

Supporting Information for:

**Self-Assembled Nanostructures of Bottle-Brush Polyelectrolytes with  
Oppositely Charged Surfactants: A Computational Simulation Study**

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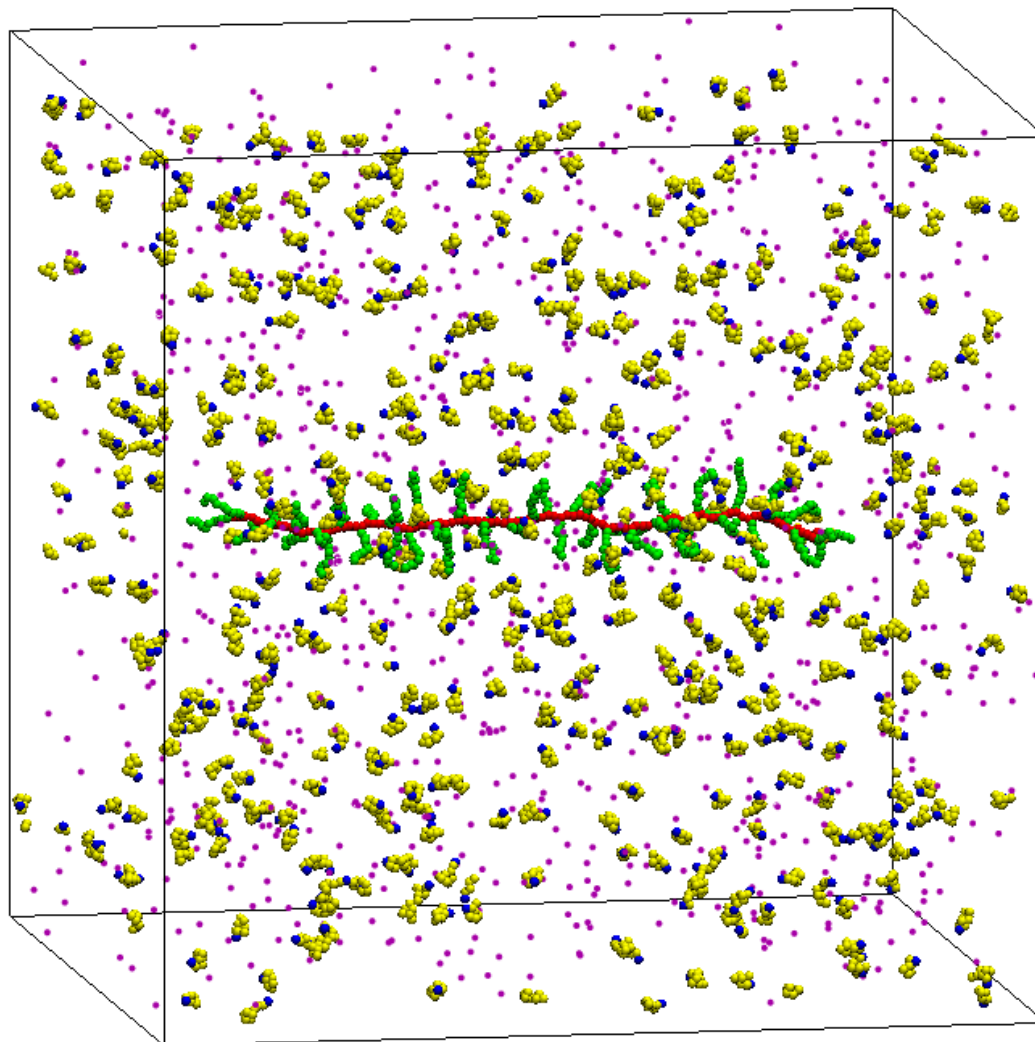
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[Contents]

1. Initial configuration of the simulated system (Figure S1)
2. Self-assembled nanostructures for two cases of highly rigid and fully flexible backbone (Figure S2-S3)
3. Additional simulation results for effects of the backbone stiffness and the charge ratio (Figure S4)
4. Additional simulation results for effects of the surfactant length (Figure S5-S6)

## Supplementary Information 1

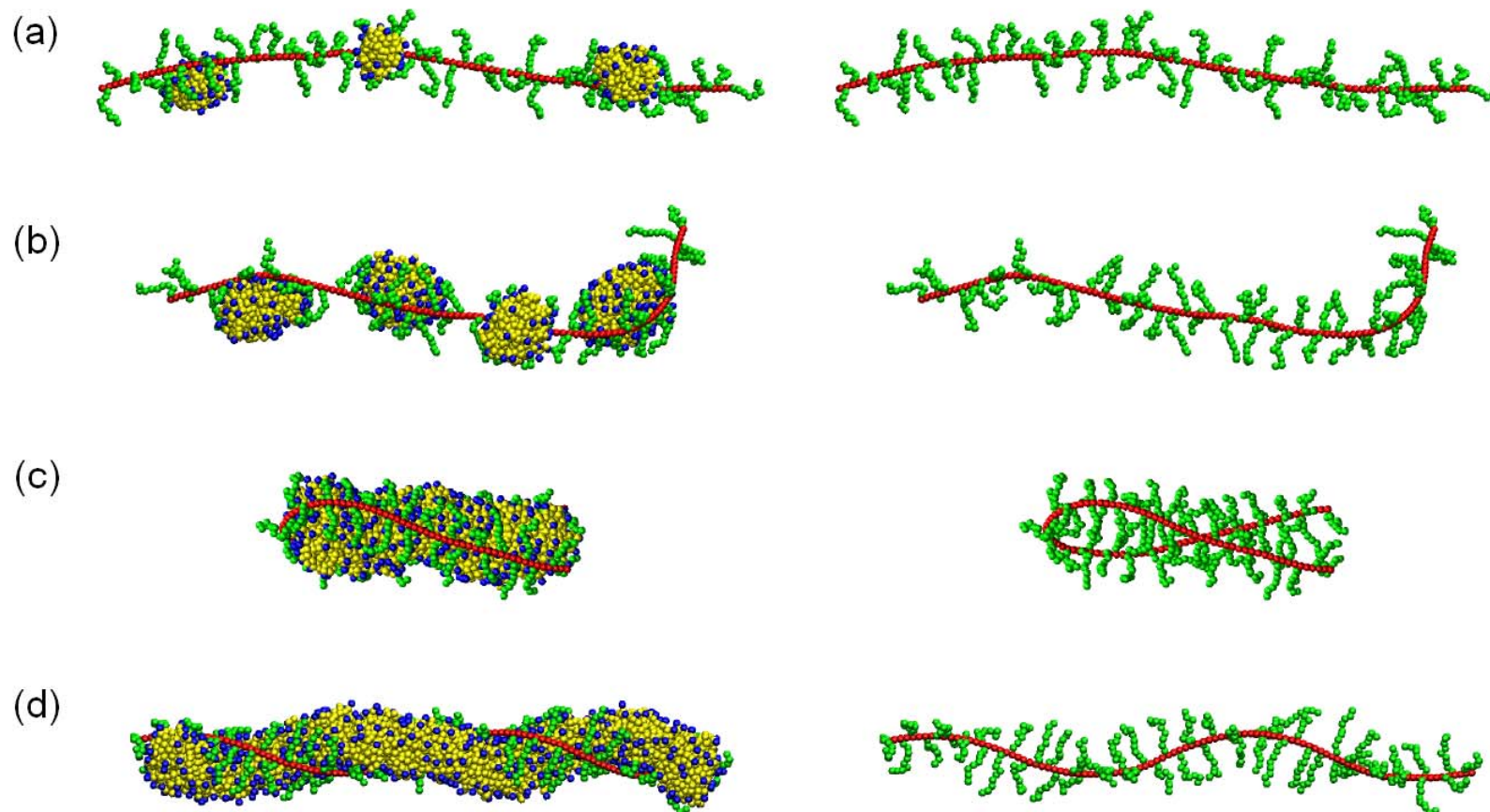
### *Initial configuration of the simulated system*



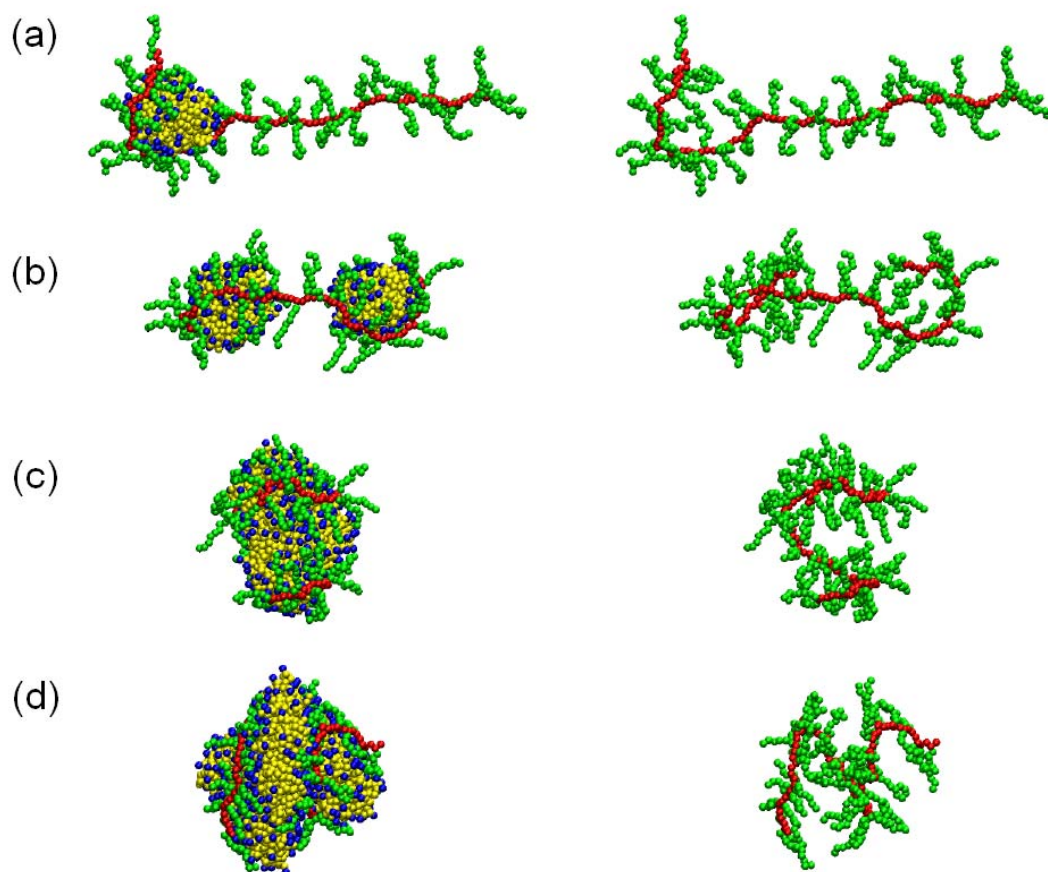
**Figure S1.** Simulation snapshot of the initial model system. The BPE is in an extended state. Surfactant molecules and small counterions are distributed randomly in the simulation box. Blue and yellow spheres are head and tail groups of the surfactant molecules, respectively. The backbone and side chains are represented red and green spheres, respectively. Purple dots are either counterions from charged side chains or ones from surfactant heads

## **Supplementary Information 2**

### *Self-Assembled Nanostructures for Two Cases of Highly Rigid and Fully Flexible Backbone*



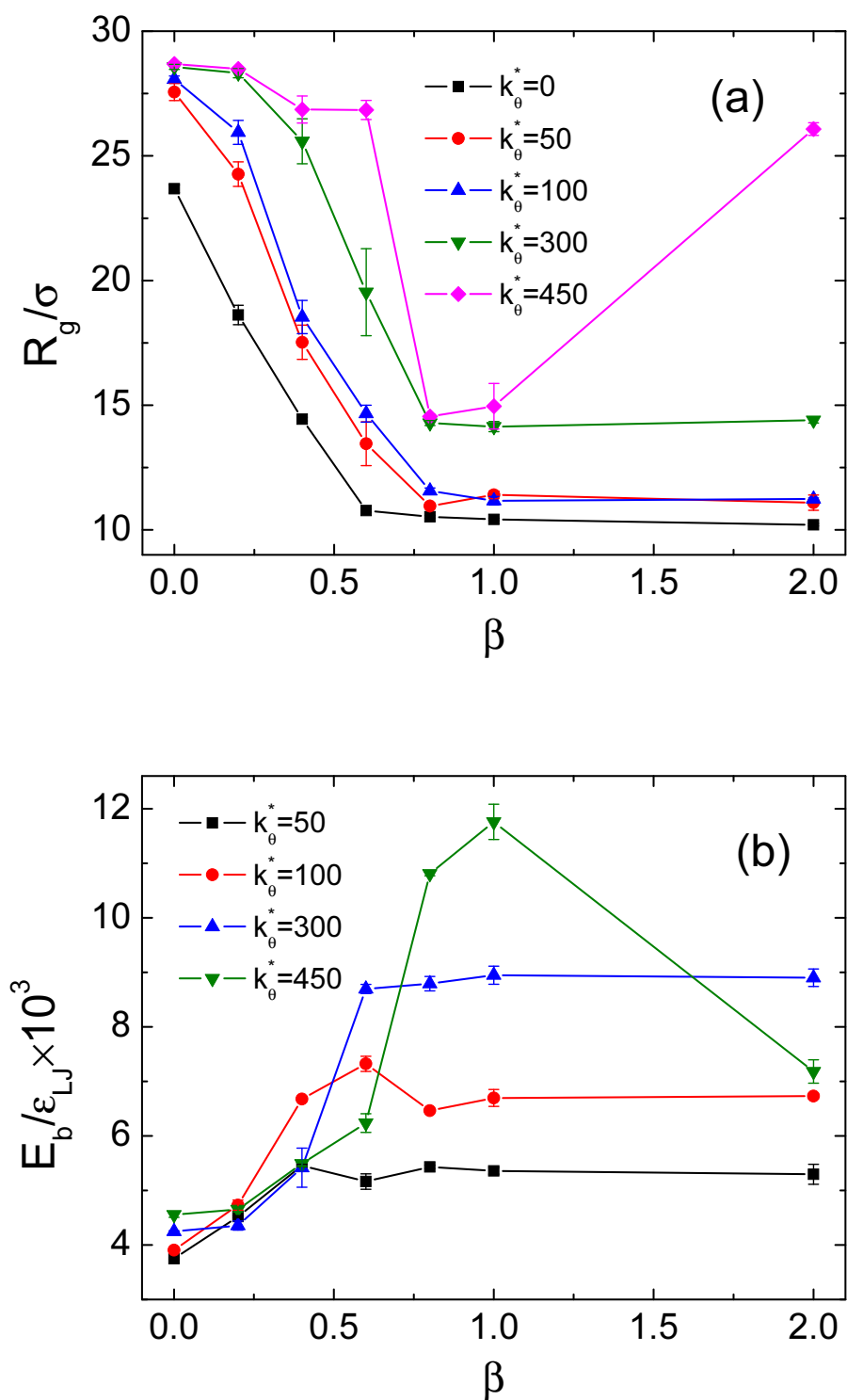
**Figure S2.** Representative equilibrium snapshots of the complex (left) and only BPE (right) for the case of the backbone stiffness  $k_{\theta}^* = 450$ . Color scheme is the same as that in Figure S1. At low charge ratios (a)  $\beta = 0.2$  and (b)  $0.6$ , surfactant molecules form a varying number and size of micelles depending on the charge ratio. With increasing the surfactant amount, such as (c)  $\beta = 0.8$  and (d)  $2.0$ , they can aggregate into a cylinder-like nanostructure. One should note that the surfactant concentration has a strong influence on the morphology of nanocylinder consisting of adsorbed surfactants and the conformation of BPE. At  $\beta = 0.8$ , the backbone folds back on itself to form a double-helix-like structure, which may become more apparent when the surfactant becomes longer. Moreover, surfactants aggregate into a cylinder-shaped rod (diameter about  $12\sigma$ ) surrounded by charged side chains. It is interesting that, at a higher charge ratio of  $\beta = 2.0$ , the backbone and the surfactant nanocylinder (diameter about  $10\sigma$ ) exhibit an extended helix state, respectively. Moreover, they adopt a double-helix configuration together. However, this kind structure has not been observed in recent experiments.<sup>S1-S3</sup>



**Figure S3.** Representative equilibrium snapshots of the complex (left) and only BPE (right) with fully flexible backbone. At a low charge ratio of (a)  $\beta = 0.2$ , the surfactants can self-assemble into a sphere-like micelle located at one end of BPE. A dumbbell-shaped complex is formed at (b)  $\beta = 0.4$ . In cases of higher surfactant amount, such as (c)  $\beta = 0.6$  and (d) 2.0, the BPE/surfactant complex tends to form an irregular aggregation and the backbone shows a helix-like structure. Color scheme is the same as that in Figure S1.

### Supplementary Information 3

Additional simulation results for effects of the backbone stiffness and the charge ratio



**Figure S4.** (a) Root-mean-square radius of gyration  $R_g$  of the BPE and (b) elastic restoring energy of the backbone as a function of  $\beta$  under different backbone stiffness.

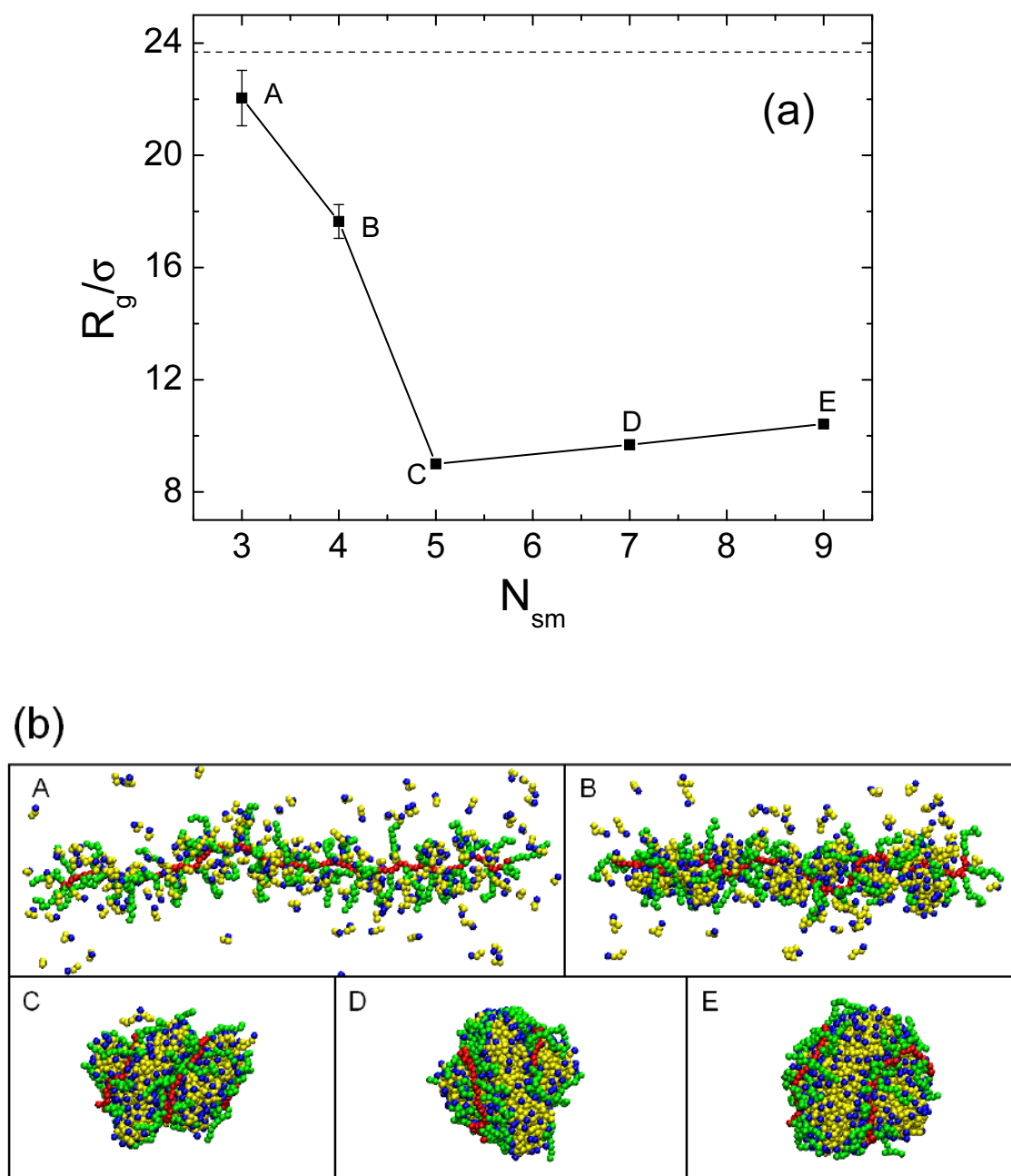
When  $\beta$  increases from 1.0 to 2.0, the size of the BPE and the elastic energy of the backbone undergo a sharp transition at  $k_{\theta}^* = 450$ . In contrast, there are slight changes for other cases when  $\beta > 0.8$ . Therefore, a reswelling of the BPE induced by increasing the surfactant amount requires a sufficiently rigid backbone.

## **Supplementary Information 4**

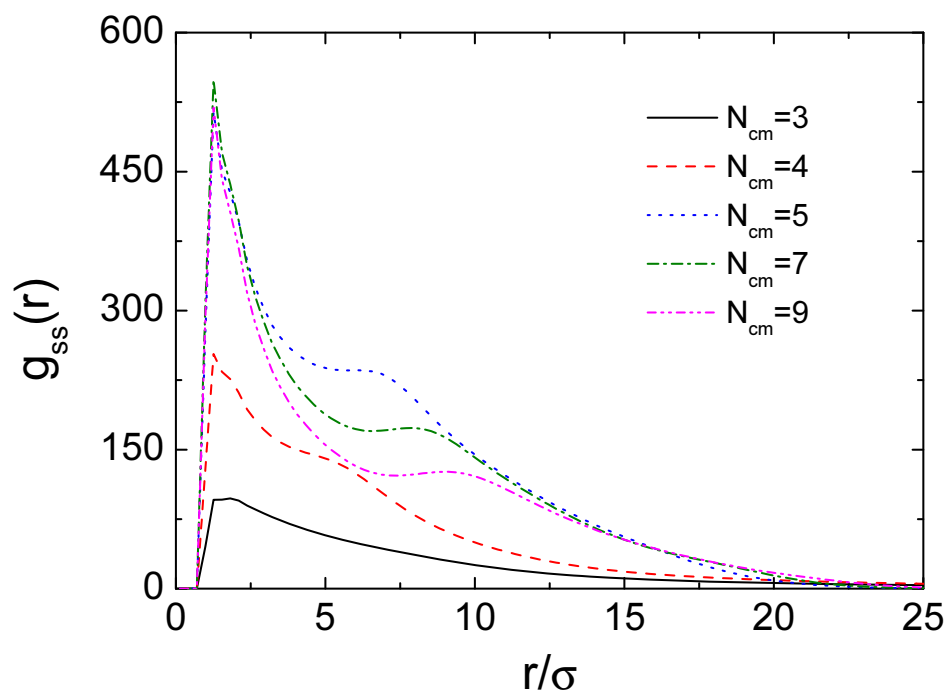
### *Additional simulation results for effects of the surfactant length*

We also perform computer simulations to gain an insight into the structural characteristics of self-assembled complexes at different surfactant lengths. The simulations are carried out in cases of fully flexible backbone and a charge ratio of  $\beta = 1.0$ . Here, we do not intend to discuss the case deeply. It is found that when the surfactant length is larger than a certain value of  $N_{sm} = 4$ , the BPE bears a collapsed conformation and wraps helically around the aggregate surface (Figure S5a and S5bC-E). The BPE reaches its smallest size at  $N_{sm} = 5$ . Further increasing the surfactant length leads to a reswelling behavior of the BPE. A completely extended conformation is observed at  $N_{sm} = 3$  (Figure S5bA). Similarly, Cong et al. observed that when the surfactant length becomes sufficiently short, the backbone will not form a helical structure due to weak hydrophobic interaction.<sup>S2</sup> Note that in the case of  $N_{sm} = 4$ , surfactant molecules are assembled into multiple small aggregates on the BPE with an extended conformation. The radical distribution functions between side chains and surfactant heads are also given in Figure S6 to describe the correlation effect between them. It is clear that the higher the first peak, the stronger the binding of surfactants to the BPE. When  $N_{sm} \geq 5$ , no significant differences in the height of the first peak are observed. The shift of the second peak towards larger  $r$  indicates an increase in the aggregate size. At  $N_{sm} = 3$  and 4, a decrease of peak height corresponds to a reduced correlation between the BPE and surfactants, or the cooperative binding ability of surfactants is weakened significantly.





**Figure S5.** (a) Effect of the surfactant length on the root-mean-square radius of gyration  $R_g$  of the BPE with fully flexible backbone at  $\beta = 1.0$ . The dashed line represents the size of the BPE in the absence of surfactants. (b) Typical snapshots of the BPE/surfactant complex with varying surfactant length. A-E correspond to those in (a). Color scheme is the same as that in Figure S1.



**Figure S6.** Radical distribution functions between side chains and surfactant heads in cases of different surfactant lengths.

## References

- S1 N. Gunari, Y. Cong, B. Zhang, K. Fischer, A. Janshoff and M. Schmidt, *Macromol. Rapid Commun.*, 2008, **29**, 821.
- S2 Y. Cong, N. Gunari, B. Zhang, A. Janshoff and M. Schmidt, *Langmuir*, 2009, **25**, 6392.
- S3 Y. Xu, S. Bolisetty, M. Ballauff and A. H. E. Muller, *J. Am. Chem. Soc.*, 2009, **131**, 1640.