Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Self-assembly of block copolymers on lithographically patterned template with ordered posts

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1. Why does the film thickness is set as around 6 layers of cylinders in our simulation?

The choice of 6 layers of cylinders as the film thickness is based on the following consideration: regarding the model of self-assembly on the flat template, adding the top template as an additional confinement is technically necessary for completely removing the periodic boundary condition at the z-axis (e.g., Macromolecules, 2009, 42, 2863; Macromolecules, 2011, 44, 8650; J. Chem. Phys., 2010, 132, 044903). However, the problem is that it introduces new interface between the polymers and the top template. If we set the distance between the two templates as $2 \sim 3L_0$, it turns out to be the self-assembly of BCP thin film confined between narrow walls. The top template greatly affects the self-assembly behavior in our particle-based simulations (although the top template is set as neutral to both blocks). Another choice to avoid this problem is that we still set the distance between two templates as high as 6 layers of cylinders, while only a thin film of BCPs corresponding to the thickness of 2 or 3 layers of cylinders are filled close to the bottom template. The top vacuum space is completely filled with the solvent particles to simulate an open air environment above the film as that in experiments. However the problem of this strategy addresses that it is not easy to find the parameters that match the real condition like open air. As a consequence, the interaction between the solvent and the BCP film on their interface still greatly disturbs the self-assembly of BCPs (in experiments, the external influence from the environment should be trivial and can be neglected). For searching a balance between reasonably eliminating the influence of the top template and still keeping the correct behavior of the BCP films as that in experiment, we find setting the film thickness as around 6 layers of cylinders is a good choice. Since the far-away top template has almost no influence on the bottom 2 or 3 layers of cylinders, the latter can only feel the interaction from the bottom template. Thus as the effective thickness of film, the bottom 2 or 3 layers of cylinders should correctly reproduce the directed self-assembly behavior with template. In Fig.1, focusing on a typical system, we make a comparison of the bottom and sub-bottom layer morphologies with the above different conditions. It is clear that with the completely same interaction parameters, when the influence of the top template is considered

(e.g., Fig.S1b and c), the morphologies of the bottom and sub-bottom layers are different from that without the influence from the top template (Fig.S1a). By the comparison between Fig.S1a and d, we find that it is not a good choice by adding the solvent layer above the BCP film to simulate the open air environment. In sum, it is reasonable to set the height between the top and bottom template as around 6 layers of cylinders in our simulations.

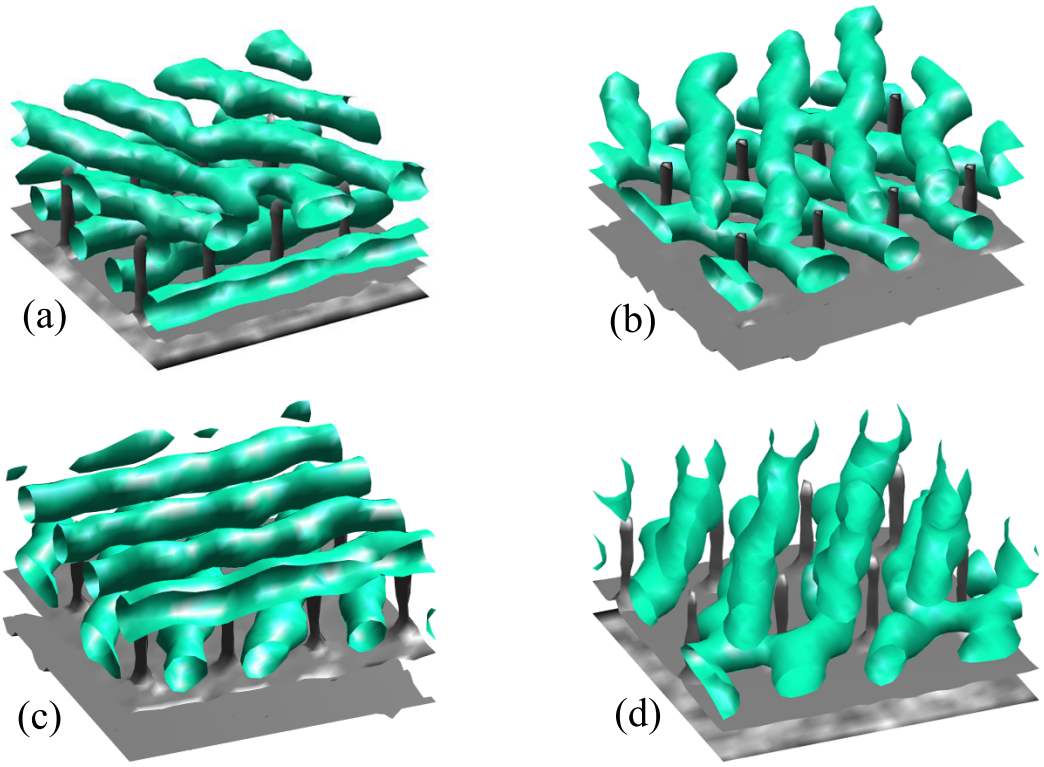

Figure S1: The morphologies of bottom and sub-bottom layers with different distances between top and bottom template: (a) the distance corresponds to 6 layers of cylinders and completely filled with BCPs; (b) the distance corresponds to 2 layers of cylinders and completely filled with BCPs; (c) the distance corresponds to 3 layers of cylinders and completely filled with BCPs; (d) the distance corresponds to 6 layers of cylinders, but only a thin film of BCPs as thick as 2 layers of cylinders are filled and the above space is filled with solvent particles. The DPD interactions are as follows: $\alpha_{TA} = 45$, $\alpha_{TB} = 25$, $\triangle\alpha = -20$ (post selectivity), and the repulsion strengths between the solvent particle and the BCP are set as $\alpha_{SA} = 45$ and $\alpha_{SB} = 45$.

2. Why does the substrate is set as minority-unfavored in the systems of Fig. 2 and 3?

In experiments the posts and the bottom substrate of template are often spin-coated as the same selectivity to the minority and majority blocks of the BCP. For example, in the experiments of Ross and co-workers (Science, 2012, 336, 1294), the substrates and posts were chemically functionalized with hydroxyl-terminated polystyrene, i.e.,the majority block of the BCP. As the corresponding simulations, we set the substrate and the posts to disfavor the minority block in the systems such as those included in Fig.4, 6 and 8 of our paper. In (Nat. Nanotechnol., 2010, 5, 256) and (Nat. Commun., 2014, 5, 3305), the substrates and posts were chemically functionalized with hydroxyl-terminated polydimethylsiloxane (PDMS) to ensure that they had an affinity for the minority block of the BCP. On this point, we do not have accurate correspondence with the experiments since we still set the bottom substrate to disfavors the minority. As the authors indicated in the paper (Science, 2008, 321, 939), "in this process, a surface layer of PDMS forms at the substrate-BCP and BCP-air interacts due to the low surface energy of PDMS". This phenomenon also appeared in another work (Science, 2008, 321, 939, i.e., Ref.10 of the above paper). Actually we also make similar simulations with minority-favored substrate, and certainly similar flat thin layer of minority block sticking on the substrate were observed, see Fig. S2a. Because of this affinity between the substrate and the minority, the bottom flat minority layer is actually made of the first layer of the cylinders from the original total of 6 layers. After the directed self-assembly in this condition, the observed ordered morphology of the bottom layer is actually from the original sub-bottom layer of cylinders, while the sub-bottom layer is actually from the original third-bottom layer of cylinders. The problem is that it turns to be difficult to make parallel comparison of the morphologies of bottom and sub-bottom layer with other systems, since the bottom flat minority layer introduces unexpected penalty of the effect from post height. Meanwhile we find this flat minority thin layer does not actually change the morphologies of the layers above it, thus its existence is meaningless. For avoiding the unnecessary factor in simulation studies, we simply set the substrate as always minority-unfavored, since it has no influence on the result of BCP self-assembly,

as shown the comparisons between Fig. S2a and b.

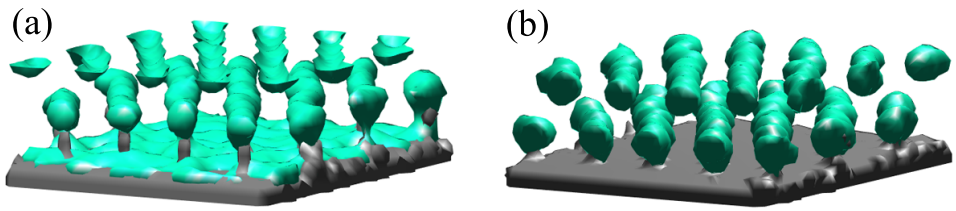

Figure S2: Comparison of the morphologies of bottom and sub-bottom layers in the conditions of: (a) posts and bottom substrate both favor the minority block of BCP; (b) posts favor the minority but the bottom substrate disfavors the minority. This system corresponds to the hexagonally arranged posts with $P_0 = 8$, $r = 1$ and $h = 4$.

3. Phase diagram of the morphologies dependent on the post height and radius with rectangularly arranged minority-unfavored posts

For a comparison of the phase diagram of morphology dependent on post radius and height made in the paper published on Science (Science, 2012, 336, 1294), we plot Fig. S3. By eliminating most metastable structures, we obtain less kinds of structures as compared. While we believe our basic rule is consistent with the former. For example, as the post turns thicker, the morphology changes from the structure labeled as brown triangle to that labeled as pink circle, and then to orange diamond, which is consistent with Cao et al.'s results (Polymer 2015, 72, 10) as well. Besides, by increasing the height of the post, the cylindrical morphology changes from brown triangle to pink circle, i.e., the orientations from parallel to perpendicular, also consistent with Cao et al.'s results.

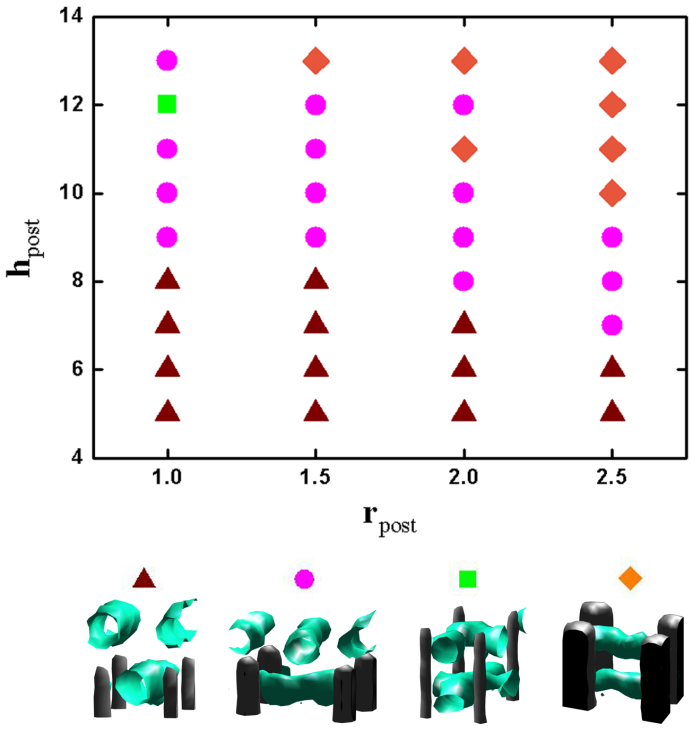

Figure S3: Phase diagram of the morphologies dependent on the post height and radius with $P_x = 12$ and $P_y = 7$ in the systems with rectangularly arranged minority-unfavored posts.