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Supporting Information for:

Striped patterns self-assembled from rod-coil diblock copolymers on spherical substrates

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1. Statistical results of stripe width and pattern pitch

As revealed by the simulations in the main text (Figure 2), regular striped patterns can be formed on the spherical substrates. The stripes are parallel except at defect sites. We further examined the stripe width and pattern pitch of the structures for various spherical radii. The statistical results are shown in Figure S1. Figure S1 (a) presents the definitions of stripe width and pattern pitch in the structures. Figure S1 (b) shows the profiles of the two parameters as a function of the spherical radius. Both parameters remain nearly unchanged at different sphere radii. Additionally, the values of the pattern pitch are larger than those of the stripe width. The average stripe width and pattern pitch are $5.0r_c$ and $6.7r_c$, respectively.

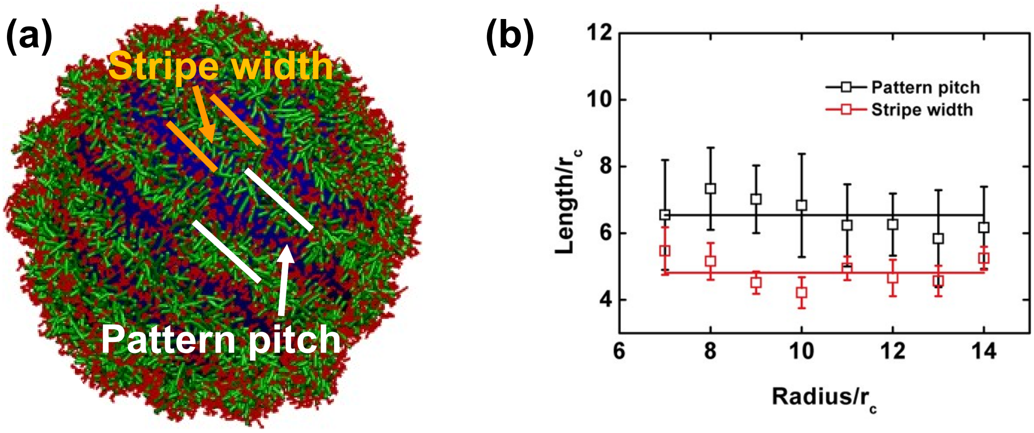

Figure S1. (a) Morphology of the structure self-assembled from rod-coil diblock copolymers on a spherical substrate. The stripe width and patterns pitch are indicated by orange and white lines, respectively. (b) Stripe width and pattern pitch as a function of spherical radii.

2. Simulation parameter settings for the comparison between simulation and experimental results

Interaction parameter. In the experiments, the solubility of PEG decreases as the temperature increases,^{S1} which means that the Flory-Huggins parameter between the solvent (water) and hydrophilic PEG segments ($\chi_{\text{PEG-water}}$) is larger at higher temperatures. Because $a_{ij} = a_{ii} + 3.27\chi_{ij}$, we tune the a_{CS} parameter according to the temperature increase.[S2] An increase in the repulsive strength a_{CS} between the coil blocks and solvents corresponds to a temperature increase in the experiments. The $\chi_{\text{PEG-water}}$ can range from negative to positive in the simulations studying the effect of self-assembling temperature. Accordingly, a_{CS} was increased from 20 to 40, corresponding to the temperature increase in the experiments. $a_{\mathrm{CS}} = 20$ corresponds to negative $\chi_{\text{PEG-water}}$ and strong hydrophilicity of PEG, while $a_{\mathrm{CS}} = 40$ represents the weak hydrophilicity of PEG.

Model of block copolymers. The model of block copolymers was chosen such that the bulk density of pure species[S3] or the relative lengths of the blocks[S4] matched the experimental data. In the simulations, the copolymer model was chosen by renormalizing both the bulk weight densities and block lengths. From the experiments, we learned that the M_{n} values for the PBLG block and the PEG block in PBLG-*b*-PEG copolymers are 12100 and 5000, respectively. The number of DPD beads was renormalized by keeping the bulk density identical in the simulations and experiments, and a ratio of 12100/5000 was obtained. In this case, 3.6 monomers in the PBLG block can form a 0.54 nm helix,[S4] while 1 monomer in the PEG block occupies 0.35 nm.[S5] Second, the number of DPD beads was renormalized by the length of rod block and coil block, and we obtained the relative number of beads for rod and coil blocks as $(12100 \times 0.54/3.6)$: $(5000 \times 0.35/1) \approx 4: 3.86$. As a result, the model of R_4C_4 rod-coil block copolymers (containing 4 rod beads and 4 coil beads) was adopted in the simulations, which captures the essential features of PBLG-*b*-PEG block copolymers in the experiments.

3. -1/2 charged disclination in experimental observations

As discussed in the main text, in our previous experiments[S2], the appearance of defects in the aggregated structures was not noted. In the following analysis of SEM images, only two types of topological defects were found in the self-assembled striped patterns, which are dislocations and

+1/2 charged disclinations. However, in the present simulations, four types of defects are observed in the striped patterns. We predicted two additional types of defects: +1 and -1/2 charged disclinations. To understand the defects in the experiments, an additional experiment regarding their structures was carried out and compared with simulation results.

Materials and sample preparation. α-Methoxy-ω-amino poly(ethylene glycol) (mPEG-NH_2, M_n = 5000) was purchased from Sigma-Aldrich. The dialysis bag (Membra-cel, 3500 molecular weight cutoff) was provided by Serva Electrophoresis GmbH. All the other reagents were purchased from Adamas-beta and used as received. *N*-carboxyl-benzyl-L-glutamate anhydride (BLG-NCA) was synthesized as described previously.[S5-S7] Poly(γ-benzyl-L-glutamate)-*block*-poly(ethylene glycol) (PBLG-*b*-PEG) block copolymers were synthesized by ring-opening polymerization of BLG-NCA in anhydrous 1,4-dioxane initiated by a mPEG-NH_2 macroinitiator according to our previous work.[S4,S8] Polystyrene (PS) homopolymer was synthesized by atom transfer radical polymerization (ATRP) with EtBriB as an initiator. Spherical aggregates were prepared according to the method in our previous experiments.[S2] First, PBLG-*b*-PEG block copolymers and PS homopolymers were dissolved in tetrahydrofuran (THF)/N,N'-dimethylformamide (DMF) (1/1, v/v) mixed solvents. Then, water was added to the polymer solution. A two-step self-assembly procedure occurred. The homopolymers first aggregated into spheres due to the low critical water content of PS (CWC = 9.1 vol%). As PBLG-*b*-PEG has higher CWC (14.4 vol%), the block copolymers remained dissolved in solution. As more water was added, the block copolymers began self-assembling on the substrates of PS-formed spheres, and wool-ball-like structures were observed. Finally, the solution was dialyzed against deionized water and samples were prepared. The morphologies of the aggregates were observed by Field Emission SEM (S4800, HITACHI) operated at an accelerating voltage of 15 kV.

Observation results. After carefully examining the SEM images of the prepared samples, -1/2 charged disclinations were found in the striped patterns. We further compared the observed -1/2 charged disclination with our simulation result. The results are shown in Figure S2. Figure S2(a) represents the SEM image of the prepared spheres with stripe-patterned surfaces. The inset in Figure S2(a) is the enlarged SEM images of one sphere, and a -1/2 charged disclination can be seen. Figure S2(b) presents the morphologies of a simulated striped pattern on spherical substrate, where the -1/2 charged disclination is marked. The morphology of the -1/2 charged disclination in the simulation is identical to that in the experiment. The stripes are bent 120° and oriented in three different directions around the core of disclination. The +1 charged disclinations have not be found in our experimental observations. This null result may be due to an increasing energy barrier for the formation of +1 charged disclinations, as discussed in the main text.

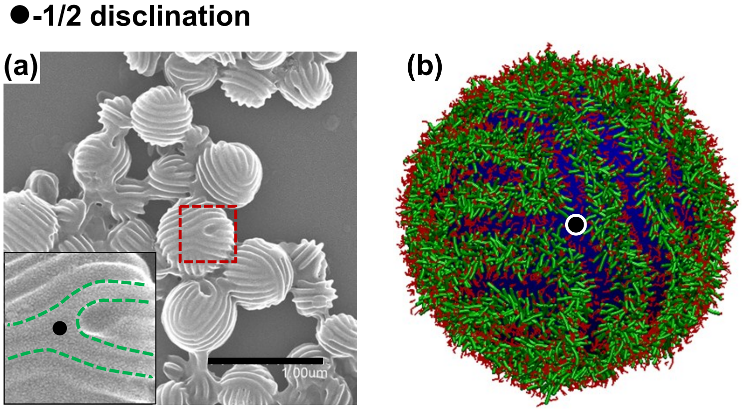

Figure S2. (a) SEM image of the aggregates prepared from the $PBLG_{141}$-b-PEG_{112}/PS_{664} mixtures (the subscripts represent the degree of polymerization for each segment). Scale bar: 1 µm. The inset in (a) represents the enlarged SEM image of one sphere marked with red dashed line. (b) Morphology of the simulated structure for rod-coil diblock copolymers self-assembled on spherical substrate. The -1/2 disclinations are marked in both the inset of SEM image and simulated morphology with black points.

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