

Structural Evolution and Alignment of Cylinder-Forming PS-*b*-PEP Thin Films in Confinement Studied by Time-Lapse Atomic Force Microscopy

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ABSTRACT

We have utilized time-resolved high-temperature atomic force microscopy (AFM) to investigate the mechanism by which topographic templates induce alignment of cylinder-forming diblock copolymer thin films. By tracking the same sample spot during thermal annealing, we observed that the structural evolution and alignment of thin films in confinement involve an intermediate state with disordered morphology and the evolution and annihilation of disclination quadrupoles guided by the channel edges, which ultimately lead to the essentially perfect alignment of cylindrical microdomains.

INTRODUCTION

The generation of nanostructures with controlled orientation and a high degree of structural perfection has attracted significant attention due to many potential technological applications. Previous studies from our group have focused on details of defect dynamics in thin polymer films [1] and the utilization of templated grating substrates to produce essentially defect-free diblock copolymer “nanowires” (Figure 1) by combining “top-down” and “bottom-up” assembly techniques [2, 3]. Thermal annealing of cylinder-forming polystyrene-*block*-poly (ethylene-*alt*-propylene) thin films deposited on physically patterned substrates at carefully selected temperatures drives the confined system into a lower energy state in which the cylinders align parallel to the grating due to interactions with the edge of the channel wall.

These previous AFM investigations required repeated cycles of imaging followed by *ex-situ* thermal annealing. Moreover, they only gave glimpses of the details of the competing kinetic and thermodynamic processes which drove the time-evolution of the system. To address these concerns, we have now developed time-lapse high-temperature AFM experiments in order to study *in-situ* the mechanistic details of these processes. In this article, the step-by-step structural evolution and realignment in confined copolymer thin films have been explored. The defects evolve to perfect configuration by first disrupting the initial morphological order of misaligned cylinders in the grating, forming disclination pairs, and finally aligning from the side of the channel inwards. In sum, the alignment process is significantly governed by interactions with the edges of the spatially-confining grating.

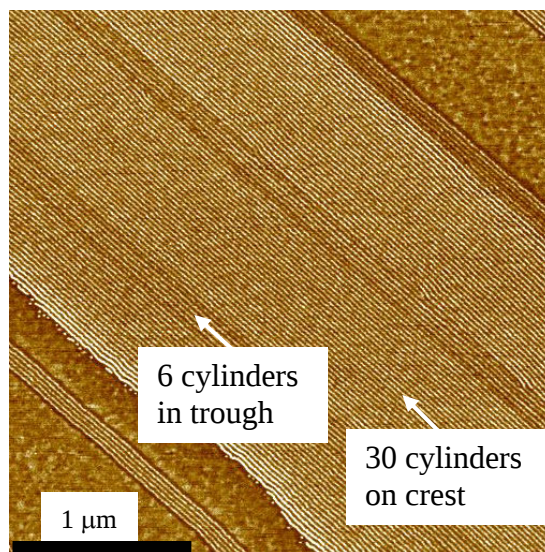


Figure 1. AFM image showing macroscopic alignment of in-plane cylindrical copolymer microdomains. In the thin film region, copolymers align inside nanochannels, whereas in the thick film region, alignment extends to the crest regions, resulting in global alignment.

EXPERIMENTAL DETAILS

Silicon nitride substrates were lithographically patterned by electron beam writing followed by reactive ion etching. The resulting square-wave grating patterns contained 100 μm -long nanochannels with widths ranging from 100 nm to 8 μm .

Polystyrene (6,100)-*block*-polyisoprene (16,000) (SI) was purchased from Polymer Source, Inc. Double bonds in the polyisoprene block were selectively saturated with Ni-Al homogeneous catalyst in order to convert SI precursors to polystyrene-*block*-poly (ethylene-*alt*-propylene) (SEP). The resulting polymer had a weight-average molecular mass M_w of 22,600 g/mol, and polydispersity M_w/M_n less than 1.10. NMR spectra indicated that the degree of hydrogenation was above 99%, with the PS blocks left intact. The volume fraction of the PS block was calculated to be 23%.

SEP samples were prepared by spin-casting dilute SEP solution in toluene. Subsequent annealing was performed at temperatures above the copolymer glass temperature (temperature ranges from 403 K to 443K) in either ovens having an inert argon atmosphere or in the high-temperature AFM chamber purged with helium. Surface morphology images at ambient conditions were obtained using tapping-mode AFM with a NanoScope IIIa or IV controller and TESP silicon tips (Veeco, Santa Barbara, CA). High-temperature AFM was employed to probe the polymeric samples *in-situ* at various elevated temperatures (samples were quenched to 348 K for imaging with good contrast, and then returned to elevated temperatures for further morphological evolution of the system). Upon annealing, SEP copolymer self-assembled into PS cylinders in a PEP matrix, with a repeat spacing of 27.1 nm. PS blocks appeared brighter in AFM images because of its stiffer mechanical nature [4].

RESULTS & DISCUSSION

The directed alignment of SEP copolymer microdomains in confinement nucleates along the nanochannel sidewalls due to preferential affinity between the PS component and the substrate. This preferred orientation then gradually proceeds towards the center of the nanochannels. After additional annealing, regions with perfect alignment assimilate regions with less perfect alignment. In this way, cylinder orientation parallel to the long axis of the channels is achieved across the entire channel width. This conclusion was originally based on *ex-situ* AFM. However, the details of domain coarsening and defect annihilation were still lacking. *In-situ* time-lapse high-temperature AFM has enabled us to examine the actual step-by-step morphological changes and alignment mechanism, revealing new insights into the dynamics of domain coarsening in confinement.

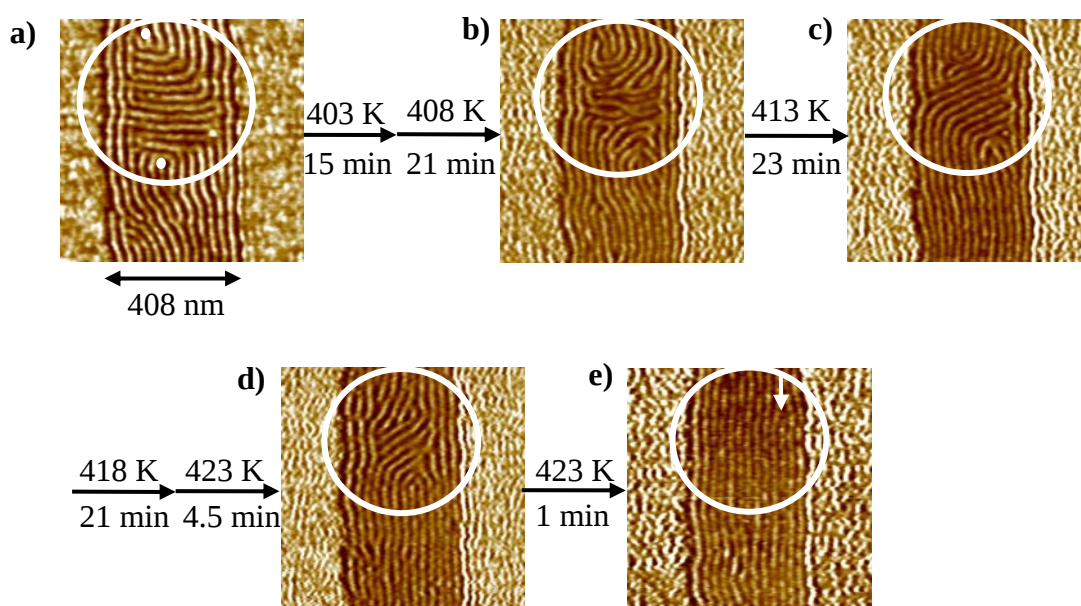


Figure 2. Time-lapse high-temperature AFM images of domain coarsening in confinement. Images were taken at 348 K to obtain good contrast, see text. The approximate positions of the two disclination cores are indicated by white dots in panel (a), while the remnant dislocation after defect annihilation is indicated by the white arrow in panel (e).

Figure 2 displays the detailed route through which cylindrical microdomains with orientation perpendicular to channel edges achieve the preferred spatial orientation. The system of interest has better registration with the channel edges at the upper and lower end of channel, whereas the cylindrical copolymer domains in the middle of the channel orient normal to the long axis, presumably due to the capillary flow from the crests to the troughs during the early stage of microphase separation. The initial state, having intermediate separation (ca. 10 domain spacing) between two disclination cores, resembles a disclination quadrupole previously seen in unconfined film geometry [4].

Interestingly, thermal annealing leads to the disruption of the original morphology of the perpendicular cylindrical domains (step 1, image a→b), similar to the intermediate state of

symmetric block copolymers during the microdomain reorientation in an electric field [5]. Upon further annealing, the disclination quadrupole transforms to two disclination pairs with oppositely oriented Burgers vectors (step 2, image b→c). As a result, the middle cylindrical domains orient with a non-normal angle to the channel sidewalls. At step 3 (image c→d), the two disclination pairs begin to evolve. Alignment is introduced from the edges of the channel, and advances inwards. And finally (step 4, image d→e) the two disclination pairs annihilate and leave perfect alignment inside the channel. The original nonzero net Burger vector is also conserved, resulting in one dislocation after domain coarsening.

CONCLUSIONS

In this article, we have described how preferred spatial orientation is achieved in lithographic confinement. Sequential high-temperature AFM images show that the domain orientation rearrangement inside lithographic structures is achieved by grating guided defect movement and annihilation. Such processes can differ from those occurring on unrestricted smooth surfaces. The original orientation normal to channel edges is destroyed to facilitate the formation of disclination pairs, which, in turn, annihilate and leave high orientational order across the channel.

ACKNOWLEDGEMENTS

This research was supported by NSF-Materials Research Science and Engineering Center at the University of Chicago, NSF-DMR-0213745. Support is also acknowledged from the University of Chicago-Argonne National Laboratory Consortium for Nanoscience Research.

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