Confinement-induced self-assembly of diblock copolymer within a non-uniform cylindrical nanopore

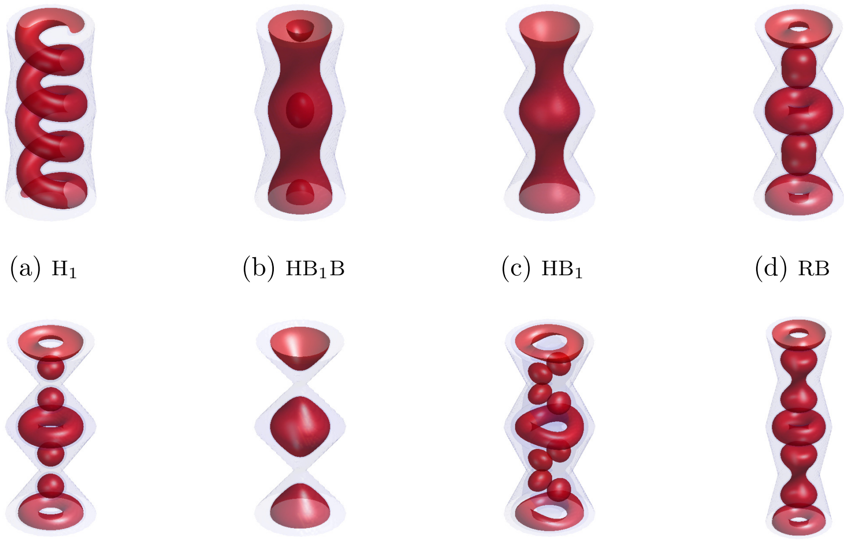
Jagat Singh, Supriya Gupta, and Paresh Chokshi

Supplementary Information

The confinement geometry is a non-uniform nanopore with an axially varying radius. Over the half-length of the pore, $L/2$, the pore radius linearly varies from R_1 to R_2 and then from R_2 to R_1 in the other half. In a real system, this may represent a non-uniform pore with a periodic variation in pore radius over the entire length of the pore. In this case, the non-uniform pore with axial length L examined in the present study can be understood as a unit cell that repeats periodically in the axial direction. The periodic repetition of the converging-diverging shape could represent a real non-uniform pore. Alternatively, the presence of a single cell of non-uniform pore with length L can be considered as a defect in a cylindrical nanopore. In this case, the structure appears as a defect in the confined ordered phases. For the former scenario, the microstructures presented in the main article represent a unit cell of periodic structures in periodically non-uniform long confinement. Here, the ordered phases reported in the main text can be visualized as periodically repeating structures. To help this visualization, we depict some of the ordered phases reported in the main article as periodic structures in this Supplementary Information. This is merely aimed at providing an alternate visualization of the reported structures. Figure S1 plots the density isosurface plots of morphologies formed by AB diblock copolymer showing two repeating unit cells.

Table S1 provides two different visualizations of the microstructures in a unit cell. In one, the ordered phases are shown for a non-uniform pore in which the radius varies axially as R_1-R_2-R_1, that is converging-diverging part of the cell (same as shown in the main text), and in another one, in which the axial variation of pore radius is R_2-R_1-R_2, that diverging-converging part of the cell.

Figure S2 provides an alternate presentation of the phase diagram shown in Figure 4 of the main article.

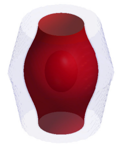
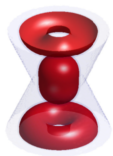
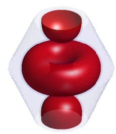
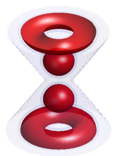
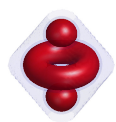
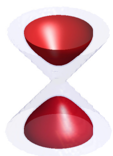


(a) H_1 (b) HB_1B (c) HB_1 (d) RB

(e) RS_2 (f) HB_2 (g) RS_4 (h) RHB_1

Figure S1: Density isosurface plots of ordered phases of AB diblock copolymer under non-uniform confinement showing two repeating unit cells. Red indicates minority B-block segments and light blue surrounding the red domain represents the majority A-block segments covering the pore surface.

Table S1: Different visualizations of the ordered phases for non-uniform pore with axial variation in radius as R_1-R_2-R_1 and R_2-R_1-R_2.

Morphology	R_1-R_2-R_1	R_2-R_1-R_2
HB_1B		
HB_1		
RB		
RS_2		
HB_2		

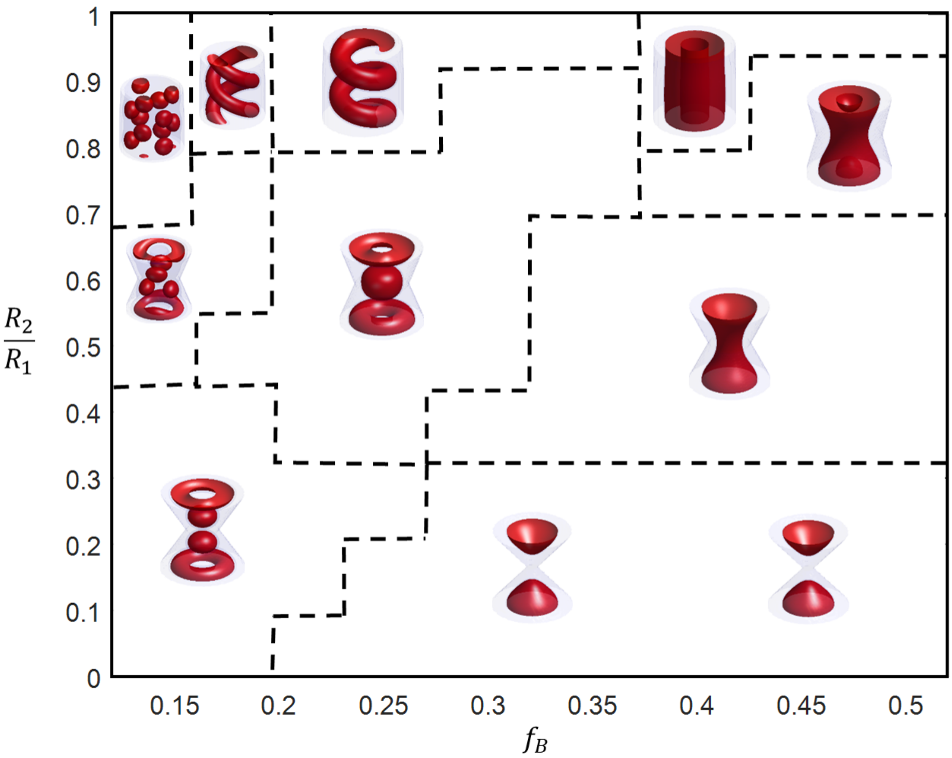


Figure S2: Different presentation of the phase diagram shown in Figure 4 of the article (same parameters). Here, the broken lines do not indicate the exact phase boundaries. The lines are drawn only as a guide to the eyes. The calculations are carried out only at the discrete points in the phase diagram as shown by symbols in Figure 4 of the main article.

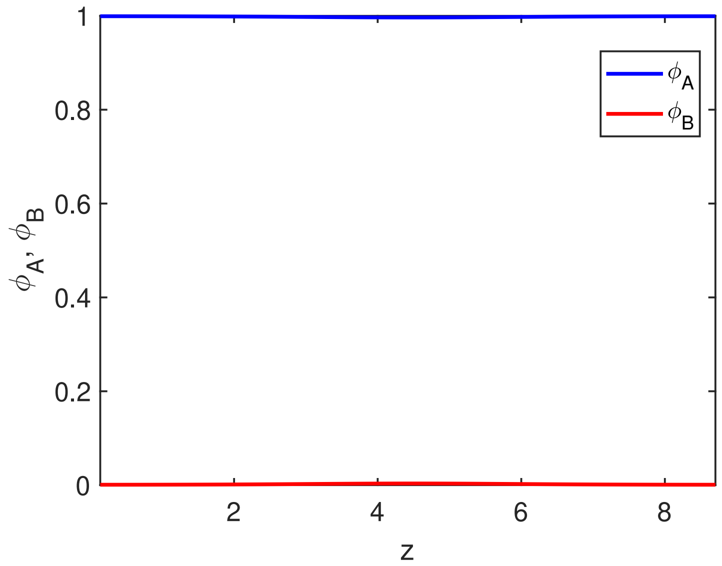


Figure S3: Composition profiles of A and B segments along the pore axis (*i.e.* z-direction at $x = y = 0$) for concentric lamella (CL_1) phase for $f_B = 0.40$, $R_1 = 4R_g$, $R_2 = 3.5R_g$, $L = 8.7R_g$, and $\chi N = 35$.

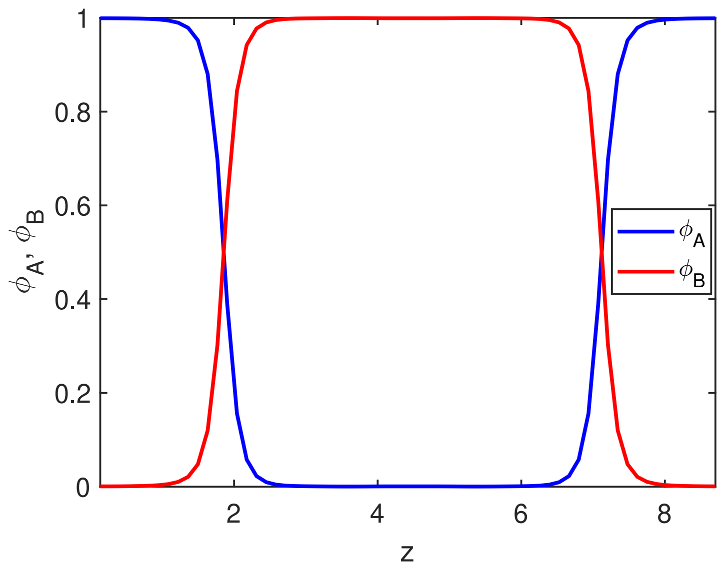


Figure S4: Composition profiles of A and B segments along the pore axis (*i.e.* z-direction at $x = y = 0$) for one-sheeted hyperboloid with bowls (HB_1B) phase for $f_B = 0.40$, $R_1 = 4R_g$, $R_2 = 3R_g$, $L = 8.7R_g$, and $\chi N = 35$.

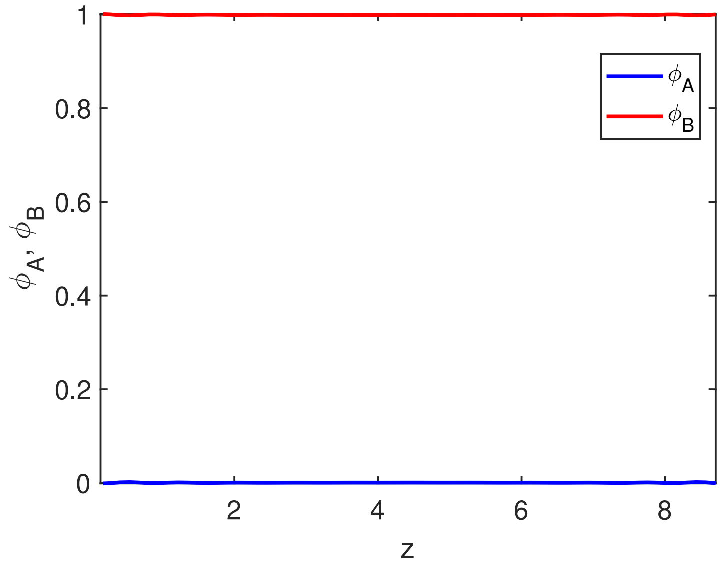


Figure S5: Composition profiles of A and B segments along the pore axis (*i.e.* z-direction at $x = y = 0$) for single-sheeted hyperboliod (HB_1) phase for $f_B = 0.40$, $R_1 = 4R_g$, $R_2 = 2.5R_g$, $L = 8.7R_g$, and $\chi N = 35$.