

Achieving Complete Photonic Band Gaps in a Low-symmetric Rectangular Cross-sectional Columnar Phase Self-assembled from Block Copolymers

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 Electronic Supplementary Information

Abstract A significant challenge in developing block copolymer photonic crystals is constructing low-symmetric ordered phases, which are essential for achieving a complete photonic band gap. Here, we propose a promising strategy to create low-symmetric ordered morphologies by incorporating shape-anisotropic rod-like side chains into block copolymers. Using dissipative particle dynamics simulations, we demonstrate that block copolymers with longer rod-like side chains can self-assemble into a hexagonally packed columnar phase characterized by a low-symmetric rectangular cross-section. Photonic band structure calculations reveal that this low-symmetric columnar phase can exhibit a complete photonic band gap, with the gap size dependent on the aspect ratio of the rectangular cross-sections of the columns. Our findings suggest an effective approach to constructing low-symmetric photonic crystals through the self-assembly of block copolymers with shape-anisotropic segments.

Keywords Photonic band gaps; Low-symmetric phase; Self-assembly; Block copolymers

Citation: Weng, H. Y.; Li, Z. W.; Li, Y. C.; Lu, Z. Y. Achieving complete photonic band gaps in a low-symmetric rectangular cross-sectional columnar phase self-assembled from block copolymers. *Chinese J. Polym. Sci.* 2025, 43, 1059–1066.

INTRODUCTION

Photonic crystals (PCs) are optical materials whose permittivity varies periodically in one (1D), two (2D), or three (3D) directions on a spatial scale comparable to the wavelength of light. One of the most remarkable properties of PCs is the photonic band gap (PBG). When light with the same frequency as PBGs is incident on PCs in a certain direction, it is completely reflected and is unable to propagate into PCs. Since PCs can affect the propagation of light, they have potential applications in displays,^[1–3] reflective coatings,^[4,5] sensors,^[6,7] information security,^[8,9] and so on. Top-down and bottom-up methods are mainly employed in the fabrication of PCs. Compared with top-down methods such as lithography, laser direct writing, and nanoimprint, the bottom-up method is both cost-effective and relatively simple.^[10] Self-assembly of block copolymers (BCPs) has emerged as a promising bottom-up method for the fabrication of PCs,^[11–13] because it allows for a broader range of materials, may incorporate various nanoparticle additives^[14,15] and possess responsiveness to external stimuli.^[16–19]

However, the fabrication of PCs by self-assembly of BCPs

remains a grand challenge, since a variety of complex factors can determine the existence of PBGs. Great efforts had been made to improve the design of PCs via self-assembly of BCPs, for example, by manipulating lattice parameters of ordered domains and increasing dielectric contrasts between different domains in a material. It had been theoretically proven that, PBGs may benefit from using non-cylindrical scatterers or even rotating scatterers to reduce structure symmetry.^[20–24] Nevertheless, the self-assembly of BCPs commonly results in symmetrical structures such as spherical, cylindrical, and lamellar morphologies, because the interfaces between domains tend to possess a constant average curvature to minimize the interfacial tension.^[25,26] Shape-anisotropic building blocks are thought to contribute to the development of low-symmetric structures because of the inherent anisotropy.^[27–30]

Herein, we design the BCPs incorporating shape-anisotropic rod-like side chains, and explore the effect of the shape-anisotropy and symmetry of BCPs on the symmetry of self-assembled structures, using dissipative particle dynamics (DPD) simulation method. A class of ordered structures, especially rectangular cross-sectional columnar phase, can be obtained by increasing the length of rod-like side chains. Further photonic band structure calculations demonstrate how the symmetry of obtained rectangular cross-sectional columnar phase affects its PBG properties. This study suggests a feasi-

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Received January 20, 2025; Accepted March 5, 2025; Published online May 8, 2025

ble route to construct low-symmetric block copolymer photonic crystals with a complete band gap.

SIMULATION METHOD

The details of simulation method can be found in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

As a mesoscopic simulation method, DPD has been proven to be successful in simulating self-assembly of BCPs.^[31–33] In DPD, all coarse-grained particles obey Newton's equations of

motion.^[34] In our simulations, three types of particles makeup the model of BCPs containing rod-like side chains, as illustrated in Fig. 1(a). The flexible main chain consists of A (blue) block bonded by x particles and B (ivory) block bonded by 8 particles. Four rod-like C side chains (green, each made up of y particles) are laterally bonded to alternating B-type particles. This BCP is represented by $A_x - b - (B_8 - g - 4C_y)$, where b and g stand for "block" and "graft", respectively. Particles of the same type are compatible, while particles of different types are incompatible in our model. The rod-like side chain is simulated as a rigid body,^[35,36] and the modified conservative force is adopted between C-type particles to avoid bond crossing and particle over-

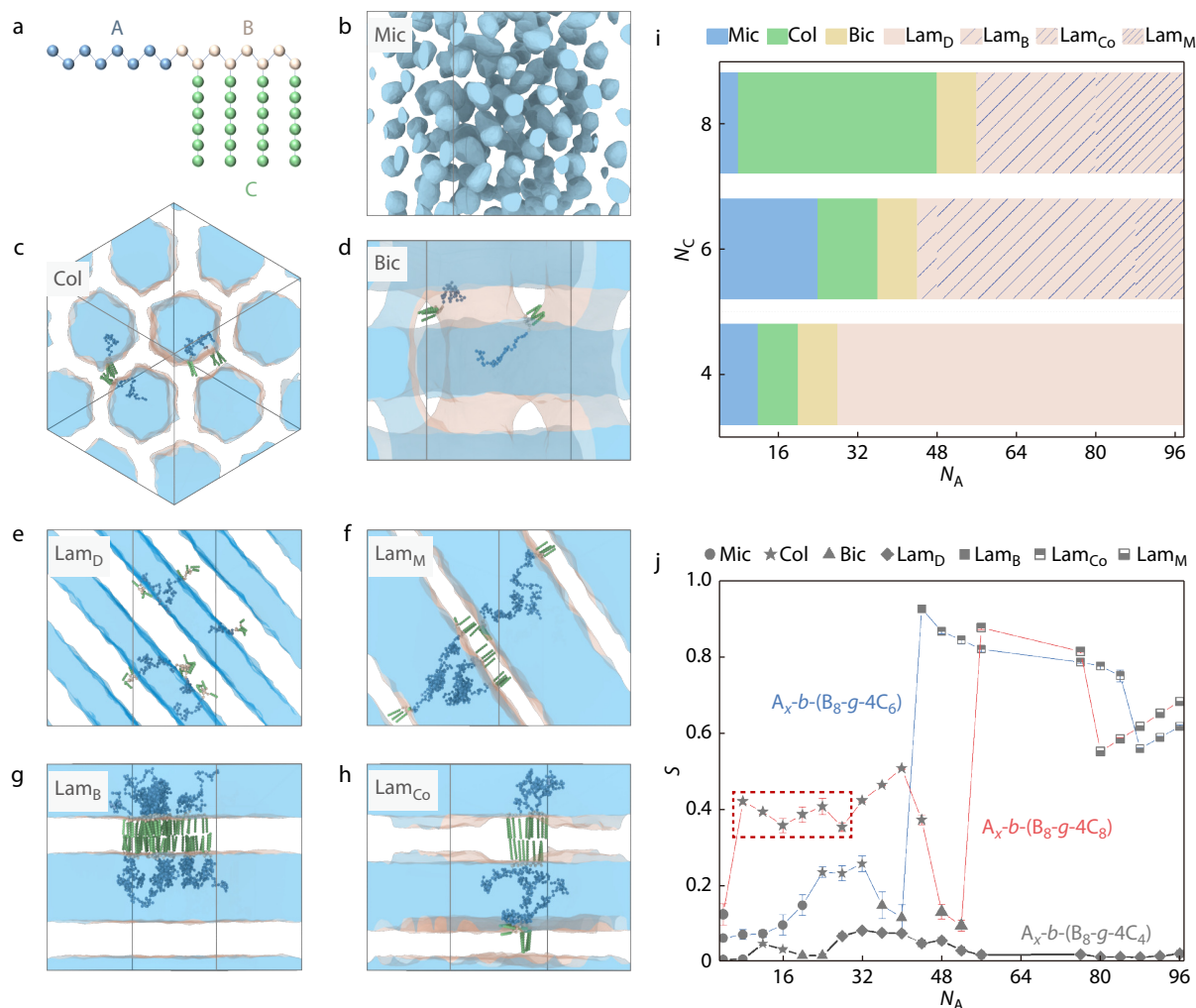


Fig. 1 (a) Schematic illustration of the model of BCP containing rod-like side chains, denoted by $A_x - b - (B_8 - g - 4C_y)$. x and y are the particle numbers of A-type block (blue) and each C-type side chain (green), respectively. (b)–(h) show typical self-assembled phases of $A_x - b - (B_8 - g - 4C_y)$: (b) micellar phase formed by A blocks (Mic) in the system with $A_4 - b - (B_8 - g - 4C_4)$, (c) columnar phase formed by A blocks (Col) in the system with $A_{28} - b - (B_8 - g - 4C_6)$, (d) bicontinuous phase (Bic) in the system with $A_{36} - b - (B_8 - g - 4C_6)$, (e) lamellar phase where rod-like side chains are disordered (Lam_D) in the system with $A_{28} - b - (B_8 - g - 4C_4)$, (f) lamellar phase where rod-like side chains are highly interdigitated in monolayers (Lam_M) in the system with $A_{92} - b - (B_8 - g - 4C_6)$, (g) lamellar phase where rod-like side chains are arranged in bilayer smectic phase (Lam_B) in the system with $A_{44} - b - (B_8 - g - 4C_6)$, (h) coexisting lamellar phase of both Lam_M and Lam_B (Lam_{Co}) in the system with $A_{56} - b - (B_8 - g - 4C_8)$. For clarity, the isodensity surface is rendered translucent, while representative chain configurations are displayed in (c)–(h). (i) Self-assembly diagram of $A_x - b - (B_8 - g - 4C_y)$ in parameter space of the number of A-type particles in each block copolymer ($N_A = x$), and the number of C-type particles in each side chain ($N_C = y$). (j) Orientational order parameter (S) of rod-like side chains as a function of N_A for systems with different N_C . The error bars represent standard deviations obtained after running five independent simulations.

lapping, which can effectively ensure the rigidity of the side chains.^[37] In this way, the side chains become shape-anisotropic rods. The increasing incompatibility between these blocks will lead to stronger phase separation. A cubic box of size $40 \times 40 \times 40$ in reduced units with periodic boundary conditions is used in our simulations, and the number density of particles is fixed at 3.0.^[38] All simulations are performed in canonical ensemble with a time step $\Delta t = 0.01$. More simulation details are given in ESI.

The shape-anisotropy and symmetry of BCPs in Fig. 1(a) are mainly determined by the number of C-type particles in each side chain (N_C), and the number of A-type particles in each block copolymer (N_A). To clarify the effect of the shape-anisotropy and symmetry of BCPs on the symmetry of self-assembled structures, the self-assembly “structure diagram”, obtained by changing N_C to 4, 6, and 8, as well as N_A from 4 to 96 in increments of 4, is summarized in Fig. 1(i). Similar to the self-assembly behavior of common BCPs, with increasing N_A while keeping N_C fixed, the BCPs containing rod-like side chains can sequentially self-assemble into micellar phase (Mic, Fig. 1b), columnar phase (Col, Fig. 1c), bicontinuous phase (Bic, Fig. 1d), and lamellar phases (Figs. 1e–1h). To provide a clear visual representation, the 3D rotational views of the phase structures are shown in Movies S1–S3 (in ESI). Among different phase structures, the arrangement of rod-like side chains varies significantly in detail, as evidenced by the chain conformations in Figs. 1(c)–1(h). To quantitatively measure the arrangement of the rod-like side chains, we calculate the orientational order parameter (S) of rod-like side chains,^[39] $S = \langle 3(\hat{u}_i \cdot \mathbf{n})^2 - 1 \rangle / 2$, where $\mathbf{n}$ is the director describing the direction of preferred orientation of rod-like side

chains, and $\hat{u}_i$ is the unit vector along the principal axis of rod-like side chain i . As shown in Fig. 1(j), in the system with $A_x - b - (B_8 - g - 4C_4)$, generally lower S indicates the disordered arrangement of shorter side chains as illustrated in the lamellar phase (Lam_D, Fig. 1e). In contrast, in the system with longer side chains, such as $A_x - b - (B_8 - g - 4C_6)$ or $A_x - b - (B_8 - g - 4C_8)$, S varies significantly with the phase structures, suggesting that longer side chains exhibit ordered arrangements, either locally or globally. Specifically, in lamellar phases with high S , the arrangement of longer side chains differs. When $N_C = 6$, with increasing N_A , a transition occurs from Lam_B (lamellar phase where rod-like side chains are arranged in bilayer smectic phase, Fig. 1g), to Lam_{C0} (lamellar phase where rod-like side chains are arranged in a manner of coexistence in both bilayers and monolayers, similar to Fig. 1h), and finally to Lam_M (lamellar phase where rod-like side chains are highly interdigitated in monolayers, Fig. 1f). Moreover, taking the system of $A_{96} - b - (B_8 - g - 4C_6)$ as an example, which forms Lam_M, we observe the formation of Lam_{C0} when the incompatibility between A-type and C-type particles increases (as shown in Fig. S1 in ESI). Analogously, when $N_C = 8$, increasing N_A induces a change from Lam_{C0} to Lam_M. These findings clearly demonstrate that N_A and the incompatibility between A-type and C-type particles can modulate lamellar substructures by adjusting the degree of interdigitation of rod-like side chains within the lamellar phases. Thus, it turns to be a facile method for adjusting the domain size of 1D photonic crystals through tuning the proportion of rod-like side chains and compatibility between A-type and C-type particles.

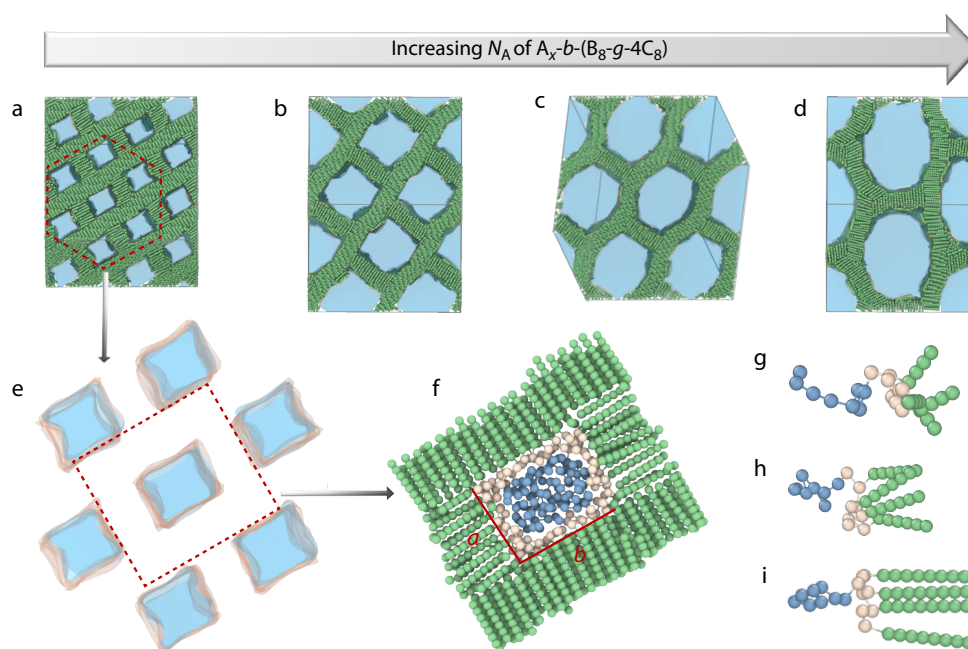


Fig. 2 (a)–(d) show hexagonally packed columnar phases with non-round cross-section formed by the systems of $A_8 - b - (B_8 - g - 4C_8)$, $A_{28} - b - (B_8 - g - 4C_8)$, $A_{40} - b - (B_8 - g - 4C_8)$, and $A_{44} - b - (B_8 - g - 4C_8)$, respectively. (e) is the isodensity surface obtained from the enlarged dashed area in (a), with C-type particles omitted for clarity. Similarly, (f) provides an enlarged view showing the slice of the dashed area in (e), where b and a represent length and width of the rectangular cross-section, respectively. In the system of $A_8 - b - (B_8 - g - 4C_8)$, the average length b and average width a are 6.92 and 6.38, respectively. (g)–(i) display chain conformations derived from the self-assembled structures of $A_8 - b - (B_8 - g - 4C_4)$, $A_8 - b - (B_8 - g - 4C_6)$, and $A_8 - b - (B_8 - g - 4C_8)$, respectively.

For $N_C = 8$, the columnar phase region in the structure diagram significantly expands, as shown in Fig. 1(i). Furthermore, the cross-sections of columns are non-round, as depicted in Figs. 2(a)–2(d). As N_A increases, the columns remain arranged in a hexagonal lattice; however, their cross-sectional shapes are changed. From $N_A = 8$ to 28, the A-type and B-type particles aggregate into columns with low-symmetric rectangular cross-sections (Figs. 2a and 2b). A typical rectangular cross-sectional columnar phase is locally magnified in Fig. 2(e), and a detailed slice of the dashed area in Fig. 2(e) is presented in Fig. 2(f). We observe that A-type particles are positioned at the center of cross-sections, with B-type particles encircling them, thereby forming the columns, with rectangular cross-sections. Outside the columns, rod-like side chains are packed in an orientationally ordered manner, and mostly perpendicular to the long axis of the columns. The rectangular cross-sections of columns are deformed as N_A increases (Fig. 2c). For $N_A = 44$, the elliptical cross-sectional columnar phase emerges (Fig. 2d).

To better understand the formation of the low-symmetric columnar phase, we monitor the time evolution of S during the self-assembly of systems with $A_8 - b - (B_8 - g - 4C_8)$ and $A_{44} - b - (B_8 - g - 4C_8)$, as shown in Figs. 3(i) and 3(s). For the system with $A_8 - b - (B_8 - g - 4C_8)$, the initial configuration is randomly generated, with rod-like side chains arranged in a disordered manner (Fig. 3a). After a period of simulation, S of the rod-like side chains remains low (Fig. 3b). To achieve a more stable and ordered structure, two thermal annealing simulations are performed, with parameters detailed in ESI. During the first heating period, the side chains begin to move, resulting in a decrease of S (Fig. 3c). With the first cooling process underway, the packing of rod-like side chains becomes increasingly ordered, and A-type particles aggregate into large micelles (Fig. 3d). In the second heating period, the metastable large micelles are decomposed, forming smaller micelles (Fig. 3e). In the cooling process, the smaller micelles gradually gather to form a hexagonally packed cylindrical structure (Fig. 3f). Subsequently, the rod-like side chains pack in an ordered way (Fig. 3g), ultimately resulting in rectangular cross-sectional columnar phase (Fig. 3h).

However, for the system with $A_{44} - b - (B_8 - g - 4C_8)$, after the first annealing cycle, a defective lamellar structure appears (Fig. 3n). After the second heating period, the lamellar structure becomes curled (Fig. 3o) and rapidly transforms into a cylindrical structure (Fig. 3p). Then the rod-like side chains gradually arrange in an ordered manner (Fig. 3q), causing A-type and B-type particles form the columns with elliptical cross-sections (Fig. 3r). To verify the stability of these self-assembled structures, we performed annealing simulation once again, and confirmed that the non-round cross-sections of columns remained stable, as shown in Fig. S2 (in ESI). In summary, the region of the columnar phase in the structure diagram is expanded due to the instability of the micellar structure or the defective lamellar structure, and the formation of columns with low-symmetric cross-sections is caused by the ordered arrangement of longer rod-like side chains.

For BCPs containing rod-like side chains, the shape entropy of the shape-anisotropic rod-like side chains has a significant impact on the self-assembled structure. Shape entropy describes how shape-anisotropic assembly units in

crowded systems are arranged in an ordered manner by optimizing local packing to maximize entropy,^[40,41] which is a concept widely applied in materials science and biology.^[42,43] In our simulation, due to the incompatibility and bonding among different blocks, rod-like side chains are confined in limited space. This leads to the parallel arrangement of rod-like side chains, which helps to increase the translational entropy. Moreover, the ordered packing of rod-like side chains increases the configuration entropy by leaving more space for accessing various configurations of main chains. As a result, the total entropy is maximized. As N_C increases, the tendency of parallel arrangement of rod-like side chains becomes stronger. Figs. 2(g)–2(i) show the representative chain configurations derived from the self-assembled structures with $N_C = 4, 6$, and 8, respectively. Contrasting to the less ordered state with $N_C = 4$, when $N_C = 8$, the rod-like side chains pack more orderly, facilitating the formation of flat interfaces with zero Gaussian curvature. This also elucidates why the columnar phase with non-round cross-section frequently appears as the rectangular cross-sectional columnar phase, as highlighted in the boxed region of Fig. 1(j). Thus, incorporating shape-anisotropic segments into block copolymers offers a feasible way to reduce the symmetry of self-assembled structures.

Theoretical simulation has suggested that lowering the symmetry of the building blocks or the crystalline lattices can potentially open a complete PBG.^[24] The rectangular cross-sectional columnar phase assembled from block copolymers with shape-anisotropic segments possesses lower symmetry compared to the conventional hexagonal columnar phase. We calculate the photonic band structure of obtained rectangular cross-sectional columnar phase in the system with $A_8 - b - (B_8 - g - 4C_8)$ using the freely available MIT Photonic-Bands (MPB) software package.^[44–46] The calculations are performed at the dielectric contrast $\epsilon = 12$.^[46–48] As shown in Fig. 4(a), the obtained rectangular cross-sectional columnar phase possesses a complete photonic band gap with a relative gap size of 3.1%, which is attributed to the overlap of transverse-electric (TE) gap between the second and third TE-polarized bands with transverse-magnetic (TM) gap between the third and fourth TM-polarized bands. As a comparison, the photonic band structure of cylindrical columns arranged in hexagonal lattice with high symmetry is also computed, but there is no complete PBG, as shown in Fig. S3 (in ESI).

The aspect ratio of the rectangular cross-section of columns and the orientation angle θ (the angle between the short axis of the rectangular cross-section and the lattice vector direction; see the inset in Fig. 4b) are the key factors that affect the symmetry of the rectangular cross-sectional columnar phase. Thus, we explore the effect of the orientation angle and the aspect ratio of rectangular cross-section of columns on the relative gap size. As illustrated in Fig. 4(b), the gap size increases with the increasing orientation angle, which is contributed to the lower symmetry at larger orientation angles. In Fig. 4(c), the aspect ratio is represented by b/a , where a is fixed and b is variable in the calculations. The symmetry will be reduced by increasing or decreasing the aspect ratio b/a from 1.0. The red point represents the rectangular cross-sectional columnar phase obtained in the system with

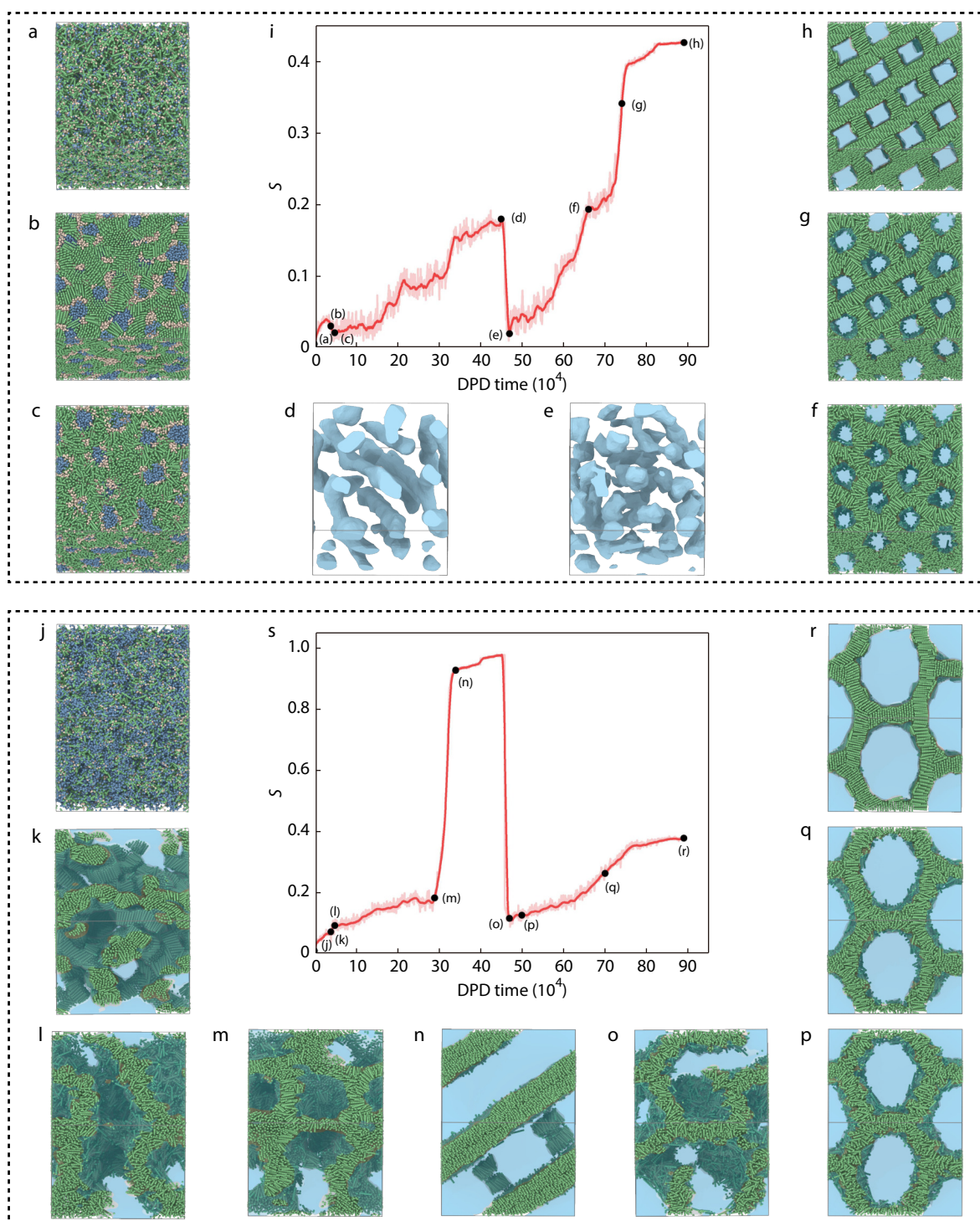


Fig. 3 (a)–(h) and (i) respectively show the structures and the variation of the orientational order parameter (S) of the rod-like side chains during the self-assembly of $A_8 - b - (B_8 - g - 4C_8)$. The black data points in (i) correspond to (a)–(h). (j)–(r) and (s) respectively show the structures and the variation of S during the self-assembly of $A_{44} - b - (B_8 - g - 4C_8)$. The black data points in (s) correspond to (j)–(r). In all simulation snapshots, the component's color settings are the same as those in Fig. 1(a). All types of particles are displayed in (a)–(c) and (j) to more clearly illustrate the disordered state of the systems. In other snapshots, we have used the isodensity surface. The rod-like side chains are presented in (h)–(g) and (k)–(r), where the isodensity surface is rendered translucent for clarity.

$A_8 - b - (B_8 - g - 4C_8)$. As shown in Fig. 4(c), the relative gap size of rectangular cross-sectional columnar phases depends on the aspect ratio of rectangular cross-section of columns.

When b/a is 0.76, the gap size of rectangular cross-sectional columnar phase can reach the maximum value of 5.1%, mostly due to its low symmetry. When the value of b/a increases

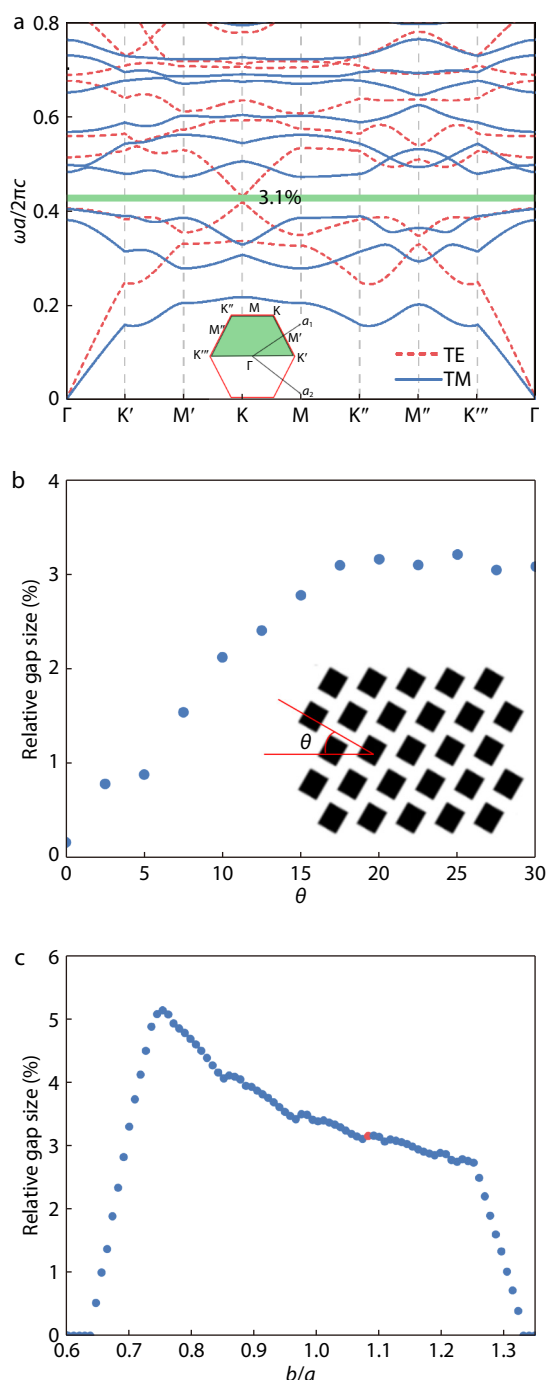


Fig. 4 (a) Photonic band structure for rectangular cross-sectional columnar phase with hexagonal lattice in the system with $A_8 - b - (B_8 - g - 4C_8)$ in air. The red lines represent transverse-electric (TE) modes, and the blue lines represent transverse-magnetic (TM) modes. (b) Relative gap size as a function of the orientation angle θ (the angle between the short axis of the rectangular cross-section and the lattice vector direction). The inset shows the corresponding 2D projection of rectangular cross-sectional columnar phase. (c) Relative gap size as a function of the aspect ratio b/a of cross-section of columns in rectangular cross-sectional columnar phase with hexagonal lattice in air. The calculation is performed at the dielectric contrast $\epsilon = 12$. Red point corresponds to the relative gap size reported in (a).

more than 1.0, although the symmetry is also reduced, the relative gap size gradually reduces due to the higher filling ratio. Large refractive index contrast is necessary to open a complete photonic band gap, which can be fulfilled by blending with polymer-functionalized inorganic nanoparticles that are selective for the domains formed by A- or B-type particles.^[46] Then the dielectric rectangular cross-sectional columns could be obtained by removing the domains formed by C-type particles through physical or chemical methods.^[49] Therefore, the rectangular cross-sectional columnar phase is a good candidate for 2D photonic crystals with a large complete band gap.

CONCLUSIONS

In summary, we present a promising strategy to construct low-symmetric ordered morphologies from block copolymers with shape-anisotropic segments. Our simulations demonstrate that the block copolymers containing shape-anisotropic rod-like side chains can self-assemble into low-symmetric rectangular cross-sectional columnar phase, due to shape entropy of long rod-like side chains. This rectangular cross-sectional columnar phase features a complete photonic band gap, and the relative gap size can be tuned by changing the aspect ratio of rectangular cross-section of columns. Thus, it holds great promise for potential applications, such as reflectors for extreme ultraviolet lithography.^[50,51] This study not only provides an effective route to achieving 2D photonic crystals with complete band gaps via block copolymer self-assembly, but also opens new possibilities for the design of photonic crystals by tuning block copolymer architectures.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3329-3>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The author's contact information: luzhy@jlu.edu.cn.

ACKNOWLEDGMENTS

This work was financially supported by the National Key R&D Program of China (No. 2022YFB3707300) and the National Natural Science Foundation of China (Nos. 22133002, 22373089). Z.W.L. acknowledges the support from the Excellent Youth Foundation of Henan Scientific Committee (No. 242300421032).

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