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Nanoscale spirals by directed self-assembly

Hong Kyoon Choi1,2,8, Jae-Byum Chang1,3,8, Adam F Hannon1,4, Joel K W Yang5,6, Karl K Berggren7, Alfredo Alexander-Katz1 and Caroline A Ross1

1 Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States of America
2 Division of Advanced Materials Engineering, Kongju National University, Cheonan, Republic of Korea
3 Department of Biomedical Engineering, Sungkyunkwan University, Seoul, Republic of Korea
4 Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States of America
5 Singapore University of Technology and Design, 8 Somapah Road, Singapore 487372, Singapore
6 Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, #08-03, Innovis, Singapore 138634, Singapore
7 Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, United States of America
8 These authors contributed equally.

E-mail: carross@mit.edu

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Abstract

Archimedean spiral patterns are formed by the directed self-assembly of diblock copolymer thin films within a circular template. The presence of a notch in the template promotes the formation of a spiral compared to concentric rings, and the notch shape determines the chirality of the spiral. Double spirals occur when the notch width is increased or when there are two notches. The spiral followed an Archimedean form with exponent \( \approx 0.9 \). Self-consistent field theory reproduces the experimentally observed morphologies and demonstrates the templating of spirals in cylindrical-morphology block copolymer films.

1. Introduction

There has been extensive work on the templated self-assembly of diblock copolymer (BCP) thin films, forming both periodic and aperiodic arrays of microdomains which have applications in diverse fields including nanofabrication, filtration, or photonics [1–7]. The microphase separation of BCPs can be templated using topographical or chemical patterns on a substrate which register the microdomains at specific locations, and which can generate structures not found in bulk, such as cylinders or lamellae with bends and junctions [8–12]. Commensurability between the template and the period \( L_0 \) of the BCP has a critical influence on the templating of microdomains in BCP thin films. For example, the number of lamellar, cylindrical or spherical microdomains that form within a trench depends on the ratio of the trench width to \( L_0 \) [13].

How BCPs self-assemble within curved templates has been a question of long-standing interest [14–18]. BCPs or BCP blends with lamellar or cylindrical microdomains have been templated within 3D spherical or cylindrical pores, leading to a range of microdomain geometries including concentric cylinders or vesicles, stacked tori or disks, helices, or pea-pod structures [19–32]. Helical structures have also been reported in chiral block copolymers [33, 34], triblock terpolymers [35, 36], terpolymer micelles [37], and BCP globules [38]. There have been reports of concentric ring formation in BCP films confined in circular templates [39–43], and from half-onion structures formed in hemispheres [44, 45], which have applications in the fabrication of sensors based on surface-enhanced Raman scattering [44, 45]. BCPs assembling on a spherical surface are predicted to form spiral structures [46], and we reported a spiral made from a cylindrical microdomain formed within a hexagonal template [47]. However, there has been little work on the control of the chirality of helical structures or spirals using BCP self-assembly.
Chiral nanostructures are especially attractive due to their interesting optical properties such as circular dichroism or optical rotatory dispersion which can be used in the analysis of molecular chirality in DNA, amino acid and proteins [48]. There have been studies on the fabrication of artificial chiral nanostructures to manipulate circular dichroism and optical activity using several lithographic methods such as direct laser writing, holographic lithography, photolithography and even DNA origami [49–52].

In this article, we demonstrate the formation of both spirals and concentric rings from a cylindrical-morphology BCP in circular confinement and show how the chirality of the spirals can be controlled in 2D. The length of the spiral increases with the diameter of the template. The results are compared with self-consistent field theory (SCFT) simulations that show the templating of spirals in cylindrical-forming BCP films.

2. Materials and methods

A polystyrene–b-polydimethylsiloxane (PS-b-PDMS) BCP was used with molecular weight $M_N = 45.5$ kg mol$^{-1}$ and volume fraction $f_{\text{PDMS}} = 0.335$. In bulk this material forms close-packed cylinders of PDMS within a PS matrix. Oxidized silicon substrates were patterned with topographical features consisting of circular pits or notched pits written in hydrogen silsesquioxane (HSQ) resist by electron beam lithography, as described previously [39, 47]. The exposed and developed HSQ formed a silica-like material with a thickness of 40 nm. The surface of the substrate and HSQ patterns was functionalized with a hydroxy-terminated PS brush ($M_N = 11$ kg mol$^{-1}$) which was spin-coated from solution, baked overnight then rinsed. This made the substrates preferentially attractive to the PS block of the PS–b-PDMS.

The PS-b-PDMS was spin-coated on the patterned substrates to a thickness of 33 nm, then annealed by placing the samples in a chamber containing a reservoir of liquid solvent (5:1 volumetric mixture of toluene and heptane) for 3 h, then removing the lid and allowing the sample to dry within seconds. Varying the toluene:heptane ratio produces different microdomain morphologies, and the solvent vapor from the 5:1 solvent mixture is known to produce a chiral morphology in the 45.5 kg mol$^{-1}$ PS–b-PDMS [53, 54]. The film thickness was chosen to form one layer of in-plane cylindrical PDMS microdomains in a PS matrix. A PDMS layer is also present at the polymer–air interface due to the low surface energy of PDMS. The microdomain morphology was determined by etching the film, first with a short 5 s CF$_4$ reactive ion etch to remove the PDMS surface layer, then a 22 s oxygen etch to remove the PS and oxidize the PDMS cylindrical microdomains. The morphology was imaged in an SEM (Helios NanoLab 600, FEI). Oxidized PDMS cylinders on a smooth substrate formed a fingerprint-like pattern with spacing of $L_0 = 36$ nm.

SCFT simulations were performed both in 2D and in 3D to examine how the shape of the confinement leads to the formation of ring-shaped or spiral microdomains. Details of the SCFT simulations are available in prior work [53, 55]. The simulations used circular boundary conditions, some of which included internal notched features. The template features were modeled using constraints to the pressure fields with large fixed values $P$ and the preferential surface boundary conditions were modeled with constrained exchange fields with values denoted by $W$. Positive $W$ values are attractive to PDMS and negative to PS. The 2D simulations were performed on a 64 by 64 grid. The 3D simulations used a fixed monolayer film thickness with 22 grid points in the thickness direction. In the 2D simulations, a volume fraction $f_{\text{PDMS}} = 0.5$ was used based on the approximate observed area fraction of PDMS after etching, whereas in the 3D simulations, $f_{\text{PDMS}} = 0.335$. The inner diameter $d$ of the templates was varied from 0.4 to 8.7 $L_0$, where $L_0$ is found from a set of simulations in which the free energy was determined for a single commensurate line feature within a rectangular confinement box of varying size in units of $R_g$. The free energy minimum occurs for a commensurate line when $L_0 \cong 3.6 R_g \chi N$ was set to 18, where $\chi$ is the Flory–Huggins interaction parameter and $N$ the degree of polymerization.

3. Results and discussion

3.1. Formation of spirals and concentric rings

Examples of the rings and spirals that formed in either the circular or notched templates are shown in figure 1. The inner diameter $d$ of figures 1(e)–(g) was 350 nm. Circular templates (figure 1(e)) produced a set of four concentric rings for this diameter, similar to those we reported previously in which PDMS-functionalized circular templates produced concentric tori from the same cylindrical-morphology PS–b-PDMS annealed in toluene vapor [39]. However, introducing a notch in the circular template breaks the geometrical symmetry of the template and promotes a spiral PDMS microdomain. The notch width, $w_{\text{NS}}$, is 38 nm which is comparable to the periodicity of the block copolymer ($L_0 \cong 36$ nm). The chirality of the spiral was determined by the orientation of the notch, and the spirals formed reproducibly in multiple notched templates.

In general, a spiral microdomain has two ends, one at the center and one at the outer edge of the spiral. However, in the spiral PDMS microdomain formed in the notched templates, the outer end facing the radial
edge of the notch was usually connected to the inner spiral arc and formed a Y junction instead of a termination as shown in figure S1 (see supporting information SI available online at stacks.iop.org/NANO/1/015001/mmedia). The density of Y junctions and terminations is influenced by the volume fraction and the annealing conditions [56]. The results here suggest that in our BCP system, the energetic cost of forming a Y junction is lower than that of forming a termination. Supplementary SCFT simulations varying the notch shape were performed to further investigate the formation of either Y junctions or terminations with the PDMS spirals (see SI1).

Figure 2 shows the effect of the inner diameter of the template \(d\) on the ring and spiral patterns. In the circular templates (figures 2(a) and (c)) the central feature was either a PDMS sphere or a hole corresponding to PS that was removed by the reactive ion etching. The number of PDMS rings increased stepwise as \(d\) increased, shown in figure 2(c). This behavior parallels that seen in [39], in which the cylinder spacing was smaller (34.2 nm) and the transition from \(n\) to \(n + 1\) PDMS rings occurred at smaller \(d\). For example, the transition from 3 rings plus a central sphere to 4 rings occurred at \(d \approx 270\) nm in [39] and at \(d \approx 310\) nm in figure 2(c). Reference [39] used a PDMS brush unlike the PS brush used here, which would increase the transition diameter; however, the PS-\(b\)-PDMS in [39] exhibited smaller periodicity (due to the different solvent vapor environment used) which would lower the transition diameter. In the notched templates, figure 2(b), the length of the spiral increased with \(d\), and the number of rotations is plotted versus \(d\) in figure 2(d). There is a monotonic increase in spiral length with \(d\) within measurement error.

### 3.2. The effect of notch width

When the notch width \(w_N\) is comparable with \(L_o\) (36 nm), a spiral is always energetically favorable compared to concentric rings as shown in figure 2. However, if we introduce a narrower notch, \(w_N = 25\) nm, either spiral or concentric rings can form depending on the commensurability between template diameter \(d\) and \(L_o\) as shown in figure 3. For commensurate templates the narrower notch could not induce a spiral, and concentric rings with distortion around the notch were formed as shown in figure 3(a). This observation indicates that the energetic cost of two terminations (or one termination and one Y junction) is higher than the cost of the distortion of rings around a narrower notch. On the other hand, when \(d\) is incommensurate with \(L_o\), the additional incommensurate strain in the rings combined with the bending energy from the distortion of rings around the notch stabilizes a spiral as shown in figure 3(b). Figure 3(c) shows the transition as a function of \(d\) for the narrower notch. We examined 16 templates for each \(d\). For most diameters both concentric rings and the spiral structure were produced in different templates, and figure 3(c) indicates the most frequent structure. The details of the image analysis are described in figure S3 (see SI). Figure 3(c) clearly shows that for \(d\) near the transition where the number of concentric rings changes and the strain due to incommensuration is greatest, a spiral becomes the favorable structure. The transition diameter is not exactly the same as that in figure 2(c); this deviation may be due to the distortion around the notch in concentric rings.

When we introduce a wider notch, \(w_N = 55\) nm, the dimension of the notch is sufficient to initiate two spiral ends which results in double spiral as shown in figures 4(b) and (e). A double spiral can also be formed in an alternative manner: placing two notches at opposite sides of the template forms a double spiral as shown in

![Figure 1](image-url)
figures 4(c) and (f). In both cases the center of the pattern contained two terminations because the PDMS cylinders did not join.

3.3. SCFT modeling of spirals and rings

Figure 5 shows the geometry of the templates used in simulations, and examples of 3D model results for notched and unnotched templates. The BCP thickness for these 3D simulations was \( \approx 1.4L_0 \) and PS template wetting conditions were used. The top-down projection of the 3D results agreed well with the corresponding 2D model confirming the validity of using 2D simulations, and therefore a 2D model was used for subsequent simulations due to the faster computation speed. These SCFT results are general for any BCP of similar \( \chi_N \) and \( f \) implying the formation of such spiral and ring nanostructures is not limited to PS-\( b \)-PDMS.

Figure 6 shows the results of 2D simulations for a circular template with its internal surface attractive to the PS block (PS is red and PDMS is blue). As \( d \) increased, the morphology evolved from having no internal structure to having a PDMS dot inside the wetting ring, a PS wetting ring, an internal PS dot, a PS ring, a PS ring around a PS dot, and so forth. The transition between these structures was governed by the commensuration of the rings with the hole diameter. The transitions from a PS ring to a dot at the center occurred close to an even integer
Figure 4. Schematic (a)–(c) and experimental result (d)–(f) of spirals: (a), (d) single spiral; (b), (e) double spiral from a wider notch; (c), (f) double spiral from a pair of notches. The notch width of (d), (e) and (f) are 38 nm, 55 nm and 38 nm respectively.

Figure 5. (a) Boundary conditions used in simulations for circular (left) and notched (middle) templates. The gray regions are where the BCP was excluded by a large pressure field with \( P = 20 \), red where the brush was modeled with a field attractive to the PS block \( W = -10 \), and light blue where the BCP evolved without constraint. Zoomed-in view of the notches are detailed (right) with base width \( b \) and height \( h \). (b) Top-down and side views of 3D simulations illustrate the top-down projection matches the 2D result for a monolayer of features. Blue features are the minority PDMS and the red region represents the confining hole template with PS preferentiality.

Figure 6. Plot of the number of internal (not counting the outer wetting ring) PS rings, \( N_{\text{PSRings}} \) versus the normalized confining diameter \( d/L_0 \). Gold cross points indicate structures that had no internal feature inside the outer wetting layer, dot points indicate a PS dot at the center, and circular points indicate a PS ring (PDMS dot) at the center. Red dots show no outer ring, blue dots show one outer ring, magenta dots show two outer rings, and crimson dots show three outer rings. Aqua circles show only one PDMS dot inside the wetting ring, green circles show one ring, yellow circles show two rings, and cyan circles show three rings. Representative density maps are given on the right for the PDMS regions (blue) and PS regions (red) with approximate \( d/L_0 \) ranges noted for each morphology. Colors around the confinement region correspond to the colors of the points in the plot on the left.
value of $d/L_0$, while transitions from a PS dot to a ring occurred at odd integer values of $d/L_0$. The regions over which a given number of rings persists is in the range of $\approx 0.7–1.7$ times the number of chain segment regions from the edge of the diameter to the center of the hole (see figure S4 in SI for a schematic illustration). One would expect the actual range to be symmetric from 0.5 to 1.5, but BCPs domains tend to tolerate larger tensile strain values than compressive strain [57] in addition to the circular confinement distorting the equilibrium $L_0$ values [39]. Prior work has examined concentric ring structures from an analytical perspective [39]. Since the curvature of the PDMS microdomains into tori introduces an additional energy term, the lowest energy ring spacing varies slightly with radius.

To examine how the addition of a notch induces spirals, two different notch geometries were simulated. Simulation results for both notch shapes at different $d/L_0$ values are shown in figure 7(a). The smaller of the two notch shapes induced spirals when $d/L_0 \approx 5.0$ while the larger notch shape induced spirals when $d/L_0 \approx 3.0$. The spiral chirality was determined by the notch orientation. In the model the notch size scaled with $d$, unlike the experiment where the notch size was the same for all $d$. This meant that rings rather than spirals formed for smaller $d$ because the notch was proportionately smaller compared to $L_0$ and distorted the outer ring to a lesser extent.

The spiral arc length was measured in the simulations as a function of the template diameter. From a simple geometric consideration, an Archimedean spiral would be the most likely type of spiral to form since such spirals are characterized by a constant distance between successive turns [58, 59]. Archimedean spirals have the general polar equation form $\rho = b\theta^m$ where $b$ is related to the spiral arm separation distance, $\rho$ is the polar radius coordinate, $\theta$ is the polar angle coordinate, and $m$ is a parameter that determines how tightly the spiral arm is wrapped. The classic case known simply as an Archimedes’ spiral occurs when $m = 1$. The arc length of the spirals as a function of the radius was calculated by numerical integration using the relationship

$$S = \int_{0}^{\theta_{max}} \sqrt{\rho^2 + \left(\frac{d\rho}{d\theta}\right)^2} \, d\theta,$$

where $\rho = d/2$ is the radius and $\theta$ is the polar angle integration variable. The spiral lengths were calculated using image analysis of the SCFT simulation results that defined a line at the center of the PS spiral and counted the number of grid points that were contained in the line as shown in figure 7(b). The length of the model spirals was less than that of an ideal Archimedes spiral, and $S_{\text{model}} \approx 0.918$, indicating the BCP spirals are more tightly wound than an ideal Archimedes’ spiral. This is evidenced by the domain lengths contracting towards the center of the confining hole. The implications of these results are interesting as there are few cases in nature of Archimedean type spirals: most naturally occurring spirals are logarithmic [60–62].

Formation of a spiral avoids the energetic costs associated with strain in concentric rings because its energy does not fluctuate according to the commensurability between the template diameter and $L_0$. However, the spiral has two terminations (or a termination and a Y junction) which are associated with an energetic cost. Whether a spiral forms or concentric rings form depends on the balance between the energy of the spiral terminations and that of the rings, which includes strain from an incommensurate template and bending due to distortion by the notch. In our system a circular pit of any diameter produced rings, so incommensurate strain by itself was not sufficient to produce a spiral. However, larger notches typically produced spirals whether or not the template was commensurate, whereas smaller notches produced spirals when the template was incommensurate. This suggests the energy penalty for distortion of the outer rings by the notch was the
determining factor in driving spiral formation, but commensurability played a role when the distortion was less significant.

Supplemental SCFT simulations were performed that examined the effect of the notch on the stability of the spiral. In these simulations, a fixed diameter $d = 4.0 \ L_0$ and notch height $h = 7d/32$ was chosen. The free energies of the relaxed concentric ring structure and the spiral structure were calculated in three cases: when the structure formed from a random seeding, from a spiral seed or from a concentric ring seed as the initial field condition. Table 1 summarizes the results of these calculations. The random seeding yielded a spiral structure in the notch template and a ring structure in the circular template. The concentric ring structure had the lower free energy under the circular template boundary conditions while the spiral structure had the lower free energy under the notched template boundary conditions. If the seeded structures are allowed to evolve, a seeded concentric structure in a notch will eventually form a spiral structure. However, a spiral structure can be retained in the circular hole boundary conditions, implying the spiral structure is metastable in the circular template.

Table 1. Comparison of the free energy differences from a disordered state (normalized by $kT$ and simulation volume). The left columns show the structure that was seeded to calculate the free energy difference while the top rows show the template used. For the random seeding cases, the circular template formed concentric rings and the notch template formed a spiral.

<table>
<thead>
<tr>
<th>Seeded structure</th>
<th>Circular</th>
<th>Notch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentric rings</td>
<td>$-2.73$</td>
<td>$-3.17$</td>
</tr>
<tr>
<td>Spiral</td>
<td>$-2.68$</td>
<td>$-3.27$</td>
</tr>
<tr>
<td>Random seeding</td>
<td>$-2.73$</td>
<td>$-3.27$</td>
</tr>
</tbody>
</table>

Figure 8. SEM images showing the spontaneous formation of spirals within hexagonal HSQ templates (brighter lines) treated with a PDMS brush. (a) Formation of a right-handed (false-colorized in orange) lone spiral among concentric ring patterns. (b) Right-handed spiral with outer end terminating at the wall of the template. Left-handed (false-colorized in teal) spirals with Y branch at one (c) and two (d) PDMS rings away from the template. (e) Double spiral from two Y branches. Scale bars denote 100 nm.

3.4. Spirals in hexagonal templates

As a final comment, we note that spirals also formed spontaneously in non-circular pits. Figure 8(a) shows a spiral formed in a hexagonal confinement, and with a PDMS brush instead of the PS brush used in the other samples described here. In the hexagonal spiral, the termination occurred near one of the corners [47], i.e. a notch was not required. The straight edges of the hexagons promote the alignment of the cylinders to the walls, with bends at the corners. The spiral originated as the cylinder formed a junction with an edge of the PDMS-coated template to relieve the bending strain.

Figures 8(b)–(e) shows spirals in larger diameter templates. The spirals originated from the template edge (figure 8(b)), the outer ring (figure 8(c)) or an inner ring (figure 8(d)). Nucleation of two Y junctions led to a double spiral (figure 8(e)). In all cases the microdomain leading to the outer termination or branch of the spiral is perpendicular to an edge of the hexagonal template. Due to the symmetry of the template, right and left-handed spirals were equally probable. This shows that spiral formation may be promoted if the geometry of the edge of
the template contains features such as corners or as well as notches that introduce strain energy that can be relieved by a termination or Y-junction.

4. Conclusion

We show that confinement of a cylindrical-morphology BCP in a shallow circular pit can produce either concentric rings or a spiral. A spiral is promoted by the presence of a notch-shaped feature within the template which controls the spiral chirality. Design of the notch geometry enabled double spirals to be formed. A notch of width \( \approx L_0 \) promotes spirals even for commensurate pit sizes indicating the critical importance of the inner shape of the template. For smaller notches, spirals formed for incommensurate template diameters and rings for commensurate template diameters. Analogous to using a notch to initiate a spiral in a circular pit, our approach could be extended to guide the chirality of 3D helical spirals formed in cylindrical confections with a helical ramp template as shown in S3 in the SI. 2D and 3D chiral nanostructures have a range of potential applications in the sensing of molecular chirality or as chiral metamaterials [63]. Chiral nanostructures have so far only been fabricated by top-down lithography or self-assembly of nanoparticles interacted with chiral molecules [50–52, 63], and this study provides an effective alternative route to fabricate chiral nanostructures via directed self-assembly.

5. Experimental section

5.1. Template fabrication

Templates in this work were fabricated by electron-beam irradiation of an electron lithography resist hydrogen silsesquioxane (HSQ; Dow Corning XR-1541, 2%). First, HSQ films were spin-coated on a silicon substrate with a thickness of 40 nm. Templates (donut-shaped polygons with and without notches) were exposed in a Raith 150 electron-beam lithography system operating at 30 kV acceleration voltage. Next, the exposed substrates were developed in saline development solution for 4 min, as described previously [64]. The substrates were then treated with \( \mathrm{O}_2/\mathrm{He} \) plasma (50 W) for 10 s to convert HSQ templates into silicon oxide.

5.2. Block copolymer self-assembly

The patterned substrates were treated with a hydroxyl-terminated PS brush layer (\( M_N = 11 \text{ kg mol}^{-1} \), Polymer Source Inc., 170 °C for 12 h) to promote formation of a PS wetting layer on the template. A 2 wt% of PS-\( \mathrm{b-} \)PDMS (\( M_N = 45.5 \text{ kg mol}^{-1}, f_{\text{PDMS}} = 35.5\% \), Polymer Source Inc.) solution in propylene glycol monomethyl ether acetate was spin-coated on the prepared substrate to a thickness of 33 nm. The BCP film was solvent annealed by placing the samples in a chamber containing a reservoir of a 5:1 mixture of toluene and heptane for 3 h.

Acknowledgments

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