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Control of Orientational Order in Block Copolymer Thin Films by Electric Fields: A Combinatorial Approach

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Block copolymers are ideal candidates for the structuring of surfaces on the nanometer scale as they form highly regular microdomain structures via self-assembly on the order of some tens of nanometers in bulk as well as in thin films. Unfortunately, these microdomains only exhibit short-range order within a grain. Therefore, it is still a challenge to align the microdomains in such a way as to yield macroscopic orientation or even a single domain structure. In the past, various methods were devised to induce long-range orientation and order in thin block copolymer films. External fields, such as shear fields,[1,2] temperature gradients,[3] selective solvent evaporation,[4] directional solidification,[5] or graphoepitaxy,[6] were employed successfully. In addition, the large potential of electric fields for the generation of in-plane and out-of-plane alignment of block copolymer microdomains has been shown.[7−10]

Various parameters play a key role in the control of the alignment process of block copolymers in electric fields. For example, the field strength at which interfacial interactions are overcome allowing for the microdomains to orient along the electric field vector has to be identified.[11−15] This threshold electric field strength, E_{tresh}, can be described with respect to the difference between the interfacial energy of each block with the substrate, $\Delta\gamma$, the static dielectric constants of the respective blocks, ε_{A} and ε_{B}, and the film thickness d:[15,16]

$$E_{\mathrm{tresh}} = \Delta\gamma^{1/2}\frac{2(\varepsilon_{\mathrm{A}}+\varepsilon_{\mathrm{B}})^{1/2}}{\varepsilon_{\mathrm{A}}-\varepsilon_{\mathrm{B}}}d^{-1/2} \qquad (1)$$

From eq 1 it can be seen that a small film thickness, a large $\Delta\gamma$, and a small dielectric contrast between the blocks $\Delta\varepsilon = \varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}}$ lead to an increase of the threshold field strength E_{tresh}. In order to decide whether a given block copolymer system can be aligned using an electric field, usually, many tedious and time-consuming experiments are required to determine a minimum field strength at which the nanostructure orients in the applied field. The same holds true for the maximum possible degree of order in the aligned thin films. In this Communication, we demonstrate a combinatorial approach allowing the simultaneous determination of the above-described parameters in one experiment under constant environmental conditions (e.g., temperature, solvent vapor) by a fixed voltage as a function of the electrode distance.

Two lamellar block copolymers polystyrene-*b*-poly(2-hydroxyethyl methacrylate)-*b*-poly(methyl methacrylate) (consisting of 47 wt % polystyrene (PS), 10 wt % poly(2-hydroxyethyl methacrylate) (PHEMA), and 43 wt % poly(methyl methacrylate) (PMMA) with a total number-average molecular weight $M_{\mathrm{n}} = 82$ kg/mol, denoted as $\mathrm{S_{47}H_{10}M_{43}}^{82}$) and polystyrene-*b*-poly(2-vinylpyridine) (denoted as $\mathrm{S_{50}V_{50}}^{78}$) were synthesized by sequential living anionic polymerization as described in detail elsewhere.[9,17,18] The static dielectric constants of the PS, PMMA, and PVP amount to 2.4, 3.6, and 7.5, respectively.[19] Thus, the dielectric contrast between the respective blocks $\Delta\varepsilon$ yields 1.2 for PS/PMMA and 5.1 for PS/PVP. For the electric field studies, films of the respective block copolymers with lamellar orientations perpendicular to the substrate were prepared as reported earlier. This resulted in film thicknesses of 37 ± 2 nm for $\mathrm{S_{47}H_{10}M_{43}}^{82}$ and 745 ± 2 nm for $\mathrm{S_{50}V_{50}}^{78}$.[9,17,20]

In order to study the influence of the electric field strength on the degree of alignment, ex-situ experiments with gradient gold electrodes on a glass substrate were performed. The electrode distance was chosen as a linear gradient ranging from 5 to 50 μm. The height of the electrodes was around 55 nm (this height corresponds to the film thickness of the $\mathrm{S_{47}H_{10}M_{43}}^{82}$ block copolymer film swollen during the solvent vapor treatment).[9] We note here that the limited electrode height does not influence the electric field-induced ordering process due to the dominating in-plane component of the electric field on and in between the electrodes even in the case of films which are significantly thicker than the ones used here. A schematic of the electrode geometry is shown in Figure 1. Because of the very large aspect ratio between electrode spacing and the electrode length (6 mm), the electric field can be considered homogeneous. A voltage of 75 V/150 V was applied resulting in a field strength gradient ranging from 1.5 to 30 V/μm. The microdomain orientation as a function of the electric field strength was monitored by a series of SFM images taken in the center between the electrodes screening the whole electrode length of 6 mm in steps of a few tens of microns. From the azimuthal intensity distribution of the 2D Fourier transforms of the SFM images, the orientational order parameter P_2 was calculated according to $P_2 = (3\langle\cos^2\varphi\rangle - 1)/2$, as described previously.[9] Here the angle φ quantifies the in-plane direction with $\varphi = 0°$ corresponding to the direction perpendicular to the electric field vector. For an alignment of the lamellae along the field direction (maximum of azimuthal intensity distribution

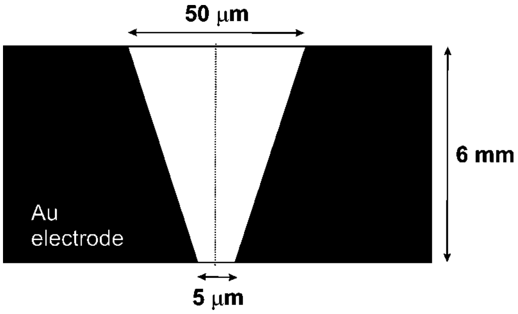

Figure 1. Schematic top view of gradient electrodes on a glass substrate. The height of the electrodes amounts to 55 nm. The electrode gap is not true to scale and the gradient (5−50 μm) has been exaggerated for clarity. The dotted line shows the axis along which the SFM images were taken.

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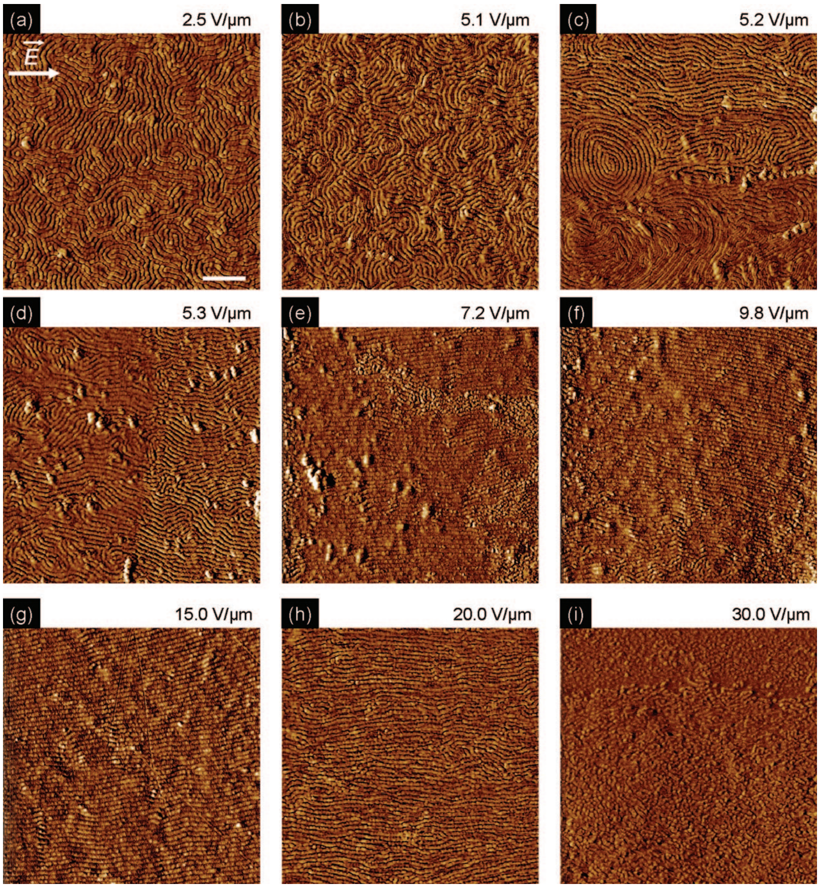

Figure 2. Series of SFM phase images (*z*-range: 0−10°) of a 39 nm thick $S_{47}H_{10}M_{43}{}^{82}$ film after annealing for 6.5 h in saturated toluene vapor in the gradient electrode setup. The arrow in (a) indicates the direction of the electric field vector, and the scale bar represents 500 nm.

at $\varphi = 90°$), P_2 ranges from 0 to -0.5 with $P_2 = -0.5$ corresponding to the fully oriented case.

To achieve in-plane alignment in a lamellar block copolymer thin film, the lamellae have to be oriented perpendicular to the plane of the film in the first place. As we have shown earlier, in the block copolymer system $S_{47}H_{10}M_{43}{}^{82}$ perpendicular alignment of the lamellae is achieved spontaneously at zero electric field.[9,17] In short, a thin brush layer of the block copolymer is adsorbed onto the (polar) substrate via the PHEMA middle block, resulting in a stripe pattern of the two majority components PS and PMMA. In thicker films this brush layer seems to serve as a template for perpendicular lamellae.[21,22] This can be seen in Figure 2a, which show an SFM image of a thin $S_{47}H_{10}M_{43}{}^{82}$ film annealed for 6.5 h in saturated toluene vapor at a position between the gradient electrodes with an electric field strength of 2.5 V/μm. The image exhibits a striped surface structure which can be interpreted as upstanding lamellae. The characteristic lateral spacing amounts to some 55 ± 8 nm, in reasonable agreement with the bulk spacing reported earlier. However, the stripe pattern exhibits a large number of defects and does not show any long-range order. Increasing the electric field strength E from 5.1 to 5.2 V/μm yields some grains with a preferred orientation of the lamellae parallel to the electric field vector. This onset of alignment is not markedly reflected in a decrease of the order parameter P_2, which yields $P_2 = -0.11$ for the image in Figure 2b and $P_2 = -0.12$ for the image in Figure 2c (P_2 data shown in Figure 3b,c). At a slightly larger electric field strength of $E = 5.3$ V/μm (Figure 2d) the predominant alignment of the lamellae parallel to the electric field vector is found to be more pronounced, which is also reflected in the decreased order parameter of $P_2 = -0.16$ (Figure 3d), which is about 50% of the value finally achieved in this experiment. Thus, from the SFM images and the onset of the ordering process, the threshold field, which is needed to align the lamellae of the polymer $S_{47}H_{10}M_{43}{}^{82}$ parallel to the electric field lines, under the given environmental conditions and in the time frame of our experiment, is determined to a range of $E_{\text{tresh}} = 5.2-5.3$ V/μm. For electric field strengths less than $E = 5.2$ V/μm an alignment of the lamellae parallel to the electric field lines cannot be achieved, even after longer annealing times. Increasing the electric field

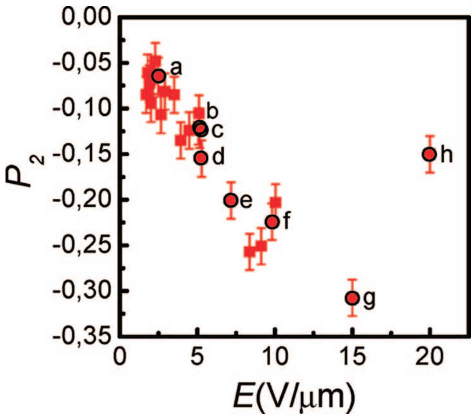

Figure 3. Evolution of orientational order parameter P_2 at different electrode distances plotted versus the electric field strength E. The numbering of the marked values corresponds to the SFM images in Figure 2. The error of the order parameter due to inhomogeneities in the film, and the phase contrast can be estimated to be about ±0.02.

strength further from 7.2 to 15 V/μm (as shown in Figures 2e−g) leads to a structure with a rather limited number of defects and a predominant alignment parallel to the electric field lines. This is also reflected in a continuing decrease of the order parameter from a value of $P_2 = -0.20$ (Figures 2e and 3e) to $P_2 = -0.31$ (Figures 2g and 3g). We note here that even longer annealing times at $E = 15$ V/μm did not improve the orientational order significantly. Thus, the block copolymer film was subjected to higher field strengths. However, 20 V/μm and more lead to a decrease in the order parameter to a value of $P_2 = -0.15$ (Figures 2h and 3h). From the SFM image in Figure 2h, it is found that the intensity of the phase signal strongly decreases, pointing to changes in the polymeric structure. This observation is supported by the SFM image of the film at 30 V/μm, where severe damages to the film can be seen (Figure 2i). Moreover, a significant decrease in film thickness is observed with time. In this high voltage range, the electric breakdown voltage has been reached, leading to ionization of the surrounding gas atmosphere, which finally results in the formation of a gas plasma. Thus, we can deduce that the film is ablated by a plasma etching process. Thus, besides the threshold field, also an upper limit of the field strengths in the range of 20−30 V/μm can be identified. The fact that the ideal value of $P_2 = -0.5$ describing perfect alignment is not reached during the experiments can be explained as follows: From a technical point of view, the low contrast ratio between the different polymer phases in the raw data leads to a rather noisy Fourier spectrum, which deteriorates the numerical value of P_2. In addition, we note that the value of P_2 is similar to the ones determined for bulk solutions of the same polymer via real-time SAXS measurements.[11] This finding points to a more fundamental reason. Since the electrodynamic driving force scales with $\cos^2 \theta$, where θ is the tilt angle of the lamellar normal vector with respect to the electric field vector, the energy gain for improved alignment is expected to continuously decrease as the angle between the lamellae and the electric field direction is approaching zero.[23] Therefore, within finite annealing times, no "perfect alignment" is to be expected. The observed limiting value for P_2 is likely to be determined by a combination of the above reasons.

The evolution of the order parameter as a function of the electric field strength as plotted in Figure 3 shows a linear dependence up to the onset of polymer decomposition. With increasing electric field strengths the order parameter decreases; i.e., the lamellar structure increasingly aligns parallel to the electric field vector. The difference in the free energy between the aligned and nonaligned state, ΔF, is predicted to be proportional to $[(\varepsilon_A - \varepsilon_B)^2/(\varepsilon_A + \varepsilon_B)]E^2$.[23,24] However, there is no direct link to the expected degree of order, especially as the electric-field-induced driving force strongly depends on the tilt angle of the lamellar normal vector with respect to the electric field vector as pointed out above.

In order to demonstrate the applicability of our method to other block copolymer systems, we exposed a thick diblock copolymer film of $S_{50}V_{50}{}^{78}$ with upstanding lamellae (generated by selective solvent vapor treatment in toluene[20]) to an electric field in the same gradient electrode geometry as described above. As the dielectric contrast between the PS and the PVP is larger than the one for PS and PMMA, only from the dielectric term in eq 1 would one expect a threshold field for $S_{50}V_{50}{}^{78}$ which is about 3 times lower than for $S_{47}H_{10}M_{43}{}^{82}$. In addition, according to the larger dielectric contrast between the blocks in $S_{50}V_{50}{}^{78}$ compared to $S_{47}H_{10}M_{43}{}^{82}$, the gain in free energy and thus the electrodynamic driving force is about an order of magnitude larger for the PVP-based block copolymer. In Figure 4 a series of SFM phase images of a 745 ± 2 nm thick $S_{50}V_{50}{}^{78}$ film after 20 h of annealing with saturated toluene vapor under a gradient electric field is shown. All images reveal a stripe pattern of upstanding lamellae. Even at the largest electrode spacing of the gradient electrode (which corresponds to an electric field strength of 2.5 V/μm) a preferential orientation of the lamellae parallel to the electric field lines is observed (Figure 4a). Therefore, the threshold electric field strength for the alignment of the lamellae of $S_{50}V_{50}{}^{78}$ is smaller than 2.5 V/μm. Larger field strengths lead to a significant increase of the degree of orientation (Figure 4b−d). At $E = 15$ V/μm an almost defect-free structure is found (Figure 4d). These observations are in good agreement with the predictions from theory.[15,23] Unfortunately, because of the low contrast between the different polymer phases in the raw data of the SFM images, leading to a Fourier spectrum with a low signal-to-noise ratio, a reliable order parameter P_2 could not be determined from the images. However, our data clearly show that by increasing the dielectric contrast of the polymer blocks a reduced threshold field strength and an improved orientation of the lamellae can be achieved. Furthermore, this valuable information was gained in a single combinatorial experiment using a gradient electric field setup under constant environmental conditions, thereby establishing an efficient testing method for the processability of various polymer systems with electric fields and their applicability for electric-field-based surface patterning procedures.

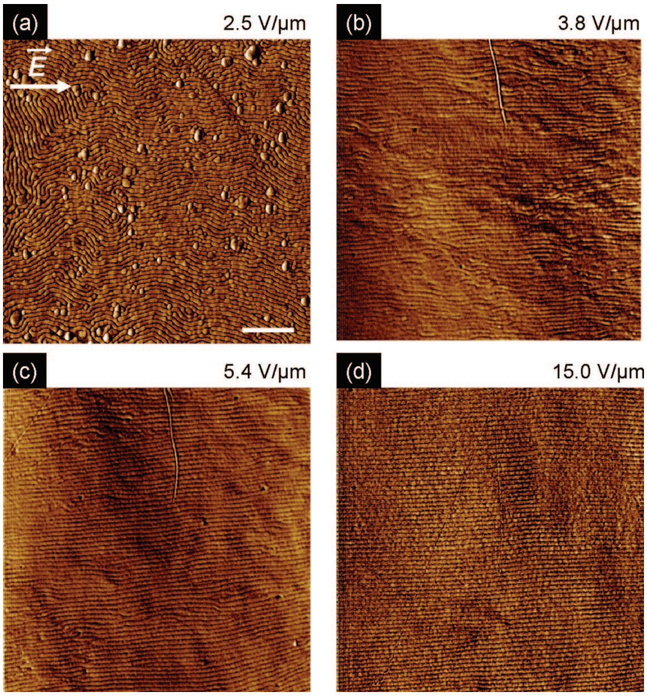

Figure 4. Series of SFM phase images (z-range: 0−20°) of a 745 ± 2 nm thick $S_{50}V_{50}{}^{78}$ film after annealing for 20 h in saturated toluene vapor in the gradient electrode setup. The arrow in (a) indicates the direction of the electric field vector, and the scale bar represents 500 nm.

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Supporting Information Available: Experimental details and calculation of the orientational order parameter. This material is available free of charge via the Internet at http://pubs.acs.org.

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