Chiral selection of single helix formed by diblock copolymers confined in nanopores

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Chiral selection has attracted tremendous attention from the scientific communities, especially from biologists, due to the mysterious origin of homochirality in life. The self-assembly of achiral block copolymers confined in nanopores offers a simple but useful model of forming helical structures, where the helical structures possess random chirality selection, i.e. equal probability of left-handedness and right-handedness. Based on this model, we study the stimulus-response of chiral selection to external conditions by introducing a designed chiral pattern onto the inner surface of a nanopore, aiming to obtain a defect-free helix with controllable homochirality. A cell dynamics simulation based on the time-dependent Ginzburg-Landau theory is carried out to demonstrate the tuning effect of the patterned surface on the chiral selection. Our results illustrate that the chirality of the helix can be successfully controlled to be consistent with that of the tailored surface patterns. This work provides a successful example for the stimulus response of the chiral selection of self-assembled morphologies from achiral macromolecules to external conditions, and hence sheds light on the understanding of the mechanism of the stimulus response.

Chirality, or called dissymmetry, is an unique feature of an object that cannot be superposed onto its mirror image.1,2 Chiral objects in the form of small molecules or large assemblies are ubiquitous in nature as well as in manmade materials, and thus have attracted tremendous attention from the scientific communities of biology, chemistry, physics, and materials.3–5 In biology, amino acids, as one of the most important constituents, of life are chiral and nearly all of those in proteins are left-handed, while all sugars in DNA and RNA are right-handed.6–7 Moreover, there are many helical structures in the form of chiral assemblies in biological systems, such as α-helices in proteins, DNA double-strand helices, tendrils, and the coiled shells of gastropod species.8–10 In particular, the origin of homochirality in life remains mysterious though many efforts have been devoted to this topic.6,11,12 In contrast, the chemical synthesis of chiral compounds from achiral reagents always yields a racemic mixture of equally represented enantiomers.13 From the perspectives of both fundamental research and the technological applications, this presents an interesting challenge to control the imparted chirality of molecules or helical structures. In experiments, diverse external chemical and physical chiral conditions have been devised to induce chiral selection.5,14–19 However, the induction process of chiral control has been much less explored by theory.20–22

Block copolymer self-assembly has attracted abiding interest because it provides a powerful platform for the formation of ordered nanostructures which have potential applications in a wide range of fields.23–25 In particular, the self-assembly behavior can be readily enriched by the diverse molecular architectures of block copolymers as well as its facile stimulus response to external conditions. It has been established that the simplest bicomponent (or AB-type) block copolymer, AB diblock copolymer, can self-assemble into a set of ordered phases including lamellar, cylindrical, spherical, or gyroid (or Fddd) networks.26,27 Although the structure library from the self-assembly of bicomponent block copolymers cannot be expanded dramatically, a few new phases have been stabilized in AB-type triblock copolymers with various topological architectures.27–29 For example, the perforated lamellar morphology that is usually metastable in simple AB diblock or ABA triblock copolymers becomes stable in comb-like or branched AB-type block copolymers.27 More interestingly, a few non-classical phases, including square cylinders, graphene-like cylinders, and honeycomb-like networks, have been predicted by theory in AB-type block copolymers with purposely designed miktoarm architectures following useful guiding principles.29 Moreover, a large number of new structures in the form of binary mesocrystals have been obtained from the self-assembly of designed B₂AB₂CB₃ multiblock terpolymers.30
As a typical soft matter system, the self-assembly of block copolymers has a strong responsive capability to external conditions, e.g. the confinement imposed by geometrical boundaries.\textsuperscript{31} The geometrical confinement not only breaks the translational symmetry of the periodic phases in the bulk but also alters the domain geometry, leading to a lot of intriguing novel morphologies differing from the bulk phases.\textsuperscript{32–40} One of the most extensively studied geometrical confinements is cylindrical confinement. Many attractive morphologies have been observed in the self-assembly of block copolymers confined in nanopores by experiments,\textsuperscript{32–34} computer simulations,\textsuperscript{35,36} and theoretical calculations.\textsuperscript{37–40} One type of surprising morphology is the helical structure from the self-assembly of achiral block copolymers under cylindrical confinement. The fundamental formation mechanism has been established; the mismatched lengths between the nanopore and the cylinder, due to a preferred diameter of the latter for a given block copolymer, drive the longer cylinder to curve into helices.\textsuperscript{35,37} Similarly, helical structures can be self-assembled by linear and star triblock copolymers softly confined by solvent environments.\textsuperscript{41,42} In addition to the self-assembly of block copolymers, the cylindrical confinement can also induce the formation of helical structures in small molecule systems. For instance, nanotubes (e.g. carbon nanotube) have been applied to template the assembly behavior of surfactants\textsuperscript{43} or water molecules.\textsuperscript{21,44} In particular, a variety of helical structures have been predicted by molecular dynamics simulations in the high-density nano-ice confined in carbon nanotubes.\textsuperscript{21}

Due to the intrinsic achiral property of the block copolymer systems, the formation of helical structures possesses a random selection of chirality, \textit{i.e.} equal probability of left-handedness or right-handedness.\textsuperscript{35,37} Similar to the racemic mixture in chemically synthesized chiral compounds where the enantiomers have identical free energy, the left-handed and right-handed helices are degenerate in free energy. Besides the cylindrically confined system, this phenomenon has also been observed with bulk achiral block copolymer systems, such as in the self-assembly of linear ABC triblock copolymers in helical supercylindrical structures.\textsuperscript{45} For a cylindrically confined system that is quasi-one-dimensional, helical structures with a random chirality are spontaneously formed at any position along the axial direction of the nanopore, and thus usually exhibit nonuniform chirality in a macroscopically long nanopore. As a result, defects are unavoidably caused at the interfaces between the morphological pieces with different chirality, thus destroying the one-dimensional long-range order. A variety of defects have been explored in confined systems with a large length by cell dynamics simulation (CDS) based on time-dependent Ginzburg–Landau theory (TDGL).\textsuperscript{46} Note that the loss of long-range order in the one-dimensional system is robust for one-dimensional condensed matter systems, which originates from the dominant effect of the entropy over the interfacial energy or the defective energy.

It is apparent that helical structures with controllable and uniform chirality are more likely to satisfy practical applications. How to control the chirality of the helical structures by the self-assembly of cylindrically confined block copolymers presents an interesting question. A number of strategies have been proposed in experiments to control the chiral selection of helical structures formed by self-assembled systems.\textsuperscript{14–19} For example, Yang and coworkers utilized chiral templates and chiral terminals, respectively, to induce the formation of helical structures with desired chirality in various self-assembly systems without chiral selection.\textsuperscript{14,15,17} More instructively, Yao \textit{et al.} added small chiral molecules to regulate the self-assembly of helical superstructures with controllable chirality from achiral diblock copolymers, which is a typical stimulus response process.\textsuperscript{16} However, this interesting topic is rarely explored by theory due to the vast challenge in methodology. On the one hand, an appropriate theoretical model is needed to simulate the self-assembly process of helical structures that typically involves nano- or mesoscale system sizes. On the other hand, the model must be capable of capturing the chiral nature of the external environment at the molecular level.

In this work, we take the single-helix morphology formed by the cylindrically confined diblock copolymers as an example model to study the stimuli-response of chirality of helical structures to external conditions. Instead of dealing with the chiral conditions at the molecular level, we simply design a chiral wall surface of the nanopore to mimic the external chiral conditions, thus investigating the induction effect of the chiral confining conditions on the chirality of the single helix inside the nanopore. The pore surface is patterned with a set of correlated patches with a distinct surface potential from the non-patched area, which is characterized by the size, shape and distribution of the patches as well as the contrast of the surface potential between the patched and non-patched area. Our main goal is to optimize the surface pattern for the controlled selection of chirality of the helical structure by systematically simulating the formation kinetics of the single helix under the confinement with variable chiral surfaces using the TDGL theory, and accordingly to unveil the stimulus response of the chirality of the helical structures to external chiral environments. The CDS of TDGL theory has been proven to be a high-efficiency dynamic simulation method for the simulation of the collective kinetics of block copolymer self-assembly.\textsuperscript{17–50}

Model and theory

We consider an incompressible melt of asymmetric AB diblock copolymers with a fixed volume fraction of the A block $f = N_A/N$, where $N_A$ and $N$ are the polymerization degrees of the A block and the entire polymer chain, respectively, confined in a cylindrical nanopore of diameter $D$. The order parameter, as a spatial function that characterizes the phase separation of the diblock copolymer melt, is chosen as $\phi(r) = \phi_A(r) - \phi_B(r)$, where $\phi_A(r)$ and $\phi_B(r)$ are the compositional distributions of the A and B components. Under the mean-field approximation, the free energy of this system can be expressed as a functional of $\phi(r)$, which is composed of three contributions,
short-range, long-range, and the surface energy of the pore wall:

\[ F[\phi] = F_s[\phi] + F_l[\phi] + \int_{|r|<D/2} d\mathbf{r} H_{\text{surf}}(\mathbf{r}) \phi(\mathbf{r}), \]  

(1)

where the integration is restricted inside the nanopore. The short-range term \(F_s\) is the usual Ginzburg-Landau type free energy and can be written as

\[ F_s[\phi] = \int_{|r|<D/2} d\mathbf{r} \left\{ \frac{C}{2} |\nabla \phi(\mathbf{r})|^2 + W(\phi) \right\}, \]

(2)

where the first term with a positive constant \(C\) is applied to suppress the short wavelength fluctuations, and the second term \(W(\phi)\) is the local interaction contribution and it can be conveniently specified by its derivative form,

\[ \frac{dW(\phi)}{d\phi} = -A_0 \tanh(\phi) + \phi. \]  

(3)

The above constant \(A_0 > 1\) gives rise to the phase separation between the two immiscible components. The long-range contribution is originally derived by Ohta and Kawasaki from the second-order vertex function obtained by the random phase approximation to alter the phase separation from macroscopic in A/B blends to microscopic in AB diblock copolymers, which is expressed as

\[ F_l(\phi) = \frac{a}{2} \int d\mathbf{r} G(\mathbf{r} - \mathbf{r}') \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}). \]  

(4)

where \(\delta\phi(\mathbf{r}) = \phi(\mathbf{r}) - \bar{\phi}\) and \(\bar{\phi} = 2f - 1\) is the spatial average of \(\phi(\mathbf{r})\). In the above expression, the positive constant, \(a\), is inherent to the characteristics of the block copolymer, and thereby dictates the segregation degree as well as the domain spacing. The long-range feature stems from the Green function \(G(\mathbf{r} - \mathbf{r}')\) because it shares the Coulomb potential form. In practice, the Laplacian equation of the Green function is more convenient, which is

\[ -\nabla^2 G(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \]  

(5)

In the last term of eqn (1), the spatial function of \(H_{\text{surf}}(\mathbf{r})\) is implemented to mimic the preferential interaction potentials of the pore wall on the two species. In order to include the chiral property of the pore surface, \(H_{\text{surf}}(\mathbf{r})\) has to be modified from a simple function of the radial distance \(r\) to be a more complex function of not only \(r\) but also the polar angle \(\theta\) and the \(z\) coordinate along the pore axis. First, we define a general surface potential for the entire pore surface, \(H_{\text{pore}}(\mathbf{r})\), as

\[ H_{\text{pore}}(\mathbf{r}) = \frac{1}{2} V_0 \{ \tanh[(\sigma - d(\mathbf{r}))/\epsilon] + 1 \}, \]  

(6)

where \(d(\mathbf{r})\) is the distance to the boundary along the radial direction, and \(\sigma\) and \(\epsilon\) specify the interaction distance and shape of the external potential along the radial direction, respectively. The constant \(V_0\) gives the potential strength of the non-patched area.

The pore surface is then patterned via introducing \(N_p\) correlated patches onto the surface, whose distribution is characterized by a set of positional parameters \((h_i, \theta_i) (i = 1, 2, ..., N_p)\), where \(h_i\) and \(\theta_i\) indicate the axial position and the polar angle of patch \(i\), respectively (Fig. 1(b)). In practice, the pattern of each patch is realized by using an elliptic cylinder with the major axis \(2R_p\) and the minor axis \(R_p\) to “cut” the nanopore, thus dividing the surface potential into the patched and non-patched area. In other words, the projection of each patch along the radial direction is an ellipse with the major and minor axes as \(2R_p\) and \(R_p\), respectively. The surface potential in the patched area delimited by the elliptic cylinder is set to be distinguished from that of the non-patched area with \(H_{\text{surf}} = H_{\text{pore}}\) by a modification factor, \(k\), i.e. \(H_{\text{surf}} = kH_{\text{pore}}\). Note that the surface potential is not ideally restricted on the pore surface, but it is indeed extended into the pore due to the certain interaction range.

With the above explicit free-energy functional, the phase-separation dynamics of the block copolymer system can be described by the Cahn–Hilliard dynamic equation (Model B),

\[ \frac{\partial \phi}{\partial t} = M \nabla^2 \frac{\delta F[\phi]}{\delta \phi} + \zeta(\mathbf{r}, t), \]  

(7)

where \(M\) is relevant to the chain mobility, set to \(M = 1\), and \(\zeta(\mathbf{r}, t)\) is a random noise term with zero average and a second moment of \(\langle \zeta(\mathbf{r}, t)\zeta(\mathbf{r}', t') \rangle = -\zeta_0 M \nabla^2 \delta(\mathbf{r} - \mathbf{r}')\delta(t - t');\) here \(\zeta_0\) is the noise strength.

We choose the group of parameters to be \(f = 0.38, A_0 = 1.28,\) and \(a = 0.02\), to obtain a typical hexagonal cylinder phase in

![Fig. 1](image-url)  
(a) Schematic plot of the self-assembly system of cylinder-forming AB diblock copolymers under the confinement of a nanopore with length \(L\) and diameter \(D\). The cylinder-to-cylinder distance of the bulk phase of the diblock copolymer is indicated by \(L_0\). The pore surface is patterned with a set of patches, which are chirally and periodically distributed along the pore and thus have correlated positions \((h_i, \theta_i)\). The shape of each patch is specified by its projection along the radial direction that is an ellipse with the lengths of the major and minor axes as \(2R_p\) and \(R_p\), respectively, and with the minor axis aligning along the pore axis. (b) Fluctuating proportion of the right-handed helix of all helical morphologies formed in the nanopores with a non-patterened surface and fixed diameter \(D = 1.74 L_0\) for a varying number of running samples. The helical pitch is indicated by \(d_p\), \(N_{\text{patt}}\), and \(N_{\text{un}}\) indicates the number of left-handed and right-handed helices, respectively.
the bulk, and specify these parameters of the surface potential as \( V_0 = 0.015 \) (for majority-attraction), \( \sigma = 0.15 \) \( L_0 \), and \( \varepsilon = 0.5 \) \( L_0 \) (\( L_0 \) is the cylinder-to-cylinder distance in the bulk cylinder phase). The standard CDS method, where the forward Euler algorithm is applied for the time integration and the explicit finite differential scheme is applied for the space, has been proven to be efficient to solve the TDGL equations.\(^{50}\) In our simulations, the lattice spacing in the CDS simulations is fixed as \( \Delta x = \Delta y = \Delta z \equiv \Delta = 0.50 \), and accordingly the time step \( \Delta t \) is chosen as 0.1 to ensure the solution stability of the dynamic equations. \( L_0 \) is determined to be about 16.5 \( \Delta \) by the simulation of the bulk system. Periodic boundary conditions are imposed on the \( z \) direction. For reading convenience, the main parameters are summarized in the Appendix.

**Results and discussion**

The self-assembly of cylinder-forming AB diblock copolymers under cylindrical confinement has been examined previously using CDS simulations.\(^{46}\) The kinetically stable region of various morphologies, including single cylinder, stacked disks, single helix, and double helices, have been determined with respect to the pore diameter. Accordingly, we fix the pore diameter as \( D = 1.74 \) \( L_0 \), which is located almost at the center of the phase region of the single helix, to ensure the formation of single helix during the kinetics. In principle, the structure formation in this quasi one-dimensional system is sensitive to the pore length with a periodic boundary condition at two ends. Only when the pore is short, such as a few \( L_0 \), a single helix with a uniform chirality is likely to be formed, but the chiral selection of each independent run of the dynamic simulations is random between the left-handed and right-handed types. Otherwise, the morphologies are formed in a long pore, typically with a length of tens of \( L_0 \), consisting of helical pieces with mixed left-handed and right-handed chirality, thus exhibiting defects at the interface of different chiralities. This implies two equivalent examination strategies for the chiral selection of single helix in the currently considered system. One strategy is to statistically count the probability of a single helix with a given chirality from a large number of simulation runs on the cylindrically confined system in a short nanopore where the single helix of a uniform chirality is mainly formed. The other is to determine the proportion of the single-helical morphology with a given chirality formed in a macroscopically long pore. In this work, we first adopt the former strategy to investigate the tuning effect of the designed patterns on the chiral selection, hence fixing the pore length as \( l = 9.68 \) \( L_0 \), with a nanopore in which a helix of five pitches is formed as \( l \approx 5 \) \( d_0 \) and \( d_0 \approx 1.94 \) \( L_0 \).

In Fig. 1(b), the proportion of the right-handed single helix formed in the nanopores with a non-patterned surface is shown for various numbers of running samples. Obviously, it fluctuates and the fluctuation amplitude attenuates as the samples are added, finally approaching 50\%, i.e. an equal chance of selection for the right-handed and left-handed helices. Then we start with a simple case of patterned surface, in which the patches with a fixed size of \( R_p = 0.25 \) \( L_0 \) are uniformly distributed in the entire pore and their polar angles are associated with their positions forming a right-handed chiral distribution. The patch distribution is specified by \( \theta_i = (i - 1/2)\pi/N_p \) and \( h_i = 2\pi i/N_p \) \( (i = 1, 2, ..., N_p) \) with \( N_p = 4 \) (Fig. 1(a)). Here we refer to this distribution as the uniform distribution. The proportion of the right-handed helix is estimated with sample numbers 100 and 500, respectively, and is shown in Fig. 2. The large sample number of 500 leads to results with reasonably low statistical errors. Note that there is still some probability for the system to form imperfect helical morphologies in such short nanopores, which is also counted in our simulations and is presented in Fig. 2.

The modification factor \( k = 1 \) corresponds to a nanopore with non-patterned surface that does not exhibit any chirality. In this case, the pore surface is uniformly attractive to the majority component. As a consequence, the formed helical morphology selects the left-handed and right-handed chirality with an equal probability of 50\%. Moreover, the random selection of chirality leads to a possibility as high as around 40\% of forming defective morphologies composed of helical pieces with different chirality (Fig. 2). When \( k \) is varied to be different from 1, a right-handed chiral property is introduced to the pore surface due to the distinguished surface interaction of these patterned patches from the non-patterned area, thus leading to the selection of right-handed chirality. Note that the right-handed chiral feature is dictated by the contrast of the surface potential between the patterned and non-patterned area, which holds equally for the two cases of \( k > 1 \) and \( k < 1 \). As \( k \) deviates from 1 more and more, the proportion of the right-handed helix increases, which is accompanied by the

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**Fig. 2** Proportion of right-handed helical morphologies as well as defective morphologies self-assembled by the diblock copolymers confined in the nanopores with patterned surface and a given length \( l = 9.68 \) \( L_0 \), as a function of the modification factor \( k \). The pattern is composed of four patches with size \( R_p = 0.25 \) \( L_0 \) whose positions along the pore axis and associated polar angles are \( h_i = \theta_i = 1/2\pi/4 \) and \( \theta_i = \pi i / (2 \theta_i = 1, 2, 3, 4) \). Two groups of data for the sample numbers of 100 and 500 are presented. \( N_{DM} \) indicates the number of defective morphologies.
decreasing proportion of defective morphologies. For \( k \geq 1.4 \), the right-handed and defect-free helix is formed exclusively in the nanopore. Obviously, the pattern with \( k < 1 \) is also able to tune the chiral selection. However, small \( k \), e.g. \( k < 0.8 \), will weaken the surface attraction to the majority component, accordingly raising the possibility of creating defects as a new mechanism differing from that arising from the uncontrolled selection of chirality. Therefore, we do not extend our simulation to the further end of \( k < 0.8 \).

To testify the tuning effect of the designed chiral pattern on the chiral selection in an alternative way, we simulated the self-assembly of the system with a pore length triple that of the previous one, \( i.e. \ l = 3 \times 9.68 L_0 \approx 15 d_0 \), for three typical values of the modification factor, \( k = 1.0, 1.2, \) and \( 1.4 \) (Fig. 3). With the non-patterned surface of \( k = 1.0 \), although a piece of right-handed helix (in green color) is formed in the pore, two pieces of other distinct morphologies are also formed, including the left-handed helix and tilted toroids, interfering with the uniform formation of right-handed helix throughout the entire pore. In contrast, for the chiral pattern of \( k = 1.2 \), the proportion of the desired right-handed helix in the pore is enhanced significantly. Finally, with \( k = 1.4 \), the right-handed helix is self-assembled throughout the nanopore, corresponding to a defect-free helical morphology. This observation is consistent with that from the results on the formation probability of the right-handed helix in the short nanopores of \( l \) = 9.68 \( L_0 \). In brief, the designed pattern of patches on the pore surface with tailored chiral properties has been demonstrated to be able to guide chiral selection for the self-assembly of helical morphologies from achiral block copolymers confined in the nanopores, and thus lead to the formation of defect-free helical morphologies in the quasi one-dimensional system.

Besides the critical variable of the modification factor \( k \), the chiral property of the surface pattern can also be regulated by a few other parameters, such as the patch size \( R_p \), number \( N_p \), and distribution \((h, \theta)\). In Fig. 4, three different sizes of patches are considered: \( R_p = 0.20 L_0, 0.25 L_0 \), and \( 0.30 L_0 \) for the same number and distribution of patches as in Fig. 2.

Fig. 5 Three morphological samples formed in the cylindrically confined block copolymer system with a large pore length of \( l = 29.04 L_0 \) for various values of the modification factor, \( k = 1.0, 1.2, \) and \( 1.4 \) (from top to bottom). For reasons of clarity, the desired right-handed helical pieces are shown in green color, while the other morphological pieces are plotted in a darker color. The nanopore is totally decorated with \( N_p = 12 \) patches, which are distributed into \( n_p = 3 \) pattern periods each of which consists of 4 patches.

Obviously, the surface pattern with larger patches leads to the formation of a higher proportion of the right-handed helix for a given value of \( k \) smaller than the critical value at which 100% of the right-handed helix is formed, indicating a larger tuning effect on the chiral selection. However, we can speculate that the patch size might have a limit for increasing the tuning effect, which will be discussed later.

In above examples, we fix the number of patches \( N_p = 4 \). Now we attempt to change \( N_p \) to examine its influence on the tuning effect of chirality. In Fig. 5, the results on the proportion of the right-handed helix for three values, \( N_p = 3, 4, \) and 5, are presented, where the uniform distribution of the patches is considered. In contrast to the variable \( R_p \), \( N_p \) has a more remarkable impact on the tuning effect of chirality. The tuning effect of \( N_p = 5 \) becomes considerably worse than that of \( N_p = 4 \), even though the chiral property is strengthened. This observation implies that the tuning effect of chirality is
not simply dictated by the magnitude of the chiral property of the patterned surface. The chiral properties of the external conditions have to be commensurate with those of the helical morphologies. More interestingly, for $N_p = 3$, the low proportion of the right-handed helix reveals that the formation of the left-handed helix is more likely to be induced by a surface pattern with the opposite chiral property. However, from the point of view of forming unique chirality, the tuning effect is also worse than that of $N_p = 4$ because there is still a small portion of the right-handed helix when $k = 1.5$.

To probe the formation mechanism of the helical morphology with opposite chirality to the external guiding conditions, we focus on the case of $N_p = 3$ and attempt to modify the distribution of the patches aiming to regulate the tuning effect of chirality for the formation of a single helix with a consistent chirality to the surface pattern. For the uniform distribution of $N_p = 3$, we plotted the density iso-surface of the right-handed helix in the patched nanopore in Fig. 6. It is shown that two patches are located on the pore surface where the helical domain passes by (denoted as 1 and 3), whereas the other is located on the surface between two neighboring pitches of the helix (denoted as 2). Accordingly, the stronger surface attraction to the majority imposed by patches 1 and 3 is unfavored by the right-handed helix, thus leading to its low formation probability, lower than 10% at $k = 1.5$, when the patch distribution is altered to be nonuniform by moving patches 1 and 3 in the uniform distribution upward and downward by a half pitch, respectively, such that the two patches like patch 2 are located on the surface between two pitches. The patch distribution can be specified by $N_{p} = 3$ and attempt to modify the distribution of the patches for an ideal tuning effect can be simply derived from the characteristic parameters of the pattern, such as the modification factor $k$ that characterizes the contrast of the surface interactions between the patterned and non-patterned areas, and the patch size $R_p$. Moreover, the number of patches as well as their distribution has a subtle influence on the tuning effect of the surface pattern on chiral selection. Surprisingly, the pattern with $N_p = 5$ leads to a considerably worse tuning effect than that of $N_p = 4$. This observation implies that a commensurability is required between the guiding pattern and the self-assembled helical morphology, for instance, in the periodicity. More interestingly, the chirality of the single helix formed in the patterned nanopore with $N_p = 3$ can be controlled to be consistent or opposite to that of the chiral pattern by tailoring the distribution of the patterned patches. By probing the induction mechanism of the chiral pattern on the chiral selection of the helix, an ideal distribution of the patches is derived.

The significance of our work is two-fold. On the one hand, it provides a simple but useful model system for studying the stimulus response of the chiral selection to external con-
ditions. Although, our system may exhibit technical difficulties in the preparation of the surface pattern of nanopores, this technical problem will hopefully be solved as nanotechnology advances. For example, there is experimental research attempting to fabricate chiral mesopores via the self-assembly of chiral amphiphilic molecules. These mesopores, with tunable diameter and chiral period, may provide a useful template to guide block copolymers to self-assemble into single helical morphologies with desired chirality. Moreover, the chiral nanopore may be effectively made from chiral materials. For example, zigzag carbon nanotubes are chiral. Though the diameter of carbon nanotubes is too small for block copolymers, they should be able to induce small molecules (e.g., water) to form helical structures with a given handedness. Therefore, our results are instructive for experiments to obtain defect-free homochiral helices in a macroscopically long nanopore that may have promising applications in nanotechnology. On the other hand, our results reveal that chiral interaction on the pore surface is transferred into the self-assembly of the entire system and thus successfully induces the chiral selection of the helix. This conclusion for the stimulus response mechanism of chiral selection may hold robustly for the self-assembly of other helical structures from achiral constituents, and thus shed light on the understanding of the origin of homochirality in life. Importantly, the precise conditions of the chiral pattern associated with helical geometry is predicted in a quantitative manner for the induction of a homochiral helix.

### Appendix

#### List of the main parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physical meaning</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>Volume fraction of the minority block of AB diblock copolymer</td>
<td>0.38</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>Model parameter controlling the degree of phase separation</td>
<td>1.28</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Model parameter dictating the segregation degree as well as the domain spacing</td>
<td>0.02</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Lattice spacing</td>
<td>0.5</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time step</td>
<td>0.1</td>
</tr>
<tr>
<td>$L_0$</td>
<td>Cylinder-to-cylinder distance in the bulk</td>
<td>16.5 $\Delta$</td>
</tr>
<tr>
<td>$d_0$</td>
<td>Helical pitch of the single helix</td>
<td>1.94 $L_0$</td>
</tr>
<tr>
<td>$l$</td>
<td>Length of the nanopore</td>
<td>9.68 $L_0$ ($5d_0$), 29.04 $L_0$ ($15d_0$)</td>
</tr>
<tr>
<td>$D$</td>
<td>Diameter of the nanopore</td>
<td>1.74 $L_0$</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Strength of the surface potential of the non-patched area</td>
<td>0.015 $L_0$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Interaction distance of the surface potential</td>
<td>0.15 $L_0$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Steepness of the surface potential</td>
<td>0.5 $L_0$</td>
</tr>
<tr>
<td>$k$</td>
<td>Modification factor of the surface potential of the patches relative to the non-patched area</td>
<td>0.8–1.5</td>
</tr>
<tr>
<td>$N_p$</td>
<td>Number of the patches</td>
<td>3, 4, 5, 12</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Size of the patches</td>
<td>0.20 $L_0$, 0.25 $L_0$, 0.30 $L_0$</td>
</tr>
<tr>
<td>$m_p$</td>
<td>Number of periods of the surface pattern</td>
<td>1, 3</td>
</tr>
</tbody>
</table>

### Acknowledgements

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### References

16. L. Yao, X. Lu, S. Chen and J. J. Watkins, Formation of helical phases in achiral block copolymers by simple


