Supporting Information

Morphological transitions of micelles induced by the block arrangements of copolymer blocks: Dissipative particle dynamics simulation.

Fusheng Zhang, § Shiyuan Peng, § JianchangXu, Chengzhi Cai, Lijuan Zhang*

DPD theory

DPD simulation adopts a soft repulsive potential and a momentum-conserving thermostat together to control the interactions between beads representing a group of atoms. The force $\mathbf{f}_i$ acting on bead i can be described as the equation (S1). [1]

$$\mathbf{f}_i = \sum_{i \neq j}\left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R\right) + \mathbf{f}_i^S + \mathbf{f}_i^A \qquad (S1)$$

The conservation force ($\mathbf{F}_{ij}^C$) is defined by soft repulsive force to ensure excluded volume. The dissipative force ($\mathbf{F}_{ij}^D$) corresponds to the viscous drag that depends both on the position and relative velocities. The random force ($\mathbf{F}_{ij}^R$) maintains energy input into the system to eliminate the dissipation. $\mathbf{F}_{ij}^D$ and $\mathbf{F}_{ij}^R$ serve jointly as a momentum-conserving thermostat. The spring forces $\mathbf{f}_i^S$ and $\mathbf{f}_i^A$ describe the bond-stretching and bond-bending interactions respectively. Excluded volume $\mathbf{F}_{ij}^C$ is given as the equation (S2).

$$\mathbf{F}_{ij}^C = \begin{cases} a_{ij}\left(1 - r_{ij}\right)\hat{\mathbf{r}}_{ij} & r_{ij} < 1 \\ 0 & r_{ij} \geq 1 \end{cases} \qquad (S2)$$

Where a_{ij} describes the strength of repulsive interaction between particle i and j. $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$.

The repulsive parameters a_{ij} between beads i and j can be obtained from the underlying atomistic interaction that is linearly related to the Flory-Huggins parameters (χ_{ij}). [2]

$$a_{ij} = a_{ii} + 3.50\chi_{ij} \qquad (S3)$$

Herein, $a_{ii} = 25 k_B T$ at a density $\rho = 3$, and the value of $k_B T$ is defined as 1. k_B is the boltzmann constant and T is temperature. The χ_{ij} values can be calculated from the solubility parameters using the equation (4), which establishes a connection between atomistic molecular dynamics (MD) and mesoscale DPD methods.

$$\chi_{ij} = \frac{\Delta E^{mix} V_r}{RT\Phi_i\Phi_j V} \qquad (S4)$$

Here, R is the gas constant. Φ_i and Φ_j are the volume fractions of bead i and j, respectively. V and V_r are the total volume and reference volume, respectively. ΔE^{mix} is the mixing energy of two different types of beads, which can be calculated by the equation (S5)

$$\Delta E^{mix} = E_{ij} - \left(E_i + E_j\right) \qquad (S5)$$

where E_{ij} is the potential energy of binary mixture, E_i and E_j are the potential energies of pure components i and j, respectively.

The calculation process of repulsion parameters

The repulsion parameters were calculated as a modified method of the published protocol. [3]

To calculate χ_{ij}, molecular dynamics simulation (MD) was performed for pure and binary components. Pure components included the all-atom models of M, AE1, AE2, C1, C2 and W. Every two models above were also mixed into binary components. All the components were represented by the COMPASS II force field, in which the total potential energy (E_{pot}) was expressed,

$$E_{pot} = E_{bonded} + E_{nonbond} + E_{cross}$$
$$= \left(E_b + E_\theta + E_\phi + E_\chi\right) + \left(E_{vdW} + E_{coulombic}\right) + E_{cross} \qquad (S6)$$

where E_b is bond stretching energy, E_θ is bending energy, E_ϕ is dihedral torsion energy, and E_χ is out-of-plane energy; the sum of these four items is bonded energy (E_{bonded}). E_{vdW} is van der Waals energy, $E_{coulombic}$ is electrostatic energy; and the sum is nonbonded energy ($E_{nonbond}$). E_{cross} is the energy of cross terms between any two of bonded items in the COMPASS II force field, such as bond-angle and bond-bond cross terms.

Each system (either pure or binary mixture) was constructed by the Amorphous Cell in Materials Studio (Accelrys Inc.). As for pure system, the number of each component was set to be 100 except water for 600. The number of each component in a binary system was same with pure system. To eliminate unfavorable contacts, the initial configurations were subjected to 10000 steps of energy minimization with an energy convergence threshold of 1×10^{-4} kcal·mol^{-1} and a force convergence of 0.005 kcal·mol^{-1}·Å^{-1}. The van der Waals interactions were calculated with a cutoff of 12.5Å, a spline width of 1Å, and a buffer width of 0.5Å. Moreover, the Ewald summation with an accuracy of 0.001kcal·mol^{-1} was used to calculate the Coulombic interactions. Next, thermal annealing from 500 to 300K was taken to ensure the full relaxation of the system at a targeting density. Then, 5ns MD equilibrium simulation at isothermal and isobaric (*NPT*) conditions was conducted to determine the equilibrium density of pure and binary systems. The temperature was maintained at 298K by Nośe thermostat and the pressure was maintained at 1bar by Andersen method. Finally, 5ns MD

equilibrium simulation was performed at isothermal and isochoric (*NVT*) conditions. The temperature was also maintained at 298K and the final 1.5ns trajectory was used to calculate potential energy. Therefore, χ_{ij} was calculated through equation (S5) and (S4), and further taken into equation (S3) to obtain a_{ij}.

Definition of radius of gyration (R_g)

Radius of gyration (R_g) of the copolymer chains was also calculated to pursue a further understanding of the extensibility of the copolymer chains in micelles. R_g was obtained from the equation (S7). [4]

$$< R_g >^2 = \frac{\sum_{i=1}^{N} m_i s_i^2}{\sum_{i=1}^{N} m_i} \qquad (S7)$$

Where m_i was the mass of bead i, s_i represented the distance of i_{th} bead from the mass center of the copolymer chains, and N denoted the total amount of beads.
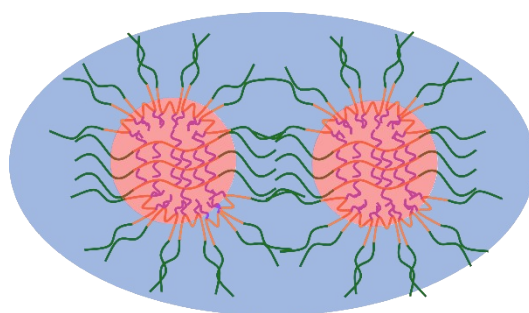

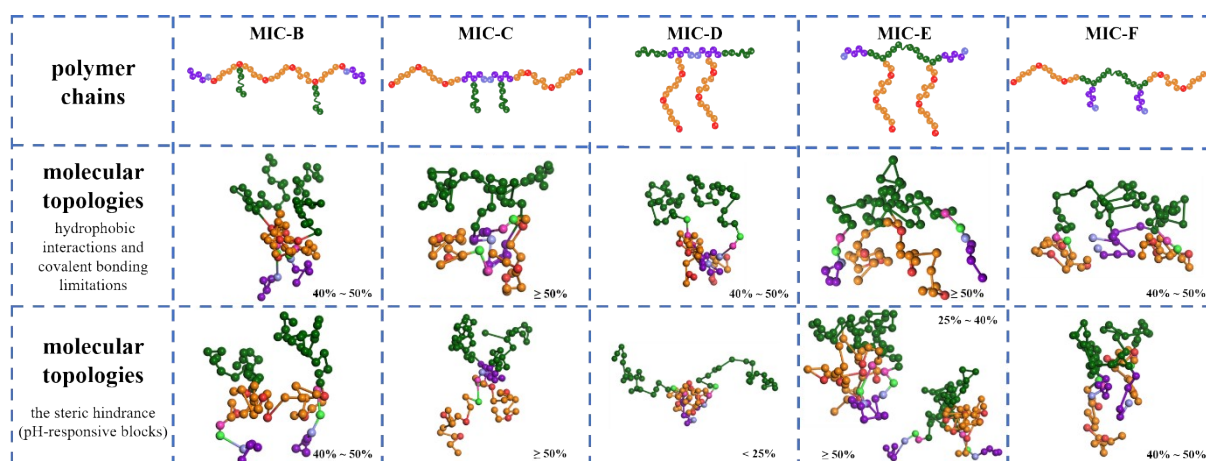**Figure S1.** The formation mechanism of hydrophobic ring.

Figure S2. Molecular topologies (configurations) of copolymer chains in self-assembled micelles (MIC. B ~ E).
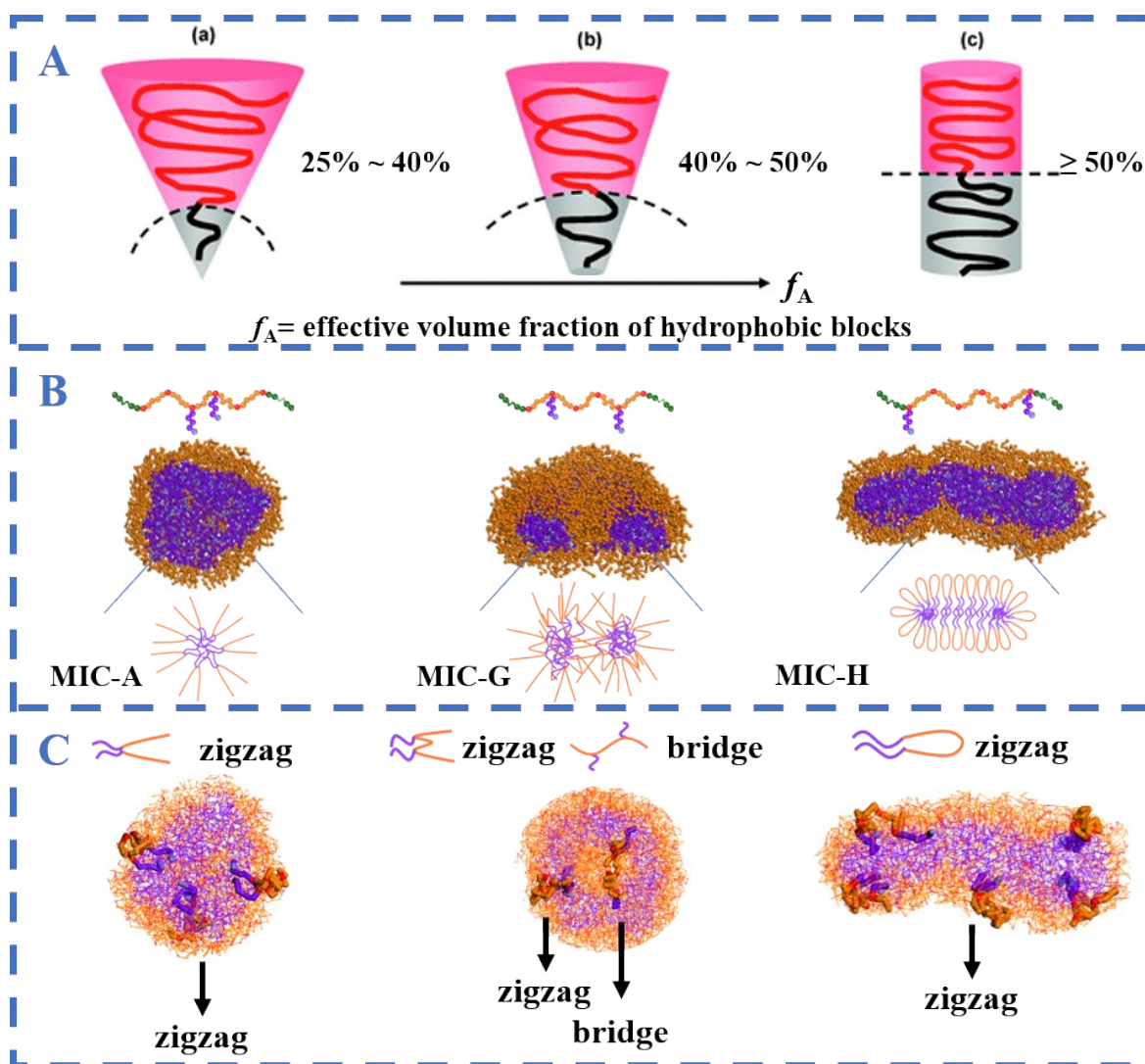
Figure S3. Schematic illustration of the cone−column mechanism for morphological transitions from sphere (a) to cylinder (b) and to lamella (c), as the volume fraction (f_A) of the hydrophobic blocks (black) increases to ∼0.5 (A); Morphological snapshots and molecule packing models of self-assembled micelles (hydrophilic blocks were hidden) (B).

References

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