Supporting Information for "Enhanced sampling of cylindrical microphase separation via shell-averaged bond orientational order parameter"

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I. BOND-ORIENTATIONAL ORDER PARAMETERS (BOP)

Figure S1 shows two characteristic symmetries of hexagonal cylinder systems: two-fold in-cylinder symmetry and six-fold inter-cylinder symmetry. Note that in Fig. S1(b), the in-cylinder neighbors as in Fig. 2 of the main text are not shown: this figure is intended to show only the idealized arrangement of cylinders, represented by six bond vectors in the plane perpendicular to the running direction of cylinders. The BOP values for these two bond vector distributions are shown in Table S1 for all degrees from 2 to 12. Two important aspects are worth noting in Table S1. First, all even-degree BOPs show maximal response of 1.0 to the two-fold symmetric distribution in Fig. S1(a). This means that even-degree BOPs, including q_6 , might show false-positive responses when numerous two-fold symmetric noises are included in the bond vector distribution, which is the case in Fig. 2(c-d) in the main text. Second, considering the planar six-fold symmetric distribution representing the hexagonal cylinder arrangement, q_6 indeed shows strongest response of 0.741, indicating that q_6 is the relevant order parameter for detecting the six-fold symmetry of hexagonal cylinder phase given that the neighbor set is properly defined to exclude in-cylinder neighbors.



FIG. S1. Bond vector distribution of (a) two-fold, (b) six-fold and (c) four-fold symmetric neighbor sets. The central and neighbor atoms are expressed as black dots, and the bond vectors are represented as arrows.

,	qı			7	q_l		
	(a)	(b)	(c)	ι	(a)	(b)	(c)
-	-	-	-	2	1.000	0.500	0.500
3	0.000	0.000	0.000	4	1.000	0.375	0.829
5	0.000	0.000	0.000	6	1.000	0.741	0.586
7	0.000	0.000	0.000	8	1.000	0.533	0.798
9	0.000	0.000	0.000	10	1.000	0.456	0.614
11	0.000	0.000	0.000	12	1.000	0.699	0.783

TABLE S1. BOP (q_l) values of the three bond vector distributions shown in Fig. S1(a-c), for degrees $l \in \{2, \dots, 12\}$. For the definition of q_l , see main text.

II. LAMELLAR SPACING AND CYLINDER-CYLINDER DISTANCES

In this section, we provide the two length scales, the lamellar spacing and cylinder-cylinder distances, for the systems studied in the main text. These values are estimated from time averages of the box sizes for NPT simulation cells of well-oriented mesophases. For the Kumar-Molinero (KM) system [1], two simulation cells were used. For both simulation cells, the temperature was fixed to 417 K and zero pressure was applied. Anisotropic pressure



FIG. S2. Snapshot of the simulation cells used for calculation of (a) lamellar spacing in the KM system, (b) cylinder-cylinder distance in the KM system, and (c) cylinder-cylinder distance in DPD simulation of block copolymers (see the main text for computational details). Pink beads and cyan beads represent the minority and the majority block, respectively. Periodic boundary condition was applied for all three Cartesian directions.

coupling (coupled in x and y directions) was used for lamellar spacing calculation, whereas isotropic pressure coupling was used for cylinder-cylinder distance calculation. The first simulation cell in Fig. S2 (a) consisted of 18 alternating lamellar layers formed by 8000 particles with the number fraction $f_A = 0.5$. The layers were stacked in the z direction whose side length is denoted by L_z . Then the lamellar spacing can be estimated from the time average of $L_z/9$ measured as 2.0748 \pm 0.0025. The second simulation cell in Fig. S2 (b) consisted of 43 hexagonally-arranged cylinders oriented along 111 orientation formed by 1000 particles with the number fraction $f_A = 0.76$. Denoting the three side lengths of the simulation cell by L_x , L_y , and L_z , the cylinder-cylinder distance can be estimated from the time average of $(L_x L_y L_z)^{1/3}/4$ measured as 2.4151 \pm 0.0092. The cylinder-cylinder distance obtained from a larger system with 8,000 particles were 2.4148 \pm 0.0021. For the dissipative particle dynamics (DPD) simulation, the snapshot in Fig. S2 (c) show the cylinders arranged within the xy plane. Let side lengths of simulation box in x and y directions be denoted L_x and L_y , respectively. Then distance between cylinder cores estimated from the time average of $L_y/2$ and $L_x/\sqrt{3}$ during the simulation was 7.7477 \pm 0.0459.

III. BIASED MOLECULAR DYNAMICS SIMULATION

To evaluate structures represented by different sets of collective variables (CVs), biased molecular dynamics simulations were performed with LAMMPS package patched with PLUMED 2.4 [2, 3] using RESTRAINT module. During the NVT simulation, the temperature was set to 700 K using Nóse-Hoover thermostat with time constant of $5\Delta t$. Disordered state of 1000 KM particles with the number fraction $f_A = 0.76$ equilibrated at 700 K were

Critaria	SET 1		SE	Τ2	SET 3	
Criteria	\bar{q}_2	\bar{q}_6	\bar{q}_2	\bar{q}_8	\bar{q}_2	\bar{q}_8
r_{cut}	2.075	-	1.91	3.39	2.075	-
r_{in}	-	2.0	-	-	-	3.0
r_{out}	-	2.5	-	-	-	4.0
r_{LD}	2.5	2.5	1.91	3.39	2.5	4.0

TABLE S2. The cutoff criterion used for the bias molecular dynamics simulations. See main text for the definitions of BOPs \bar{q}_l and the cutoff criterion r_{cut}, r_{in}, r_{out} , and r_{LD} .



FIG. S3. Snapshot of the generated structures using the set of CVs (a) $\bar{q}_2 = 0.781$ and shell-based $\bar{q}_6 = 0.461$, (b) $\bar{q}_2 = 0.931$ and $\bar{q}_8 = 0.244$, and (c) $\bar{q}_2 = 0.781$ and shell-based $\bar{q}_8 = 0.272$. Red beads and transparent black beads represent the minority and the majority block, respectively. Periodic boundary condition was applied for all three Cartesian directions.

used as the initial configuration. The simulations were run for 100τ timesteps during which a harmonic potential with the force constant $\kappa = 10^5$ was applied. The minima of the harmonic potentials were placed at the corresponding values of the CVs obtained from a trajectory of the hexagonal phase equilibrated at 300 K. The cutoff choices are summarized in Table S2.

IV. CONVERGENCE OF METADYNAMICS SIMULATIONS

The simulation time for various metadynamics simulations has been decided from observation of the free energy differences between the disordered and ordered basins in our system of interest: $f_{\rm A} = 0.76$. The free energy differences of three independent runs for the temperatures of 400 K and 425 K converge to the same value around $5 \times 10^4 \tau$. As for 375 K, the average value oscillates around 11.99 ± 1.58 kcal/mol. This is partly due to the small terrace formed at the location of the metastable basin. Nevertheless, the resulting transition temperatures using the data for 375 K at $5 \times 10^4 \tau$ and $7.5 \times 10^4 \tau$ are $417.4 \pm 0.6K$ and $417.4 \pm 0.2K$, respectively. These values are reasonably in agreement, and therefore we concluded that the simulation time of 5×10^4 (or 10^7 timesteps) is enough.



FIG. S4. Free energy differences between the disordered and ordered basins during metadynamics simulations for (red) 375 K, (blue) 400 K, and (black) 425 K.

V. FINITE TEMPERATURE STRING METHOD FOR DISORDERED-TO-HEXAGONAL TRANSITION AT 350 K

For the order-disorder transition in the system of f = 0.76 at 350 K, there is a local minimum at $\bar{q}_2 = 0.5$ and $\bar{q}_6 = 0.128$ on the concerning free energy surface. The depth of this basin was analyzed using MATLAB implementation of the Finite Temperature String (FTS) algorithm [4, 5]. The string converged to a principal curve in 10⁴ iterations at temperature $\mu = 2.7$. The final string, transition tube, and relative free energy along the curve are shown in Fig. S5. Fig. S5 (c) indicates that there is indeed a local minimum with its relative free energy of around 3 kcal/mol separated from the global minimum by a low barrier.



FIG. S5. Results of the finite temperature string method: (a) Final string and associated isocommittor surfaces at 350 K with respect to \bar{q}_2 and \bar{q}_6 . (b) Transition tube at 350 K with respect to \bar{q}_2 and \bar{q}_6 . (c) Relative free energy along the possible minimum energy path.

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