Supporting Information for

Planet-satellite micellar superstructures formed by ABCB terpolymers in solution

Chao Duan, Weihua Li*, Feng Qiu, An-Chang Shi

Email: weihuali@fudan.edu.cn

This PDF file includes:
Theoretical Methods and Parameter Setting
Tables S1 to S4
Figures S1 to S6
Videos S1 to S4
Theoretical Methods and Parameter Setting

Dissipative Particle Dynamics Simulation (DPD)

Dissipative particle dynamics (DPD) method is a highly coarse-grained model in which each particle represents tens of monomeric repeat units. The coarse-graining treatment in simulations brings a few obvious advantages at the expense of some chemical details [S1, S2]. On the coarse-graining level, the center-of-mass positions may overlap without violating the excluded volume condition for the atomistic constituents. Therefore the non-bonded interactions between coarse-grained particles can be modeled by soft potentials. The largely reduced number of particles as well as the implementation of the soft potentials dramatically increases the length and time scales accessed by computer simulations in contrast to the full atomistic model, and thus enables examining the phase-separating dynamics of block copolymer systems that evolves the length of tens of nanometers and the time from seconds to hours.

In the NVT canonical ensemble [S1, S2], the force $\mathbf{F}_i$ acting on the $i$-th DPD particle is the sum of the conservative force $\mathbf{F}_{ij}^C$, the dissipative force $\mathbf{F}_{ij}^D$, and the random force $\mathbf{F}_{ij}^R$, i.e.

$$\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \quad \text{(S1)}$$

with

$$\mathbf{F}_{ij}^C = a_{ij} \left[ \omega_{ij}(r_{ij}) \right]^{1/2} \mathbf{r}_{ij} \quad \text{(S2)}$$

$$\mathbf{F}_{ij}^D = -\gamma \omega_{ij}^D(r_{ij}) (\mathbf{r}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{r}_{ij} \quad \text{(S3)}$$

$$\mathbf{F}_{ij}^R = \sigma \omega_{ij}^R(r_{ij}) \zeta_{ij} \Delta t^{-1/2} \mathbf{r}_{ij} \quad \text{(S4)}$$

where the cutoff radius $r_c$, the mass of DPD particles $m$, and the temperature (or energy) $k_B T$ are all set to be unit. $a_{ij}$ represent the interaction parameters which are listed in Table S1 and the weight functions $\omega_{ij}^D(r_{ij}) = \left[ \omega_{ij}^R(r_{ij}) \right]^2 = \omega_{ij}(r_{ij}) = (1 - r_{ij}/r_c)^2 \theta(r_c - r_{ij})$ with the Heaviside function $\theta(x) = 1$ if $x > 0$, and otherwise $\theta(x) = 0$. The time step is set as $\Delta t = 0.06 \tau$ with $\tau = (mr_c^2/k_B T)^{1/2}$. The particle number density is selected as $\rho = 3$. We take the noise amplitude $\sigma = 3.0$, and then the friction coefficient $\gamma = \sigma^2/2k_B T = 4.5$. 

2
\( \zeta_{ij} \) denotes a randomly fluctuating variable with zero mean and unit variance. The beads of polymer chain are connected by the harmonic spring force \( F_{ij}^S = -C \mathbf{r}_{ij} \) with \( C = 4.0 \). Simulations are carried out by the modified velocity-Verlet algorithm with \( \lambda = 0.65 \) in a cubic box with \( V = (30.0r_c)^3 \). Periodic boundary conditions are imposed on all three directions. The solution systems of tetrablock terpolymers A_9B_xC_3B_y with \( x + y = 18 \) are mainly simulated with a fixed volume fraction of copolymers \( \phi_{Co} = 0.1 \). The initial configurations are randomly generated, and then at least \( 5 \times 10^5 \) time steps are used to equilibrate the systems. For a fully equilibrated system, the number of satellites maintains unchanged for a long period. However, different simulations with the same group of parameters but different initial conditions can lead to different numbers of satellites. Therefore, \( N_{\text{satellite}} \) as well as its statistical error is estimated by averaging five independent simulations, which is in contrast to the certain integer in SCFT.

Table S1: Interaction parameters \( a_{ij} \) for all types of DPD particles, which are selected to generate a roughly similar set of Flory-Huggins interaction parameters in SCFT according to the relation \( \Delta a_{ij} = a_{ij} - a_{ii} \sim \chi_{ij}N \) [S2].

<table>
<thead>
<tr>
<th>( a_{ij} )</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25</td>
<td>55</td>
<td>115</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>—</td>
<td>25</td>
<td>55</td>
<td>28.75</td>
</tr>
<tr>
<td>C</td>
<td>—</td>
<td>—</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>S</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>25</td>
</tr>
</tbody>
</table>
Self-Consistent Field Theory (SCFT)

We consider a polymer solution in a volume of $V$, composed of linear tetrablock terpolymer chains $AB_1CB_2$ with a fixed concentration of $\phi_{Co} = 0.1$ and the solvents $S$ that are mimicked by very short homopolymers. The terpolymer length is indicated by the total number of segments $N$, and the length of each block is specified by $f_{A}N$, $f_{B_1}N$, $f_{C}N$, and $f_{B_2}N$, respectively. The length of the homopolymer is selected as $N_S = \gamma N$ with $\gamma = 0.05$. The repulsive interactions between the four dissimilar segments are characterized by a set of Flory-Huggins interaction parameters, $\chi_{ij}$ ($i, j = A, B, C, S$). The micellar structures are characterized by the spatial distributions of four components, $\phi_i(r)$ ($i = A, B, C, S$). The blending system is assumed to be incompressible, i.e. $\phi_A(r) + \phi_B(r) + \phi_C(r) + \phi_S(r) = 1$. Moreover, we assume that all polymers have equal Kuhn length $b$ and segment density $\rho_0$.

Within the standard SCFT based on the Gaussian-chain model, the free energy density in the unit of thermal energy $k_B T$ for a given temperature $T$, where $k_B$ is the Boltzmann constant, can be expressed as

$$\frac{NF}{V \rho_0 k_B T} = -\phi_P \ln Q_P - \frac{(1 - \phi_P)}{\gamma} \ln Q_S + \frac{1}{V} \int dr \left\{ \sum_{i<j} \chi_{ij} N \phi_i(r) \phi_j(r) - \sum_i w_i(r) \phi_i(r) - \eta(r) \left[ 1 - \sum_i \phi_i(r) \right] \right\}, \quad (i, j = A, B, C, S)$$

where the spatial function $\eta(r)$ is a Lagrange multiplier used to enforce the incompressibility conditions. The two quantities $Q_P$ and $Q_S$ are the single chain partition functions of the tetrablock terpolymer and homopolymer-representing “solvent”, respectively, interacting with the mean fields of $w_i(r)$ ($i = A, B, C, S$) produced by surrounding chains, and are given by

$$Q_\alpha = \frac{1}{V} \int dr \ q_\alpha(r,s) q_\alpha^\dagger(r,s), \quad (\alpha = P, S)$$

Here $q_\alpha(r,s)$ and $q_\alpha^\dagger(r,s)$ are the propagator functions of segments for the two polymer chains, satisfying the following modified diffusion equations

$$\frac{\partial q_\alpha(r,s)}{\partial s} = -\nabla^2 q_\alpha(r,s) - w(r,s)q_\alpha(r,s)$$

$$-\frac{\partial q_\alpha^\dagger(r,s)}{\partial s} = -\nabla^2 q_\alpha^\dagger(r,s) - w(r,s)q_\alpha^\dagger(r,s), \quad (\alpha = P, S)$$

4
where \( w(r, s) = w_i(r) \) when \( s \) belongs to the \( i \)-component blocks along the polymer chains. The above expressions imply that \( R_g = (N/6)^{1/2}b \) is chosen as the unit of spatial length, and \( s \in [0, 1] \) for the tetrablock terpolymer, while \( s \in [0, \gamma] \) for the short homopolymer. The initial conditions of the propagator functions are \( q_\alpha(r, 0) = 1 \) (\( \alpha = P, S \)), \( q^\dagger_P(r, 1) = 1 \), and \( q^\dagger_S(r, \gamma) = 1 \). Minimization of the free energy with respect to the monomer densities and the mean fields leads to the following SCFT equations,

\[
\begin{align*}
    w_i(r) &= \eta(r) + \sum_{j \neq i} \chi_{ij} N \phi_j(r) \\
    \phi_A(r) &= \frac{\phi_P}{Q_P} \int_0^{f_A} ds q_P(r, s) q^\dagger_P(r, s), \\
    \phi_B(r) &= \frac{\phi_P}{Q_P} \left[ \int_{f_A}^{f_A+f_{B1}} ds q_P(r, s) q^\dagger_P(r, s) + \int_{1-f_{B2}}^{1} ds q_P(r, s) q^\dagger_P(r, s) \right], \\
    \phi_C(r) &= \frac{\phi_P}{Q_P} \int_{f_A+f_{B1}}^{1-f_{B2}} ds q_P(r, s) q^\dagger_P(r, s), \\
    \phi_S(r) &= \frac{(1-\phi_P)}{\gamma Q_S} \int_{0}^{\gamma} ds q_S(r, s) q^\dagger_S(r, s).
\end{align*}
\]  

(S8)

The modified diffusion equations are solved using pseudo-spectral method with periodic boundary conditions imposed on all three directions. The polymer solutions are considered to be placed in a cubic box that is discretized into a \( 64^3 \) lattice, of which the maximal lattice spacing is smaller than \( 0.2 R_g \). The chain contour is divided into 100 points. To determine the stability of micellar structure, the method of optimizing the size of simulation box at the constant copolymer concentration proposed by Greenall et al. \[S5, S6\] is used. Although the two approaches of the DPD simulation and the SCFT calculation can lead to qualitatively consistent results about the self-assembly of diverse block copolymer systems, it is essential to emphasize the considerable difference between them. One of the most pronounced differences arises from the difficulty in matching the characteristic parameters between the two models. For instance, the interaction parameters are barely perfectly matched when the compositions are set to be exactly same. As a consequence, in Figure 2, in order to achieve reasonably matched interaction parameters between the DPD and SCFT models, a small deviation of the compositions is generated. On the other hand, the slightly different compositions facilitate the choice of the bead numbers for each block in the multiblock copolymer.
Table S2: Normalized radius $R_A$ of the planet with the volume fraction of $A$-block and the box size $L_{\text{box}}$ by SCFT. RSD indicates “Relative Standard Deviation”.

<table>
<thead>
<tr>
<th>$R_A / \left( f_A^{1/3} \cdot L_{\text{box}} \right)$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_A$</td>
<td>0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>Mean</td>
<td>0.28626</td>
<td>0.28752</td>
</tr>
<tr>
<td>RSD</td>
<td>0.154%</td>
<td>0.066%</td>
</tr>
</tbody>
</table>

Table S3: List of possible non-satellite structures formed in the $\eta - f_A$ phase diagram of Figure 3 by SCFT.

<table>
<thead>
<tr>
<th>NS$_1$</th>
<th>NS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform C phase</td>
<td>Connected structures</td>
</tr>
</tbody>
</table>
Table S4: List of possible non-satellite (NS) structures formed at smaller or larger $f_C$ for fixed $f_A = 0.30$ by SCFT.

<table>
<thead>
<tr>
<th>$f_A = 0.30$</th>
<th>$f_C &lt; 0.10$</th>
<th>$f_C &gt; 0.14$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform C phase</td>
<td>Elongated structure</td>
<td></td>
</tr>
</tbody>
</table>

![Uniform C phase](image1)  ![Elongated structure](image2)
Figure S1: Planet radius $R_A$ in the unit of $R_g$ as a function of $\eta$ for fixed $f_C = 0.10$ obtained by SCFT.

Figure S2: Typical plot of energy for the DPD simulation on the self-assembly of $A_9B_{10}C_3B_8$ copolymers in solution. A number of intermediate morphologies are presented, represented by full three-component (above row) and two-component (A and C) (bottom row) particle distributions, respectively.
Figure S3: Distance $l_{PS}$ between the satellite center and the planet surface (empty symbols for the left longitudinal coordinate) and the radius $R_C$ of $C$-satellites as a function of $\eta$ with fixed $f_C = 1.0$ for $f_A = 0.25$ and $f_A = 0.30$. 
Figure S4: (a) Circularly averaged density distributions $\phi_S(r)$ of solvents along the radial direction of the micellar superstructures for fixed $f_A = 0.25$ and $f_C = 0.10$ and various $\eta$. (b) Derivatives of the distribution functions $d\phi_S(r)/dr$. It is found that the local minima of the derivative curves roughly correspond to the central position of C-satellites. (c) Solvent density $\phi_S^* \eta$ at the central position of C-satellites defined in Figure (b).
Figure S5: (a) Variations of satellite number $N_{\text{satellite}}$ with $f_C$ for fixed $f_A = 0.30$. (b) Optimization of free energy with respect to the box size illustrating that the planet-satellite superstructures may transform into non-satellite structures when $\eta = 0$ (also can be seen from Video S3). This observation reveals the significant role of the terminal $B_2$-block in $A B_1 C B_2$ tetrablock copolymers on stabilizing the planet-satellite superstructures in contrast to the ABC linear triblock copolymers (Video S4).

Figure S6: Schematic plots demonstrating the mechanism leading to the Coulomb-like interactions between the satellites proposed by Semenov [S7, S8]. At the top row, BC diblock copolymers with hydrophobic C-block and hydrophilic B-block self-assemble into micelles in solution. When two micelles approach each other, they will experience a Coulomb-like repulsive interaction due to the loss of configurational entropy of the compressed B-blocks. In the bottom row of the planet-satellite superstructures, there is a similar Coulomb-like repulsive interaction between the C-satellites when neglecting the influence of the presence of the A-planet.
Figure S7: SCFT Phase diagrams at the $\eta$-$\chi_{AC}N$ plane for $\chi_{AB}N = \chi_{BC}N = 40$, $f_A = 0.3$, and $f_C = 0.1$ (a), and at the $\eta$-$\chi_N$ plane for $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = \chi_{N}$, $f_A = 0.3$, and $f_C = 0.11$. The interaction parameters between the three components of the tetrablock terpolymer and the solvent are same as those in Figure 3, i.e. $\chi_{BS}N = 5$ and $\chi_{AS}N = \chi_{CS}N = 100$. The results indicate that the planet-satellite superstructures could be formed robustly with the tetrablock terpolymer but not limited to a specific one.

References

107, 4423-4435.


