Tunable helical structures formed by ABC triblock copolymers under cylindrical confinement

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Block copolymers confined in nanopores provide unique achiral systems for the formation of helical structures. With AB diblock copolymers, stable single and double helical structures are observed. Aiming to obtain more different helical structures, we replace the AB diblock copolymer with linear ABC triblock copolymers. We speculate that a core–shell superstructure is formed within the nanopore, which is composed of a C-core cylinder wrapped by B-helices within the A-shell. Accordingly, the pore surface is set to be most attractive to the majority A-block and a typical set of interaction parameters is chosen as \( \chi_{AC}N \ll \chi_{AB}N = \chi_{BC}N = 80 \) to generate the frustrated interfaces. Furthermore, the volume fraction of B-block is fixed as \( f_B = 0.1 \) to form helical cylinders. A number of helical structures with strands ranging from 1 to 5 are predicted by self-consistent field theory, and in general, the number of strands decreases as the volume fraction of C-block \( f_C \) increases in a given nanopore. More surprisingly, the variation of helical strand in the confined system has an opposite trend to that in the bulk, which mainly results from the constraint of the cylindrical confinement on the change of the curvature between the outer A-layer and the inner B/C-superdomain. Our work demonstrates a facile way to fabricate different helical superstructures.

1 Introduction

Block copolymers, composed of two or more dissimilar blocks linked by covalent bonds, have attracted increasing interest due to their unique self-assembly ability into rich ordered nanostructures that exhibit promising applications in a wide range of fields.1,2 For a given block copolymer, the self-assembly behavior is controlled by its characteristic parameters including the interaction parameters and composition. For example, the phase behavior of an AB diblock copolymer is mainly dictated by two parameters, i.e. the volume fraction of A-block (\( f \)) and the product \( \chi N \) where \( \chi \) is the Flory–Huggins interaction parameter and \( N \) is the total number of statistical segments on the polymer chain. By a concerted interplay between theory and experiment in the past decades, more and more ordered structures were gradually identified in AB diblock copolymers, finally leading to a relatively complete phase diagram of AB diblock copolymers. This two-dimensional phase diagram in the \( f-\chi N \) plane mainly consists of hexagonally close-packed (hcp) spheres, body-centered cubic (bcc) spheres, hexagonal cylinders (C), double gyroids (G), Fddd (O\(^{19}\)) and lamellae (L).3–6

Of course, a direct way to alter the phase behavior of block copolymers is to change their molecular architectures, i.e. make new block copolymers. Especially, advanced modern synthesis techniques are able to make many different types of block copolymers with variable numbers of components as well as topological architectures, and thus provide a lot of opportunities for the fabrication of novel nanostructures.7,8 For block copolymers with given components, different molecular architectures often shift the phase boundaries considerably,6,9,10 and some purposely designed architectures can even stabilize novel ordered phases.9,11–15 On the other hand, usually adding more components into a block copolymer enriches its phase behavior drastically. For example, ABC linear triblock copolymer, made by adding a third-component C-block onto an AB diblock, exhibits much richer ordered phases than AB diblock.7 In particular, when its three interaction parameters satisfy a special condition of \( \chi_{AC}N \ll \chi_{AB}N \sim \chi_{BC}N \), ABC linear triblock copolymer can self-assemble into many exotic hierarchical superstructures, such as double/triple-helical superradials and knitted patterns, where the formation of A/C interfaces frustrates the A/B/C topological sequence.16–20 Moreover, if the linear architecture is changed to be a star, ABC triblock copolymer can form other different interesting morphologies like the Archimedean tiling patterns.21–26

A facile way to change the self-assembly behavior of block copolymers is to impose some external conditions on them.
One of the most used external conditions is geometrical confinement. The self-assembly of block copolymers under various geometrical confinements has been intensively studied by experiment, simulation and theory. The influence of confinement is exerted by breaking the translational symmetry of the bulk periodic phases as well as by the surface interaction of the confining geometry, leading to the formation of novel structures without periodicity in the confined directions. According to the confinement dimensions, the confinement is categorized into 1D (e.g. two parallel walls), 2D (nanopores) and 3D (cavities). In particular, the self-assembly of block copolymers confined in cylindrical nanopores is of great interest. Under cylindrical confinement, simple AB diblock copolymers can self-assemble into some interesting structures, of which the helical structures are extremely appealing. The system is so simple that it can be systematically studied by experiment, simulation and theory. More importantly, the results from these different studies are in good agreement with each other and thus lead to a common understanding for the formation mechanism of helical structures.

Typically for the cylinder-forming diblock copolymer, the delicate balance between the interfacial energy and the stretching energy leads to a preferred diameter \( d_0 \) of the cylindrical domain that is hardly influenced by the nanopore size \( D \). When the pore wall attracts the majority block (e.g. B-block), there should be a suitable pore diameter for perfectly accommodating one minority cylinder at the center of the pore, i.e. \( D_0 \sim d_0 f^{1/2} \). As the pore size is expanded, the minority cylinder becomes longer than the nanopore under the assumption that it maintains a nearly constant diameter \( d_0 \). The length ratio can be roughly estimated as \( \gamma \sim (D/d_0)^2 \). The most efficient way to pack the longer cylinder into the nanopore at a low cost of energy is to curve the cylinder uniformly into helices. As \( \gamma \) is increased by increasing \( D \), the straight cylinder located at the pore center transfers to a single helix going through a narrow region of intermediate structure of stacked disks, and then to double helices. However, the increasing trend of strands does not continue to triple helices as \( D \) is gradually increased. Instead, an additional domain is generated at the pore center to release the high stretching, and no stable triple-helical structure is observed in the outer layer. To the best of our knowledge, helical structures with four and five strands are rarely observed in block copolymer systems. Even with ABC star triblock copolymers confined in nanopores, Song et al. did not observe helical structures with helical strands larger than three.

In this work, we investigate the self-assembly of ABC linear triblock copolymers confined in nanopores, aiming to obtain more different helical structures, especially with various strands of helices. As this confined ABC system consists of a large number of parameters, at least including three interaction parameters \( \lambda_{ABN}, \lambda_{BCN} \) and \( \lambda_{ACN} \), two independent block ratios, the pore diameter and the surface interactions of the nanopore and the three blocks, it is infeasible to search in such a huge parameter space for the desired structures. Therefore, we need to judiciously choose some parameters and thus narrow the searching parameter space. We speculate a category of helical superstructures, which is composed of B-helical domains sitting at the concentric A/C interface. Without loss of generality, we assume that the pore wall is most attractive to A-blocks, driving the A/C-blocks to self-assemble into a core–shell structure with A-shell and C-core. According to this scenario, we choose \( \lambda_{ACN} = \lambda_{BCN} = 80 \) to generate A/C interfaces frustrating the A/B/C topological sequence, and fix \( f_B = 0.1 \) to ensure the formation of helical B-domains. Note that a B-block with smaller \( f_B \) tends to form spheres while that with a larger \( f_B \) will form perforated lamellae. Therefore, the volume fraction of C-block \( f_C \), the pore diameter \( D \) and \( \lambda_{ACN} \) are three control parameters for the formation of helical superstructures. We construct two-dimensional phase diagrams with respect to two of the three control parameters using self-consistent field theory (SCFT), focusing on the exploration of different helical superstructures.

### 2 Theory and method

We consider an incompressible melt of ABC linear triblock copolymers confined in a cylindrical nanopore of diameter \( D \). The total number of segments on each copolymer chain is specified by \( N \), and those on the A/B/C-blocks are given by \( f_A N, f_B N \) and \( f_C N \) (\( f_A + f_B + f_C = 1 \)), respectively. For simplicity, we assume that all segments have equal length \( b \) and density \( \rho_0 \).

Within the mean-field approximation and under the Gaussian-chain approximation, the free energy functional \( F \) per chain for \( n \) ABC triblock copolymer chains confined in the nanopore of volume \( V \) can be expressed as

\[
\frac{F}{nk_B T} = -\ln Q + \frac{1}{T} \int_{|r| \leq D/2} dr \left[ \lambda_{AB} N \phi_A(r) \phi_B(r) + \lambda_{BC} N \phi_B(r) \phi_C(r) + \lambda_{AC} \phi_A(r) \phi_C(r) - w_C(r) \phi_C(r) + H_{ext}(r) \phi_C(r) - \phi_B(r) - \phi_C(r) \right] - \eta(r) \left[ 1 - \phi_A(r) - \phi_B(r) - \phi_C(r) \right],
\]

where \( k_B \) is the Boltzmann constant, \( \phi_A(r), \phi_B(r), \) and \( \phi_C(r) \) are the spatial distributions of volume fractions of A, B and C blocks, and \( w_A(r), w_B(r) \) and \( w_C(r) \) are their conjugate potential fields, respectively. The constant quantity \( Q \) is the single-chain partition function within the mean fields \( w_A, w_B \) and \( w_C \) produced by the surrounding chains. For simplicity, only one spatial function \( H_{ext}(r) \) is introduced to mimic the surface potentials of the pore wall on the three components. The term of surface interactions in the free energy functional implies that the surface potential on A-block is \( H_{ext}(r) \), while that on both B- and C-blocks is \( -H_{ext}(r) \). Similar to previous work, we choose

\[
\frac{H_{ext}(r)}{\lambda_{AB} N} = A_0 \{ \exp(\sigma + |r| - D/2)/\lambda - 1 \}
\]

when \( D/2 - \sigma \leq |r| \leq D/2 \), while \( H_{ext}(r) = 0 \) for \( |r| \leq D/2 - \sigma \). Here, \( A_0, \sigma \) and \( \lambda \) quantify the strength, interaction range and steepness of the surface potential, respectively. Note that the magnitudes of \( \sigma \) and \( \lambda \) do not influence the phase behavior significantly except for changing the effective pore size, and therefore
we choose $\sigma = 0.5R_g$ and $\lambda = 0.25R_g$ that are used in our previous work,51 where $R_g = N^{1/2}b/\sqrt{6}$ is the radius of gyration of an unperturbed homopolymer chain with $N$ segments. The sign of $A_o$ dictates the surface preference, i.e. $A_o < 0$ means that the pore wall attracts A-block, while repulsing B- and C-blocks. In this work, we fixed $A_o = -0.1$.51

Minimization of the free-energy with respect to the three volume fraction distributions and three mean fields leads to the following standard SCFT equations43

$$w_A(r) = Z_{AB}N^\beta \phi_A(r) + Z_{AC}N\phi_C(r) + H_{\text{ext}}(r) + \eta(r)$$

(3)

$$w_B(r) = Z_{AB}N^\beta \phi_A(r) + Z_{BC}N\phi_C(r) - H_{\text{ext}}(r) + \eta(r)$$

(4)

$$w_C(r) = Z_{AC}N\phi_A(r) + Z_{BC}N\phi_B(r) - H_{\text{ext}}(r) + \eta(r)$$

(5)

$$\phi_A(r) = \frac{1}{Q} \int_0^{r_A} \text{d}r \phi_A(r,s) q^I(r,s)$$

(6)

$$\phi_B(r) = \frac{1}{Q} \int_{r_A}^{r_B} \text{d}r \phi_A(r,s) q^I(r,s)$$

(7)

$$\phi_C(r) = \frac{1}{Q} \int_{r_B}^{r_C} \text{d}r \phi_A(r,s) q^I(r,s)$$

(8)

$$Q = \frac{1}{P} \int \text{d}q(r,s) q^I(r,s)$$

(9)

$$\phi_A(r) + \phi_B(r) + \phi_C(r) = 1$$

(10)

where the spatial function $\eta(r)$ is a Lagrange multiplier used to enforce the incompressibility condition, $\phi_A(r) + \phi_B(r) + \phi_C(r) = 1$. In the above equations, $q(r,s)$ and $q^I(r,s)$ are two end-segment distribution functions starting from two distinguishable ends, respectively. The two propagator functions satisfy the modified diffusion equations

$$\frac{\partial q(r,s)}{\partial s} = \nabla^2 q(r,s) - w(r,s) q(r,s)$$

(11)

$$\frac{\partial q^I(r,s)}{\partial s} = \nabla^2 q^I(r,s) - w(r,s) q^I(r,s)$$

(12)

where $w(r,s) = w_A(r)$ for $s \leq f_A, w(r,s) = w_B(r)$ for $f_A \leq s \leq f_A + f_B$, and $w(r,s) = w_C(r)$ for $1 - f_C \leq s \leq 1$. The initial conditions of the above two equations are $q(r,0) = q^I(r,1) = 1$. For numerical solution, we employ the pseudo-spectral method44,65 to solve the modified diffusion equations for the end-segment distribution functions. Similar to our previous work,44,54,66 the cross-section of the pore is put into a rectangular cell in the $xy$ plane, which is slightly larger than the diameter of the pore, while the pore axis is aligned along the $z$ direction. Then, we discretize the cell into an $N_x \times N_y \times N_z = 96 \times 96 \times 64$ lattice, and divide the chain contour into 100 pieces. Periodic boundary conditions are imposed in three directions. The free energy of each periodic structure is minimized with respect to the pore length. More details of the calculations can be found in our previous work.44,54,66

3 Results and discussion

In the bulk, the critical condition for the formation of helical supercylinders is to spontaneously create the A/C curvature, and thus it requires a small volume fraction of C-block $f_C$ (or large $f_A$) for a fixed $f_B = 0.1$. In contrast, the concentric A/C interface is enforced by the inner surface of the nanopore in the cylindrically confined system. In other words, a spontaneous curvature in the pore-confined system is not essential. For instance, lamellae are forced to curve into concentric structures inside a nanopore. As a consequence, the helical superstructures could be formed in a wider range of $f_C$ in the confined system than in the bulk, therefore resulting in a possible variation of helical strands to a larger extent.

According to the previous works on the self-assembly behaviors of ABC triblock copolymers with frustrated interactions of $\chi_{ACN} = 20 < \chi_{ABN} = \chi_{BCN} = 80$, a few ordered phases in the bulk may be relevant to the formation of helical superstructures in the confined system, such as cylinders-within-lamellae (LC), double-helical supercylinders (H$_2$) and triple-helical supercylinders (H$_3$). The transition sequence of the three phases in the bulk should be instructive for understanding the self-assembly behaviors of the ABC triblock copolymers in nanopores. In Fig. 1, we present the density plots of these ordered structures (a), the stable phase sequence (b) and the free-energy comparison (c) in the bulk. To demonstrate the relative stability between more helical superstructures, we also consider the single-helical superstructure (H$_1$) and quadruple-helical superstructure (H$_4$). The transition sequence of stable phases in the considered range of $0.12 \leq f_C \leq 0.33$ is BCC$_2 \rightarrow$ H$_2 \rightarrow$ H$_3 \rightarrow$ LC, whereas H$_1$ and H$_4$ are only metastable. For $f_C < 0.154$, the B/C-superdomains transform from cylinder-like to sphere-like, and they are arranged onto a bcc lattice. Three kinds of spherical superstructures are considered with each C-core domain decorated by a B-ring on its equator and two B-dots on two poles (BCC$_4$), by six B-dots arranged on the six vertices of an octahedron (BCC$_3$), and by a perforated B-layer (BCC$_5$), respectively. The superstructure of BCC$_2$ is metastable, and it continuously transforms into BCC$_3$ as $f_C$ decreases.

Although the mechanism accounting for the relative stability between different helical structures has been discussed by Li et al.,16 it is not fully understood. In the previous work, the length ratio of the B-helical domains to the C-core domain was proposed to dictate the number of helices, i.e. a large length ratio usually gives rise to more strands of helices. The length ratio $\gamma$ is defined as $\gamma = m/sin\theta$, where $m$ and $\theta$ are the number of helical strands and pitch angle. The pitch angle $\theta$ can be estimated by $\theta = tan^{-1}(L_d/\pi d_h)$, where $L_d$ and $d_h$ are the pitch length and the rotational diameter of B-helix around C-core. However, the magnitudes of $\gamma$ of the four different helical phases shown in Fig. 2 are not notably distinguishable, and thus they cannot be applied to rationalize the relative stability between the four helical phases. Very recently, Zhang et al.15 argued that there are more factors impacting the formation of helical strands.

Therefore, we attempt to interpret the transition from H$_2$ to H$_3$ as $f_C$ increases from another aspect. Nevertheless, the comparison of various contributions of free energy between
these different helical phases is always a good starting point. For the ABC triblock copolymers, the free energy of each ordered phase can be divided into four contributions: A/B interfacial energy \(U_{AB}\), B/C interfacial energy \(U_{BC}\), A/C interfacial energy \(U_{AC}\), and the entropic contribution \(-TS\), which are expressed as

\[
\begin{align*}
U_{AB} &= \frac{1}{nk_B T} \int d\mathbf{r}_{AB} N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) \\
U_{BC} &= \frac{1}{nk_B T} \int d\mathbf{r}_{BC} N \phi_B(\mathbf{r}) \phi_C(\mathbf{r}) \\
U_{AC} &= \frac{1}{nk_B T} \int d\mathbf{r}_{AC} N \phi_A(\mathbf{r}) \phi_C(\mathbf{r}) \\
S &= -nk_B \ln Q - \frac{1}{nk_B T} \int d\mathbf{r} [w_A(\mathbf{r}) \phi_A(\mathbf{r}) + w_B(\mathbf{r}) \phi_B(\mathbf{r}) + w_C(\mathbf{r}) \phi_C(\mathbf{r})].
\end{align*}
\]

For the reason of clarity, we plot the above four contributions of the free energy of different helical phases relative to \(H_2\) as a function of \(f_C\) in Fig. 3. The comparisons indicate \(U_{AB}\) in a descending order while the entropic contribution has an ascending order tendency as the helical strand increases. The relationship
of A/B interfacial energy as well as the entropic contribution mainly results from the largely different shapes of B-domains of these different helical phases. In Fig. 4, we present the cross-sections of different helical supercylinders upon changing $f_C$. Obviously, the B-domain of the superstructure with smaller helical strands is more expanded in circumference, and consequently, the B/C interface is more curved toward the C-core. In particular, the B-domain in H1 is remarkably prolonged in circumference forming a crescent shape. The reason for the expansion of B-domain is to diminish the entropy loss arising from the constraint of discrete B-domains on the chain configurations. In contrast to H1, the elongation of B-domains in H2 is significantly reduced, leading to a much less bent crescent shape. In H3, the bending of B-domains almost vanishes, while the shape of B-domains in H4 is already close to an ellipse. The expansion of helical B-domains in circumference is favorable for the chain configurations, especially for uniformly stretching A-blocks, and thus leading to more favorable entropy with less strands in Fig. 3(d) but higher A/B interfacial energy in Fig. 3(a). A highly unfavorable A/B interfacial energy and entropic contribution make H1 and H4 less likely to become stable, respectively.

For the two main competitive H2 and H3 phases, another critical factor arises from the variation of $U_{BC}$. We can see that the B/C interfacial energy of H3 in contrast to that of H2 changes from unfavorable to favorable as $f_C$ increases, driving the transition from H2 to H3. This variation trend of $U_{BC}$ directly results from the change of the shape of B/C interfaces. The aim of changing the domain shape is to increase A/B interfacial area by expelling B-domains from the C-domain because $U_{AB}$ becomes less and less dominant over the increasing $U_{BC}$ as $f_C$ increases. Obviously, the curvature of the B/C interface of H1 is the most negative toward B-domain, while that of H4 is the most positive. As a consequence, the high B/C curvature makes H1 and H4 have higher B/C interfacial energy than H2 and H3. The negative B/C curvature of H2 is milder than that of H1 and attenuates gradually, while the positive B/C curvature of H3 is smaller than that of H4 and tapers to almost zero, as $f_C$ increases. Nevertheless, the large magnitude of B/C curvature gives rise to higher B/C interfacial energy.

After understanding the formation mechanism of helical supercylinders with different strands in the bulk, we turn to exploring the formation of helical supercylinders from the self-assembly of ABC triblock copolymers confined in nanopores. In Fig. 5, the phase diagram with respect to $f_C$ and $D$ for the self-assembly of ABC triblock copolymers with $\chi_{AB} N = \chi_{BC} N = 80$, $\chi_{AC} N = 20$ and $f_B = 0.1$ under the confinement of nanopores, where two vertical dashed lines indicate the corresponding transition sequence of H2 $\rightarrow$ H3 $\rightarrow$ LC in the bulk. Moreover, the blue and red dashed curves indicate the effective diameters of one-layer concentric copolymers around each helical supercylinder of H2 and H3, respectively, defined as $D_{eff} = (2\sqrt{3}/\pi)^{1/3}L_0$, where $L_0$ is the supercylinder-to-supercylinder distance in the bulk.

![Fig. 4](image-url) Cross-sections of different helical supercylinders upon changing $f_C$ in Fig. 1(b). From bottom to top rows, the results are for H1, H2, H3, and H4, respectively.

![Fig. 5](image-url) Phase diagram with respect to $f_C$ and $D$ for the self-assembly of ABC triblock copolymers with $\chi_{AB} N = \chi_{BC} N = 80$, $\chi_{AC} N = 20$ and $f_B = 0.1$ under the confinement of nanopores, where two vertical dashed lines indicate the corresponding transition sequence of H2 $\rightarrow$ H3 $\rightarrow$ LC in the bulk. Moreover, the blue and red dashed curves indicate the effective diameters of one-layer concentric copolymers around each helical supercylinder of H2 and H3, respectively, defined as $D_{eff} = (2\sqrt{3}/\pi)^{1/3}L_0$, where $L_0$ is the supercylinder-to-supercylinder distance in the bulk.

![Fig. 6](image-url) Three-dimensional density plots of considered ordered structures when constructing the phase diagram in Fig. 5. For the reason of clarity, the isosurfaces of B-domains or even inner A/B-domains of some complex superstructures are plotted separately.
the helical strand varies to a larger extent. Helical structures with four and five strands are rarely reported in block copolymers. To the best of our knowledge, Jinnai and coworkers observed a small portion of four-stranded helical structure in the bulk blend of ABC triblock copolymer and C homopolymer that mainly self-assembled into the three-stranded one.\(^6\) Therefore, we mainly focus on rationalizing the transition mechanism of these helical structures on the basis of the formation mechanism of the helical supercylinders in the bulk.

In the phase diagram of Fig. 5, one of the most remarkable features lies in a transition sequence from single-helical structure to double-helical structure and then to triple-helical structure. Here, the helical structure with \(m\) strands is composed of \(m\) helical B-domains wrapping around a C-core domain centering in the nanopore, and it is denoted as \(H_mC\) where C is added to indicate the central C-cylinder and also to distinguish it from the hexagonal array of \(m\)-stranded helical supercylinders \(H_m\) in the bulk. All the three helical structures (\(m = 1, 2\) and 3) exhibit considerably large stability windows. Moreover, this transition trend of helical strands even extends to a quadruple-helical structure in a noticeable region of pore diameter \(7.4R_g \leq D < 7.8R_g\), which is evidenced by the free-energy comparison in Fig. 7. Within this sequence, the helical strand increases as \(f_C\) decreases, which seems to be in contrast to that in the bulk system where \(H_3\) transfers to \(H_2\) as \(f_C\) decreases. Moreover, the presence of stable \(H_4C\) and \(H_5C\) is in great contrast to the absence of \(H_1\) and \(H_4\) in the bulk.

To discuss the relative stability between the different helical superstructures formed in the confined system, we still start from the comparison of various contributions of their free energies, which is provided in Fig. 8. When we compare the results in Fig. 8 to those of the bulk system in Fig. 3, we find that the relative magnitudes as well as their variation trends are highly different, especially those of \(U_{BC}\) and \(-TS\). No doubt these differences should originate from the confinement of the nanopore. In the bulk system, the free energy can be minimized by freely adjusting its different contributions. Concomitantly, the minimization of free energy results in the preferred curvatures of interfaces. However, in the nanopore-confined system, the confinement imposes a severe constraint on the overall chain stretching as well as the curvature of the interface between the A-domain and B/C-superdomain or the diameter of B/C-superdomain in the helical superstructure of \(H_mC\). In other words, the stretching length of the copolymer chain in \(H_mC\) is solely dictated by the pore radius in the nanopore with given surface potentials, and thus the stretching energy or the entropic contribution to free energy cannot be tuned freely to minimize the free energy. Moreover, the diameter of B/C-superdomain is roughly proportional to \((f_B + f_C)^{1/2}\). In return, the constraint significantly impacts the competition between the interfacial energy and the entropic contribution, and thus the relative stability of different structures.

In general, the stretching length of a copolymer in the bulk \(H_2\) or \(H_3\) structure changes as \(f_C\) varies. As \(f_C\) decreases, the overall segregation of the copolymer decreases, and thus the entropic contribution increases, leading to less stretched chains. To illustrate the different stretching degrees between the bulk system and the confined system, we introduce an effective diameter \(D_{eff}\) to quantify the mean stretching length of copolymer in the bulk helical superstructures, determined by \(D_{eff} = (2\sqrt{3/\pi})^{1/2}L_0\). The curves of \(D_{eff}\) as a function of \(f_C\) for
H$_2$ and H$_3$ are plotted in the phase diagram of Fig. 5, indicated by the blue and red dashed lines, respectively. Note that the values of $D_{\text{eff}}$ of H$_2$ and H$_3$ are very close and both decrease as $f_C$ decreases. Within the stability region 0.174 $\leq f_C \leq$ 0.30 of the bulk H$_1$, H$_4$C is stable in a large window of $D$. When $D$ is reduced to be smaller than $D_{\text{eff}}$, the confinement compresses the copolymer chains in contrast to them in the bulk increasing the curvature of B/C-supercylinder, which is similar to the effect of decreasing $f_C$ on the curvature. As a consequence, $U_{BC}$ of H$_4$C becomes rapidly unfavorable, driving H$_4$C to transform into H$_3$C like the H$_3$ $\rightarrow$ H$_4$ transition in the bulk. Oppositely, when $D$ increases, the curvature of B/C-superdomain is gradually decreased. Meanwhile, the disadvantage due to the unfavorable B/C interfacial energy in the helical superstructure with a large number of strands is alleviated. In addition, when the copolymer chain is more stretched, the constraint of divided domains on the configurations becomes more severe, benefiting the formation of H$_n$C with more strands. Specifically, the entropic contribution of H$_4$C becomes lower than that of H$_1$C in Fig. 8(d). As a result, H$_4$C becomes stable against H$_1$C in a noticeable region of large $D$ in the phase diagram. Note that the phase region of H$_4$C is truncated by the formation of other kinds of superstructures in the direction of increasing $D$.

When $f_C$ is increased to approach a symmetric A/C composition, the overall segregation of the copolymer increases leading to a stable lamella-like phase against H$_1$ in the bulk (e.g. LC). Accordingly, the copolymer chain exhibits increasing stretching as $f_C$ increases. When the A/C-layering structure is forced to curve into an A/C-concentric structure by the cylindrical confinement of the nanopore of a given size, it experiences an increasingly severe confining effect as $f_C$ increases. In other words, the curvature of B/C-superdomain relative to its bulk value is increasingly enlarged. Similar to the above mechanism, increasing curvature of B/C-superdomain drives the transition of H$_n$C toward decreasing $m$, i.e. H$_1$C $\rightarrow$ H$_2$C $\rightarrow$ H$_3$C. In brief, the effect of the confinement on the curvature of B/C-superdomain is the main factor impacting the formation of helical strands. Specifically, more the curvature of B/C superdomain is increased by the confinement relative to the bulk value, less helical strands are formed with the helical superstructure, and vice versa.

In the top portion of the phase diagram, an additional layer of inner domains is formed at the center to release the increasingly high stretching due to the mismatch between the pore size and the domain spacing. For the formation of B-helices, the direct effect is to decrease the curvature of the interface between the outer A-layer and the neighboring B/C-superdomain. As a result, the helical strand is added, e.g. from H$_1$C $\rightarrow$ H$_2$C $\rightarrow$ H$_3$C $\rightarrow$ H$_4$C to H$_2$CS $\rightarrow$ H$_3$CS $\rightarrow$ H$_4$CS $\rightarrow$ H$_5$CS, where S denotes the B-spheres zigzag-arranged axially within the A-cylinder at the center of the nanopore. Besides these helical superstructures, some other interesting structures are predicted in the phase diagram, which mainly consist of various toroidal structures. In fact, toroidal structures are widely observed in block copolymers under geometrical confinement.\textsuperscript{13,46,47} The formation of toroids arranged along the axial direction provides an alternative way to release the high stretching of blocks as the majority blocks can be packed along both the radial direction and the axial direction. Another interesting structure formed in a noticeable region with rather small $D$ and low $f_C$ is denoted by P$_b$, which is composed of dice-like B/C-superdomains arranged within the A-matrix and where 6 indicates the cubic B-frame with six holes. Apparently, the formation of P$_b$ is mainly due to a low overall B/C volume fraction that leads to the high curvature of B/C-superdomain.

As we know, the interaction parameters must satisfy a prerequisite of $\chi_{ACN} < \chi_{ABN} \sim \chi_{BCN}$ for the formation of these helical superstructures with A/C interfaces. Therefore, it is necessary to demonstrate if the transition sequence of helical superstructures is generic for varying $\chi_{ACN}$. In Fig. 9, we present the phase diagram in the $f_C$-$\chi_{ACN}$ plane for $\chi_{ABN} = \chi_{BCN} = 80$, $f_B = 0.1$ and $D = 7.6R_p$. Importantly, the transition sequence of H$_1$C $\rightarrow$ H$_2$C $\rightarrow$ H$_3$C $\rightarrow$ H$_4$C as $f_C$ decreases is generic before the B-helical domains transform into the perforated B-layer as $\chi_{ACN}$ increases. The superstructure composed of a perforated B-layer covering the C-core domain is denoted as PC. Note that there are various PC superstructures that exhibit different arrangements of holes within the B-layer, which are nearly degenerate in free energy. In Fig. 9, only one PC superstructure is considered to estimate the boundaries (indicated by dotted lines) between the PC phases and these helical phases.

### 4 Conclusions

In summary, the self-assembly of linear ABC triblock copolymers under the confinement of nanopores is investigated using self-consistent field theory, focusing on the exploration of more helical superstructures. Instead of simply searching the huge parameter space, we judiciously fix a number of parameters such as the interaction parameters $\chi_{ACN} = 20 \ll \chi_{ABN} = \chi_{BCN} = 80$ and $f_B = 0.1$ according to the bulk self-assembly behaviors. Upon increasing the control parameter, the volume fraction of C-block ($f_C$), the double-helical superstructure (H$_3$) transfers to the triple-helical one (H$_4$) in the bulk. We find that the H$_2$ $\rightarrow$ H$_3$ transition
is mainly induced by the variation of A/B/C interfaces in response to the change of $f_C$. Then, we calculate the phase diagram with respect to $f_C$ and the pore diameter $D$ for the ABC triblock copolymer confined in a nanopore with fixed surface interaction attraction to A-block. Surprisingly, a number of helical superstructures are predicted in the phase diagram, whose helical strands continuously vary from 1 to 5. Moreover, in contrast to the bulk system where the helical strand increases as $f_C$ increases, the helical strand in the confined system changes in an opposite trend. The opposite trend results from the constraint of the cylindrical confinement on the change of the curvatures of A/B/C interfaces, especially the interface between the outer A-layer and the inner B/C-superdomain. When the curvature is increased, the helical strand tends to decrease, and otherwise it increases. Furthermore, we find that the transition sequence of $H_2C \rightarrow H_3C \rightarrow H_4C \rightarrow H_5C$ as $f_C$ decreases is generic within the range of $20 \leq \Delta N \leq 60$ for fixed $\Delta N = N = 80$. In addition to these helical superstructures, more interesting structures are predicted, e.g. a number of toroidal structures. This cylindrically confined ABC triblock copolymer system provides a facile way to generate various helical superstructures.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**