1. The detailed information about the coarse-grained DPD models.

The amphiphilic hyperbranched multiarm copolymers HBPO-star-PEO with one hydrophobic hyperbranched HBPO core and many hydrophilic linear PEO arms (ref. 23) could be considered as the representative prototype for the coarse-grained DPD model used in this paper. As listed in Table S1, the volumes of the repeat units in the HBPO-star-PEO molecule can be calculated according to the experimental density and molecular weight. Because all of the beads are assumed to possess the same volume in DPD simulation, so we used one A bead (the yellow bead) in the model to represent one repeat unit of HBPO, while one B bead (the cyan bead) represents three repeat units of PEO. Moreover, when the solvent is water ($V = 30 \, \text{Å}^3$), one S bead represents six water molecules.

Table S1 Molecular parameters in the system of HBPO-star-PEO copolymers.

<table>
<thead>
<tr>
<th>Bead type</th>
<th>Molecular weight $M$ (g/mol)</th>
<th>Density $\rho$ (g/cm$^3$)</th>
<th>Monomer volume $V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Hydrophobic HBPO)</td>
<td>116</td>
<td>1.0</td>
<td>193</td>
</tr>
<tr>
<td>B (Hydrophilic PEO)</td>
<td>44</td>
<td>1.12</td>
<td>65</td>
</tr>
</tbody>
</table>

2. The explanation for the interaction between water molecules by applying soft repulsion potential.

According to the reports by Groot and Warren (ref. 61), the dimensionless compressibility can be described by $\kappa^{-1} \approx 1 + 0.2\alpha_{ii}\rho/k_B T$, where $\alpha_{ii}$ is repulsion parameter between the same type of bead, $\rho$ is number density, and the temperature $k_B T$ is taken as the reduced units. Considering that $\kappa^{-1}$ equals 15.9835 for water at room temperature (300K), the repulsion parameter $\alpha_{ii}$ is calculated to be 25 when $\rho$ equals 3. Therefore, it is correct to describe interaction between water molecules by applying soft repulsion potential in DPD simulations.
3. HOOMD scripts used for DPD simulations.

```python
from hoomd_script import *
init.read_xml(filename="xxxxxx.xml")  # xxxxx.xml is the input file

# specify interaction parameters between particle pairs
dpd = pair.dpd(r_cut=1.0, T=1.0)
dpd.pair_coeff.set('A', 'A', A=25.00, gamma = 4.5)
dpd.pair_coeff.set('A', 'B', A=50.0, gamma = 4.5)
dpd.pair_coeff.set('A', 'S', A=as.0, gamma = 4.5)  # as.0 is the value of $\alpha_{AS}$

dpd.pair_coeff.set('B', 'B', A=25.00, gamma = 4.5)
dpd.pair_coeff.set('B', 'S', A=bs.0, gamma = 4.5)  # bs.0 is the value of $\alpha_{BS}$

dpd.pair_coeff.set('S', 'S', A=25.00, gamma = 4.5)
dpd.set_params(T = 1.0)

nlist.set_params(r_buff = 0.25)
nlist.reset_exclusions(exclusions = [])

harmonic = bond.harmonic()
harmonic.set_coeff('bond1', k=4.0, r0=0.0)  # k=4.0 is the coefficient of harmonic spring force

# define the type
groupA = group.type(name='groupA', type='A')
groupB = group.type(name='groupB', type='B')
groupAB = group.union(name="groupAB", a=groupA, b=groupB)
groupC = group.type(name='groupC', type='S')
groupABC = group.union(name="groupABC", a=groupAB, b=groupC)

integrate.mode_standard(dt=0.02)  # dt=0.02 is the integration time step
integrate.nve(group=group.all())
```
# output files
analyze.log(filename="dpdnve_energy.log", quantities=['potential_energy', 'kinetic_energy'], period=100, header_prefix='#', overwrite=True)
analyze.log(filename='dpdmomentum.log', quantities=['momentum'], period=100, header_prefix='#', overwrite=True)
analyze.log(filename='dpdtemperature.log', quantities=['temperature'], period=100, header_prefix='#', overwrite=True)

xml = dump.xml(filename="particles", period=1000000)
xm1.set_params(position=True, type=True, bond=True)
dump.bin(filename="particles", period=2000000)

mol2 = dump.mol2()
mol2.write(filename="zinitial.mol2")
dump.dcd(filename="ztrajectory.dcd", period=10000, group=groupAB)

# run 4000000 time steps
run(4000001)
Fig. S1 The morphological snapshots of the spherical micelles formed by $A_{42}B_{20}$ at $\alpha_{BS} = 5$ and $\alpha_{AS} = 50$ (a), $\alpha_{BS} = 23$ and $\alpha_{AS} = 50$ (b); (c) the relationships between $N_{\text{micelle}}$ and $\alpha_{BS}$ (blue curve), mean aggregation number and $\alpha_{BS}$ (green curve) at $\alpha_{AS} = 50$, respectively. Error bars are obtained by averaging five parallel samples. The solvent beads are omitted for clarity. The color codes are the same as those in Fig. 2.
Fig. S2 Sequential snapshots of the formation of the vesicle with a membrane inside self-assembled from Fig. 4c at $1.50 \times 10^5$ steps (a), $1.90 \times 10^5$ steps (b), $2.20 \times 10^5$ steps (c), $2.80 \times 10^5$ steps (d), $7.90 \times 10^5$ steps (e), to $1.65 \times 10^6$ steps (f). For each image, the upper one is the 3D view, while the lower one is the cross-section view. The solvent beads are omitted for clarity. The color codes are the same as those in Fig. 2.
Fig. S3 The fine structure of one vesicle: (a) cross-sectional view of the vesicle showing the membrane structure, and the arrow indicates the two labelled molecules extracted from the vesicle to show the molecular packing model. (b) Radial density distributions of A (yellow) and B (cyan) segments across the membrane of the vesicle. The distance from the centre of mass to the outside of the vesicle is $r$. Hydrophobic hyperbranched core: yellow, red, and purple beads; hydrophilic linear arms: cyan, green, and blue beads.
Fig. S4 (a) The side view of a helical micelle structure from Fig. 8b of the main text, (b) and (c) are the decomposition charts of (a) in order to observe the helical micelle clearly.

4. Further investigation for SMAs in a larger cubic box of $100 \times 100 \times 100r_c^3$.  

Furthermore, we have carried out the simulation for the formation of small micelle aggregates (SMAs) in a larger cubic box of $100 \times 100 \times 100r_c^3$ ($\alpha_{BS} = 29$, $\alpha_{AS} = 80$). There are a total of seven SMAs in the box at $4.00 \times 10^6$ time steps (Fig. S5). Among the seven SMAs, five of them are separated into several aggregates on the wall of the box by the periodic boundary conditions applied in all three dimensions. Then, we calculated the distribution of the aggregation number ($N_{agg}$) versus the simulation time. As depicted in Fig. S6, with the increase of the simulation time, $N_{agg}$ first decreases and then levels off from $1.00 \times 10^6$ to $4.00 \times 10^6$ time steps. Such a result indicated that the polymers began to self-assemble and then reached equilibrium in the simulation box. Moreover, we also calculated the time evolution of conservative energy $E_{AS}$ (Fig. S7). At the beginning, $E_{AS}$ decreases sharply and quickly, and then decreases slowly and finally reaches a relative dynamic equilibrium state. The average shape factor of the seven SMAs is 0.425, and the variance of the average shape factor is 0.264, which attributes to the different number of small spherical micelle in every SMAs.

![Fig. S5](image-url)

**Fig. S5** The final snapshot of SMAs at $4.00 \times 10^6$ time steps in a cubic box of $100 \times 100 \times 100r_c^3$. The left one is the 3D view, while the right one is the isosurface view of type A. The solvent beads are omitted for clarity.
Fig. S6 The distribution of $N_{agg}$ versus the simulation time for the SMAs.

Fig. S7 Conservative energy between the hyperbranched core beads and the solvents, $E_{AS}$ versus simulation time.