Hierarchical Nanostructures Self-Assembled from a Mixture System Containing Rod-Coil Block Copolymers and Rigid Homopolymers

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Self-assembly behavior of a mixture system containing rod-coil block copolymers and rigid homopolymers was investigated by using Brownian dynamics simulations. The morphologies of formed hierarchical self-assemblies were found to be dependent on the Lennard-Jones (LJ) interaction $\varepsilon_{RR}$ between rod blocks, lengths of rod and coil blocks in copolymer, and mixture ratio of block copolymers to homopolymers. As the $\varepsilon_{RR}$ value decreases, the self-assembled structures of mixtures are transformed from an abacus-like structure to a helical structure, to a plain fiber, and finally are broken into unimers. The order parameter of rod blocks was calculated to confirm the structure transition. Through varying the length of rod and coil blocks, the regions of thermodynamic stability of abacus, helix, plain fiber, and unimers were mapped. Moreover, it was discovered that two levels of rod block ordering exist in the helices. The block copolymers are helically wrapped on the homopolymer bundles to form helical string, while the rod blocks are twistingly packed inside the string. In addition, the simulation results are in good agreement with experimental observations. The present work reveals the mechanism behind the formation of helical (experimentally super-helical) structures and may provide useful information for design and preparation of the complex structures.

Amphiphilic block copolymers have a capability to self-assemble into ordered nanostructures in selective solvents, such as spherical micelles, cylindrical micelles, and vesicles. These nanostructures have attracted considerable interests due to their wide applications in drug delivery, coating, cosmetics, nanoreactors, and so on. So far number of researches have been directed toward the self-assembly of flexible block copolymers. In contrast with the flexible block copolymers, block copolymers containing rigid blocks can organize into more well-ordered nanostructures, since the rigid segments can lead to orientation organization. The self-assembly mechanism is relatively complicated for rod-coil block copolymers in selective solvents and it is a challenging task to understand exactly how the observed structures were formed.

Blending a second component with the block copolymer systems is an efficient approach to manipulate the aggregate structures relative to the design of a new copolymer with novel molecular structures. The second component may be a block copolymer or homopolymer. The aggregate structures can be easily tuned by variation of properties of the mixture system such as the mixture ratio and interaction parameters. The cooperative self-assembly of two-component polymers has received much attentions in
To examine the self-assembly behavior of rod-coil block copolymer/rigid homopolymer mixtures, the aggregate structures were examined, and various structures including abacus-like, helical structures, disk micelles were observed. When the two copolymers are mixed, cylindrical hybrid micelles are observed. In addition, we have carried out a preliminary study on the self-assembly behavior of PBLG-b-PEG/PBLG mixtures in aqueous solution. The experiments revealed that the PBLG homopolymers packed side-by-side to form bundles, and the PBLG-b-PEG block copolymers wrapped on the homopolymer bundles. Supramolecular structures such as abacus-like (beads-on-wire) structures, super-helices, and plain fibers can be sequentially observed as the self-assembling temperature decreases. However, the detailed structure and important information of these hierarchical aggregates cannot be provided through the experimental method, such as the chain ordering and twisting information. Moreover, the formation mechanism of these superstructures should be further verified.

Apart from the experimental investigations, theory and computer simulations have emerged as powerful tools to study the self-assembly behavior of two-component polymers. They can provide more straightforward results than pure experiments, and overcome the limitation inherent in experiments. So far, various approaches, such as self-consistent field theory (SCFT), molecular dynamics (MD) simulations, and dissipative particle dynamics (DPD) simulations, have been successfully employed to investigate the aggregation behavior of polymer mixtures in solution. For example, Xu and coworkers used the SCFT method to investigate the self-assembly of homopolymer and diblock copolymer mixtures in selective solvents. By varying the mixture ratio and homopolymer chain length, various morphologies including vesicles, circle- and line-like micelles, and their mixtures were predicted. Zhong et al. simulated the micellization of linear and star ABC triblock copolymer mixtures. The structures of multicompartment micelles were found to be governed by mixture ratio and copolymer composition. So far, the publications on the two-component polymers are mainly focused on flexible polymers, and the theoretical and simulation studies on the mixtures with rod-coil copolymers or rigid homopolymers are very limited. Brownian dynamics (BD), as a solvent-free molecular dynamics method, presents more predominant in simulating rod-coil copolymers and computation efficiency. We have applied the BD method to the study of micelle structures of rod-coil diblock copolymers. Twisting string and disk micelles were observed. Such success of the BD simulation made it to be successfully extended to examine the self-assembly behavior of rod-coil block copolymer/rigid homopolymer mixtures. The preliminary simulations well reproduced the general features of the self-assembly from such a mixture system. However, many important issues remain unsolved in such complex systems, and the mixture systems need to be explored further.

In the present work, we performed a Brownian dynamics simulation to study the self-assembly behavior of mixture systems consisting of rod-coil block copolymers and rigid homopolymers in dilute solution. The effects of interaction parameter between rod blocks, block length, and mixture ratio on the aggregate structures were examined, and various structures including abacus-like, helical structures, plain fiber, and unimers were obtained. The thermodynamic stability regions of these structures in space of and block length were constructed. The ordering information of rod blocks and twisting information in the helical structures were also provided to reveal the formation mechanism of these complex structures.

Results

Very recently, we have discovered that a mixture of rod-coil block copolymers and rigid homopolymers was able to co-assemble into supramolecular structures such as super-helices. The preliminary results suggest that a number of parameters, including the interactions between rods, mixture ratio, and chain length, etc., play important roles in determining the aggregate structures of the mixtures. It is therefore worth to carry out further studies in order to understand the underlying mechanism of the cooperative self-assembly. In this work, self-assembly of rod-coil block copolymer/rigid homopolymer mixtures was studied, and the effect of interactions between rods, chain length, and mixture ratio was examined. A coarse-grained model of mixture was constructed as typically shown in Fig. 1a. The rod block length and coil block length in block copolymer are denoted by the bead numbers of and blocks in one copolymer chain, respectively (i.e.,\(L_{R} = m\),\(L_{C} = n\)). The mixture ratio of block copolymer to homopolymers is defined as the chain number ratio of the block copolymers to homopolymers. The simulation details are presented in Methods section. In what follows, the effects of these parameters were...
examined. In all simulations, the homopolymer chain number was fixed as 4, and the bead number in one homopolymer chain was set to be 150. The chain number of \( R \) block copolymers was set as 660, except for the study of the dependence of aggregate structures on mixture ratio \( \phi \).

**Effect of Interaction Strength between Rod Blocks on Aggregate Structure.** As revealed by previous communication\(^2\), the interactions between rods (\( \varepsilon_{RR} \)), which can be related to temperature in experiments, is an important factor determining the self-assembled structures of rod-coil block copolymer/rigid homopolymer. In this sub-section, the effect of such interactions was examined. The mixtures contain 660 \( R_7C_3 \) copolymers and 4 \( R_{150} \) homopolymers. The total bead number is 7200, therefore the number density of the system is roughly 0.0021. The \( \varepsilon_{RR} \) was varied from 2.7 to 1.3. The larger the value of \( \varepsilon_{RR} \), the more hydrophobic the \( R \) blocks.

Figure 1 presents the effect of \( \varepsilon_{RR} \) on the simulation results. When \( \varepsilon_{RR} \) is higher (\( \varepsilon_{RR} \geq 2.5 \)), the \( R_7C_3/R_{150} \) mixtures self-assemble into an abacus-like structure (beads-on-wire), in which \( R_7C_3 \) block copolymers aggregate into separating disks around \( R_{150} \) bundles (Fig. 1b1). Inside the abacus-like structure, the homopolymer rods are packed closely forming the inner axis. We can also see the orientation packing of rod blocks in each disk. As \( \varepsilon_{RR} \) decreases to the range between 2.4 and 2.1, the \( R_7C_3 \) block copolymers become helically wrapped on the \( R_{150} \) bundles, as shown in Fig. 1b2. The block copolymers continuously form a helical string along the major axis of homopolymer bundles, in which rod blocks are also aligned twistingly with each other. With further decreasing \( \varepsilon_{RR} \), the block copolymers cannot enwrap Figure 2. Order parameter \( S \) of \( R \) blocks in the aggregates formed by \( R_7C_3/R_{150} \) mixtures as a function of \( \varepsilon_{RR} \). The insert shows the typical morphology snapshots of aggregates at various \( \varepsilon_{RR} \). The regions of different structures are separated by dashed lines.
fully the homopolymer bundles, as seen from the snapshot of $\varepsilon_{RR} = 1.6$ in Fig. 1b. The $R_{70}$ bundles are randomly coated with $R_{7}C_{3}$ copolymers, but many $R_{7}C_{3}$ chains are freely dispersed in the simulation cell. The aggregate is no longer a helical fiber but a plain fiber. Finally, all unimers come out from the fiber, and no aggregates are formed (snapshot is not included).

From Fig. 1b, we learn that a structure transition from abacus to helix, to plain fiber, and finally to unimers appears for $R_{7}C_{3}/R_{150}$ mixtures with decreasing interaction strength $\varepsilon_{RR}$ between rod blocks. To identify the structural transition of aggregates and molecular packing of rod blocks, the order parameter $S$ of $R_{7}$ blocks in the aggregates was calculated. The $S$ as a function of $\varepsilon_{RR}$ is shown in Fig. 2. The insert shows the typical morphology snapshots of aggregates at various $\varepsilon_{RR}$. As can be seen, $S$ is larger than 0.7 in the abacus region when $\varepsilon_{RR} \geq 2.5$ and then sharply decreases to about 0.2 with decreasing $\varepsilon_{RR}$. The higher $S$ value indicates that the rod blocks are orientated and packed regularly in the copolymer disks. The sharp decrease of $S$ is ascribed to the abacus-helix transition. In the helix region, the $R_{7}$ blocks are twistingly packed in the helical string, therefore $S$ decreases dramatically. With further decreasing $\varepsilon_{RR}$, the $S$ is very low, implying the packing of rod blocks is disordered in the fiber and unimer regions.

As mentioned above, in the self-assembly of mixture, the block copolymers are wrapped on the surface of homopolymer bundles to form structures such as helical string. To illustrate the structure of helical string more clearly, we show schematic representations of the helical structure and the domain of rod blocks of block copolymers in Fig. 3a–b. It can be seen that the homopolymer bundles form the inner axis and block copolymers form the screw through ordered packing of the rod blocks. The rod blocks tend to align in an orientation vector, and such a vector is gradually changed along the axis of the bundle, which can be seen in the enlarged view of local packing of rod blocks (Fig. 3b). The global helical distribution of block copolymers is in a large-length-scale, while the local twisting packing of rod blocks is in a small-length-scale. The interplay of these two scale orderings determines the final hierarchical structures. In addition, two structural parameters of helix, i.e., screw pitch and twisted angle, were defined, and the sketch of their definitions is shown in Fig. 3b. The screw pitch $P_{1}$ of helix is the length along the long axis of the helix string in a helix period, and the twisted angle $\theta$ is the angle between each rod block and orientation direction. Figure 3c shows a typical result of $\cos(\theta)$ as a function of position along the long axis in the helical fiber of $R_{7}C_{3}/R_{150}$ mixtures at $\varepsilon_{RR} = 2.1$. The distance between dashed lines was defined as the local twisting pitch $P_{2}$ of rod blocks.

Figure 3. (a–b) Schematic representation for the helical structure and domain of rod blocks of block copolymers. In figure (b), the enlarged view indicates the local twisting packing of rod blocks. The sketch of definitions of screw pitch $P_{1}$ and twisted angle $\theta$ is also shown. (c) Typical result of $\cos(\theta)$ as a function of position along the long axis in the helical fiber of $R_{7}C_{3}/R_{150}$ mixtures at $\varepsilon_{RR} = 2.1$. The distance between dashed lines was defined as the local twisting pitch $P_{2}$ of rod blocks.
a single-twisting structure (no global helix). The double-twisting structure formed by introducing long rigid homopolymers was found for the first time. The homopolymer bundles provide a surface for block copolymers to assemble on, and at certain interaction strength the block copolymers form a helical string wrapping the homopolymer bundles. The local twisting packing of rod blocks is analogous to the packing manner of rod blocks in a string micelle formed by pure rod-coil block copolymers. They are both examples of twisting structures formed by nonchiral polymers, which provide new strategies for preparing helical superstructures. However, in rod-coil block copolymer systems, the string micelle could split into smaller string micelles when the number of copolymers is large enough\(^4\). Compared to that, in the rod-coil block copolymer/rigid homopolymer mixture systems, the helical string can be elongated under the directing of homopolymer bundles regardless of the number of copolymers.

Effect of Block Length on Aggregate Structure. The block length of copolymers is another important parameter determining the cooperative self-assembly behaviors. We then examined the effect of rod block lengths \(L_R\) and coil block lengths \(L_C\) on the structures of self-assembled aggregate. The simulations were carried out for two cases. One is that the \(L_R\) was varied from 6 to 9, while the \(L_C\) was fixed as 3. The other scenario is that the \(L_C\) was changed from 3 to 6, while the \(L_R\) kept unchanged (\(L_R = 7\)). Combing the effect of interaction strength \(\varepsilon_{RR}\), the thermodynamic stability regions of aggregate structures for various block lengths were constructed.

Figure 4a,b shows the morphology stability regions in space of \(L_R\) vs \(\varepsilon_{RR}\) and \(L_C\) vs \(\varepsilon_{RR}\), respectively. The morphology includes abacus, helix, plain fiber, and unimers. As shown in Fig. 4a, the rod-coil block copolymer/rigid homopolymer mixtures (e.g., \(R_6C_3/R_{150}\) mixtures) form an abacus-like structure at higher \(\varepsilon_{RR}\). As the \(\varepsilon_{RR}\) decreases, a transition from abacus-like structure to helical structure and then to plain fiber was shown. With further decreasing \(\varepsilon_{RR}\), the system gets into the unimer region. On the other hand, with increasing the rod block length \(L_R\), the region of helix becomes wider, while the region width of plain fiber keeps unchanged roughly. The boundaries of these regions tend to shift toward lower \(\varepsilon_{RR}\). It suggests that at a constant \(\varepsilon_{RR}\) the abacus-like structure is easier to form than the helical structure and plain fiber for longer rod block. Figure 4b shows the region widths of helix and plain fiber have a slight change, while the region boundaries move to higher \(\varepsilon_{RR}\) as the coil block length \(L_C\) increases, which is opposite to the effect of \(L_R\). The mixtures tend to form the abacus-like structure for shorter coil block but form the helical structure or plain fiber for longer coil block at a constant \(\varepsilon_{RR}\).
From the simulation results, we learn that the lengths of both rod and coil blocks affect the structural transition of aggregates. In fact, for a given aggregate structure, the block length may also affect the structure details of the aggregates. For example, the helical structures which occupy the major part of the morphology stability regions may possess different pitches at various block lengths. We then examined the screw pitches $P_1$ of helical structures and local twisting pitch $P_2$ of rod blocks as a function of $L_R$ and $L_C$. The results are presented in Fig. 5. Figure 5a presents the pitches $P_1$ of helical structures with various $L_R$ at $\varepsilon_{RR} = 1.9, 2.2, \text{and } 2.4$. The insert shows the $P_2$ as a function of $L_R$ at various $\varepsilon_{RR}$. These two pitches were both found to increase markedly with increasing $L_R$ at a fixed $\varepsilon_{RR}$. For example, at $\varepsilon_{RR} = 2.2$, for $L_R = 6$ the pitch $P_1$ is 17.7σ (σ is the diameter of LJ bead, $P_2 = 13.4\sigma$), while for $L_R = 9$ the $P_1$ is up to 41.2σ ($P_2 = 25.6\sigma$). These results indicate that the helical wrapping of block copolymers on homopolymer bundles is in a more extended manner for longer rod block, and the local twisting of rod blocks is easier to occur for shorter rod block. We can also view the effect of $\varepsilon_{RR}$ on the screw pitch $P_1$ and twisting pitch $P_2$. With decreasing $\varepsilon_{RR}$, the two pitches both decrease. It suggests that the block copolymers are easier to be helically distributed and rod blocks are easier to twistingly pack at lower $\varepsilon_{RR}$. Figure 5b shows the screw pitches $P_1$ of helical structures as a function of $L_C$ at $\varepsilon_{RR} = 2.0, 2.2, \text{and } 2.4$. The insert shows the $P_2$ versus $L_C$ at various $\varepsilon_{RR}$. As can be seen, $P_1$ and $P_2$ decrease slightly with $L_C$ increases, while the pitches increase markedly with increasing $\varepsilon_{RR}$. The structure diversity of helices for various $L_C$ is not obvious relative to the helices formed by mixtures with different $L_R$.

**Effect of Mixture Ratio on Aggregate Structure.** The effect of mixture ratio $\phi$ (block copolymer/homopolymer) on the aggregate structures was further examined. We mainly focused on the helical structure and explored the relationship between the structure of helices and mixture ratio. The interaction parameter $\varepsilon_{RR}$ was chosen to ensure the formation of helical structures. The chain number of homopolymer rods kept constant, while the chain number of $R_7C_3$ block copolymers was varied to realize various mixture ratios.

Figure 6 shows the screw pitches $P_1$ of helices formed by mixtures with various $\phi$ at $\varepsilon_{RR} = 1.9, 2.1, \text{and } 2.4$. The insert shows the local twisting pitches $P_2$ of rod blocks as a function of $\phi$ at various $\varepsilon_{RR}$. The value of $\phi$ was changed from 120 to 180, as the chain number of block copolymers was set in the range of 480 and 720. From the figure, we can see both the effects of $\phi$ and $\varepsilon_{RR}$. For any $\varepsilon_{RR}$, the pitches...
**Figure 6.** Screw pitches $P_1$ of helices formed by $R_bC_7/R_{150}$ mixtures with various mixture ratios $\varphi$. The interaction strength of rod blocks is $\varepsilon_{RR} = 1.9$, 2.1, or 2.4. The insert shows the local twisting pitches $P_2$ of rod blocks as a function of $\varphi$ at various $\varepsilon_{RR}$.

$P_1$ and $P_2$ decrease rapidly with increasing $\varphi$ from 120 to 180. At a fixed $\varphi$, two pitches have an increase with the increase of $\varepsilon_{RR}$. When the value of $\varphi$ is smaller, the helical wrapping of block copolymers on homopolymer bundles is more extended ($P_1$ is larger), and the rod blocks take on a smaller twisting degree ($P_2$ is larger). As the $\varphi$ increases, the helical wrapping of copolymers becomes more sufficient (the pitch $P_1$ becomes smaller) and the contact between the homopolymer surface and solvents decreases. The decrease of screw pitch $P_1$ could be ascribed to the increase in chain number of block copolymers. The helical string on homopolymer bundle surface becomes longer, but the homopolymer bundles keep a fixed length. To wrap the homopolymer bundle surface effectively, the block copolymers have to be packed in a relatively shrinking manner. The closer packing of rod blocks also leads to the decrease of twisting pitch $P_2$ of rod blocks. Figure 6 indicates that the mixture ratio has a prominent effect on the screw pitches of formed helical structures and local twisting pitches of rod blocks. However, only the results of systems with larger mixture ratio were presented here. The effect of mixture ratio on the aggregate structures at smaller $\varphi$ is revealed in the next section, through a comparison with the experimental results.

**Comparison with Experimental Observations.** In previous work\textsuperscript{24,25}, we reported a study of cooperative self-assembly of a mixture of PBLG-$b$-PEG block copolymers and PBLG homopolymers. The PBLG blocks take rigid $\alpha$-helix conformation, while the PEG are flexible chains. They can correspond to the rod and coil blocks in the simulations. We have examined the effect of self-assembling temperature on the aggregate structures. The results show that the PBLG$_{\text{141}}$-$b$-PEG$_{\text{112}}$/PBLG$_{\text{141}}$ binary system (the subscripts denote the polymerization degree (DP) for each segment) self-assemble into abacus-like structures at 40 °C. With decreasing the temperature to 20 °C, the super-helical structures were observed. Further decreasing the temperature, plain fibers were formed at 5 °C. The experiments indicated that the self-assembling temperature has a prominent influence on the aggregate structures.

In the experiments, the solubility of PEG decreases with increasing temperature\textsuperscript{44}, which means that the interaction between solvent (water) and hydrophilic PEG segments is weaker at higher temperature. In this case, the PEG block becomes more hydrophobic and PBLG-$b$-PEG copolymers have stronger tendency to aggregate at higher temperature. Since there are no solvents in Brownian dynamics simulation, the strong aggregation tendency of the PBLG-$b$-PEG copolymers was realized by tuning the parameter of $\varepsilon_{RR}$\textsuperscript{25}. A decrease of interaction strength $\varepsilon_{RR}$ between the $R$ blocks corresponds to a decrease of temperature in the experiments.

In the simulations, as shown in Fig. 1b, the $R_bC_7/R_{150}$ mixtures self-assemble into an abacus-like structure with $R_bC_7$ disks around $R_{150}$ bundles at $\varepsilon_{RR} = 2.4$, where the parameter settings are according to the experiments. In the experiments, the number average molecular weight ($M_n$) of PBLG homopolymer is 528000 (DP = 2411), and the $M_n$ for typical PBLG-$b$-PEG is 36000 (PBLG: $M_n = 31000$, DP = 141; and PEG: $M_n = 5000$, DP = 112). Therefore, the ratio of PBLG to PBLG-$b$-PEG (in terms of $M_n$) is nearly 15. In the simulations, the number ratio of rigid homopolymer to copolymer model is set to be 15, where the coarse-grained homopolymer contains 150 beads and the copolymer model contains 10 beads. Meanwhile, the ratio of molecular weight $M_n$ of PBLG homopolymer to that of PBLG block of PBLG-$b$-PEG is about 17, and the setting ratio of $R_{150}$ homopolymer to $R_b$ block in the simulation model is close to this value.

In addition, the model of block copolymer was chosen such that the bulk density of pure species\textsuperscript{45} or the relative lengths of the blocks\textsuperscript{46} matches the experimental data. In the simulations, the copolymer model was chosen by renormalizing both the bulk weight densities and block lengths. From the experiments, we learned that the $M_n$ of PBLG block and PEG block in PBLG-$b$-PEG copolymers are 31000
and 5000, respectively. First, the number of BD beads was renormalized by keeping the bulk density identical in the simulations and experiments, and then a ratio of 31000 / 5000 was obtained. In this case, 3.6 beads for the PBLG block can form a 0.54 nm helix, while 1 bead for the PEG block occupies 0.35 nm. Second, the number of BD beads was renormalized by the length of rod block and coil block, and we obtained the relative number of beads for R and C blocks as (31000 × 0.54/3.6) : (5000 × 0.35/1) = 7 : 2.63. As a result, the model of R_C block copolymers (contains 7 R beads and 3 C beads) was adopted in the simulations, which can capture the essential feature of PBLG-b-PEG block copolymers in the experiments. As the εRR decreases, the aggregate morphology was transformed to a helical structure with R_C helically wrapping on R_C bundles (at εRR = 2.1) and a plain fiber with R_C randomly packing on R_C bundle surface (at εRR = 1.5). The transition from abacus to helix and then to plain fiber is in good accordance with the experimental observations.

Here, we carried out further comparisons between the simulations and experiments. The experimental details are available in Supporting Information. In addition to temperature, the mixture ratio is another factor influencing the cooperative self-assembly. The experimental results, as shown in Fig. 7a-d, indicate that the helices are clearly visible when the molar ratio of PBLG-b-PEG block copolymer to PBLG homopolymer is larger (130). With decreasing the molar ratio, the helical structures tend to be less visible, and then fibers with no helical structure but a rough surface appear. Finally, completely plain fibers are obtained (for details, see sections 1 and 2 of Supporting Information). The simulations obtained similar results, as shown in Fig. 7e-h. The parameter setting of the simulation models corresponds to the essential feature of the experimental samples. For example, φ is changed from 165 to 52.5, according to the molar ratio of PBLG-b-PEG copolymer to PBLG homopolymer varying from 130 to 6 in experiments. As can be seen, with decreasing the mixture ratio φ, the regular helical structure is gradually transformed into fibers without regular helical structures. When the φ is small enough (52.5), the block copolymer simply covered the homopolymers, and plain fibers were formed. The block copolymers tend to protect the homopolymer surface from being exposed to the solvents, but the block copolymer chains cannot cover the homopolymer bundles sufficiently, and no helical structures are formed. We can find that a good qualitative agreement between simulations and experiments was shown again.

The simulation and experiment results regarding the screw pitches of helices were also compared. The simulation results shown in Fig. 5 are replotted in Fig. 8 for a comparison with experiments. As shown in Fig. 8a, the simulated pitch P1 of helical structures at εRR = 2.2 increases gradually as the rod block length L increases. In the experiments, we measured the screw pitches of super-helices self-assembled from PBLG-b-PEG112/PBLG2411 mixtures with various polymerization degrees of PBLG (nPBLG) in PBLG-b-PEG copolymer by collecting a number of micelles from SEM images. The value of nPBLG corresponds to the length of rod blocks (the experimental details are available in section 3 of Supporting Information). It was found that the experimental screw pitch increases with increasing nPBLG which is in qualitative accordance with the simulation calculations. Figure 8b shows the simulated P1 as a function of L_C and experimental screw pitches with respect to the polymerization degree of PEG (nPEG). The P1 has a slight decrease as L_C increases, and the experimental screw pitch is also slightly affected by nPEG (for details, see section 3 of Supporting Information). The tiny difference between them may be due to the statistical deviation. Our simulations can not only reproduce the general features of self-assembly of PBLG-b-PEG/PBLG mixtures, but also provide chain packing information and allow us to get a deep insight into the formation mechanism of these hierarchical assemblies.

**Discussion**

Based on the simulation results, the physical principle of structural transition governed by interaction strength εRR was proposed. A transition from plain fibers to helical structures to abacus-like structures...
was found with increasing $\varepsilon_{RB}$. The interesting structures are the helical structures, which are formed at moderate values of $\varepsilon_{RB}$. The reason that the helical structures appear instead of abacus-like structures (higher $\varepsilon_{RB}$) and plain fibers (lower $\varepsilon_{RB}$) at moderate $\varepsilon_{RB}$ can be explained as follows. Provided that the abacus-like structures are formed, the translational entropy of block copolymers is lost as compared with the helical structures. This is because the rod blocks tend to be packed more ordered in the abacus-like structures than that in helical structures. Although the interfacial enthalpy is more favorable, it still cannot compensate for the loss of translational entropy, and thus the total free energy increases. On the other hand, if the plain fibers are formed, the rod blocks can be distributed more dispersedly than that in helical structures, and thus the translational entropy is more favorable. However, the interfacial enthalpy dramatically increases due to the dispersed packing of rod blocks, leading to the increase of total free energy. Therefore, a balance between the translational entropy and interfacial enthalpy decides the helical structures at moderate values of $\varepsilon_{RB}$. The formation of other structures at other $\varepsilon_{RB}$ is also due to the similar mechanism.

It should be noted that in the simulations, the chirality of polymers is not considered and the system is treated as a blend of achiral block copolymers and achiral homopolymers, although the polymers are chiral in the experiments. Due to the achiral feature of the simulation models, the co-existence of left-handed and right-handed helical structures could exist in the simulations, and in principle there should be equal number of left-handed and right-handed helical structures in a given system.

Regarding the effect of block length on the aggregate structures, the changes of rod and coil block length can bring about changes of balance between the interfacial enthalpy and entropy loss. As the rod block length $L_R$ increases, the hydrophobic blocks are more exposed to the solvents, inducing the interfacial enthalpy to increase. To maintain the system balance, the screw pitch $P_1$ of helical structures and twisting pitch $P_2$ of rod blocks both increase with increasing $L_R$ as shown in Fig. 5a (decreasing the entropy loss). On the other hand, with increasing the coil block length $L_C$, the coil blocks can cover the hydrophobic blocks more effectively, and the interfacial enthalpy decreases. However, the higher density of coil blocks at the rod-coil interface makes the entropy loss increase. Under the interplay between interfacial enthalpy and entropy loss, the pitches $P_1$ and $P_2$ have a slight change with increasing $L_C$ (see Fig. 5b).
Cooperative self-assembly of multi-component polymers provides a promising strategy to prepare complex aggregates with controlled structures. The multi-component polymers exhibit prominent advantages over single-component polymers in achieving controllable and multi-functional properties, facilitating the applications such as in drug delivery and nanoreactors. In this work, we reported the cooperative self-assembly of rod-coil block copolymers and rigid homopolymers. A variety of hierarchical nanostructures were predicted, such as helical and abacus-like structures. The helices with a homopolymer bundles covered by block copolymer chains are reminiscent of the structure of tobacco mosaic virus, in which proteins spontaneously assemble around the RNA template. The present research on the formation mechanism of hierarchical assemblies can be of practical significance for the construction of complicated biological analogs such as a model virus and subsequent investigation of its physiological behavior, e.g., cell penetration. Understanding the cooperative self-assembly of multi-component polymers also provides important information for the design and fabrication of advanced materials.

In summary, we applied Brownian dynamics simulations to investigate the self-assembly behavior of mixture systems containing rod-coil block copolymers and rigid homopolymers. The aggregate morphologies of mixture systems were found to be dependent on the interaction parameter \( \varepsilon_{RR} \), rod block length \( L_R \), coil block length \( L_C \), and mixture ratio \( \phi \). At higher \( \varepsilon_{RR} \), an abacus-like structure is formed. With decreasing \( \varepsilon_{RR} \), the morphology is transformed to helix, plain fiber, and then to unimers. The ordering information of rod blocks was provided. For the super-helices, two levels of the chain ordering were discovered. The block copolymers were helically wrapped on the homopolymer bundles to form helical string. Meanwhile the packing mode of the rod block exhibited a twisting manner. Based on simulation results, we constructed a phase diagram of morphology stability regions in space of \( L_R \) and \( \varepsilon_{RR} \) (or \( L_C \) and \( \varepsilon_{RR} \)). The screw pitches of the helical structures and twisting pitches of rod blocks were also calculated. The pitches increase with increasing \( L_R \), while they decrease slightly as \( L_C \) increases. In addition, the mixture ratio \( \phi \) also affects the pitches of helices. The simulation results were compared with experimental observations, and an agreement was obtained. The present work provides an insight into the formation mechanism of complex structures self-assembled from rod-coil block copolymer/rigid homopolymer mixtures.

Methods

The simulations were carried out by applying the simulator, coarse-grained molecular dynamics program (COGNAC) of OCTA. The simulator was developed by Doi’s group, which is public on a Web site. The reduced units used in COGNAC can be converted to real ones, which have been described in our previous work.

We considered a mixture system containing rod-coil diblock copolymers and rigid homopolymers, and constructed a coarse-grained model. The rod-coil block copolymer was modeled as a linear chain with \( m \) R beads of rod block and \( n \) C beads of coil block, denoted by the type of \( R_mC_n \). The rigid homopolymer molecule was represented by a rigid chain with \( x \) R beads (denoted by \( R \)). Figure 1a shows the illustration of \( R_mC_n \) block copolymer \( / R \), homopolymer mixture (for instance, \( R_CC_R \) mixture) model. The beads colored by red, green, and blue are hydrophobic rod block, hydrophilic coil block, and hydrophobic homopolymer, respectively.

To construct rod-coil block copolymer and rigid homopolymer molecules, potentials that should be given are bonding potential \( U_{mol} \) and nonbonding potential \( U_r \). The former can construct a desired molecule from atoms, while the latter describes intermolecular interactions. For rigid segments, the \( U_{mol} \) is composed of bond stretching potential \( U_{bond}(r) \) and angle bending potential \( U_{angle}(\theta) \). For flexible segments, there is no angle bending potential.

The bond stretching potential is a function of distance \( r \) between the chemically bonded beads, which is given by a harmonic potential

\[
U_{bond}(r) = \frac{1}{2} k_b (r - r_0)^2
\]

(1)

where \( k_b \) is the bond spring constant and \( r_0 \) is the equilibrium bond length. In this work, the value of \( k_b \) was set to be 10000 for all bonds to avoid the over-stretching of bonds. The bond length \( r_0 \) was set as 0.75 and 1.0 for the rod and coil blocks. The angle bending potential \( U_{angle}(\theta) \) for the rod block is given by a cosine harmonic function of the angle \( \theta \) between every two consecutive bonds:

\[
U_{angle}(\theta) = \frac{1}{2} k_\theta (\cos \theta - \cos \theta_0)^2
\]

(2)

where \( k_\theta \) is the angle spring constant, and \( \theta_0 \) is the equilibrium angle. The larger the \( k_\theta \) value, the more rigidity of the molecule chain. The magnitude of the constant \( k_\theta \) was set to be 10000 in all cases. To realize the rod block, the equilibrium angle \( \theta_0 \) was set as a value of 0.1° (close to zero), which is not zero so that the bond angle can be adjusted. More detailed information of the choice of simulation parameters can be found in our previous work.

The nonbonding potential \( U_r \) is given by the standard Lennard-Jones 12:6 potential acting between any pair of beads \( i \) and \( j \):
The twisting pitch can be calculated from the plot of $\cos(\theta_i)$ versus position along the axis.

The twisting of rod blocks can be described by $\cos(\theta)$ as a function of position of the rod block along the major axis of the helical string. The position of rod block is defined as the projection of the mass center of each rod block onto the major axis of helical string. For a rigid fiber, the major axis can be illustrated by the homopolymer bundle axis, while for a slightly flexible fiber, the major axis should be divided into 2 or 3 subaxes. The twisting pitch can be calculated from the plot of $\cos(\theta)$ versus position along the axis.

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Author Contributions
Y. L. and T. J. carried out the simulations and wrote the manuscript. C. C. and X. Z. designed and carried out the experiments. S. L. and J. L. directed the research and revised the manuscript. All authors reviewed the manuscript.

Additional Information
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