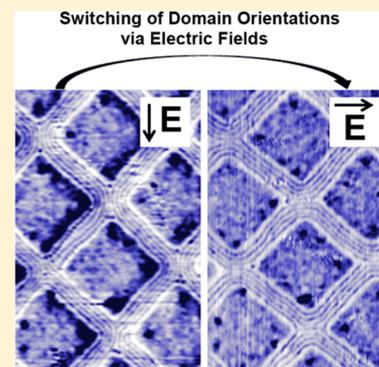


Electric-Field-Induced Control and Switching of Block Copolymer Domain Orientations in Nanoconfined Channel Architectures

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ABSTRACT: Successfully controlling and switching cylinder-forming diblock copolymer domain orientations located in nanoconfining channel architectures has been achieved by the application of electric fields. Two degenerate structures result when the block copolymer thin films are confined in intersecting crossed channels. Here, cylinder domains align in one of two energetically degenerate structures having orientations of 45° or 135° with respect to the channels in the crossed areas. Electric fields are then introduced to further control the orientation of microdomains in both as-cast and phase-separated films. The cylinder domains then become oriented parallel to the electric field, and a single structure is obtained in the crossed areas. Finally, by introducing quadrupolar electrodes, we demonstrate the ability to switch block copolymer domain orientations between the two degenerate structures. These results suggest many follow-on applications in fundamental polymer physical chemistry as well as new approaches for static and dynamic nanostructure design and control.



INTRODUCTION

Self-assembly has become increasingly valuable due to its utilization in the large-scale fabrication of nanoscale structures. Diblock copolymer thin films are well-known examples of self-assembling systems as they spontaneously form periodic microdomain structures of various symmetries, including, for example, spherical, cylindrical, and lamellar domains. These self-assembled patterns have been used as nanolithographic masks to create patterns on substrates^{1–3} as well as templates for the further synthesis of metallic dots^{4,5} and nanowires.^{6,7} However, the precise control over pattern registration and formation of long-range-ordered nanostructures free from defects remains a crucial issue. Techniques that have been used to guide the orientation of polymer domains and eliminate defects include electric fields,^{8–10} flow fields,^{11–13} directional crystallization,¹⁴ chemical patterning,^{15–19} and graphoepitaxy.^{20–29}

Graphoepitaxy utilizes substrate topography to order microdomains. This technique was first used to achieve long-range order of spherical domains^{20–22} and has since been used to align striped patterns of cylinder-forming^{23–26,28,29} or lamella-forming²⁷ block copolymers with both perpendicular and parallel orientations. This new “bottom-up” approach of creating highly dense, ordered patterns presents a potentially powerful option for next-generation lithographic technology and magnetic storage.

Electric fields, which take advantage of dielectric contrast between two polymer blocks, have successfully been used to achieve long-range order in copolymer nanostructures.^{10,23,30–32} The microdomains orient parallel to the electric fields to lower the free energy of the system. Electric-field-induced orientation of block copolymer domains has been studied experimentally with both in situ^{8,33} and ex situ^{7,9,23,34}

methods. Rotation of grains, nucleation and growth, and selective disordering have been suggested as the three mechanisms for electric-field-induced reorientation of microdomains.^{35–38}

In this paper, we have examined the alignment of cylinder-forming PS-*b*-PEP thin films confined in crossed nanochannels. Two structures were observed, with cylinders aligning along either of the two energetically degenerate diagonal directions in the crossed areas. Electric fields were used to further orient the microdomains and remove one of the degenerate structures. The combination of graphoepitaxy and electric field alignment enables us to precisely control the polymer patterns. Moreover, the utilization of quadrupolar electrodes surrounding the areas of channel intersection has allowed us to demonstrate the ability to readily switch between the two otherwise degenerate geometric arrangements, suggesting many new applications in lithography, data storage, and nanofluidics.

EXPERIMENTAL SECTION

Polystyrene (6,100)-*block*-polyisoprene (16 000) with a polydispersity of 1.07 was purchased from Polymer Source, Inc. of Dorval, Quebec. It was then modified to polystyrene-*block*-poly(ethylene-*alt*-propylene) (PS-*b*-PEP) by selective hydrogenation of the polyisoprene block. PS-*b*-PEP has 27 wt % PS so that the copolymer forms hexagonally packed PS cylinders in the PEP matrix.

Electrodes on silicon nitride substrates were fabricated using optical lithography followed by evaporation of 5 nm titanium and 25 nm gold. The topographic patterns were then prepared

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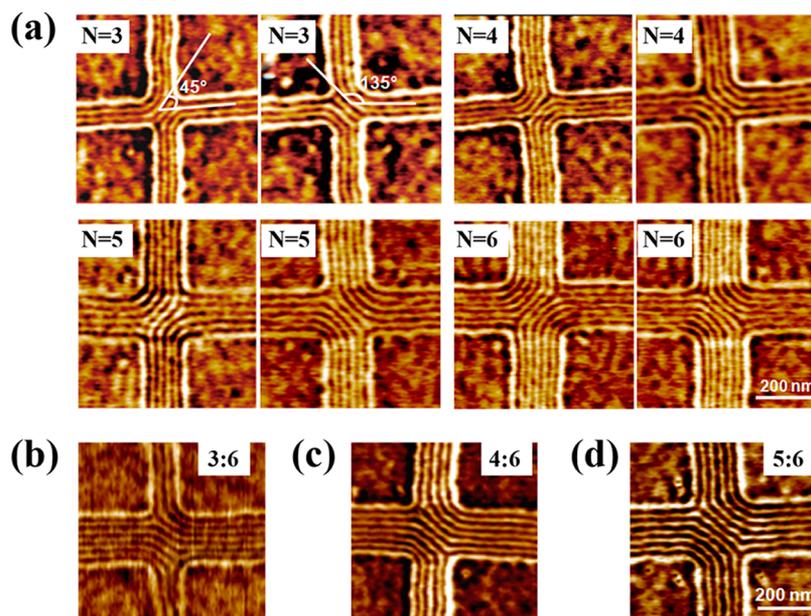


Figure 1. (a) AFM phase images of the alignment of PS-*b*-PEP thin films in crosses with arms of equal widths. The arms contain ordered cylinder domains with $N = 3$ – 6 rows. The samples have been annealed in an argon atmosphere at $175\text{ }^{\circ}\text{C}$ for 12 h to reach their equilibrium structures. Two degenerate structures are observed, and the cylinders are aligned along a 45° or 135° direction to the horizontal arms. (b–d) AFM phase images of the alignment of PS-*b*-PEP thin films in crosses with arms of different widths. One pair of the arms contains six cylinders, while the other pair contains three to five cylinders. The cylinder domains in the crossed areas align along a direction that is 45° or 135° to the horizontal arms. The extra cylinders in the wider arm are connected to the cylinders in the wider arm on the other side.

by electron beam lithography using a Hitachi S-2700 scanning electron microscope and reactive ion etching.²⁸

The nanopatterned substrates were cleaned with toluene, acetone, and methanol using an ultrasonic cleaner and dried with nitrogen. The washed substrates were spin-coated with PS-*b*-PEP block copolymer in 0.5% toluene solution at 4000–5500 rpm for 60 s and then annealed at 448 K under an argon atmosphere for 4–12 h with or without the application of electric fields.

The samples were imaged by Asylum Research's MFP-3D atomic force microscope in ac (tapping) mode using AppNano ACTA cantilevers with a spring constant of $\sim 50\text{ N/m}$.

RESULTS AND DISCUSSION

The alignment of cylindrical domains in the crossed channels with arms of equal widths is shown in Figure 1a. The crossed patterns created by electron beam lithography are 50 nm deep. Asymmetric wetting of PS-*b*-PEP occurs on the nanopatterned silicon nitride substrate. PS prefers to wet the silicon nitride/polymer interface, whereas PEP exhibits an affinity for the polymer/air interface. The crests appear featureless, corresponding to an $L/2$ thick film, where L is the natural thickness of one layer of cylinders. The troughs are filled with a layer of PS cylinders embedded in a PEP matrix ($3L/2$ thick film), which show fingerprint structures.²⁶ The preferential interaction of PS with the arm's sidewalls drives the alignment along the arms. In the crossed areas, it is observed that the cylinders next to the sidewalls follow the edge contour of the template and the cylinders can form two degenerate structures. They can align along either of the two diagonal directions in the crossed areas, which is consistent with previous simulation results.³⁹ By counting over 500 crosses, the ratio between the two degenerate structures is determined to be 50:50. For crossed channels with arms of nonequal widths, the cylinder domains in the crossed areas also align along a direction that is 45° or 135°

to the horizontal arms, as shown in Figure 1b–d. Let us assume that two arms have n and N ($N > n$) cylinder domains. The first n cylinders in the wider arm will connect to the n cylinders in the narrower arm next to it, while the rest of the $N - n$ cylinders in the wider arm will follow the 45° (or 135°) direction and connect to the cylinders in the wider arm on the opposite side. For example, as shown in Figure 1b, the vertical and horizontal arms contain three and six cylinder domains, respectively. The three cylinder domains on the top of the right arm are connected to the three cylinders in the top arm, while the rest of the three cylinders at the bottom of the right arm follow the 135° direction and are connected to the three cylinders on the top of the left arm. Therefore, for crosses with arms of nonequal widths, the cylinder domains in the crossed areas also align along a direction that is 45° or 135° with respect to the horizontal arms, with the extra cylinders in the wider arm connected to the cylinders in the wider arm on the other side.

The use of block copolymer thin films to generate nanostructured surfaces for device and other applications requires precise control of the domain orientation. Next, we illustrate our approach to remove the degeneracy of the structures in the crossed areas by applying an electric field (E). Owing to the different dielectric properties of the two blocks, an orientation of cylinder microdomains parallel to the external electric fields is energetically favored. The free energy of cylinder-forming diblock copolymer thin films in an electric field is³⁴

$$F - F_0 = \frac{1}{8\pi} \epsilon_D |E_0|^2 \left[\frac{1}{2} \left(\frac{\beta}{\epsilon_D} \right)^2 \langle \bar{\psi}^2 \rangle [1 - (\hat{\epsilon}_c \cdot \hat{\epsilon}_z)^2] - \frac{\langle \epsilon \rangle}{\epsilon_D} \right]$$

where F is the free energy of the system, F_0 is the free energy without an electric field, E_0 is the applied electric field, $\bar{\psi}$ is the

amplitude of the composition pattern, $\langle \epsilon \rangle$ is the space-averaged dielectric constant, ϵ_D is the dielectric constant in the limit of vanishing stationary composition pattern, β is the sensitivity of the dielectric constant to composition change, \hat{e}_c is the unit vector in the direction of the cylindrical axes, and \hat{e}_z is the unit vector in the direction of the applied field. According to this equation, the free energy of the system is minimized when the cylindrical axes are parallel to the field.

A schematic of the electrode geometry is shown in Figure 2. A 5 nm thick titanium and 25 nm thick gold film are evaporated

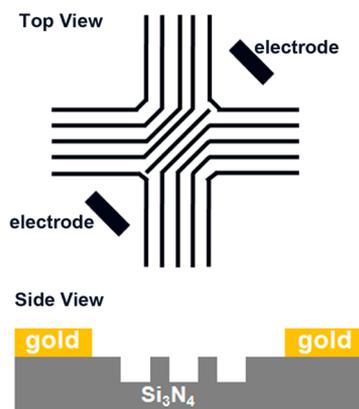


Figure 2. Schematic illustrations giving the top and side views of the electrode arrangement. A 5 nm thick titanium and 25 nm thick gold film are evaporated onto the substrates to form the electrodes. The separation distance between the two electrodes is about 4 μm . The crossed patterns created by electron beam lithography are 50 nm deep.

onto the substrates to form the electrodes. The separation distance between the two electrodes is about 4 μm . The electric field strength chosen in this study is $\sim 30 \text{ V}/\mu\text{m}$, which is necessary to align the cylinders parallel to the electric field lines in the time frame of our experiment. Lower field strengths result in no orientation of the PS-*b*-PEP domains. This observation is consistent with a previous study on the alignment of PS-*b*-PI, which has a threshold field strength of 18 $\text{V}/\mu\text{m}$.³³

Studies were performed with the block copolymer thin films in different initial states. First, we investigated the samples having a disordered initial alignment. After spin-coating with the diblock copolymer solution, the samples were annealed in an argon atmosphere at 175 $^\circ\text{C}$ for 4 h, under an applied, in-plane electric field of 30 $\text{V}/\mu\text{m}$. Parts a and b of Figure 3 show the alignment of copolymer domains on flat and nanopatterned substrates annealed with the application of electric fields, respectively. On the flat substrates, alignment in the direction of the applied fields is achieved. For the as-cast samples, it has been demonstrated that alignment along the electric fields proceeds via growth of the favorable orientation at the expense of neighboring regions.^{40,41} On nanopatterned substrates, the domains align along the template sidewalls in the arms due to the preferential wetting of PS blocks. The applied electric fields are not sufficiently high to overcome the interfacial interactions. Previous studies have also discussed the competition between electric fields and interfacial energy.^{7,42–44} In contrast, in the crossed areas, both of the degenerate structures stated above have the same interfacial energy, and preferential cylinder alignment is only driven by a decrease in electrostatic energy. Therefore, the cylinder domains in the crossed areas adopt the structure oriented parallel to the electric fields, as shown in

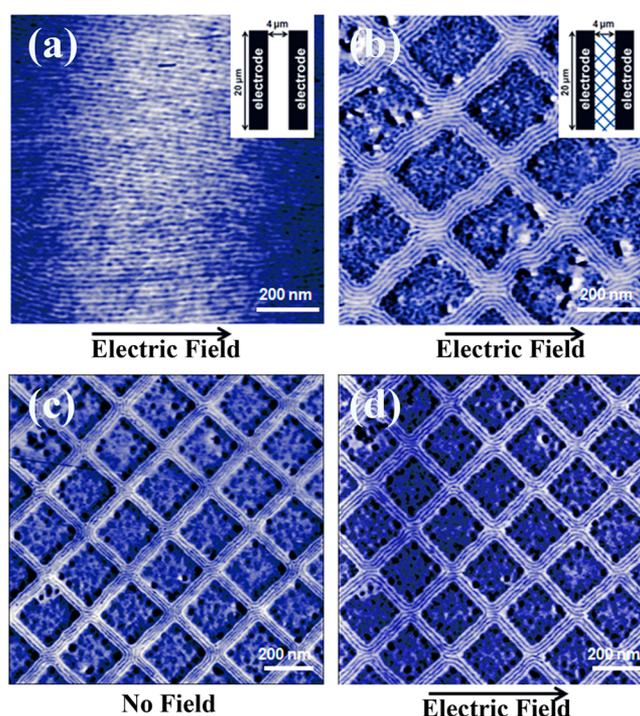


Figure 3. AFM phase images of the alignment of cylinder domains (a) on a flat substrate and (b) on a nanopatterned substrate. The samples are annealed in an argon atmosphere at 175 $^\circ\text{C}$ for 4 h under an applied, in-plane electric field of 30 $\text{V}/\mu\text{m}$. The cylinders on the flat substrates and in the crossed areas are oriented parallel to the electric fields. A schematic of the electrode geometry is shown in the inset panels of (a) and (b). AFM phase images of the alignment of cylinder domains (c) prior to and (d) after the application of a 33 $\text{V}/\mu\text{m}$ electric field. Electric-field-induced reorientation of cylinder domains is observed in initially microphase-separated block copolymer thin films.

Figure 3b. Using electric fields in combination with topological templates, we are capable of removing one of the two degenerate structures in the crossed areas to achieve a single orientation.

Next, let us turn to the orientation of initially microphase-separated copolymers. Figure 3c shows the alignment prior to the application of electric fields. The sample has been annealed at 175 $^\circ\text{C}$ for 6 h in the absence of electric fields. As expected, two degenerate structures coexist in the crosses at about a 50:50 ratio in Figure 3c. After subsequent exposure to an electric field of 33 $\text{V}/\mu\text{m}$ for 4 h at 175 $^\circ\text{C}$, the same area is scanned, and the AFM image is shown in Figure 3d. The electric fields successfully induce reorientation of the cylinders in the crossed areas, and all of the crosses adopt the degenerate structure that is oriented parallel to the electric fields. Previous work has shown that, for initially microphase-separated copolymers, electric-field-induced alignment proceeds through disruption and reorientation of the originally misaligned domains.⁸

Quadrupolar electrodes, shown in Figure 4a, were designed to switch the polymer domain orientation between the two degenerate structures. Here the two pairs of electrodes are arranged perpendicularly to each other. By connecting the top and bottom electrodes, a vertical electric field is applied; by connecting the left and right electrodes, a horizontal electric field is applied. First, we apply an electric field of 33 $\text{V}/\mu\text{m}$ between the top and bottom electrodes on a flat substrate for 4 h and observe that the cylinder domains at the center of the

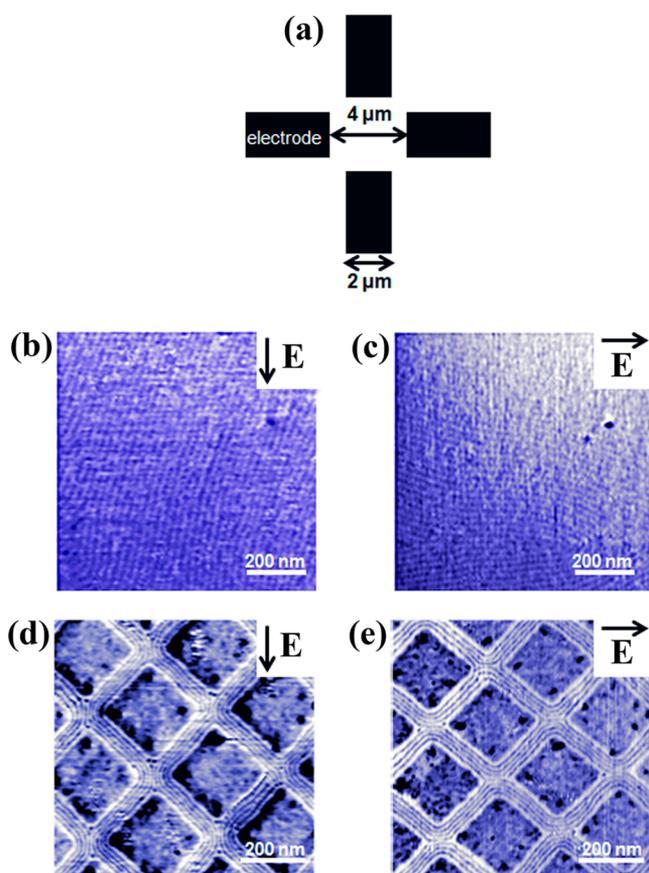


Figure 4. (a) Schematic illustration presenting the top view of the quadropolar electrodes. (b, c) AFM phase images showing the alignment of cylinder domains on flat substrates by applying an electric field of $33 \text{ V}/\mu\text{m}$ between the top and bottom electrodes (b) and subsequently between the left and right electrodes (c). The switching of polymer domain orientations is observed. AFM phase images of the alignment of cylinder domains in crosses by applying an electric field of $33 \text{ V}/\mu\text{m}$ between the top and bottom electrodes (d) and subsequently between the left and right electrodes (e). The cylinders are readily switched between the two degenerate structures in the crossed areas via electric fields.

quadropolar electrodes become oriented parallel to the electric field, vertically arranged in Figure 4b. The electric field is subsequently applied between the left and right electrodes for another 4 h; all the cylinders now switch to a horizontal orientation, Figure 4c. This confirms that we can switch the polymer domain orientation upon the application of two perpendicular electric fields.

Next, we turn to the alignment of cylinder domains in crossed patterns. Again, by applying an electric field of $33 \text{ V}/\mu\text{m}$ between the top and bottom electrodes for 4 h at 175°C , the cylinder domains in the crossed areas become oriented with the direction of the vertical electric fields, as shown in Figure 4d. The electric field is subsequently applied between the left and right electrodes for another 4 h, and all of the cylinders in the same crossed areas switch to the horizontal direction, Figure 4e. The cylinder domains in the crossed areas are reconnected with the domains in the arms after switching. Using such quadropolar electrodes, we can therefore switch between the two degenerate structures using applied electric fields, offering a new conduit to technological applications such as controlled circuit design and data storage.

CONCLUSIONS

In summary, we have demonstrated that the alignment of cylinder-forming PS-*b*-PEP thin films confined in crossed nanochannels can be controlled by the application of appropriate electric fields. Initially, before application of such fields, two structures occur in the crossed areas, with cylinders aligning along two energetically degenerate directions that are oriented 45° or 135° with respect to the crossed channels. Electric fields were then used to further orient the microdomains in both as-coated and phase-separated block copolymer thin films. The cylinder domains in the crossed areas adopted only one of the two degenerate structures and became oriented parallel to the electric field direction. With the combined application of electric fields and topological templates, we achieved precise control over the polymer domain orientations. By introducing quadropolar electrodes, we have demonstrated the ability to readily switch between the two degenerate structures, which opens up new perspectives in controlled self-assembly for applications in lithography, flexible circuit design, data storage, and nanofluidics.

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Notes

The authors declare no competing financial interest.

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