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# Alignment of Lamellar Block Copolymers via Electrohydrodynamic-Driven Micropatterning\*\*

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The combination of top-down approaches with block copolymer bottom-up self-assembly in a single processing step<sup>[1–3]</sup> has received increasing attention because of its potential use for sub-100-nm lithography. The so far unachieved principle employs block copolymer self-assembly for the controlled formation of 10-nm-sized patterns, which are interfaced by larger structures providing the addressability of self-assembled nanodevices. The successful implementation of such a device requires a simultaneous control over the self-assembly process and the large-scale structures. Both have been demonstrated individually in a number of ways, but their combination remains elusive.

Block copolymers are ideal building blocks for 10-nm-sized structures because of their special molecular architecture. These macromolecules typically consist of two or more chemically dissimilar polymers which are covalently joined. The competition between the inherent incompatibility of the constituent polymers and their chemical linkage leads to a self-assembling process with structure sizes in the range of 5 to 50 nm.<sup>[4]</sup> The alignment of microdomains perpendicular to the substrate is important because this is a typical requirement for nanotechnological applications<sup>[5]</sup> and can be achieved by the confinement of thin block copolymer films or the application of external fields, such as mechanical shear fields and electric fields. The resulting nanostructures which are accessible from the air

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surface can for example be partially degraded thereby serving as templates for metals<sup>[6]</sup> and semiconducting<sup>[7]</sup> nanowires.

The long-range lateral control over the orientation of block copolymer domains in polymer melts and solutions has been demonstrated in a number of ways, such as the use of steady shear,<sup>[8–10]</sup> capillary extrusion,<sup>[11]</sup> and elongational flow.<sup>[12,13]</sup> The roll-casting of solutions<sup>[14–17]</sup> or shearing of block copolymer films with silicon rubber pads<sup>[18]</sup> also results in a long-range order of microphase-separated block copolymer morphologies. The alignment of block copolymer morphologies using electric fields<sup>[19,20]</sup> is particularly interesting because of the level of control that can be achieved by this method. Since the domains follow the electric field lines,<sup>[21-23]</sup> the local alignment of the microphase morphology both perpendicular<sup>[24,25]</sup> and parallel<sup>[26-30]</sup> to the film-normal is possible. The long-range nature of electric fields results in an equally long-range alignment of the microphase morphology. Additionally large-scale topographic structures can be generated in a controlled fashion by a electrohydrodynamic (EHD) film instability.

EHD pattern formation is a technique in which a liquid dielectric interface is destabilized by an electric field that is applied normal to this interface. In a homogeneous field, this gives rise to micrometer-sized columns with well defined diameter and spacing.<sup>[31,32]</sup> By using heterogeneous fields (generated, e.g., by micro-patterned electrodes) nearly any pattern can be replicated into a homopolymer film.<sup>[33]</sup> Russell and coworkers used electrostatic forces to pattern block copolymer films with a cylindrical microphase morphology to create well-ordered patterns of columns, tens of micrometers in size.<sup>[34]</sup>

Here we discuss the interplay of EHD structure formation with the structural control over a block copolymer microphase morphology. In contrast to the systematic earlier work by Russell and coworkers about cylindrical phase morphologies, we have investigated a confined lamellae-forming block copolymer in a much higher degree of lateral confinement. The main difference to the earlier work lies in the lateral anisotropy of standing lamellae and in the frustration of such a morphology when confined into a column. Upon temperature or solvent vapor annealing, initially flat block copolymer films are destabilized by electric fields leading to the formation of micrometer-sized pillars perpendicular to the substrate. This coarse pattern has a further substructure, which arises from the alignment of the microphase-separated lamellar block copolymer morphology parallel to the electric field lines, i.e., parallel to the axis of the columns (Fig. 1b).

The experimental setup is summarized in Figure 1a. Films of symmetric polystyrene (PS)-*b*-poly(methyl methacrylate)



Figure 1. Schematic drawing of the experimental procedure. a) Experimental setup of the EHD pattern formation experiments. The outer box represents the atmosphere of the experiment which is either at  $T > T_g$ of the block copolymers or a controlled solvent vapor atmosphere. The sample chamber contains a block copolymer film supported by a silicon wafer and a top electrode (either topographically structured or planar) which is placed above the polymer film leaving an air gap. A voltage is applied between the electrodes while the sample is annealed. b) EHD pattern formation: columns span the two electrodes. The columns have an internal structure consisting of lamellar microdomains which are aligned perpendicular to the electrodes and parallel to the electric field vector. c) Schematic cross-sections through the columns of (b) showing three possible in-plane configurations of the lamellar microdomains. d) Simulation representing the field distribution in an intermediate stage of the EHD structure formation of a polymer film. The simulation shows an initially 700 nm thick PS layer with a dielectric constant of 3.4 in a capacitor with a plate spacing of  $2 \,\mu$ m and an applied voltage of 80 V. The pattern is induced by a 400 nm wide, 150 nm high central protrusion on the 4.2  $\mu$ m wide top capacitor plate. The image clearly shows the lateral component in the field lines.

(PMMA) block copolymers (Table 1) were confined between two electrodes, leaving an air gap. The samples were annealed either by raising the temperature above the glass transition temperatures of the two components or in controlled solvent 
 Table 1. Characteristics of the diblock copolymers.

Polymer	Molecular weight [kg mol <sup>-1</sup> ]	Polydispersity	Source	
P(S-d8)31-b-PMMA31	62	1.09	PSS	
PS33-b-PMMA32.5	65.5	1.06	PSS	
PS89-b-PMMA95	184	1.05	PSS	

 $\mathsf{PSS} = \mathsf{Polymer \ Standards \ Service}.$ 

vapor atmospheres, and a DC voltage was applied. For high molecular weight polymers, temperature annealing is impractical because of their high melt viscosities. Solvent vapor annealing, in contrast, very effectively increases the polymer mobility at low temperatures, thereby significantly reducing the thermal degradation of the polymer.

Similar to the well-documented results using homopolymer films, the application of an electric field across a liquid/air bilayer leads to an array of polymer pillars that span the two electrodes. The pillars with a characteristic center-to-center distance are the result of the electrostatic pressure that overcomes the surface tension of the polymer-air interface. This structure formation process is well understood in terms of the balance between the destabilizing electrostatic energy (per area A),  $F_{\rm el} = 1/2 C U^2$  and the restoring surface tension  $F_{\gamma} = \gamma$ A, where U is the applied voltage, C the capacity of the film/air double layer, and  $\gamma$  the surface tension. For the capacities  $C_1$ and  $C_2$  for air and the polymer, respectively,  $F_{el}$  is lowered for a conformation that spans the electrode gap compared to the layered arrangement. Upon application of an electric field, the interplay of electrostatic destabilization and the restoring surface tension gives rise to an undulatory instability with a well-defined wavelength, leading eventually to a pattern of polymer columns. If an electrode with a design topography is used, the polymer pattern replicates the electrode pattern.

Figure 2 shows the pattern formation on the micrometer scale of films with two different molecular weights. The diameter and lateral positions of the columns are replicas of the design-pattern of the top electrode. The two annealing protocols (heating (Fig. 2a) and swelling in solvent vapor (Fig. 2b,c)) produced comparable results.

In difference to the EHD pattern formation of homopolymer films, the micrometer-sized block copolymer pillars reveal a 10 nm substructure in the high-resolution SEM images in Figure 3. These images were taken after degradation of the PMMA component by UV light and subsequent rinsing with acetic acid and Millipore water. They show individual high aspect ratio sheets of lamella, which are, aligned parallel to the axis of the pillars, along the lines of the electric field. The gaps in the polymer morphology arise from defects leading to a mechanical instability of some of the lamellar sheets, which were removed during the washing step. Only PS lamellae that extend down to the substrate survive the PMMA degradation and washing step. Interestingly, our finding that the standing lamellae extend down to the substrate differs from the recent results of Xu et al.,<sup>[29]</sup> reporting that surface-induced parallel





**Figure 2.** AFM images of micrometer-sized patterns of PS-*b*-PMMA films made by EHD lithography. a) P(S-d8)<sub>31</sub>-*b*-PMMA<sub>31</sub> film with an initial film thickness of 135 nm. The block copolymer film was annealed at 170 °C under an applied electric field of 40 V  $\mu$ m<sup>-1</sup> for 19 h. The pillar diameter of ~1  $\mu$ m and the inter-pillar spacing of 2  $\mu$ m were controlled by a topographically structured top electrode. The height of the pillars is around 410 nm. The inset shows a three dimensional view of the pillars. b) and c) Micropatterns of PS<sub>33</sub>-*b*-PMMA<sub>32,5</sub>. A 94 nm thick film was swollen in toluene vapor at *p*/*p*<sub>sat</sub> = 0.85 for 15 min, and 80 V were applied across the electrodes for 17 h. The patterned films were then slowly dried by reducing the *p*/*p*<sub>sat</sub> ratio down to 0 (pure nitrogen) in 17 steps of 30 s each, i.e., the film was dried very slowly. The samples were additionally dried in pure nitrogen for 5 min before removing the electric field. b) AFM image of 2  $\mu$ m wide and 660 nm high columns. The pattern sizes match the dimensions of the structured top electrode. c) AFM image of ~1  $\mu$ m high columns.

preferential orientation of some surface-near lamellae dominates over the electric field alignment effect.

The detailed alignment mechanism is somewhat complex and will therefore be addressed in a separate publication.<sup>[35]</sup> A brief indication of the alignment pathway is given in Figure 4, which shows the column formation at an intermediate stage. It shows an in-plane worm-like morphology of the copolymer in the parts of the film that has not yet been incorporated into the column. Inside the column this worm-like morphology is oriented along the column axis. Since the samples were not annealed before the electric field was aligned, Figure 4 indicates that the electric field perturbs the formation of laterally oriented lamellae. The resulting worm-like morphology aligns vertically in the columns partially because of the flow forming these structures, partially by the action of the electric field. In the final stage the equilibrium lamellar morphology forms inside the columns.

The in-plane arrangement of lamellae is intrinsically anisotropic. The confinement into columns therefore leads to the three different in-plane assemblies schematically shown in Figure 1c: onion-type concentric alignment of lamellae (Fig. 3a, arrow), bent lamellae pointing towards the column mantle (Fig. 3c) and parallel sheets (book sheets) (Fig. 3b). The in-plane orientation of the lamellae is the result of an interplay between surface interactions, electric field alignment during column formation, bending energy of the lamellae, and the energy associated with defects in the lamellar structure.

In particular, the small difference in PS and PMMA surface energies favors the parallel alignment of the lamellae at the column mantle. This is opposed by the in-plane components of the electric field during the intermediate stages of column formation. This effect is visualized by the outward bent field lines in the simulation of Figure 1d. Thirdly, the bending of the lamellae leads to a frustration of the polymer conformations, which also penalizes the formation of defects (bending singularities) in the lamellar morphology.

The relative importance of these three effects gives rise to the different in-plane morphologies in Figure 1c. The onion morphology is favored by a lowering of the surface energy, overcoming the lateral component in the electric field. The opposite case, that is, the dominance of the lateral field components over the reduction of surface free energy leads to the conformation of outward pointing lamellae (Fig. 1c, middle). Both conformations cause, however, the bending of lamella in the interior of the column and, because of polymer frustration, result in the formation of bending defects in the lamellar structure. The minimization of lamellar bending is the dominant effect for the book-sheet morphology, which has a non-homogeneous mantle boundary.

Interestingly, all three possible configurations are found, often on the same sample, irrespective of the type of annealing protocol and polymer molecular weight. While it is possible that the in-plane microphase morphology is not fully equilibrated, this is unlikely, given the fact that the lamellae are fully aligned along the column axis and the qualitatively similar results for both polymer molecular weights and annealing methods. This indicates that none of the free energies responsible for the three in-plane alignment described above is dominant, leading to strong fluctuations between them.

Careful examination of the SEM images in Figure 3 reveals the interplay of opposing free-energy contributions in close vicinity of the mantle. Most columns are surrounded by a single PS lamella, with the further inward lamellae pointing perpendicular to the mantle. This indicates that surface tension dominates the short-range morphology, while the longer ranged electrostatic forces dominate the lamellar arrangement in the near-mantle region further inside the column. The free energy associated with the bending of the lamellae and the creation of grain boundaries seems to be small in comparison, since all columns exhibit (sometimes elaborate) defect structures.



**Figure 3.** SEM images of the microphase morphology of PS-*b*-PMMA columns showing complete alignment of the lamellar microdomains normal to the substrate. The pillars were exposed to UV-light and rinsed in acetic acid and water to remove the PMMA phase. Before imaging, the films were coated with a 5 nm thick layer of gold. a) and b) Top view of pillars of P(S-d8)<sub>31</sub>-*b*-PMMA<sub>31</sub> formed at 170 °C with an applied voltage of 40 V for 22.5 h. Before removing the electric field, the samples were cooled down to room temperature. The initial film thickness was 135 nm, the air gap was 235 nm. The height of the pillars is 370 nm as measured by AFM. c) and d) Top view of PS<sub>89</sub>-*b*-PMMA<sub>95</sub> pillars. The initially 170 nm thick film was swollen for 20 min at  $p/p_{sat} = 0.85$  in toluene vapor and a voltage of 80 V was applied across the capacitor plates for 4.5 h. After drying the patterned films in pure nitrogen for 30 min, the electric field was removed. In the dry state, the columns are 2.5  $\mu$ m high.

In summary, we demonstrate a combined bottom-up and top-down approach based on electrohydrodynamic formation of surface patterns in thin films and the self-assembly of symmetric block copolymers within these patterns. The exposure of liquefied symmetric di-block copolymer films to an electric field gives rise to micrometer-sized columns, which can be lithographically controlled. Within each pillar the lamellar block copolymer domains are oriented parallel to the pillar axis, which is induced by the combination of shear alignment of the lamellae during EHD column formation with the direct interaction of the electric field with the block copolymer morphology. The structures formed on the micrometer length scale by the electrohydrodynamic instability compartmentalize the block copolymer microphase morphology. Three different in-plane morphologies are observed in a one-step process, which result from a interplay between the surface tension, electrostatic forces, and the frustration of polymer conformations caused by lamellar bending.



**Figure 4.** Intermediate stage of column formation of of PS-*b*-PMMA films. The contrast in the image is obtained by degrading the PMMA. The image reveals a lateral arrangement of a worm-like microphase morphology in the film surrounding the columns and the vertical arrangement of this morphology in the column, clearly indicating that the orientation of the alignment is changed during column formation.

#### Experimental

The block copolymers were obtained from Polymer Standards Service, Germany. The relative PS-PMMA volume fraction was close to 50% leading to a lamellar microphase morphology in the bulk. Samples with three different molecular weights were used to verify the universality of the reported phenomena. Thin block copolymers films were spin-cast from toluene solutions with block copolymer concentrations of 2 to 3 wt %. Typical spinning speeds were 3000 to 8000 rpm, resulting in film thicknesses between 100 and 200 nm. All silicon wafers were snow-jet [36] cleaned prior to use. Top electrodes were planar silicon wafers or topographically structured surfaces (purchased from eXtreme Lithography, Germany). Silicon top electrodes were rendered hydrophobic by the deposition of a 1H,1H,2H,2Hperfluorodecyltrichlorosilane (Fluorochem, 97%) self-assembled monolayer to reduce the adhesion of block copolymer. To ensure a good electrical contact the silicon substrates were coated on their backside with 2nm Cr and 100nm Au by thermal evaporation. ITO-coated glass slides were also used as top electrodes. The block copolymer coated bottom electrode was loaded into the sample chamber (Fig. 1a) and the upper electrode was mounted on top of the polymer film with the polished or structured side facing the film.

The as-prepared samples were annealed at temperatures above the glass transition temperature of the two blocks (T = 170 °C) or exposed to a well-controlled atmosphere of toluene vapor (a good solvent for both blocks) to induce mobility and facilitate equilibration. The solvent vapor pressure in the chamber was adjusted using a home-made apparatus [37–39]. Mass-flow controllers (MKS Instruments Model 1179A with a PR4000F readout) regulated the flux of the carrier gas N<sub>2</sub> through two lines. In one line, the N<sub>2</sub> was bubbled through a solvent-filled bottle resulting in a solvent-saturated gas stream. Both streams were mixed and passed through the sample chamber. The flow rates were individually regulated to values between 1 and 20 cm<sup>3</sup> min<sup>-1</sup>. The vapor pressure in the mixing chamber can be estimated by the ratio of the saturated ( $p_{sat}$ ) to dry (p) gas flow rates as determined by the flow-meter readout. The films were allowed to swell in the controlled

solvent atmosphere until an equilibrium film thickness was reached. The polymer concentration in the equilibrated film at a set vapor pressure is given by  $\varphi = d_0/d$ , with  $d_0$  and d the dry and swollen film thicknesses, respectively (assuming additivity of the partial volumes of polymer and solvent). At vapor pressures of  $p_{tol} = 0.85 \ p_{sat}$  the films swell to 1.7 times their dry thickness resulting in polymer concentrations of  $w_p = 0.58$ . This concentration is well above the order-disorder transition for the diblock copolymers.

Instead of using spacers to control the air gap [40], the two surfaces were brought directly into contact with each other. A finite air gap arises from deviations in the planarity of the two surfaces and from a low concentration of defects (dust particles) that are trapped between the two plates. In the case of temperature annealing a voltage of 40-80 V was applied between the two plates and the temperature of the device was raised to 170 °C for periods of time ranging from several minutes to several hours. Cooling the sample down to room temperature and removing the electric field terminated the experiment. For the solvent-vapor experiments the block copolymers were allowed to swell to their equilibrium thickness – typically ~20 min [37] and voltages of 40-80 V were applied across the sandwich for several periods of time. The removal of the solvent was performed by passing dry N<sub>2</sub> through the sample chamber. After this quenching process the electric field and the top wafer were removed.

The topography of the micro-patterned diblock copolymer films was analyzed by optical microscopy and Tapping Mode Atomic Force Microscopy (AFM, Digital Instruments D3100). AFM was also used to determine film thicknesses, which allows the calculation of the plate spacing *h* and the air gap *h*–*d*. To elucidate the lamellar microdomain structures within the columnar structures field emission scanning electron microscopy (FESEM, LEO 1530) was performed. The typical preparation of the samples for SEM was as follows: UV irradiation under vacuum for 10 min, rinsing in acetic acid for 5 min and washing with Millipore water to selectively remove the PMMA block within the block copolymer structures. Prior to SEM imaging, a thin layer of gold,  $\approx$ 5 nm, was evaporated onto the block copolymer surface to prevent charging of the polymer during imaging.

For the simulations of Figure 1d the Comsol Multiphysics package was employed, which uses a finite element method to solve for the electric field.

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