

## Biaxial alignment of block copolymer-complex lamellae†

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Microphase-separated lamellar block copolymers can be oriented perpendicular to a substrate. The application of this attractive configuration as a template for nanostructure fabrication requires additionally long-range in-plane alignment of the lamella, for which no simple procedures are available. Here we present a convenient solution to this problem by exploiting the combination of supramolecular liquid-crystalline ordering of the block copolymer in combination with PTFE rubbing technology. The mesogenic ligands incorporated in one of the blocks interact with the substrate and control the self-assembly, rendering a vertical orientation of the microdomains. In addition the vertical lamellae orient parallel to the friction-deposited PTFE layer leading to long-range lateral ordering, providing unique new possibilities for block copolymer nanotechnology.

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### Introduction

Microphase separation of block copolymers (BCPs) leads, depending on composition and molecular mass, to various highly ordered morphologies with dimensions in the nanometer range.<sup>1</sup> Thin films of BCPs are of particular interest because they can be applied as templates for large-scale nanopatterning. In this situation, the domain structure depends on the surface energies of the blocks as well as the geometrical constraints introduced by confinement. Therefore, lamellar structures have a strong tendency to orientate parallel to the substrate, leading to unstructured film surfaces. Two methods have been used to orient the block interfaces perpendicularly. First the substrate can be grafted with brush layers of a random copolymer, chosen to neutralize the BCP-substrate interactions.<sup>2</sup> In the case of a cylindrical morphology, due to the symmetry of the system, this suffices to obtain unique perpendicular patterns. To obtain a uniform structure, long-range in-plane alignment has still to be induced. Alternatively, one can use comb-coil BCPs in which the comb-like block forms a smectic liquid crystal phase with the smectic layers perpendicular to the block interfaces. In thin films the mesogenic interactions at the substrate usually lead to smectic layers parallel to

the substrate, resulting in perpendicular block interfaces almost for free.<sup>3,4</sup> Again an additional process is needed to obtain azimuthal (in-plane) alignment of the perpendicular lamellae.

Considerable research has been directed towards obtaining periodic structures of BCP films either by employing corrugated substrates<sup>5</sup> or by applying external fields. These include electric fields,<sup>6</sup> epitaxy<sup>7</sup> and graphoepitaxy,<sup>8</sup> directional crystallization,<sup>9</sup> solvent evaporation,<sup>10</sup> and shear.<sup>11</sup> In this work we concentrate on the problem of creating azimuthal long-range order of perpendicular lamellae, with which we started. We use supramolecular comb-coil BCPs to control the microphase separation and the orientation of the microdomains.<sup>12–17</sup> In this approach, molecular mesogens are grafted to the polymer backbone *via* secondary interactions (*i.e.* hydrogen bonds, ionic interactions, metal ligation) to form a block with comb-like polymers. While the comb-coil BCP self-assembles into well-defined microstructures, the mesogenic units order into smectic layers inside one of the domains. The latter provides the desired starting structure of block interfaces perpendicular to the substrate.

Unidirectional sliding of a rod of polytetrafluoroethylene (PTFE) against a smooth and rigid surface (*e.g.* glass), results in a friction-deposited layer of single-crystalline PTFE oriented along the sliding direction.<sup>18–20</sup> The properties of the resulting surface are well documented and enable uniaxially oriented growth of organic material over macroscopic scales.<sup>19–24</sup> However, reports addressing the orientation of a coil-coil BCP on such a transferred layer are still scarce. The difficulty is that the physical properties of the blocks (coil structure) are only weakly sensitive to the crystal structure of the underlying

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substrate. In this work we choose ligands that not only interact specifically with one of the blocks as mentioned above, but also adsorb physically onto a PTFE-rubbed substrate.<sup>22</sup> The interaction of the ligands with the PTFE layer controls the in-plane orientation of the microdomain structure, while the stoichiometry of the complex defines the comb-coil BCP morphology.

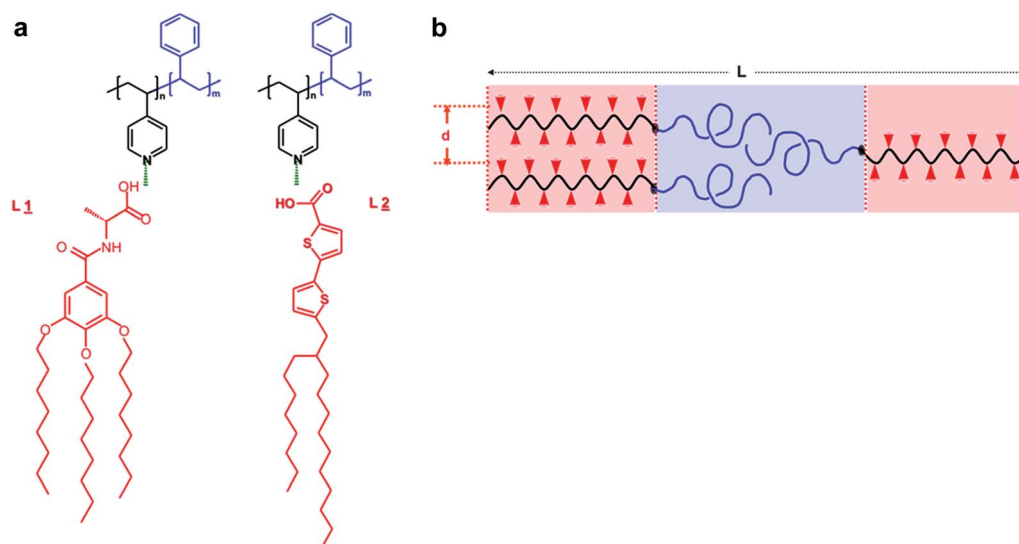
Two structurally different ligands have been selected with a terminal carboxylic acid group that forms a complex with the polybase P4VP. PS is used as the other block. In both cases thin films with 75% complexation generate lamellae. Note that this approach circumvents the need for laborious synthesis of several BCPs as the properties can be tailored by adjusting the attached mesogens. Because the ligands form stacks parallel to the SiO<sub>2</sub> substrate, the BCP lamellae orient perpendicularly to the film<sup>4</sup> but still lack azimuthal order, as anticipated. The friction-deposited PTFE layer consists of parallel stripes with an average height of about 4 nm. We find that on such a substrate, the lamellae of the BCP complex not only remain orthogonal to the interfaces but additionally align uniaxially along the PTFE stripes.

In the following we first discuss the morphology and orientational order of the lamellar ligands. We combine scanning

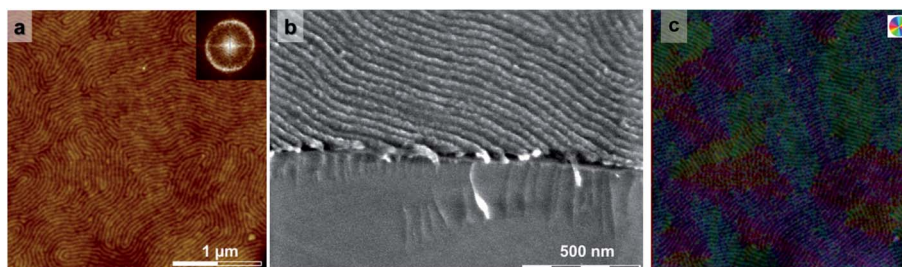
force and field-emission electron microscopy (SFM and FE-SEM) to assess the homogeneity and surface structure of films with thicknesses of 40–100 nm. FE-SEM also provides a view of the internal structure of the lamellae and their orientation relative to the support. In the second part, we present results from grazing-incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) for one of the samples. The combination of these techniques allows presenting a full quantitative model of the uniform film structure.

## Results and discussion

The first BCP under investigation is polystyrene-*block*-poly-4-vinylpyridine, PS<sub>330</sub>-P4VP<sub>130</sub>, in which the subscripts denote the degree of polymerization. By itself it microphase separates into a cylindrical morphology. The ligands, shown in Scheme 1, are denoted as **L1** and **L2**, respectively. Their properties are given in Fig. S1 and S2 of the ESI.† In short, both compounds crystallize in bulk with melting temperatures around 114 and 45 °C, respectively. In thin films they self-assemble into dimers that in turn form either columnar stacks (**L1**)<sup>25</sup> or lamellar ones (**L2**). The ligands readily bind to the pyridine unit through



**Scheme 1** (a) Structure of the ligands 4'-(3'',4'',5''-tris(octyloxy)benzamido)-propanoic acid denoted as **L1** and 5'-(2-octyldodecyl)-2,2'-bithiophene-5-carboxylic acid denoted as **L2** with hydrogen bonds between P4VP and the ligands. (b) Schematic illustration of the lamellar microphase-separated structure in the BCP complex, in which the ligands form smectic layers with the layer normal parallel to the BCP interfaces. Note that the scheme is not to scale:  $d \approx 4$  nm and  $L \approx 30$  nm.



**Fig. 1** Thin film morphology of PS<sub>330</sub>-P4VP<sub>130</sub> (**L1**)<sub>0.75</sub>. (a) SFM height image with the 2D FFT as the inset indicating an interlamellar spacing of about 45 nm, and (b) tilted cross-sectional FESEM image (45°). (c) False color orientation map of (a) indicating an average domain size of about 500–700 nm.

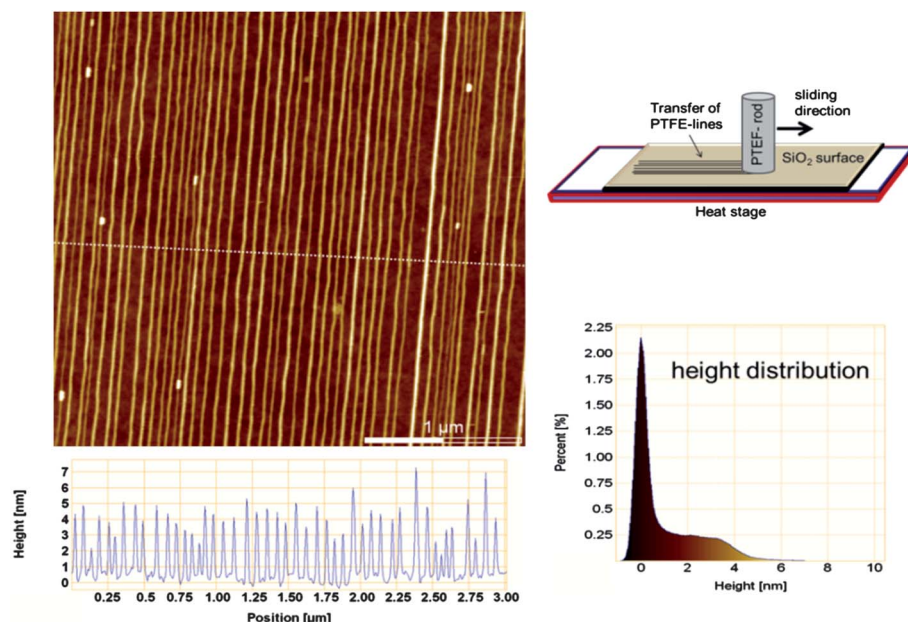


Fig. 2 SFM height image of friction-transferred PTFE stripes. The height distribution and the cross-section profile give a mean height of about 4 nm.

hydrogen bonding.<sup>12–14</sup> However, depending on the strength of the hydrogen bonds, steric interaction limits the degree of complexation  $x$  (average number of ligands per monomer) and phase separation might occur.<sup>15</sup> A value of  $x = 0.75$  ensures that the BCP complex self-assembles in a lamellar morphology while the ligands form smectic layers orthogonal to the block-interfaces. Scheme 1 illustrates schematically the hydrogen-bonded structure.

Fig. 1a shows an SFM height image of a thin film of the BCP complex PS<sub>330</sub>–P4VP<sub>130</sub> (**L1**)<sub>0.75</sub> on bare SiO<sub>2</sub>. Its 2D-FFT is a halo indicating short-range orientational order and a period of about 45 nm. A side view of the edge of a fracture (Fig. 1b) clearly indicates lamellae perpendicular to the substrate plane. From Fig. 1c we derive an average domain size of about 500–700 nm. The film thickness is about 80 nm, almost twice the BCP period. Similar results hold for the BCP complex PS<sub>190</sub>–P4VP<sub>100</sub> (**L1**)<sub>0.75</sub> with a lamellar period of 26 nm (ESI S4†). For the present thicknesses confinement effects due to the surface field can be excluded: the perpendicular orientation of the lamellae is solely associated with the ligand organization.<sup>16,17</sup>

Unidirectional sliding of a PTFE rod against an SiO<sub>2</sub> substrate causes the transfer of regular stripes (Fig. 2). The structure of the resulting PTFE films has been well studied.<sup>18,24,26</sup> Fig. 3a shows that the pure BCP forms P4VP cylinders that are randomly oriented in the PS layers. Obviously, without the ligand the microdomain structure is insensitive to the underlying PTFE configuration. However, the BCP ligand complex shows a remarkable uniaxial orientation of the lamellae parallel to the PTFE stripes (Fig. 3b and c). The 2D-FFT shows well-defined peaks orthogonal to the rubbing direction indicating a periodicity of 43 nm. Evidently, the lamellar period is not influenced by the underlying PTFE stripes. A cross-sectional view of the film (Fig. 3c) shows that the block lamellae maintain their vertical orientation.

For the second ligand (PS<sub>330</sub>–P4VP<sub>130</sub>(**L2**)<sub>0.75</sub>; see Scheme 1) again at  $x = 0.75$  a lamellar phase is formed. In thin films, the lamellae are orthogonal to the SiO<sub>2</sub>–air interface with no in-plane orientational order as before. As expected, on a friction-deposited PTFE layer the lamellae align along the PTFE stripes (Fig. 4) while the 2D-FFT indicates arcs orthogonal to the rubbing direction. From the peak position we calculate a periodicity of

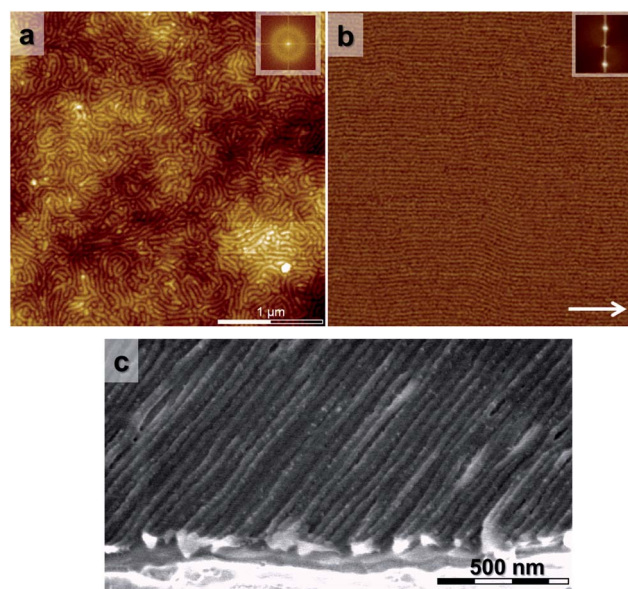
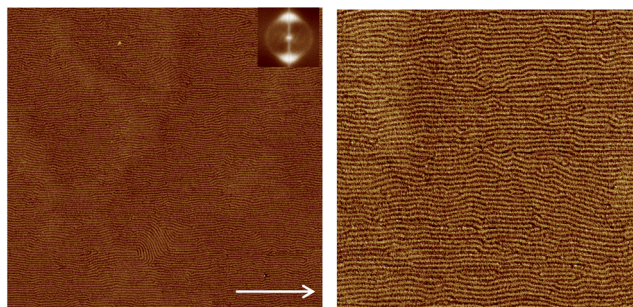


Fig. 3 Images of a thin film deposited on PTFE stripes after annealing for 24 h in benzene vapor. (a) SFM height image of the cylindrical morphology of PS<sub>330</sub>–P4VP<sub>130</sub> without ligands showing random orientations. (b) Phase SFM image of the BCP complex PS<sub>330</sub>–P4VP<sub>130</sub> (**L1**)<sub>0.75</sub> (scan size  $3 \times 3 \mu\text{m}^2$  in  $512 \times 512$  lines) with the corresponding 2D-FFT as inset from a scan of  $10 \times 10 \mu\text{m}^2$ . The arrow indicates the rubbing direction. (c) FESEM image of a cross-section viewed at a tilt angle of  $45^\circ$ .



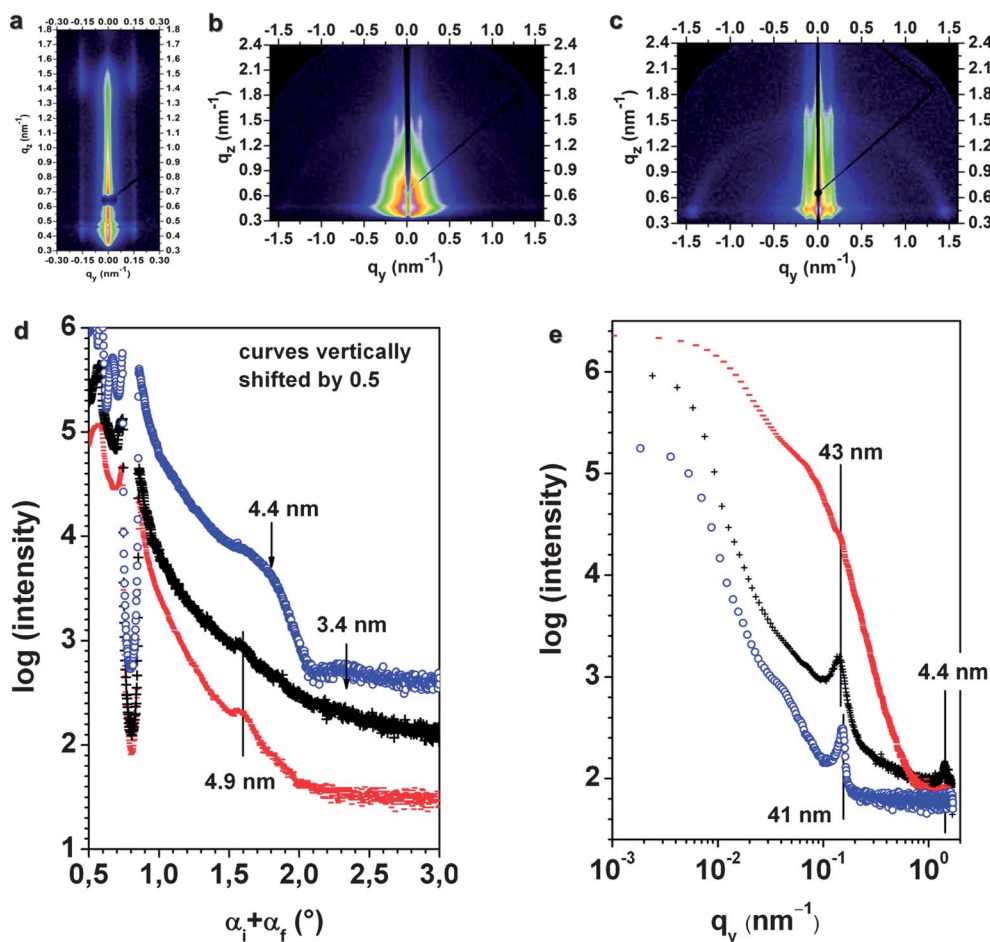


**Fig. 4** SFM phase images of PS<sub>330</sub>-P4VP<sub>130</sub>(**L2**)<sub>0.75</sub> on rubbed PTFE (scan size  $6 \times 6 \mu\text{m}^2$  in  $4096 \times 4096$  lines). The arrow indicates the rubbing direction. The inset shows the 2D FFT of a  $20 \times 20 \mu\text{m}^2$  image. The right image is an enlarged view ( $3 \times 3 \mu\text{m}^2$ ).

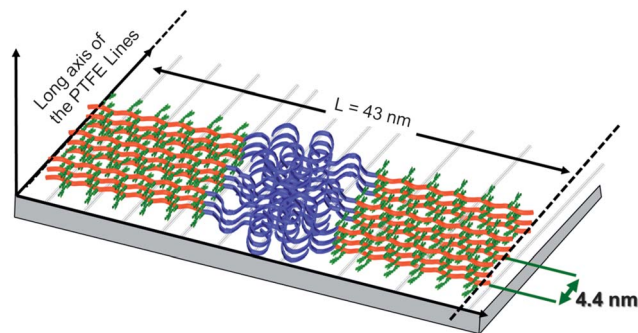
about 46 nm. We want to emphasize that these results should be considered as a proof of principle. No attempts have been made yet to optimize the rubbing procedure (so far done by hand) and thus to maximize the quality of the parallel structures.

Grazing-incidence wide and small angle X-ray scattering (GIWAXS<sup>27</sup> and GISAXS<sup>28</sup>) was performed on about 40 nm thick

films of PS<sub>330</sub>-P4VP<sub>130</sub>(**L2**)<sub>0.75</sub> in order to gain statistically relevant information about the inner film structure inaccessible to SFM. Both an unoriented sample and a sample aligned by rubbed PTFE were probed. In the latter case the X-ray beam was oriented either parallel or perpendicular to the alignment direction (long direction of the PTFE fibers). The full 2D GISAXS data and some line cuts are displayed in Fig. 5. Vertical line cuts from the 2D GISAXS data yield information about structures along the surface normal (see Fig. 5d). Horizontal line cuts from the 2D GISAXS data contain information about lateral structures, *i.e.* structures parallel to the sample surface and perpendicular to the X-ray beam (see Fig. 5e).<sup>28</sup> In the horizontal line cuts, the simplest feature is the peak corresponding to an in-plane distance of 41–43 nm, the BCP lamellar period (compared to about 45 nm from SFM). Moreover, at larger  $q_y$  values corresponding to 4.4 nm in the horizontal line cut, an additional peak is found for perpendicular PTFE orientation. In the vertical line cut two peaks/features are found at positions corresponding to 3.4 and 4.4 nm (marked in Fig. 5d), respectively. As both values occur simultaneously in the unaligned samples, none of them can originate from PTFE. The length of the **L2** ligand in a fully stretched conformation is about 1.8 nm.



**Fig. 5** Top: 2D GISAXS data of PS<sub>330</sub>-P4VP<sub>130</sub>(**L2**)<sub>0.75</sub> for (a) an unoriented sample and for oriented samples with the X-ray beam (b) parallel and (c) perpendicular to the preferred PTFE direction. Bottom: vertical detector cuts (d) and horizontal out-of-plane cuts (e). Red curves (—) correspond to parallel PTFE orientation, black curves (+) to perpendicular PTFE orientation and blue ones (O) to no orientation.



**Fig. 6** Model for the structure of PS<sub>330</sub>-P4VP<sub>130</sub> (**L2**)<sub>0.75</sub> on a rubbed PTFE substrate.

Hence the dimension of 4.4 nm corresponds to a double layer of two ligands attached in opposite directions to the P4VP chain (smectic layer period). The first dimension of 3.4 nm is close to the length of a free ligand dimer (about 3.6 nm). Indeed at  $x = 0.75$  free ligands can be expected to form a dynamic equilibrium with ligands bound to the polymer.<sup>29,30</sup> However, isolated dimers would not give an X-ray signal and we are obliged to assume that small “clusters” of free dimers exist inside the smectic layers consisting of polymer-bound ligands. Such a type of smectic demixing (in terms of short-range order, hence without macroscopic phase separation) has been proposed earlier to explain the X-ray features of another system with a hydrogen-bonded polymer with mesogenic side chains.<sup>31</sup>

Regarding the orientation of the ligand lamellae we note that in the aligned sample a signal corresponding to 4.4 nm (the smectic layer period) is only observed in the horizontal line cuts when the X-ray beam is *perpendicular* to the preferred PTFE direction. From this observation we can conclude a rather simple structure, depicted in Fig. 6 for a single block period. Both the block lamellae and the smectic layers are perpendicular to the substrate and mutually orthogonal. The origin of the in-plane order of the BCP lamellae is due to the ligands that want to minimize their orientational elasticity by lining up parallel to the PTFE stripes. This process is very similar to the situation in liquid-crystal displays,<sup>32,33</sup> in which the nematic director aligns to grooves in the substrates.

To determine the internal structure of the ligand lamellae on a smaller scale GIWAXS has been used (Fig. 7). For an unaligned

sample the only feature is a broad ring with a maximum corresponding to 0.47 nm. Bulk WAXS on the strongly related homopolymer [P2VP (**L2**), not shown here] gives a similar strong broad ring at 0.46 nm. The obvious interpretation is to attribute this bump to a short-range inner structure of the smectic ligands (stacks of ‘liquid’ layers). This situation corresponds to conventional smectic-A liquid crystals. In the GIWAXS pattern of aligned samples (ESI Fig. S5†) we still observe the broad ring. In addition a multitude of discrete peaks is found that can be assigned to the underlying PTFE structure by comparing with the GIWAXS data for a pure friction-deposited PTFE film.<sup>26</sup> No evidence has been found for crystallinity inside the smectic layers of the ligands.

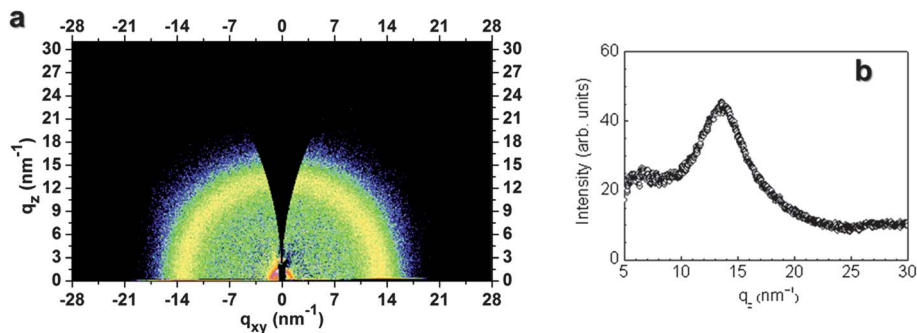
## Conclusion

We have presented the principle of a method to align block copolymer lamellae perpendicular to the air/substrate interface with additionally long-range in-plane orientational order on a macroscopic scale. This is achieved by a combination of supramolecular liquid crystal order in the block copolymer and a substrate with a thin PTFE layer produced by friction-deposition. Remarkably, the thickness of the aligning PTFE layer is only *ca.* 4 nm while the block copolymer film thickness is of the order of 100 nm. Wedge-shaped mesogens control the self-assembly of the block copolymer rendering a vertical orientation of the microdomains. In addition the vertical lamellae orientate parallel to the preferred direction in the PTFE layer leading to long-range lateral ordering. This technique has the advantages of simplicity as compared to various other approaches and creates new opportunities for manufacturing nanoscopic device components. An additional asset is the possibility to introduce functionality by altering the structure of the ligand or by selective disruption of the hydrogen bonds.

## Experimental

### Materials

Two block copolymers were investigated: PS<sub>330</sub>-P4VP<sub>130</sub> ( $M_w/M_n = 1.07$ , PS mass fraction  $\Phi_{PS} = 0.69$ ) and PS<sub>190</sub>-P4VP<sub>100</sub> ( $M_w/M_n = 1.12$ ,  $\Phi_{PS} = 0.65$ ), in which the subscripts denote the degree of polymerization. They were synthesized by living anionic polymerization, as described elsewhere.<sup>34</sup> All the chemicals and solvents were analytical pure and were purchased from Sigma-Aldrich.



**Fig. 7** (a) 2D GIWAXS data of an unoriented sample of PS<sub>330</sub>-P4VP<sub>130</sub> (**L2**)<sub>0.75</sub>. (b) Corresponding slice-integration over 80–100°.

## Synthesis of the ligands

The synthesis of ligand **L1** has been described previously.<sup>25</sup> **L2** was prepared according to the following procedure. *n*-BuLi (1.6 M, 0.95 mL, 1.52 mmol) was added dropwise at 0 °C to a solution of 5-(2-octyldodecyl)-2,2'-bithiophene<sup>35</sup> (0.50 g, 1.5 mmol) in 100 mL dry THF. After 1 h the reaction mixture was cooled down to −78 °C and CO<sub>2</sub> was flowed into the solution for 5 h. Subsequently the mixture was heated up to room temperature and stirred overnight. 1 M HCl was added dropwise, and the mixture was diluted with dichloromethane. The organic phase was dried over MgSO<sub>4</sub>. After evaporation of the solvents, the crude mixture was purified by column chromatography (SiO<sub>2</sub>, *n*-hexane : ethyl acetate, 3 : 1 (v/v)) resulting in 5'-(2-octyldodecyl)-2,2'-bithiophene-5-carboxylic acid (**L2**) as a brownish solid (0.16 g, 22%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ [ppm] = 7.74 (1H, d, *J* = 4.0 Hz, *H*<sub>4</sub>), 7.12 (1H, d, *J* = 3.6 Hz, *H*<sub>3'</sub>), 7.07 (1H, d, *J* = 4.0 Hz, *H*<sub>3</sub>), 6.68 (1H, d, *J* = 3.6 Hz, *H*<sub>4'</sub>), 2.72 (2H, d, *J* = 6.8 Hz, CH–CH<sub>2</sub>–T), 2.72 (1H, bs CH–CH<sub>2</sub>–T), 1.32–1.20 (32H, m, alkyl CH<sub>2</sub>), 2.72 (6H, t, *J* = 6.8 Hz, CH<sub>3</sub>). MS *m/z* (CI): 491 [M<sup>+</sup>]. Anal. calcd for C<sub>29</sub>H<sub>46</sub>O<sub>2</sub>S<sub>2</sub>: C 70.97, H 9.45%. Found C 70.79, H 9.46%.

## Complex preparation

The complexes were prepared according to the known literature procedure.<sup>16</sup> In brief, the BCP and the ligand were dissolved in chloroform and stirred overnight in the dark. Subsequently, the solvent was evaporated by rotary evaporation under reduced pressure. The solid was collected, re-dissolved in chloroform, and filtered with a 0.2 μm PTFE syringe filter. The final concentration of the solutions was controlled to 0.5 wt% and stored in brown GC vials. Hydrogen bonding between the BCP and the ligand was assessed with infrared spectroscopy, see ESI† for details. All solvents used were of analytical grade and were bought from VWR GmbH, Germany. Silicon wafers (100) were purchased from Si-Mat GmbH.

## Film preparation

The films were prepared by spin coating a solution of the block copolymer complex in chloroform onto a pre-cleaned silicon wafer or onto a PTFE rubbed SiO<sub>2</sub> surface. Unidirectional rubbing was carried out manually. In practice, the wafer was placed on a hot plate maintained at 300 °C and a PTFE rod was rubbed once against the hot surface of the substrate. The films were annealed for 24 h at room temperature in a closed vessel containing a small amount of benzene.

## Characterization methods

The morphology of the thin films was investigated by tapping mode SFM (NanoScope V, BrukerAXS) under ambient conditions.

Scanning electron microscopy (SEM) was performed using a Hitachi S4800 high-resolution field emission scanning electron microscope with an accelerating voltage of 1–1.5 kV. In order to avoid any artifacts no metal coating was used. To enhance the contrast the ligand was removed by washing the thin film in

ethanol, a good solvent for the ligand but not for PS. After washing the morphology of the micro-phase separation was still the same, though shrinking occurred of the domains in which the ligand was originally present.<sup>17</sup>

IR spectra were recorded using a Nicolet NEXUS 670 Fourier Transform IR spectrometer at a resolution of 4 cm<sup>−1</sup>.

Grazing incidence X-ray scattering (GIWAXS and GISAXS) was performed at the synchrotron beamline BW4 of the DORIS III storage ring (HASYLAB at DESY) in Hamburg. The X-ray wavelength used was λ = 0.138 nm. The sample-detector distances were set to 107 (GIWAXS) and 2088 mm (GISAXS). For GIWAXS the incident angle was fixed to α<sub>i</sub> = 0.2° and for GISAXS α<sub>i</sub> = 0.4°. The scattering signal was recorded with a two-dimensional (2D) detector (MARCCD, 2048 × 2048 pixels). The specular peak and/or the small angle scattering region were blocked by a (rod-shaped) beam stop. Details of the GISAXS and GIWAXS set-up can be found elsewhere.<sup>27,36</sup>

The coordinate system is chosen with the (*x*,*y*)-plane being defined by the sample surface with the *x*-axis oriented in the direction of the X-ray beam. The *z*-axis is oriented perpendicular to the sample surface. Therefore the components of the scattering vector *q* are  $q_x = 2\pi(\cos \psi \cos \alpha_f - \cos \alpha_i)/\lambda$ ,  $q_y = 2\pi(\sin \psi \cos \alpha_f)/\lambda$  and  $q_z = 2\pi(\sin \alpha_i + \sin \alpha_f)/\lambda$  with the incident and exit angles α<sub>i</sub> and α<sub>f</sub>. The scattering plane is defined by these incident and exit angles α<sub>i</sub> and α<sub>f</sub> and scattering outside this plane is probed under an out-of plane angle ψ.<sup>28</sup> In GIWAXS  $q_{xy} = \sqrt{q_x^2 + q_y^2}$  is used. More details on GISAXS can be found in ref. 37.

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