Supplementary data for

The Biphasic Effect of ABA Triblock Copolymer on Self-assembly of Surfactant: Insight from Dissipative Particle Dynamics

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1. Interaction parameters of bead–bead pairs α_{ij}

In this study, we set the interaction parameter α_{ij}, and the detailed values are shown in Table S1. W stands for water bead, A stands for hydrophilic bead of surfactant and triblock copolymer, B stands for hydrophobic bead of surfactant and triblock copolymer.

Table S1 Interaction parameters of bead–bead pairs α_{ij}

α_{ij}	A	B	W
A	25	60	20
B	60	25	60
W	20	60	25

2. Simulation detail

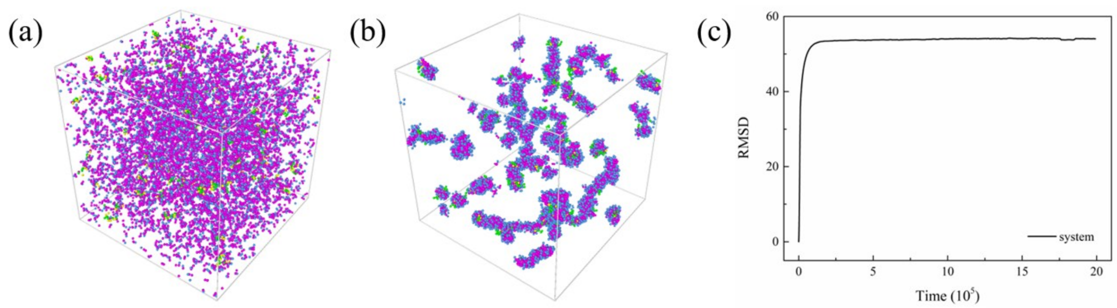

Fig. S1 Evolution of system. (a) initial configuration, (b) equilibrium configuration and (c) root-mean-square deviation of system. Solvent is not shown for clarity.

In this study, the evolution of the systems was performed during 2,000,000 steps. We made sure all the systems are not trapped in local nonequilibrium state.

3. The periodic Poiseuille flow method and fitting procedure

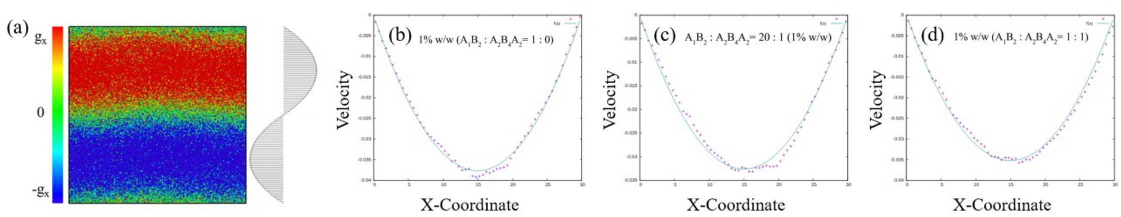

Fig. S2 The scheme of periodic Poiseuille flow method and the fitting procedure of A_1B_2:$A_2B_4A_2$ = (a) 1:0, (b) 20:1, and (c) 1:1.

Here, the Poiseuille flow method is used to measure the viscosity[1]. This periodic Poiseuille flow method can calculate viscosity of particle model fluids accurately, which has been proved by several DPD studies. As shown in Fig. S2, a periodic Poiseuille flow is chosen to test dynamic viscosity of system. The application of opposing external forces enables the use of ordinary periodic boundary conditions, and the viscosity is then related to the mean flow velocity of the two flows. Based on using periodic boundary conditions and fitting formula, the viscosity of particle model fluids can be obtained.

4. The variation of micellar structure

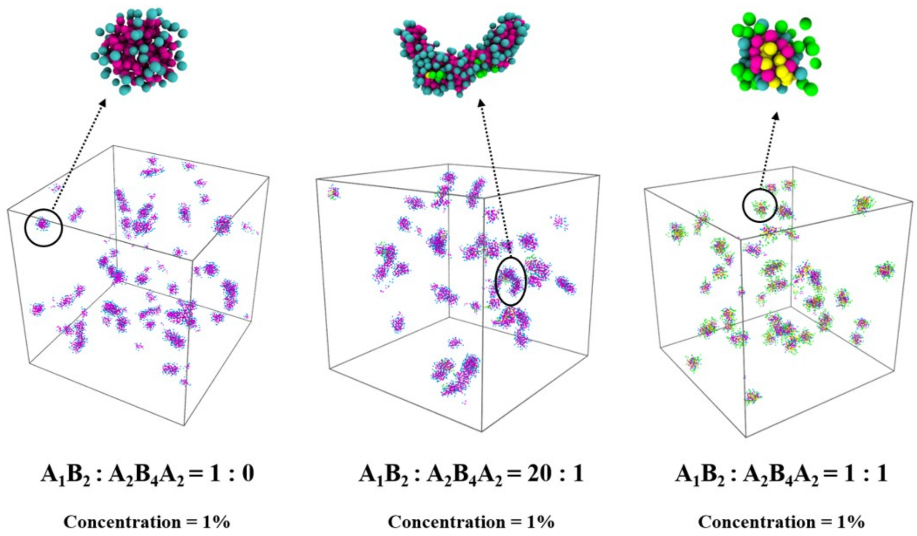

Fig. S3 Aggregates formed by the mixed A_1B_2 and $A_2B_4A_2$ at different ratio between A_1B_2 and $A_2B_4A_2$ (concentrations = 1%).

As the morphological phase diagram shows, the addition of a small amount of ABA triblock copolymer can help to promote the growth of spherical micelles.

5. The investigation of the mechanism of micellar fusion

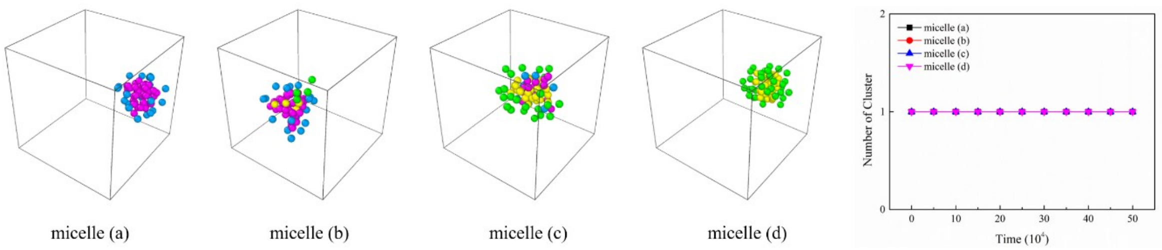

Fig. S4 Simulations for investigation of premicelles.

In order to explore the mechanism of micellar fusion, several premicelles have been built, as shown in Fig. S4. In this section, the size of simulation box is 10×10×10 r_c, and a total of 500,000 steps were carried out for sampling. To verify the stability of micelles, we examined the dynamic process and confirmed that the number of cluster is unchanged during the simulation. After that, these micelles have been used to investigate the fusion free energies (in the 10×10×20 r_c box).

6. The asphericity of premicelles

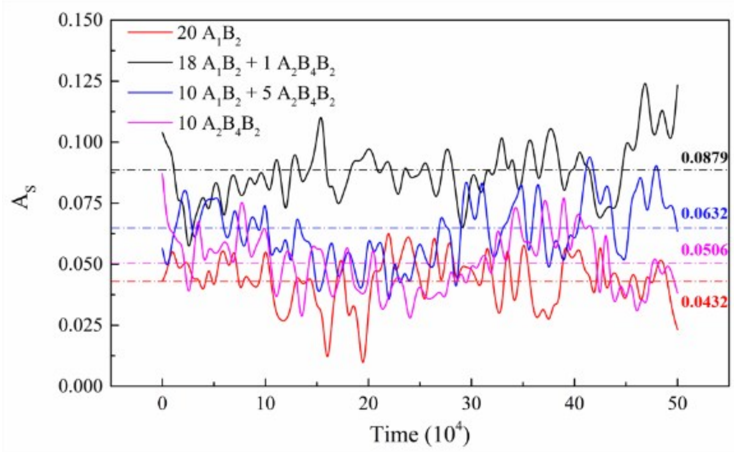

Fig. S5 Time evolution of the asphericity (A_S) of premicelles.

To analyze the shape characteristics of premicelle, we studied the asphericity of different kinds of premicelles. According to the definition of asphericity (A_s), a higher A_s corresponds to a higher anisotropic shape[2]. As can be seen from the time evolution of the asphericity of premicelles, the addition of a small amount of $A_2B_4A_2$ can result in the increase of asphericity of premicelle. With the increase in the proportion of $A_2B_4A_2$, the asphericity of premicelle gradually decrease.

7. The influence of triblock copolymer properties on co-self-assembly structure

In order to study the applicability of triblock copolymer, four other models of triblock copolymer were considered. Firstly, the influence of ratio between hydrophilic block and hydrophobic block was investigated, the equilibrium configurations of micelles are reported in Fig S6. As shown in Fig. S6 (a) and (b), in these two cases, triblock copolymer is failed to promote or inhibit the micellar growth. In addition, the loop configuration of polymer−surfactant complexes have been reported by some experimental studies[3,4]. Thus, we infer that the ratio between hydrophilic blocks and hydrophobic blocks is a key factor for the biphasic effect. When the balance between hydrophobic and hydrophilic is broken, the biphasic effect of triblock copolymer no longer exists.

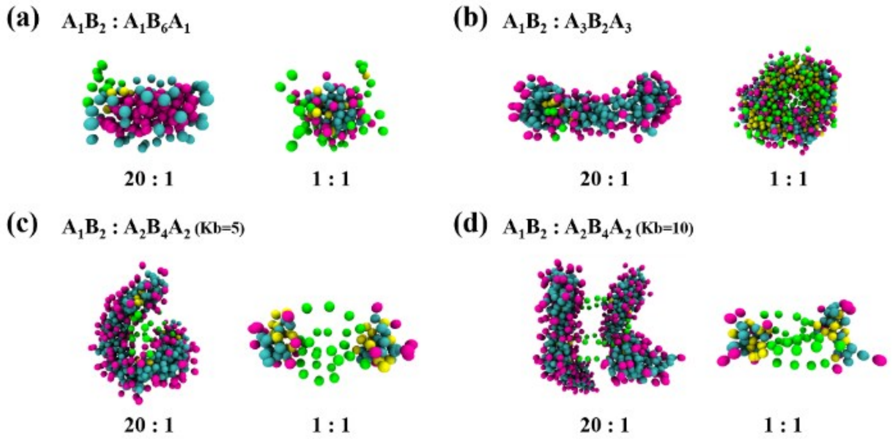

Fig. S6 The cooperative assembly structure of AB_2 with different models of $A_2B_4A_2$. Color scheme is the same as Fig. 2.

Moreover, the influence of rigidity of triblock copolymer was investigated, as shown in Fig. S6 (c) and (d). Because the $A_2B_4A_2$ is bended to anchor into the core of micelles, the self-assembly structure is sensitive to the rigidity of triblock copolymer. Hence, the biphasic effect of triblock copolymer is failed with the increased rigidity. These results indicate that the ratio between hydrophilic block and hydrophobic block and the rigidity of triblock copolymer have a marked impact on self-assembly of surfactant and triblock copolymer.

Reference

1. J. Backer, C. Lowe, H. Hoefsloot and P. Iedema, *The Journal of chemical physics*, 2005, **122**, 154503.
2. T. Zhou and S. B. Chen, *Macromolecules*, 2005, **38**, 8554-8561.
3. K. R. Francisco, M. A. da Silva, E. Sabadini, G. Karlsson and C. A. Dreiss, *Journal of colloid and interface science*, 2010, **345**, 351-359.
4. A. L. Kwiatkowski, H. Sharma, V. S. Molchanov, A. S. Orekhov, A. L. Vasiliev, E. E. Dormidontova and O. E. Philippova, *Macromolecules*, 2017, **50**, 7299-7308.