=2\sin\theta/\lambda$) was calibrated using diffraction pattern of corundum. The region of interest was selected with an on-axis optical microscope operated in reflection mode. A beam monitor installed upstream the sample provided dose-monitoring for

online exposure normalization. The sample was scanned along the pore axis with help of an x-y gantry. The diffraction patterns were collected using a step of 1.0 μm. The data reduction and analysis including geometrical and background correction, visualization and the radial as well as azimuthal integration of the 2D diffractograms were performed using home-built routines designed in Igor Pro software (Wavemetrics Ltd.).

Observation of orientational defects in the PDPenS films.

The X-ray measurements allow observing the orientational defects in the films of PDPenS. Notably, in the TD pattern, the meridional peak with the d-spacing of 11.78 Å is stronger and slightly wider than its two off-meridional counterparts, whereas they are expected to have identical intensity for the defect free film. The MD pattern displays a strong difference between the intensity of the meridional peak and the two counterparts. The likely explanation is that the high nucleation rate of PDPenS on PTFE substrates limits the time of the mesophase growth and therefore precludes formation of well-organized lamellae, which had has sufficient time to undergo thickening.

Preparation of PTFE-rubbed substrates: The PTFE rubbing was performed using a home-built machine operated at 300 °C at a deposition rate of 0.63 mm s^{-1}. During rubbing, a thin PTFE film is deposited on the substrate, in which the chains are aligned in the rubbing direction.[2] Subsequently 5 % wt polymer solution was spin-coated on top.

Impregnation of nanotemplates: The wetting of the nanoporous alumina membranes was done with the same poly(di-*n*-alkylsiloxanes) concentration as for spin-coating. The AAO templates with 200 and 35 nm pore size were supplied by Whatman Ltd. and SmartMembranes GmbH, respectively. The thickness of the template with 200 nm pores was 60 μm, while the one with 35 nm pores - 50 μm. The honeycomb morphology of the membranes consisting of isolated channels perpendicular to the surface was verified using Scanning Electron Microscopy (SEM) and Small Angle X-ray Scattering. The extent of membrane pores infilling can be appreciated for example by comparing the SAXS signal originating from the AAO template and 10 reflection from the hexagonal mesophase of PDAS.

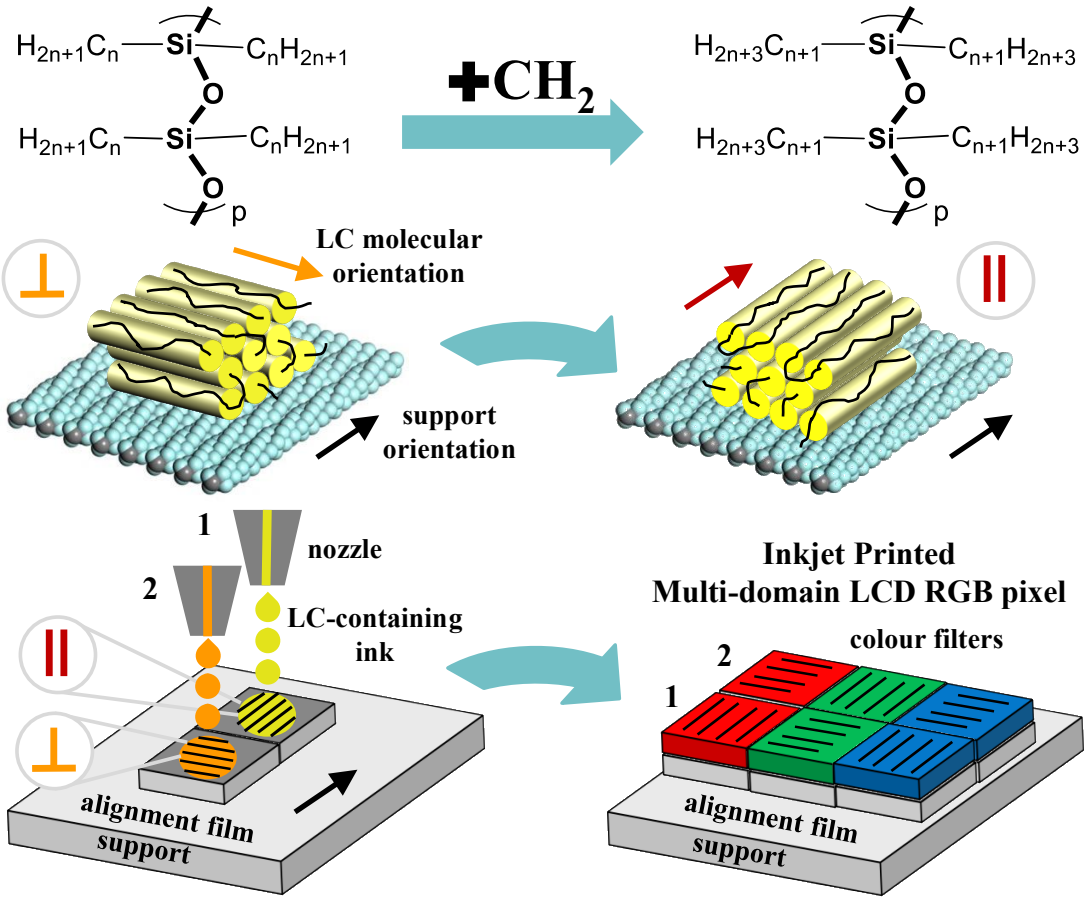

Figure S2. Schematics of the two mechanisms of the LC alignment in a series of model poly(di-*n*-alkylsiloxanes) PDAS: grapho-epitaxy (left) and molecular epitaxy (right). Addition of one CH_2 group to the side chain can change the macromolecular orientation by 90 degrees. Example of a multi-domain colour LCD where each pixel contains domains oriented according to the mechanisms of true molecular epitaxy and grapho-epitaxy. Such technology does not require buffing of the substrate for LC alignment and allows wider viewing angels.

References

(1) Out, G. J. J. Poly(di-N-Alkylsiloxane)s, Synthesis and Molecular Organization, University of Twente, The Netherlands, 1994.

(2) Wittmann, J. C.; Smith, P. Highly Oriented Thin Films of Poly(tetrafluoroethylene) as a Substrate for Oriented Growth of Materials. *Nature* **1991**, *352* (6334), 414–417.