ARTICLE TYPE

Supporting info for: Self-assembly structures of amphiphilic multiblock copolymer in dilute solution

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In this *Supporting information* file, we show all the parameters used in our simulations, quantify the relation between the simulation parameter α and the solvent condition, and show the simulation results for self-assembly of multiblock copolymer in solvent poor for both components.

1 Simulation parameters

To describe the effective attraction between hydrophobic A beads, the A-A interactions are characterized by a modified Lennard-Jones (LJ) type potential¹,

$$U_{AA}(r) = 4\varepsilon_{AA} \left[\left(\frac{\sigma}{r}\right)^{12} - \alpha \left(\frac{\sigma}{r}\right)^{6} \right].$$
(1)

The bead-bead interactions between B and B beads and between A and B beads are characterized by Weeks-Chandler-Andersen (WCA) potential,

$$U_{WCA}(r) = U_{LJ}(r) - U_{LJ}(r_{c,WCA}),$$
(2)

with $U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$. The simulation parameters used to describe the modified LJ potential and WCA potential are listed in Table 1.

2 Quantify the solvent condition

The solvent quality can be controlled by varying parameter α in modified LJ type potential (eqn. 1). For $\alpha = 1.0$, potential $U_{AA}(r)$ returns to the standard LJ potential, which corresponds to bad solvent condition in implicit solvent models. In this case, the hydrophobic *A* beads will strongly cluster together. With the decrease of α , the solvent becomes better for the hydrophobic beads. For $\alpha = 0.0$, potential $U_{AA}(r)$ is purely repulsive, which corresponds to good solvent condition. To quantify the solvent quality reflected by parameter α , we have

conducted series of Brownian dynamics simulations to obtain Flory exponent v, which is the scaling parameter between radius of gyration of the chain $(R_{g,c})$ and the chain length (N), $R_{g,c} \sim N^{\nu}$. We simulate chains consisting only bead type A with length N from 100 to 1000 with an interval of 100, at different values of α between 0.0 and 1.0. For each simulation, the total simulation time is $5 \times 10^6 \delta t$. We obtain $R_{g,c}$ with time average from $4 \times 10^6 \delta t$ to $5 \times 10^6 \delta t$ after equilibrium with an interval of $2 \times 10^5 \delta t$, and average over 10 samples with different initial chain configurations. The simulation parameters used are listed in Table 2. Parameters listed in Table 2 are exclusively used to obtain Flory exponent v by calculating $R_{g,c}$ for chains with different lengths; In these simulations, we perform 5×10^6 steps for each. For all the main simulations, *i.e.*, the simulations for elucidating self-assembly structures with different k_a and α combinations, we perform 1.5×10^7 steps for each, and the parameters are listed in Table 1.

3 Distribution of bond length

We are using standard bond potential $U_{bond}(r) = (k_b/2)(r - k_b/2)$ $(r_0)^2$ but with $r_0 = 0$ in our simulations. Moreover, the bond force constant is set as 10.0, which is quite small as compared to other simulations using harmonic bond potentials. In a simulation model at coarse-grained level, finite extensible nonlinear elastic (FENE) potential was typically used to represent chemical linkages between the beads. The characteristics of FENE potential are the limited extension of the "bonds" and the minimum energy at zero "bond" length, where the limited extension of the bonds is designed to reflect chain entanglements at coarse-grained level, and the minimum energy at zero bond length simply reflects chain connectivity. We actually follow the line of FENE potential by keeping minimum energy at zero bond length to reflect correct polymer chain connectivity, but using harmonic form of potential with small force constant instead. In this way, we model a polymer

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chain with crossable bonds. Since we are focussing on the self-assembly structures of the block copolymers, by allowing bond-crossing, we can easily bypass kinetic traps in self-assembly processes and accelerate the simulations to a large extent.² Taking $(A_{10}B_{10})_{10}$ for example, we show typical distributions of bond lengths when $k_a = 0$, $\alpha = 1$ (single flower micelle) and $k_a = 10$, $\alpha = 0$ (extended chain), respectively, in Fig. 1. The distribution is sampled by 1000 snapshots from 1.0×10^7 to 1.5×10^7 steps with an interval of 5×10^3 steps in equilibrium state.

4 Multicompartment micelles obtained from multiblock copolymer in bad solvent

We also consider the self-assembly of the multiblock copolymer in bad solvent for both components (potential type of *AA* and *BB*: LJ potential, and *AB*: WCA potential). If we start the simulation from an initially random chain in bad solvent condition, finally we can observe multicompartment micelles with lots of defects, such as branchings, different terminal caps, and irregular compartment sizes, as shown in Fig. 2, even after an annealing process.

5 Self-assembly structures of $(A_{15}B_5)_n$ and $(A_{18}B_2)_n$

We also consider the self-assembly structures of the multiblock copolymer with larger portion of hydrophobic blocks, such as $(A_{15}B_5)_n$ and $(A_{18}B_2)_n$. The crew-cut like micelles^{3–7} can be formed, as shown in Fig. 3. These extra simulations are targeted to highlight possible crew-cut micelle structures formed by our multiblock copolymers. We would like to focus on this type of systems in our further studies in detail.

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 Table 1 Simulation parameters in this paper.

Parameter	Value
Temperature	1.0
$\sigma_A = \sigma_B$	1.0
Potential type $A - A$	modified LJ
α	from 0.0 to 1.0
Potential type $A - B$ and $B - B$	WCA
$r_{cut,AA}$	3.0
$r_{cut,WCA} = r_{cut,AB} = r_{cut,BB}$	$\sqrt[6]{2}$
$arepsilon_{AA}=arepsilon_{AB}=arepsilon_{BB}$	1.0
k_b	10.0
<i>k</i> _a	from 0.0 to 10.0
δt	5×10^{-3}
Total simulation steps	1.5×10^{7}
Thermostat	Brownian dynamics
A and B represent for bead A and bead B, respectively	
LJ represents for Lennard-Jones potential	
WCA represents for Weeks-Chandler-Andersen potential	

WCA represents for Weeks-Chandler-Andersen potential

 k_b represents for bond force constant for harmonic bond potential

 k_a represents for angle force constant for harmonic angle potential

 Table 2 Simulation parameters in this paper.

Parameter	Value
Temperature	1.0
$\sigma_{\!A}$	1.0
Potential type	modified LJ
α	from 0.0 to 1.0
Ν	from 100 to 1000
$r_{cut,AA}$	3.0
k_b	10.0
δt	5×10^{-3}
Total simulation steps	$5 imes 10^{6}$
Thermostat	Brownian dynamics
A represents for bead A	

LJ represents for Lennard-Jones potential

N represents for the chain length

 k_b represents for bond force constant for harmonic bond potential

Parameters listed here are exclusively used to obtain Flory exponent v by calculating $R_{g,c}$ for chains with different lengths

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Fig. 1 Bond length distributions of $(A_{10}B_{10})_{10}$ for (a) $k_a = 0$, $\alpha = 1$ (single flower micelle), and (b) $k_a = 10$, $\alpha = 0$ (extended chain), respectively.



Fig. 2 Self-assembly structures from $(A_{10}B_{10})_n$ with initially random chain configuration in solvent bad for both components. (a) n = 20, (b) n = 40, (c) n = 60, (d) n = 80, and (e) n = 100.



Fig. 3 Self-assembly structures from multiblock copolymer in solvent selectively poor for component *A*, for $(A_{15}B_5)_n$ with (a) n = 10, (b) n = 30, (c) n = 50, (d) n = 70, (e) n = 90, and for $(A_{15}B_5)_n$ with (f) n = 10, (g) n = 30, (h) n = 50, (i) n = 70, (j) n = 90.