Bending Behaviors and Directed Self-assembly of Rod-Coil Block Copolymers

lingying shi

sichuan university <https://orcid.org/0000-0002-6620-7878>

Sangho Lee

Massachusetts Institute of Technology

Qingyang Du

Massachusetts Institute of Technology

rong ran

sichuan university

Runze Liu

Massachusetts Institute of Technology

Caroline Ross (✉ caross@mit.edu)

Massachusetts Institute of Technology <https://orcid.org/0000-0003-2262-1249>

Article

Keywords: conformational asymmetry, block copolymers, rod-coil, directed self-assembly

Posted Date: August 20th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-58565/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at ACS Applied Materials & Interfaces on February 19th, 2021. See the published version at <https://doi.org/10.1021/acsami.0c22177>.

Abstract

The formation of zig-zags, chevrons, Y-junctions and line segments is demonstrated in thin films formed from cylindrical morphology Si-containing rod-coil diblock copolymers and triblock terpolymers under solvent annealing. Directed self-assembly of the block copolymers within trenches yields well-ordered cylindrical microdomains oriented either parallel or transverse to the sidewalls depending on the chemical functionalization of the sidewalls, and the location and structure of concentric bends in the cylinders is determined by the shape of the trenches. The innate etching contrast, the spontaneous sharp bends and junctions, and the range of demonstrated periodicity and line/space ratios make these conformationally asymmetric rod-coil polymers attractive for nanoscale pattern generation.

Introduction

Block copolymers (BCPs) form a class of highly versatile materials, assembling into a variety of well-defined periodic nanostructures such as arrays of spheres, cylinders, lamellae and gyroids with periodicities typically in the range of 5–100 nm and a wide range of chemical compositions.^{1–3} BCP self-assembly provides a path towards the fabrication of complex heterogeneous structures with applications spanning energy harvesting and storage, filtration, functional surfaces, and nanoscale device fabrication.^{4–7} However, for applications in nanolithography, device-relevant features are required such as rectilinear geometries, tunable line/space ratios, and lines with bends and junctions.^{8–11} By taking advantage of traditional lithographic techniques to guide block copolymer self-assembly, directed self-assembly (DSA) has enabled the design of complex two- or three-dimensional nanopatterns governed by the interactions and the commensurability between a topographical or chemical template and the BCP.^{12–14} Most DSA has been based on coil-coil diblock copolymers or triblock copolymers or terpolymers, but the inclusion of diverse blocks such as in rod-coil BCPs has further extended the range of achievable microdomain morphologies and chemistries and raised interest in their application to nanolithography. Incorporation of a Si-containing block provides a good etch contrast and is particularly useful for pattern transfer.¹⁵

Conformationally-asymmetric block copolymers such as those containing rigid rods, polypeptides, polysaccharides, or polyhedral oligomers present self-assembled morphologies that differ qualitatively from those seen in coil-coil BCPs.^{16–20} The morphology is influenced by multiple parameters including the interaction parameter, molecular geometry, block fractions, block lengths and rigidity and the tendency of the rigid block to crystallize, and is highly dependent on the annealing process^{18,21,22} leading to a diversity of stable and metastable phases, such as zigzag smectic C-like morphologies^{21,23} and highly asymmetric lamellar structures.²⁴

We focus here on conformationally-asymmetrical rod-coil Si-containing diblock copolymers and triblock terpolymers comprising a polydimethylsiloxane (PDMS) coil block and a semi-rigid poly{2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene} (PMPCS) block.^{25,26} PMPCS is a mesogen-jacketed liquid

crystalline polymer²⁷ adopting an extended-chain conformation in solution and a columnar nematic liquid crystalline phase when thermally annealed in bulk.^{27,28} The PDMS-*b*-PMPCS (or DM) has a high interaction parameter and can microphase separate under thermal or solvent vapor annealing, with the liquid crystal (LC) ordering playing a role in the kinetic pathway determining the final morphology.^{29,30} The presence of silicon imparts a high etch selectivity between the two blocks, and is converted to silicon oxide on etching in oxygen, simplifying pattern transfer and making PDMS-containing BCPs attractive for nanolithography applications.^{15,31,32} We have produced well-ordered in-plane cylindrical silica patterns from PDMS-*b*-PMPCS thin films by thermal annealing,²⁹ and a variety of core-shell patterns from a PDMS-*b*-PS-*b*-PMPCS (or DSM) triblock terpolymer by solvent vapor annealing,²⁶ and also have generated well-ordered lamellae with out-of-plane orientation through a two-step annealing method.³⁰

In this article, we demonstrate grating patterns with spontaneous sharp bends and Y-junctions as well as a tunable periodicity and line/space ratio from a series of rod-coil DM and DSM BCPs. In our prior work, we noted the formation of cylindrical microdomains with sharp bends in a solvent-annealed DSM triblock terpolymer.²⁶ Here we show that the formation of such structures is not limited to the DSM triblock terpolymer but occurs generally for the DM diblock copolymers. The bends take the form of chevrons, Y-junctions, or discontinuous line segments depending on the bend angle and the block fraction. Furthermore, the cylinders can be aligned within topographical features with the cylinder orientation depending on the surface functionalization of the template, and concentric bends can be guided, creating device-relevant patterns by DSA.

Results

Figure 1a shows the chemical structures of the PDMS-*b*-PMPCS diblock copolymer and PDMS-*b*-PS-*b*-PMPCS triblock terpolymer, and Table 1 summarizes the properties of the materials used in this study including molecular weight (M_n), degree of polymerization N , polydispersity (PDI), volume fraction f , acetone:heptane A:H ratio used for solvent vapor annealing (SVA), and period L_0 with D, M and S subscripts representing PDMS, PMPCS and PS respectively. Syntheses of the diblock copolymer and triblock terpolymer were described in our previous work.^{25,26} The molecular weight of the PDMS block $M_{n(D)}$ was fixed while its volume fraction f_D ranges from 33–11%. Figure 1b demonstrates the fabrication steps used to convert films of DM or DSM into in-plane SiO_x line patterns on flat and patterned silicon substrates (See Supplementary Information). The surfaces of the substrates were chemically functionalized by a 3 nm PS brush layer or a 3 nm PDMS brush layer. According to the Hildebrand solubility parameters of the PDMS ($\delta_{PDMS} = 15.3 \text{ MP}^{1/2}$), PS ($\delta_{PS} = 18.5 \text{ MP}^{1/2}$) and PMPCS ($\delta_{PMPCS} = 20.7 \text{ MP}^{1/2}$)^{33–35} the solubility parameter of PS lies approximately midway between those of PMPCS and PDMS suggesting that the PS brush will not be strongly preferential to either block in the DM. In contrast, the PDMS brush is highly preferential to the PDMS block. BCP films with thickness 30–100 nm were subsequently spin-coated and solvent vapor annealed^{36,37} using an acetone/heptane mixture at room

temperature. The BCP films were etched by a two-step reactive ion etching to leave behind oxidized PDMS patterns.

Table 1
Molecular characteristics of the block copolymers, solvent annealing conditions and the structural parameters of in-plane cylinders

Sample	$N_D:N_M$ or $N_D:N_S:N_M$	$M_{n(D)}^a$ (g/mol)	$M_{n(PMPCS)}^a$ (g/mol)	PDI ^b	f_D^a (%)	f_M^a (%)	SVA (A:H)	L_0^c (nm)	Line/ space ratio
D _{4K} M _{12K}	58:30	4,300	11,700	1.07	33	66	8:1	16.5	1.2:1
D _{4K} M _{17K}	58:44	4,300	17,500	1.07	25	75	8:1	18.7	1:1.2
D _{4K} M _{21K}	58:52	4,300	21,100	1.05	22	79	7:1	20.8	1:1.6
D _{4K} M _{34K}	58:85	4,300	34,300	1.05	15	85	4.5:1	24.8	1:3
D _{4K} S _{7K} M _{40K} ^d	58:70:100	4,300	40,500	1.07	11	73	5:1	30.9	1:4
^a Determined from ¹ H NMR results of the macroinitiator and the block copolymers. ^b Determined from GPC using linear polystyrene standards. ^c Determined from SEM of etched films. f_D is the volume fraction of PDMS and f_M is the volume fraction of PMPCS. ^d In ref. [24] this polymer was named D58S70M100 representing its degree of polymerization.									

Line-space patterns with a wide range of fill factors

Solvent vapor annealing in mixed acetone/heptane vapors with appropriate composition produced in-plane cylindrical morphologies for all the BCPs. The etched top-view and cross-section SEM images of the films in Fig. 1c demonstrate highly ordered cylindrical PDMS microdomains on PS-functionalized substrates; similar results were produced on PDMS-functionalized substrates (Supplementary Information, **Fig. S1**). The preferential wetting of PDMS at the film/air surface (and at the film/substrate interface on PDMS-functionalized substrates) promotes the in-plane orientation. The acetone/heptane mixture ratio (A:H) that yielded well-ordered cylinders was 8:1 for D_{4K}M_{12K}, 7:1 for D_{4K}M_{17K} and D_{4K}M_{21K}, and 4.5:1 for D_{4K}M_{34K}, *i.e.* a greater amount of heptane was required as the PDMS volume fraction decreased, presumably because heptane selectively swells the PDMS to obtain an effective volume fraction consistent with forming a cylindrical morphology. Acetone constitutes the majority of the vapor, and the sum of the partial pressures of all solvent mixtures used here approached 30 kPa.²⁶

Line-space patterns consisting of a monolayer of cylindrical microdomains were characterized from top-view SEM images of films (Fig. 1c). The DSM triblock terpolymer presents in-plane PDMS core-PS shell cylinders²⁶ L_0 is relatively small for these rod-coil BCPs compared with that of typical coil-coil block copolymers with similar molecular weight, due to the interdigitation of the rod block in the matrix,^{25,26} and

the domain size of the PMPCS block is expected to scale almost linearly with the PMPCS molecular weight.²¹ The fill factor r varies between 0.20 and 0.55, covering a wide range that is advantageous for nanolithographic pattern generation. Cylindrical morphology BCPs typically form arrays with $r \sim 0.5$, though the range of r can be extended by annealing in selective solvents.³⁸

Lines with spontaneous kinks and Y-junctions

The most dramatic difference between the line patterns formed by the rod-coil BCPs and coil-coil BCPs is the spontaneous formation of zig-zag bends in the former, in contrast to the fingerprint patterns seen in the latter.³⁹ The zig-zag morphology is shown in Fig. 2a for $D_{4K}M_{34K}$ and in **Fig. S2-3** for all of our BCPs. The cylinders formed sharp kinks or chevrons (V) and bends with a Y-junction structure or arrow (Y-bend),²⁶ which are indicated by yellow and green circles, respectively. When the bending angle decreased to a small value, the bend is no longer continuous, and the cylinders form line segments (LS), indicated by light pink circles. The morphology therefore changes from chevrons to Y-bends to line segments as the bend angle became more acute.

The critical bending angles at which the chevrons transition to Y-junctions (θ_Y) and the Y junctions to line segments (θ_{LS}) are plotted as a function of volume fraction of PDMS (f_{Si}) for all the block copolymers in Fig. 2b. A higher volume fraction of the rod-block, hence narrower PDMS cylinders, correlates with a wider range of existence of the Y-bends. The segment length at the Y-bends, L_b , (Fig. 2a inset and **Fig. S4a**) is plotted vs θ for $D_{4K}M_{21K}$, $D_{4K}M_{34K}$ and $D_{4K}S_{7K}M_{40K}$ in **Fig. S4g**. The segment becomes longer as θ decreases because there is a larger spacing L_{cp} between the cylinders at the bend. Figure 2c shows the data normalized to L_0 , revealing that L_b/L_0 increases with the volume fraction of PMPCS at fixed θ .

Zig-zag morphologies have been observed in several lamellar rod-coil BCPs^{16,20,21,23} and their energetics and internal structure have been examined theoretically.⁴⁰⁻⁴² The zig-zag occurs in lamellar structures in which the rod block forms a liquid crystal smectic C arrangement, with the rods oriented at an angle to the intermaterial dividing surface (IMDS). The zig-zag represents a defect in which the tilt angle of the rods with respect to the IMDS is reversed. The tilting of the rods leads to a higher interface area but enables greater relaxation of the coil blocks, therefore it is stabilized by entropy of the coil block, and is promoted by annealing conditions that screen the block repulsion, e.g. the presence of a good solvent. The formation of zigzag lamellae is therefore process-dependent.²¹ In contrast, coil-coil BCPs lack the driving force provided by rod alignment, but sharp bends, kinks or zig-zags can be created by DSA⁴³ and can occur at the grain boundaries between lamellae in bulk coil-coil BCPs.⁴⁴⁻⁴⁶ The Y-bend appears analogous to the omega structures observed in tilt boundaries of lamellar coil-coil BCPs.^{44,46} However, such omega or Y-bend structures have not been reported for cylindrical coil-coil BCPs, in which the cylinders at grain boundaries tend to form bends rather than junctions.⁴⁷

Our findings therefore extend the morphologies observed in cylindrical rod-coil BCPs to include both zig-zags and Y-junctions. The change in bend morphology with angle may be understood by considering

both the origin of zig-zags in rod-coil BCPs and the chevron-to-omega transition in lamellar tilt boundaries. We first comment that the energetics of bending of microdomains in coil-coil BCPs is described in terms of the interfacial and chain stretching energies.^{48–50} The bending free energy per chain at a radius of curvature R_c is described in the Supplementary Information and **Fig. S5**, and scales with bending angle θ as:

$$\Delta G^{bend}(\theta) = \frac{\pi^2}{62.7} \cdot kT \cdot \frac{L_0^2}{W^2} \cdot \frac{1 - \sin\left(\frac{\theta}{2}\right)^2}{\sin\left(\frac{\theta}{2}\right)^4}$$

where W is the bending boundary width as shown in Fig. 2b.⁴⁶ This energy increases dramatically for sharp bends (*i.e.* low θ and low W), explaining why coil-coil BCPs favor the gradual bends seen in fingerprint patterns. Therefore, the formation of the sharp bends in the DM and DSM clearly indicates that an additional factor is stabilizing the sharp bends, namely the rod-rod interaction. It is significant that the zig-zag morphology was not seen in thermally-annealed cylindrical DM,²⁹ which instead formed a fingerprint pattern. This supports the assumption that the solvent annealing plays a key role in reducing the interfacial energy so that the morphology is dominated by the rod-rod interactions. Thermal annealing at 200 °C causes a nematic orientation and more extended chain conformation for the PMPCS ($L_{0,thermal\ anneal} = 22$ nm, $L_{0,solvent\ anneal} = 18.7$ nm) in $D_{4K}M_{17K}$ compared to the less rigid chain conformation and presumed locally smectic orientation formed during the solvent anneal. Under the solvent annealing, in which the PMPCS is swollen and the chains may form an interdigitated arrangement, the tilt of the rods could relieve the overcrowding, favoring bends and zig-zags.

The transition from chevron to Y-bend occurs with decreasing θ analogously to the chevron-to-omega transition in lamellar coil-coil BCPs: the additional line segment in the Y-bend reduces the stretching of the chains of the majority block required to fill the volume corresponding to increasing L_{cp} . The width W of the bent region (**Fig. S4a**) is larger for the chevron bends than for the Y-bends, *e.g.* in Fig. 2a, $W = 54$ nm for the chevron with $\theta = 137^\circ$, $W = 26$ nm at the transition from chevrons to Y-bends at $\theta = 120^\circ$, and $W = 12$ nm for the Y junction with $\theta = 90^\circ$. For small θ the Y-bend cannot form because there is insufficient volume to enclose the additional branched cylinder between the two straight sections of the cylinders, and the structure transitions to line segments; conformational asymmetry also favors the formation of line segments compared to bent continuous microdomains, as observed in star copolymers.⁵¹ These considerations determine the angular range over which the Y-bend is stable.

Directed Self-Assembly of Bends

We now show how the locations and angles of the bends in the DM and DSM block copolymers can be determined by directed self-assembly using a template etched into the substrate. The templates were prepared by electron beam lithography on silicon substrates, then functionalized with a ~3 nm thick PS or PDMS brush (see Supplementary Information). The sidewalls present a topographical guide and the

polymer brushes provide a chemical guide for DSA. The as-cast film thicknesses were 30–50 nm, and during solvent vapor annealing the BCP on the mesas flowed into the trenches, which resulted in 50–100 nm thick films in the 100 nm deep trenches and at most a wetting layer of BCP on the mesas.

The solvent vapor annealed DM and DSM films present in-plane cylindrical morphologies within both PS and PDMS-coated templates, with orientation dominated by the brush. PS-brushed trenches led to cylinders oriented transverse to the trench shown in Fig. 3a for 120 nm wide trenches, and **Fig. S6** for larger defect-free areas. The cylinder to cylinder distance is the same as that on the flat substrate. Transverse orientation is also produced for wide trenches (**Fig. S7a**) and in trenches with gradually changing width, Fig. 3b. In contrast, PDMS-brush functionalized trenches lead to parallel orientation of the cylindrical patterns of all the BCPs. $D_{4K}M_{12K}$, $D_{4K}M_{21K}$, $D_{4K}M_{34K}$ and $D_{4K}S_{7K}M_{40K}$ present 7, 6, 4, and 3 cylinders in 120 nm wide trenches, respectively, Fig. 3c, and **Fig. S8**. This orientation occurred for narrow trenches, *e.g.* the $D_{4K}M_{34K}$ presents a single cylinder in 30 nm wide trenches transitioning to two cylinders in 50 nm wide trenches (Fig. 3d). Figure 3e plots the number of transverse cylinders along a 625 nm long 120 nm wide PS-brushed trench, and the number of parallel cylinders in 120 nm wide PDMS-brushed trenches as function of BCP molecular weight.

The wetting behaviors of BCP films in PS-brush and PDMS-brush coated trenches are compared schematically in Fig. 3 f. In both cases, the top surfaces of the films form PDMS wetting layers because PDMS has a lower surface energy than PMPCS, implying that the morphological difference is a result of the wetting behaviors at the trench walls. PS brush coated templates preferentially adsorb the PS block of the DSM triblock terpolymer but are not strongly preferential to either block in the PDMS-*b*-PMPCS, because the solubility parameter of PS lies approximately midway between those of PMPCS and PDMS.^{33–35} The adsorption of both PMPCS and PDMS at the sidewalls for DM copolymers and the preferential adsorption of the middle block PS for DSM terpolymer favors the orientation of the PDMS cylinders perpendicular to the sidewalls, as schematically shown in Fig. 3 f. Metastable transverse orientations of cylinders have been observed due to capillary flow in other BCPs, evolving into a parallel orientation for longer annealing times,⁵² or by neutralizing the walls,⁵³ but here the conformationally asymmetrical DM and DSM systems appear to form stable transverse cylinders.

In contrast, for the PDMS brush functionalized templates, the PDMS preferentially forms wetting layers at the top, bottom and sides of the film in the trench, and the cylinders are aligned parallel to the film surface and also to the trench walls. The transverse alignment in the PS-brush coated trenches and the parallel orientation in the PDMS-brush coated trenches was found in films with a range of thicknesses, and the polymer brush modified trenches can even guide the orientation and long range ordering of films much thicker than the trench depth, **Fig. S9**.

In our previous report of directed self-assembly of $D_{4K}M_{17K}$ diblock copolymer in PS-brushed trenches by thermal annealing (200 °C, 72 hr),²⁹ ladder morphologies (consisting of transverse cylinders joined to one parallel cylinder adjacent to each sidewall) as well as cylinders parallel to the sidewalls were formed depending on the film thickness and the groove and mesa width. In comparison, the transverse

morphologies of the present study were produced consistently in DM and DSM films in PS-brushed trenches. The difference is attributed to the use of solvent annealing in the present study. The mobility of the rod-coil BCP under thermal annealing is lower than that produced by solvent annealing, and for the wider mesas not all the BCP flowed into the trenches during the thermal anneal. For solvent annealing the influence of mobility, wetting behavior and the swelling and LC configuration of the chains differ from the thermal anneal case and the ordering kinetics is faster.

In prior work, a two-step anneal of $D_{4K}M_{21K}$ consisting of solvent annealing followed by thermal annealing produced vertically-aligned lamellae in which the PMPCS exhibited a hexatic columnar nematic LC arrangement.³⁰ The response of $D_{4K}M_{21K}$ cylinders in templates to a subsequent thermal annealing process is shown in **Fig. S10**. The transverse or parallel orientation of the cylinders imparted by the PS or PDMS brush respectively during solvent annealing was preserved as they transitioned into lamellae, although some regions of in-plane lamellae were also observed. This process therefore provides a route to templating lamellae of different orientations within trenches via the surface chemistry. Lamellae are favored by larger molecular weight of the PMPCS as well as a more symmetric volume fraction.

We now describe the templating of bends by directed self-assembly within V-shaped templates coated with a PS-brush. Figure 4a-b shows the transverse alignment of $D_{4K}M_{34K}$ and $D_{4K}S_{7K}M_{40K}$ in right-angled trenches. Concentric bending occurs at the corners, and the bending angle of the PDMS cylinders θ is expected to be the supplementary angle of the bending angle of the trench ($\angle V$). The $D_{4K}M_{34K}$ and $D_{4K}S_{7K}M_{40K}$ form Y-junctions on flat substrates at a bending angle $\sim 90^\circ$, but in the trenches, wide chevrons are observed for both BCPs. The $D_{4K}M_{34K}$ was also templated in 120 nm wide trenches patterned with $\angle V = 30, 60, 90, 120$ and 150° , **Fig. S7b**. The chevron bends display $\theta = 150, 120$ and 90° for $\angle V = 30, 60$ and 90° respectively, but for $\angle V = 120^\circ$ and 150° , the cylinders are tilted with respect to the trench wall and Y-junctions are not observed. Figure 4c and **Fig. S7c-d** show the effect of other trench geometries. For PDMS-brush functionalized trenches, **Fig. S11**, the cylinders followed the sidewall contour and concentric bending was observed. These results show that in templated bends the chevrons are favored over Y-bends or line segments, and the angle at the bend is lowered by accommodating a tilt of the cylinders so that they are not perpendicular to the sidewalls. The control over transverse and parallel orientations may be useful in fabricating 3D multilayer structures relevant to microelectronic device layouts.

Summary

We demonstrate the formation of a series of grating patterns with scalable periodicity and line/space ratios from solvent annealed thin films of conformationally asymmetrical silicon-containing rod-coil block copolymers and terpolymers. Spontaneous bending leads to chevrons, Y-junctions and line segments, unlike the fingerprint patterns typically found in thin films of cylindrical or lamellar morphology BCPs. Directed self assembly within chemically functionalized topographical substrates produces a range of patterns with control over the cylinder orientation and bending. In particular, the surface

chemistry of the patterned substrate yields in-plane cylinders either transverse or parallel to the sidewalls for a range of polymer compositions and film thicknesses. Furthermore, concentric bending of the cylinders occurs in trenches with angles. These results reveal a powerful platform for designing functional 3D nanostructures or device layouts by utilizing conformationally asymmetrical block copolymers.

Methods

Characteristics of the BCPs and thin film fabrication. Four different PDMS-*b*-PMPCS diblock copolymers were synthesized by atom transfer radical polymerization and a DSM triblock terpolymer was prepared by sequential atom transfer radical polymerization using the same monodisperse PDMS macroinitiator (4300 g/mol, PDI = 1.02). 30–120 nm thick films were prepared by spin coating dilute solution of the BCP solution in toluene on the substrates. The concentration of the solution was 2~5 wt% at various spin speeds. The film thickness was measured from the reflectance spectra of the BCP thin film within a wavelength range of 300 – 1000 nm by spectral reflectometry (FilMetrics F20-UV).

Solvent vapor annealing of the BCP thin films. Solvent vapor annealing was carried out with samples supported on a stage inside a solvent reservoir annealing system consisting of a closed chamber of volume 80 cm³ with 6 mL of liquid acetone:heptane mixture inside. The volumetric ratios of the acetone:heptane mixture in the chamber used to produce cylindrical cylinders for D_{4K}M_{12K}, D_{4K}M_{17K}, D_{4K}M_{21K}, D_{4K}M_{34K} and D_{4K}S_{7K}M_{40K} were 8:1, 7:1, 7:1, 4.5:1, 5:1, respectively, corresponding to molar ratio 16:1, 14:1, 14:1, 9:1 and 10:1. The chamber had a loosely fitted lid that allowed the vapor to leak out slowly at room temperature, 23 ± 2 °C, with humidity 76%. The acetone:heptane mixture is a nonideal solution and the partial pressure of acetone is much higher than that of heptane. Based on experimental data for the binary liquid system of acetone and heptane, when the mole ratio of acetone in the mixed solvents was higher than 0.8, the total vapor pressure is estimated to approach the partial pressure of acetone at 298 K, ~30.6 kPa.^{30,54}

Patterned substrate fabrication A 300 nm thick positive ZEP 520A electron beam resist film was spin-coated onto a Si wafer with a 200 nm thermally grown oxide layer. The patterns were exposed with an Elionix EBL tool at a beam current of 10 nA. Then the exposed photoresist was developed with ZED N50 developer. A 4 min CF₄/O₂ plasma etching was used to transfer the patterns into the SiO₂ layer. Finally, a piranha clean was conducted to remove the residual resist. The patterned substrates were then chemically functionalized with polymer brushes.

Chemical functionalization of substrates. The PS brush (hydroxyl terminated PS, 11.0 kg/mol, polydispersity index (PDI) = 1.10, Polymer Source, Inc.) and PDMS brush (hydroxyl terminated PDMS, 5.0 kg/mol, polydispersity index (PDI) = 1.07, Polymer Source, Inc.) were grafted to the surface of the flat and template substrates through the dehydration reaction between hydroxyl groups of the polymer chain and silanol groups of the silicon oxide during baking at 170 °C under vacuum (20 Torr) for 20 h. After thoroughly rinsing in toluene to remove unreacted excess polymer chains, a 3 nm PS brush layer and a

2 nm PDMS brush layer were obtained respectively. During annealing the BCP flows into the trenches. For example, in the template with trench width 120 nm and mesa width 80 nm, the initial 30 nm thick film leads to an estimated 50 nm thick film in the trenches after annealing.

Reactive ion etching of BCP films. A two-step RIE (Plasma-Therm 790) method consisting of a 50W CF₄ plasma at 15 mTorr to remove the PDMS wetting layer on the surface and a 90W O₂ plasma at 6 mTorr to selectively etch the PMPCS and PS matrix was used to convert the BCP patterns to oxidized in-plane PDMS cylinders. The etching time for D_{4K}M_{12K} BCP was 5 s of CF₄ plus 5 s of O₂, and that for D_{4K}M_{12K} BCP was 5 s of CF₄ plus 8 s of O₂, and that for D_{4K}M_{34K} and D_{4K}S_{7K}M_{40K} is 3 s of CF₄ plus 8 s of O₂.

SEM imaging. Imaging of the etched samples was performed on a Zeiss Merlin SEM, with 2–5 keV accelerating voltage, ~4 mm working distance and 100–150 pA. For cross-sectional imaging, microscopy was performed on the Zeiss Merlin similar to above with the sample held at an angle of 80°.

Declarations

Acknowledgment.

Financial support from NSF DMR-1606911, the Semiconductor Research Corporation, the National Natural Science Foundation of China (Grants 51773124 and 51403132) and the Fundamental Research Funds for Central Universities are gratefully acknowledged. Shared experimental facilities of CMSE, an NSF MRSEC under award DMR-1419807, and the NanoStructures Laboratory were used.

References

1. Bates, F. S. & Fredrickson, G. H. Block copolymers—designer soft materials. *Phys. Today* **52**, 32–38 (1999).
2. Mai, Y. & Eisenberg, A. Self-assembly of block copolymers. *Chem. Soc. Rev.* **41**, 5969–5985 (2012).
3. Bates, C. M. & Bates, F. S. 50th anniversary perspective: block polymers—pure potential. *Macromolecules* **50**, 3–22 (2017).
4. Kim, H.-C., Park, S.-M. & Hinsberg, W. D. Block copolymer based nanostructures: materials, processes, and applications to electronics. *Chem. Rev.* **110**, 146–177 (2010).
5. Jackson, E. A. & Hillmyer, M. A. Nanoporous membranes derived from block copolymers: from drug delivery to water filtration. *ACS Nano* **4**, 3548–3553 (2010).
6. Sai, H. *et al.* Hierarchical porous polymer scaffolds from block copolymers. *Science* **341**, 530 (2013).
7. Tang, C., Lennon, E. M., Fredrickson, G. H., Kramer, E. J. & Hawker, C. J. Evolution of block copolymer lithography to highly ordered square arrays. *Science* **322**, 429 (2008).
8. Stoykovich, M. P. *et al.* Directed self-assembly of block copolymers for nanolithography: fabrication of isolated features and essential integrated circuit geometries. *ACS Nano* **1**, 168–175 (2007).

9. Tavakkoli K. G, A. *et al.* Templating three-dimensional self-assembled structures in bilayer block copolymer films. *Science* **336**, 1294 (2012).
10. Doerk, G. S. *et al.* Enabling complex nanoscale pattern customization using directed self-assembly. *Nat. Commun.* **5**, 5805 (2014).
11. Majewski, P. W., Rahman, A., Black, C. T. & Yager, K. G. Arbitrary lattice symmetries via block copolymer nanomeshes. *Nat. Commun.* **6**, 7448–7448 (2015).
12. Cheng, J. Y., Mayes, A. M. & Ross, C. A. Nanostructure engineering by templated self-assembly of block copolymers. *Nat. Mater.* **3**, 823–828 (2004).
13. Segalman, R. A. Directing Self-Assembly Toward Perfection. *Science* **321**, 919 (2008).
14. Li, W. & Müller, M. Directed self-assembly of block copolymers by chemical or topographical guiding patterns: optimizing molecular architecture, thin-film properties, and kinetics. *Prog. Polym. Sci.* **54–55**, 47–75 (2016).
15. Lo, T.-Y., Krishnan, M. R., Lu, K.-Y. & Ho, R.-M. Silicon-containing block copolymers for lithographic applications. *Prog. Polym. Sci.* **77**, 19–68 (2018).
16. Chen, J. T., Thomas, E. L., Ober, C. K. & Mao, G. P. Self-assembled smectic phases in rod-coil block copolymers. *Science* **273**, 343–346 (1996).
17. Hoebe, F. J. M., Jonkhøj, P., Meijer, E. W. & Schenning, A. P. H. J. About Supramolecular assemblies of π -conjugated systems. *Chem. Rev.* **105**, 1491–1546 (2005).
18. Zhang, J., Chen, X.-F., Wei, H.-B. & Wan, X.-H. Tunable assembly of amphiphilic rod–coil block copolymers in solution. *Chem. Soc. Rev.* **42**, 9127–9154 (2013).
19. Ryu, J.-H. & Lee, M. in *Liquid crystalline functional assemblies and their supramolecular structures* (ed Takashi Kato), 63–98 (Springer Berlin Heidelberg, 2008).
20. Schlaad, H., Smarsly, B. & Losik, M. The role of chain-length distribution in the formation of solid-state structures of polypeptide-based rod – coil block copolymers. *Macromolecules* **37**, 2210–2214 (2004).
21. Chen, J. T., Thomas, E. L., Ober, C. K. & Hwang, S. S. Zigzag morphology of a poly(styrene-*b*-hexyl isocyanate) rod-coil block copolymer. *Macromolecules* **28**, 1688–1697 (1995).
22. Osipov, M. A., Gorkunov, M. V., Berezkin, A. V., Antonov, A. A. & Kudryavtsev, Y. V. Molecular theory of the tilting transition and computer simulations of the tilted lamellar phase of rod–coil diblock copolymers. *J. Chem. Phys.* **152**, 184906 (2020).
23. Thomas, E. L., Chen, J. T., O'Rourke, M. J. E., Ober, C. K. & Mao, G. Influence of a liquid crystalline block on the microdomain structure of block copolymers. *Macromol. Symp.* **117**, 241–256 (1997).
24. Huang, M. *et al.* Highly asymmetric phase behaviors of polyhedral oligomeric silsesquioxane-based multiheaded giant surfactants. *ACS Nano* **12**, 1868–1877 (2018).
25. Shi, L.-Y., Zhou, Y., Fan, X.-H. & Shen, Z. Remarkably rich variety of nanostructures and order–order transitions in a rod–coil diblock copolymer. *Macromolecules* **46**, 5308–5316 (2013).

26. Shi, L.-Y. *et al.* Core-shell and zigzag nanostructures from a thin film silicon-containing conformationally asymmetric triblock terpolymer. *ACS Macro Letters*, 852–858 (2019).
27. Chen, X.-F. *et al.* Mesogen-jacketed liquid crystalline polymers. *Chem. Soc. Rev.* **39**, 3072–3101 (2010).
28. Lyu, X. *et al.* Head-tail asymmetry as the determining factor in the formation of polymer cubosomes or hexasomes in a rod-coil amphiphilic block copolymer. *Angew. Chem. Int. Ed.* **57**, 10132–10136 (2018).
29. Shi, L.-Y. *et al.* Thin film self-assembly of a silicon-containing rod-coil liquid crystalline block copolymer. *Macromolecules* **52**, 679–689 (2019).
30. Shi, L.-Y. *et al.* Vertical lamellae formed by two-step annealing of a rod-coil liquid crystalline block copolymer thin film. *ACS Nano* **14**, 4289–4297 (2020).
31. Li, L. & Yokoyama, H. Nanoscale silica capsules ordered on a substrate: Oxidation of nanocellular thin films of poly(styrene-*b*-dimethylsiloxane). *Angew. Chem. Int. Ed.* **45**, 6338–6341 (2006).
32. Oh, J. *et al.* Universal perpendicular orientation of block copolymer microdomains using a filtered plasma. *Nat. Commun.* **10**, 2912 (2019).
33. Barton, A. F. M. *Handbook of polymer-liquid interaction parameters and solubility parameters*, 1st edn, 125–147 (CRC Press, Florida, 1990).
34. Shi, L.-Y., Shen, Z. & Fan, X.-H. Order – order transition in a rod – coil diblock copolymer induced by supercritical CO₂. *Macromolecules* **44**, 2900–2907 (2011).
35. Gotrik, K. W. *et al.* Morphology control in block copolymer films using mixed solvent vapors. *ACS Nano* **6**, 8052–8059 (2012).
36. Jung, Y. S. & Ross, C. A. Solvent-vapor-induced tunability of self-assembled block copolymer patterns. *Adv. Mater.* **21**, 2540–2545 (2009).
37. Chavis, M. A., Smilgies, D.-M., Wiesner, U. B. & Ober, C. K. Widely tunable morphologies in block copolymer thin films through solvent vapor annealing using mixtures of selective solvents. *Adv. Funct. Mater.* **25**, 3057–3065 (2015).
38. Jeong, J. W., Park, W. I., Kim, M.-J., Ross, C. A. & Jung, Y. S. Highly tunable self-assembled nanostructures from a poly(2-vinylpyridine-*b*-dimethylsiloxane) block copolymer. *Nano Letters* **11**, 4095–4101 (2011).
39. Lane, A. P. *et al.* Directed Self-Assembly and Pattern Transfer of Five Nanometer Block Copolymer Lamellae. *ACS Nano* **11**, 7656–7665 (2017).
40. Li, W. & Gersappe, D. Self-assembly of rod – coil diblock copolymers. *Macromolecules* **34**, 6783–6789 (2001).
41. Pryamitsyn, V. & Ganesan, V. Self-assembly of rod-coil block copolymers. *J. Chem. Phys.* **120**, 5824–5838 (2004).
42. Gao, J., Song, W., Tang, P. & Yang, Y. Self-assembly of semiflexible block copolymers: 2D numerical implementation of self-consistent field theory. *Soft Matter* **7**, 5208–5216 (2011).

43. Ji, S. *et al.* Directed assembly of non-equilibrium ABA triblock copolymer morphologies on nanopatterned substrates. *ACS Nano* **6**, 5440–5448 (2012).
44. Matsen, M. W. Kink grain boundaries in a block copolymer lamellar phase. *J. Chem. Phys.* **107**, 8110–8119 (1997).
45. Gido, S. P. & Thomas, E. L. Lamellar diblock copolymer grain boundary morphology. 2. Scherk twist boundary energy calculations. *Macromolecules* **27**, 849–861 (1994).
46. Gido, S. P. & Thomas, E. L. Lamellar diblock copolymer grain boundary morphology. 4. Tilt boundaries. *Macromolecules* **27**, 6137–6144 (1994).
47. Jinnai, H., Yasuda, K. & Nishi, T. Three-dimensional observations of grain boundary morphologies in a cylinder-forming block copolymer. *Macromol. Symp.* **245–246**, 170–174 (2006).
48. Wang, Z. G. & Safran, S. A. Curvature elasticity of diblock copolymer monolayers. *J. Chem. Phys.* **94**, 679–687 (1991).
49. Wang, Z. G. Response and instabilities of the lamellar phase of diblock copolymers under uniaxial stress. *J. Chem. Phys.* **100**, 2298–2309 (1994).
50. Jung, Y. S., Jung, W. & Ross, C. A. Nanofabricated concentric ring structures by templated self-assembly of a diblock copolymer. *Nano Lett.* **8**, 2975–2981 (2008).
51. Yang, L., Hong, S., Gido, S. P., Velis, G. & Hadjichristidis, N. I₅S miktoarm star block copolymers: packing constraints on morphology and discontinuous chevron tilt grain boundaries. *Macromolecules* **34**, 9069–9073 (2001).
52. Jung, Y. S. & Ross, C. A. Orientation-controlled self-assembled nanolithography using a polystyrene – polydimethylsiloxane block copolymer. *Nano Lett.* **7**, 2046–2050 (2007).
53. Bai, W., Gadelrab, K., Alexander-Katz, A. & Ross, C. A. Perpendicular block copolymer microdomains in high aspect ratio templates. *Nano Lett.* **15**, 6901–6908 (2015).
54. Maripuri, V. O. & Ratcliff, G. A. Measurement of isothermal vapor-liquid equilibriums for acetone-n-heptane mixtures using modified Gillespie still. *J. Chem. Eng. Data* **17**, 366–369 (1972).

Figures

Figure 1

Self-assembly of cylindrical-morphology block copolymers. (a) Chemical structures of the PDMS-*b*-PMPCS diblock copolymer and PDMS-*b*-PS-*b*-PMPCS triblock terpolymer, and representations of their coil-rod and coil-coil-rod shapes. (b) Fabrication procedure to create silica patterns on flat and patterned silicon substrates. (c) SEM images of oxidized PDMS nanopatterns formed in DM copolymers and DSM terpolymer thin films via solvent vapor annealing. (d) The plots of L_0 and line/space ratio as function of molecular weight and volume fraction of silicon block.

Figure 2

Cylindrical bending patterns and the geometry of chevrons and Y-bends. (a) SEM images of oxidized PDMS microdomains in D4KM34K diblock copolymer thin films, in which yellow, green and pink circles represent examples of chevrons, Y-junctions and line segments, respectively, and the blue arcs represent the region of the bend with width W . (b) θ_Y and θ_{LS} of all BCP samples and (c) the curves of normalized L_b/L_0 as function of θ .

Figure 3

Directed self-assembly of transverse and parallel cylinders. (a-b) SEM image of transverse cylinders in PS-brush modified templates; (c-d) SEM images of parallel cylinders in PDMS-brush modified templates. (e) Plots of numbers of transverse cylinders in a 625 nm long trench and parallel cylinders in 120 nm wide trenches as function of molecular weight. (f) Schematic illustration of the alignment of cylinders in the polymer brush functionalized trenches.

Figure 4

Concentric bending morphology in bending trenches. SEM images of transverse cylinders in (a) right angle trenches, (b) T-shape trenches, and (c) number shaped trenches, for both DM and DSM block copolymers.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [bendingpaperSupportingInformationcr.docx](#)
- [FigS1.png](#)
- [FigS2.png](#)
- [FigS3.png](#)
- [FigS4.png](#)
- [FigS5.png](#)
- [FigS6.png](#)
- [FigS7.png](#)
- [FigS8.png](#)
- [FigS9.png](#)
- [FigS10.png](#)

- [FigS11.png](#)