Planet−Satellite Micellar Superstructures Formed by ABCB Terpolymers in Solution

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Supporting Information

ABSTRACT: The occurrence and relative stability of planet−satellite nanostructures, composed of a host micelle (the planet) accompanied by a number of guest micelles (the satellites), in ABCB tetrablock terpolymer solutions are studied using the polymeric self-consistent field theory and dissipative particle dynamics simulations. The theoretical results demonstrate that the self-assembly of the ABCB tetrablock terpolymers with solvophobic A- and C-blocks and solvophilic B-blocks could lead to the formation of various planet−satellite superstructures, where the planet and satellites are composed of the A- and C-blocks, respectively. Furthermore, the number of satellites is controlled by the ratio of the two B-blocks. The arrangement of the satellites surrounding the planet resembles the solution of the well-known Thomson’s problem concerning the optimum arrangement of a given number of electrons on a sphere. Besides providing a facile route to engineering novel multicompartment micelles with planet−satellite superstructures for potential advanced applications, the study strengthens the prospect that multiblock copolymers could become a useful platform for the fabrication of complex nanostructures.

Recently an intriguing class of nanoassemblies with multicompartment superstructures have attracted tremendous attention.1−6 Among the different types of multicompartment architectures, the unique structural feature of “planet−satellite” (PS) superstructures makes it a promising candidate for various applications.4−11 Besides of technological applications, the study of the PS superstructure is also of fundamental interest because the arrangement of a given number of satellites surrounding a planet resembles the classical Thomson’s problem12 which is a generic model of many different physiochemical systems.13−16

Experimentally, a number of strategies have been developed to obtain PS superstructures. One popular strategy is based on the assembly of nanoparticles linked by peptide5 or DNA.6−8 Recently, Vana et al. proposed an alternative method where the satellite particles are separated from the planet core by RAFT star polymers.10,11 Technically, methods to engineer PS superstructures should meet a number of requirements. First of all, the system should have only one planet particle as the central core, surrounded by multiple satellites. Second, the number of satellites, ranging from a few to a few hundred, should be controllable. Finally, the size of the planet and satellites, as well as the planet−satellite distance, should be regulated. Despite great successes in obtaining PS superstructures, the properties of PS superstructures in these strategies are far from being precisely controlled. Therefore, it is desirable to explore cost-effective and efficient routes to engineering PS superstructures, of which the number of satellites, the size of the planet and satellites, and the planet−satellite distance can be readily controlled in a systematic manner.

In the current study, we propose a bottom-up strategy of engineering PS superstructures via the self-assembly of multiblock copolymers. It is well established that the self-assembly of block copolymers provides a powerful platform for the fabrication of different ordered nanostructures.1,2,17−27 In many insightful experiments, it has been demonstrated that multiblock copolymers could be designed to obtain desired ordered phases, e.g., hierarchical lamellar structures28,29 or the complex Frank–Kasper σ-phase.30 In particular, a theoretical example is given by Xie et al., demonstrating that the composition of B1AB2CB3 linear multiblock copolymers could be purposely designed to form various binary mesocrystal phases mimicking the binary ionic crystals.31 Their results reveal that the asymmetry of the coordination numbers (CNs) in a crystal structure could be regulated by the architecture of the copolymers. Furthermore, Xie et al. have demonstrated that asymmetric AB1CB2 tetrablock copolymers are able to form...
binary crystal structures with unequal CNs, of which the A-domain has higher CN than the C-domain. It is very instructive to regard a binary crystal with unequal CNs as a crystal of PS clusters sitting on a simpler lattice. Therefore, the AB1CB2 terpolymer could provide a candidate macromolecule to obtain a desired PS structure in the form of micelles self-assembled from block copolymer solutions. From a practical perspective, this type of tetrablock terpolymer\textsuperscript{28,29} or even more complex multiblock copolymers\textsuperscript{28,29} has been successfully synthesized in experiments. Therefore, the proposed bottom-up method could be readily carried out in the laboratories.

Specifically, the route to obtain desired PS superstructures with controllable properties is constituted based on the self-assembly of AB1CB2 tetrablock copolymers in solution (Figure 1). The AB1CB2 system is specified with constraints on the

![Figure 1. Schematics of the formation of "planet—satellite" micellar structures from the self-assembly of AB1CB2 tetrablock terpolymers in solution. Domains of the solvophobic A- and C-blocks are plotted in red and blue, while those of B1 and B2 are indicated by green and yellow, respectively. The circular arrow indicates the direction of increasing the length ratio of B2-blocks \( \eta = f_{B2}/f_B \) for a fixed total B composition. The numbers below each cluster indicate the number of satellites of the structure.](image)

lengths of A- and C-blocks such that the A-blocks and C-blocks form micelles separately. Thus, the A- and C-blocks are chosen to be solvophobic, whereas the B-blocks are solvophilic. The asymmetric architecture leads to that the A-blocks would self-assemble to form the central micelle ("planet") surrounded by a number of C-micelles ("satellites"). The middle B1-blocks form an intermediate layer between the A- and C-micelles, while the terminal B2-blocks form an outer layer of the micelles, thus screening the solvophobic blocks from the solvents. The terminal B2-block plays a significant role in the formation of the complex superstructure because of two reasons. First of all, in the case of the AB1C triblock copolymer without the terminal B2-block, the B1-block has to adopt a looping configuration in order to screen the C-micelles from the solvents\textsuperscript{25,32}, thus increasing the tendency of C-micellar fusion. Second, the relative length between the middle and terminal B-blocks can be used to control the number of satellites as well as the planet—satellite distance. Third, in contrast to the AB1CB2 melt, the solvent plays additional important roles on regulating the self-assembly of the micellar superstructures. For example,

the selective swelling of the solvents to the B-blocks enhances the asymmetry between A- and C-blocks of the polymer, thus increasing the effective CN of the A-domain (e.g., the number of satellites).

The validity of the proposed route is verified using two theoretical approaches, the dissipative particle dynamics (DPD) simulations\textsuperscript{33,34} and the polymeric self-consistent field theory (SCFT) calculations.\textsuperscript{35} Details of the DPD and SCFT methods are given in the Supporting Information (SI). Although DPD and SCFT differ markedly in model details, qualitatively consistent results are obtained from these two methodologies, demonstrating the robustness of the proposed design route.

The parameter space of the AB1CB2 terpolymer solutions is extremely large. Following our previous work\textsuperscript{31} we consider the cases with fixed interaction parameters and use a set of varying block ratios, \( f_{AB}, f_{BC}, f_C \) and \( f_{B2} \) as the controlling parameters. The six interaction parameters for the SCFT model are chosen as \( \chi_{AB} = \chi_{BC} = 40 \ll \chi_{AC} = 120, \chi_{AB} = 5 \), and \( \chi_{AS} = \chi_{CS} = 100 \), where \( \chi_i \) (\( i = A, B, C, S \)) are the Flory–Huggins interaction parameter and \( N \) is the total number of statistical segments of a copolymer. It is important to emphasize that the choice of these parameters is not stringent because it just needs to ensure that the A- and C-blocks form separated spherical domains. For the DPD simulations, the corresponding interaction parameters are summarized in Table S1. For convenience, a variable \( \eta = f_{B2}/f_B \) is introduced to describe the volume fraction of the B2-block relative to the total B composition. For the two methods, the volume fraction of copolymers is fixed as \( \phi_C = 0.1 \).

We first examine the effect of B-block partitions or \( \eta \) on the satellite number \( N_{\text{satellite}} \) of the PS superstructure. Results of \( N_{\text{satellite}} \) from the DPD simulations of \( A_9B_{15}C_8B_3 \) with \( x + y = 18 \) and the SCFT calculations of \( A_{0.26}B_{13}C_{0.1}B_3 \) with \( x + y = 0.64 \) are presented in Figure 2. It is noted that the stable morphologies from the SCFT calculations are determined by a comparison of the free energy that is optimized with respect to the cubic box size \( L_{\text{box}} \) for a given copolymer concentration.\textsuperscript{28} Accordingly, the planet radius is estimated as \( R_p \sim f^{1/3}_{B2}L_{\text{box}} \) (Figure S1 and Table S2). Our DPD simulations confirm that these stable

![Figure 2. Variation of satellite number with \( \eta \) from DPD and SCFT, where copolymers \( A_9B_{15}C_8B_3 \) with \( x + y = 18 \) in DPD and \( A_{0.26}B_{13}C_{0.1}B_3 \) with \( x + y = 0.64 \) in SCFT are considered. The insets show the morphologies obtained from DPD on the top and SCFT at the bottom, respectively.](image)
structures could also be obtained in the dynamic simulations (Figure S2, Videos S1 and S2).

Although the value of \( f_A \) is slightly different in the DPD and SCFT calculations, both systems self-assemble into various PS superstructures and exhibit a similar tendency of the change of \( N_{\text{satellite}} \) as a function of \( \eta \). Specifically, \( N_{\text{satellite}} \) increases to reach a maximum at around \( \eta = 0.5-0.7 \) and then decreases. This nonmonotonic behavior is in contrast to the monotonic increase of the CN ratio between A- and C-domains of the binary crystal phase formed in the tetrablock melt as \( \eta \) increases. Moreover, we find that the planet–satellite distance \( l_{PS} \) also varies nonmonotonically as \( \eta \) and exhibits a similar trend (Figure S3), implying a close correlation between these two quantities, \( N_{\text{satellite}} \) and \( l_{PS} \).

It is obvious that the distance \( l_{PS} \) should depend on the molecular architecture, i.e., \( \eta \). When \( \eta \) is negligibly small, the B\(_1\) blocks have to screen the C-satellites from the solvents, thus forming large-loop configurations at the expense of entropy (Figure 3). In this case, the satellites prefer to be embedded into the B\(_1\)-matrix thus reducing \( l_{PS} \). As \( \eta \) increases or the tail B\(_1\)-blocks grow, B\(_2\)-blocks play more roles on wrapping up the satellites, liberating the large loops of B\(_1\)-blocks. Replacing large loops with normal bridging configurations pushes the satellites away from the planet. As \( \eta \) increases further, B\(_1\)-blocks start to experience extra stretching, and in turn, the stretching will pull the satellites back toward the planet. It is also interesting to note that the size of the whole micellar superstructure varies nonmonotonically as \( \eta \) for fixed \( f_A \) and \( f_C \), which can be simply measured by \( R_h \) (Figure S1). As a consequence, the radius variation of C-satellites becomes complex because it is impacted by the size variation of the whole superstructure as well as \( N_{\text{satellite}} \) (Figure S3).

It is important to note that the molecular architecture controls the effective CNs of the planet (the number of satellites) through the architecture asymmetry, as it does in the melts, as well as through the planet–satellite distance, \( l_{PS} \). The influence of \( l_{PS} \) on \( N_{\text{satellite}} \) is two folds. First of all, the concentration of the swelling solvents in the B-domains surrounding the C-satellites strongly depends on \( l_{PS} \). The solvent concentration decreases from its bulk value outside the PS superstructure to vanishingly small near the planet (Figure S4). It has been established that larger degree of solvent swelling tends to increase the interfacial curvature toward the C-blocks, favoring the formation of a larger number of smaller C-satellites. Second, a larger \( l_{PS} \) leads to larger separation between the satellites and thus causes more severe loss of translational entropy due to the constraint of the aggregated satellites on the B\(_2\)-blocks that prefer to form a uniform outer layer. Forming smaller satellites favors reducing the entropy loss. However, at the same time, the C-domains constitute a constraint on the distribution of the B\(_2\)-blocks that becomes stronger as \( l_{PS} \) decreases because a reduced number of bridging configurations are accessible for the B\(_2\)-blocks connecting A- and C-domains. To release this constraint drives an opposite effect, i.e., forming increasing number of satellites of reduced size as \( l_{PS} \) decreases, which shifts the peak positions of \( N_{\text{satellite}} \) from that of \( l_{PS} \).

The planet size as well as the number of satellites are also controlled by the volume fraction of the A-blocks. Comparing with the melt system where \( f_A \) is varied in a very limited range in order to ensure the formation of a spherical domain, the value of \( f_A \) in the current case can be varied within a much larger window. It is obvious that an increase of \( f_A \) lowers the spontaneous curvature of the A-domain, thus increasing the planet size. On the other hand, a larger \( f_A \) induces higher hydrophobicity of the polymer and accordingly drives up the number of polymers in a micelle, resulting in a larger micellar superstructure. Therefore, \( N_{\text{satellite}} \) increases as \( f_A \). It is expected that the effects of \( \eta \) and \( f_A \) are coupled. To gain a comprehensive picture, a phase diagram in the \( \eta-f_A \) plane is constructed from extensive SCFT calculations (Figure 4).

![Figure 3](image-url)  
**Figure 3.** Schematics demonstrating the configurational change of the B blocks in response to the length ratio \( \eta \).

![Figure 4](image-url)  
**Figure 4.** SCFT phase diagram in the \( \eta-f_A \) plane for \( f_C = 0.10 \). The cross and plus symbols indicate possible nonsatellite (NS) micelles (see Table S3), while all other symbols indicate PS superstructural micelles with different number of satellites. The dashed lines, indicating boundaries between the PS and NS superstructures, are a guide for the eyes.
Table 1. Comparison of the Satellite Arrangements in Figure 3 to the Solution of the Thomson’s Problem

<table>
<thead>
<tr>
<th>(N_{\text{satellite}})</th>
<th>SCFT Results</th>
<th>Point Groups</th>
<th>Föppl Arrangements</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(D_{3h})</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(D_{3h})</td>
<td>(1.3)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(D_{3h})</td>
<td>(1,3,1)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(O_5)</td>
<td>(1,4,1)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(D_{5h})</td>
<td>(1,5,1)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(D_{3h})</td>
<td>(4)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(D_{3h})</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>(D_{4h})</td>
<td>(1,4,2,1)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(C_{2v})</td>
<td>(1,2,4,3)</td>
<td></td>
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</tbody>
</table>

The arrangements are specified by their point groups in the Schönflies notations together with the Föppl configuration composed of a list of the number of vertices on circles formed by intersections of the sphere with consecutive planes perpendicular to the principal symmetry axis of the polyhedron or polygon. The colored rows indicate possible metastable morphologies.

A very interesting observation is that the spatial distribution of the satellites in the PS superstructure resembles the solution of the Thomson’s problem (Table 1). This similarity could be understood by considering the effective interactions between the micelles (Figure S6), which are approximately Coulomb-like as shown by Semenov. Apparently, the effective interaction between the C-satellites, which could be regarded as micelles interacting through the B-matrix when the effect of A-blocks is ignored, mainly originates from the configurational entropy of the polymers and thus has a limited interacting distance in contrast to the real Coulomb potential. Although the difference between the two types of interactions is considerable, especially when the C-micelles are separated by highly concentrated solvents, the effective interaction between the C-satellites in the PS superstructures still resembles the Coulomb interaction well because all the C-satellites are constrained on a spherical surface. Note that the key factor dictating the satellite arrangement is not the specific form of the interaction, but the long-range repulsive feature. Therefore, the spatial arrangement of the satellites in a PS superstructure is similar to the Thomson’s problem of arranging charged particles on a sphere.

In summary, we propose a facile route of generating various planet–satellite superstructures via the self-assembly of multiblock terpolymers in solution. The validity of the proposed bottom-up approach was verified by SCFT calculations and DPD simulations. The theoretical results demonstrate that the satellite number, planet size, and planet–satellite distance could be controlled by the compositions of the block copolymers. In particular, the robustness and feasibility of the proposed route are confirmed by the fact that the formation of the PS superstructures is insensitive to the choice of the copolymer species, i.e., the interaction parameters, as shown in Figure S7.

Taking together, our theoretical study predicts a large window in the parameter space for the formation of various PS superstructures, thus implying that the PS superstructures could be readily observed with the tetrablock terpolymer solutions in experiments. The polymeric superstructures provide a useful template for the fabrication of multifunctional inorganic PS superstructures. This work sheds light on the fabrication of complex micellar superstructures via designed multiblock copolymers and strengthens the concept that multiblock copolymers could become a useful platform for the engineering of complex nanostructures as long as their design principles are developed.

ASSOCIATED CONTENT

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.7b00058.

  Details about the dissipative particle dynamics method and the self-consistent field theory; figures regarding the formation of nonsatellite structures, the planet–satellite distance, the size of the planet and satellites, the formation kinetics of the planet–satellite superstructures, and the phase diagrams for other sets of parameters (PDF)
  Videos regarding the formation of planet–satellite structures in the ABC triblock copolymer solution (AVI)
  Videos regarding the formation of planet–satellite structures in the ABCB tetrablock copolymer solution (AVI)
  Videos regarding the formation of nonsatellite structures in the ABC triblock copolymer solution (AVI)
Videos regarding the effect of tetrablock architecture on the formation of planet−satellite structures (AVI)

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Notes
The authors declare no competing financial interest.

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