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Depletion driven self-assembly of block copolymer solutions by homopolymers†

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The addition of a non-adsorbing homopolymer to a block copolymer solution provides a convenient strategy for regulating its self-assembly. We systematically investigate the depletion effect from a homopolymer on the morphologies of AB diblock and BAB triblock copolymers in selective solvents. Increasing the homopolymer content results in larger spherical micelles, and the curvature of micelles is proportional to the square of homopolymer concentrations. A high enough homopolymer concentration may transfer micelles into vesicles. A deep analysis shows that the depletion effect produces attractive interaction between hydrophilic B blocks as well as their contraction on the micellar surface. The size of triblock copolymer micelles is not affected by homopolymers significantly, and spherical-to-wormlike micelle transition occurs at high homopolymer contents. These results have important applications for the precise design of self-assembled nanostructures of copolymer systems.

1 Introduction

Self-assembly of amphiphilic block copolymers in selective solvents offers a variety of nanostructures.[1–3] These nanostructures, including spherical micelles, worm-like micelles, vesicles, *etc.*, result from the delicate balance between the interfacial tension at the hydrophobic/hydrophilic interface and polymer conformational entropy. These structures have wide applications including in drug delivery,[4,5] catalysis,[6] *etc.* To control precisely and reversibly the morphology transitions of block copolymer solutions is extremely valuable for concrete applications but is also not easy. Traditionally, the morphologies can be controlled *via* changing the copolymer composition, solvent quality, temperature, and polymer concentrations. Adding non-adsorbing homopolymers to solutions provides a new strategy to regulate their self-assembly.[7] The chain length and concentration of added homopolymers can be adjusted conveniently. The depletion force, which arises from the osmotic force of homopolymer coils on two closed particles,[8] has been extensively studied in colloidal systems.[9] Similarly, the addition of homopolymers to dilute copolymer (or surfactant) solutions may induce depletion attraction between the formed micelles. Different from solid colloid particles, micelles are soft and the fusion between them may occur when the depletion force drives them to aggregation. Some experiments have revealed that macrophase separation and aggregation or flocculation of micelles can occur.[10–13] In semidilute or concentrated micelle solutions, added homopolymers result in the order–disorder phase transitions since depletion interaction affects the process of micellization itself inevitably.[14,15] It has shown that varying the molecular weight or concentration of homopolymers changes the aggregation number as well as the effective core radius of micelles.[7] Therefore, the versatility of these mixtures to produce ordered phases with a controllable structure and size could make them promising for the bottom-up assembly of copolymers for the formation of nanoscale materials. From a fundamental research viewpoint, studying the mechanism and laws of self-assembly represents one of the most important issues in polymer physics. In theoretical respect, the depletion interactions in soft polymer-based colloids mixed with linear homopolymers have been investigated by simulations.[16] However, to the best of our knowledge, there is no simulation works to handle the depletion driven self-assembly of block copolymer solutions by adding repulsive homopolymers.

Another interesting issue is whether the transition from spherical to worm-like micelles occurs only by controlling the content of added homopolymers. This morphological switch may lead to an increase of solution viscosity, which is important in therapeutic delivery[17] and secondary oil recovery.[18] Recently, it was observed that adding a small amount of homopolymer may trigger the fusion of micelles into worm-like micelles.[19] Similarly, a non-adsorbing polymer-induced sphere–cylinder transition in microemulsion droplets was observed.[20] While significant progress in experiments on depletion-induced morphology transition has been achieved, there has been a lack of in-depth understanding of the depletion effect of homopolymers so far.

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In this study, we aim at a systematic study on how the addition of repulsive homopolymers affects the phase behavior of block copolymer micellar solutions. The effects of the volume fraction of copolymers and homopolymers, interaction parameters as well as homopolymer chain length on the morphology are investigated in detail. More importantly, we found that the role of a repulsive homopolymer is two fold. One is to provide depletion force among micelles and drive them to aggregation. The other is to change the A/B interfacial tension by mainly extracting the solvents located on the micellar surface. The two factors lead to a variety of equilibrium morphologies. We revealed that the average radius of spherical micelles increases as a linear function of the square of homopolymer concentration, which provides a precise method to design micelle size and has potential application in drug delivery.

2 Model and simulation methods

Dissipative particle dynamics (DPD) simulations are used to handle polymer solutions. The detailed DPD simulation technique for polymer systems can be found in the literature.[21,22] By the use of coarse-grained beads, solvent molecules are modeled as single beads while polymers are modeled as chains connected by beads. All beads have the same size. Diblock and triblock copolymers are denoted as A_3B_1 and $B_1A_3B_1$, respectively. The subscripts denote the bead number for each component. A homopolymer is denoted as C_m where m varies from 5, 10 to 20. We choose the bead density ρR_C equal to 3 with R_C the bead diameter. As commonly used in DPD simulations we take the intracomponent repulsive parameter a_{ii} = 25 for all bead types, which simulates a liquid with the compressibility of water.[23] Other interaction parameters between different beads are a_{AB} = 60, a_{AC} = 200, a_{BC} = 100, a_{AS} = 100, a_{BS} = 20, and a_{CS} = 20. These parameters guarantee that B is hydrophilic and A is hydrophobic to selective solvent S (water), so that A constitutes the core of micelles while B forms the shell. These chosen parameters for copolymer molecules and solvents are similar to that for the system of surfactants in water proposed by Groot.[23] C is strongly repulsive compared to A and B, which represents the non-adsorbing characteristic of homopolymers to micelles. By test we find that when $a_{AC} \geq 100$ the morphology is insensitive to a_{AC}, then homopolymers form a depletion layer near the A/B interface and the entropy effect from the homopolymers plays an important role in the self-assembly of copolymer solutions. Also S is a good solvent for C. Simulations are carried out in a cubic box of $L_x = L_y = L_z = 30$ measured in units of bead diameter. Three bulk volume fractions of 2%, 5% and 10% of block copolymers (denoted as ϕ_{AB} or ϕ_{BAB}) are used. The bulk volume fraction of the added homopolymers (denoted as ϕ_c^0), which is defined as the ratio of the number of added C beads to that of all beads, varies from 0% to 15%. Simulations are performed with a certain time step value of $\Delta t = 0.05\tau$, where τ is the standard DPD unit,[21] and each simulation is considered to be in equilibrium for executing 10^5 steps. During the production run, one configuration is documented every 10^3 steps and 100 configurations are saved for further statistical analysis.

3 Results and discussion

3.1 The morphology of copolymer solutions with homopolymers

For pure diblock and triblock copolymer solutions at different bulk copolymer concentrations without C, all systems form dispersed micelles and single micelles retain their stable spherical state (left panels of Fig. 1 and 3). Increasing copolymer bulk concentration leads to an increase of the number of micelles, whereas the micelle diameters remain almost constant. For diblock copolymers, the solution with ϕ_{AB} of 10% has almost double the number of dispersed micelles compared to 5% solution. Furthermore, the micelle size of diblock copolymers is significantly larger than that of triblock copolymers. As the micellar core consists of a hydrophobic middle block of triblock copolymers, two ends of each chain have to lie on the micellar surface. This topological constraint indicates that the largest size of formed micelles should be smaller than chain length. In contrast, diblock copolymer micelles retain the A block inside, and its maximum diameter may approximately be twice the chain length.

Fig. 1 displays the influence of non-adsorbing homopolymer C_{10} on the morphologies of the A_3B_1 system with interaction parameter a_{AC} = 200. When homopolymers are added gradually,

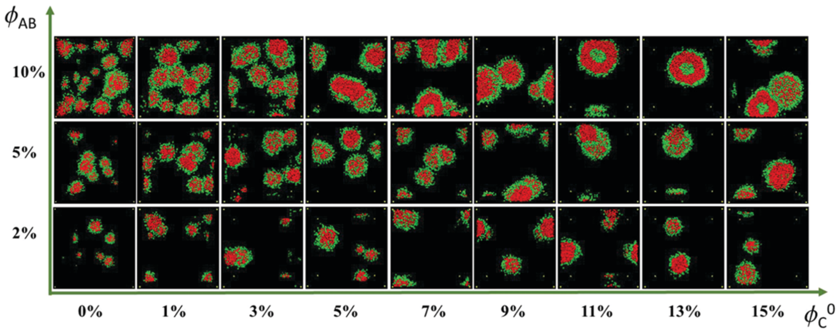

Fig. 1 The snapshots of A_3(red)B_1(green) diblock copolymer solutions with addition of homopolymer C_{10} (not display). The interaction parameters are a_{AB} = 60, a_{AC} = 200, a_{BC} = 100, a_{AS} = 100, a_{BS} = 20, and a_{CS} = 20.

the dispersed micelles decrease in number and their size increases accordingly. The decreasing number of micelles means that the aggregation number of each micelle should increase. Fig. 2 shows that the 1/*R* curvature is a linear decreasing function of ϕ_c^2 for 5% copolymer solution. Here the real concentration (effective volume fraction) of homopolymers ϕ_c is different from the bulk volume fraction ϕ_c^0. Since the beads' density remains constant in the simulation, ϕ_c is calculated by subtracting the volume occupied by all formed micelles. The calculation of *R* is carried out in the following procedure. After the system is in equilibrium, the coordinates of B beads (the surface layer) for all sphere-like micelles are obtained. For each micelle, we used the spherical or elliptical formula to fit these coordinates and obtain the volume of the micelle, and then we calculate the effective radius in terms of its volume. At last, the radius *R* is calculated by averaging the radii of different micelles. In 10% copolymer solution some micelles are aggregated, which results from the depletion force of homopolymers. Short cylindrical micelles may appear accompanied by more tight aggregation of spherical micelles. When excessive C is added, a larger spherical micelle is unstable since the strongly stretched A blocks prohibit further stretching. Alternately, vesicles may be formed with a significant lower stretching energy of A blocks. For 5% copolymer solution, two connected vesicles with rather small cores appear, whereas for 10% copolymer solution the formed vesicles have obvious large cores. The higher bulk copolymer concentration results in bigger vesicles.

The triblock copolymers display different self-assembled morphologies upon the addition of homopolymers. Fig. 3 shows how depletion force changes the phase behavior of dispersed micelles. At low copolymer content (2%), with increasing homopolymers the number of micelles decreases and their size increases accordingly. However, the increase of micelle size is not significant due to the topological feature of the triblock architecture. Since two B blocks of each chain must be located within the micelle shell, the A block inside the core can form a loop conformation when its two ends are close, it can also form a bridge conformation when its two ends almost lie on two opposite locations of a spherical (or cylindrical) surface (see the left part of Fig. 4). The topological constraint means that middle A blocks can only be stretched to some limited length for both loop and bridge conformations, which constraint the triblock micelle size and prohibits the appearance of large micelles, as shown in Fig. 4.

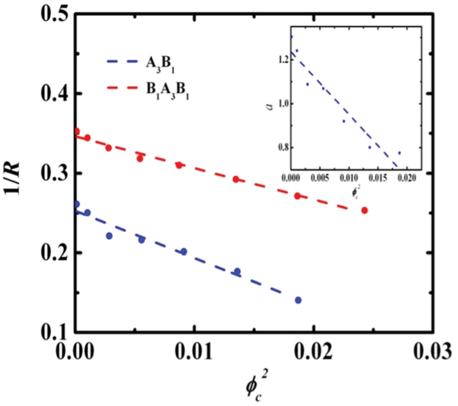

Fig. 2 The mean curvature of radius 1/*R* of diblock (blue) and triblock (red) copolymer micelles with a bulk concentration of 5% as a linear decreasing function of ϕ_c^2. The dots are from simulation results and dashed lines represent linear fittings. The inset shows that the surface area per molecule *a* in aggregated spherical micelles is inversely proportional to ϕ_c^2.

At higher copolymer content (5% and 10%) the dispersed micelles tend to aggregate firstly with adding C, a phenomenon similar to depletion-induced flocculation of colloids. Further increasing ϕ_c^0 leads to the partial fusion of aggregated micelles. Worm-like micelles begin to appear coexisting with spherical micelles. It is noted that these worm-like micelles have almost the same radius as spherical micelles. Also the average curvature of micelles displays a good linear relationship as a function of ϕ_c^2 as diblock copolymer micelles, as shown in Fig. 2. At high homopolymer content only two worm-like micelles closely packing are observed. An impressive feature for a triblock copolymer is the absence of vesicles at high ϕ_c^0, indicating the different conformational entropy loss between triblock and diblock copolymers. When enough homopolymers are added the depletion interaction makes the packing of B blocks more tightly. If triblock copolymers form a vesicle, many chains have to adopt loop conformations within the B-bead rich region. The middle A blocks will lose an amount of conformational entropy, which is unfavorable. Alternately, triblock copolymers tend to adopt cylindrical instead of spherical shape to minimize their interfacial energy as well as entropy.

One might expect that the molecular weight of homopolymers affects the phase morphologies significantly since a longer chain induces stronger depletion force between colloidal particles.[24] Here we used three homopolymers with different lengths of C_5, C_{10} and C_{20} while keeping the volume fraction of added homopolymers fixed. Counter-intuitively, the equilibrium phases do not exhibit important difference (Fig. 5–8). Therefore, the morphology is mainly controlled by the concentration of homopolymer monomers instead of chain length. The homopolymers provide driving force for approaching micelles. However, the key role of homopolymers is to vary the interfacial tension *via* changing the packing degree of copolymers, so that the self-assembled structure is independent of chain length.

The self-assembled morphology is insensitive to interaction parameter a_{AC} between C and A blocks. For a_{AC} = 100 the morphology of triblock copolymers (Fig. 9) displays a similar behavior to the case of a_{AC} = 200 (Fig. 3). Interestingly, at some special homopolymer content of ϕ_c^0 = 11% two cylindrical micelles form a helical structure under the depletion force, as shown in Fig. 10 that is an amplified picture of the correspond one in Fig. 8. Since C has some affinity to the A core, homopolymers are not strongly repulsive by micelles and only lead to moderate contraction of B beads on the surface. Consequently, the worm-like micelle has lower bending rigidity and a depletion-driven helical structure is formed from two wrapped micelles.

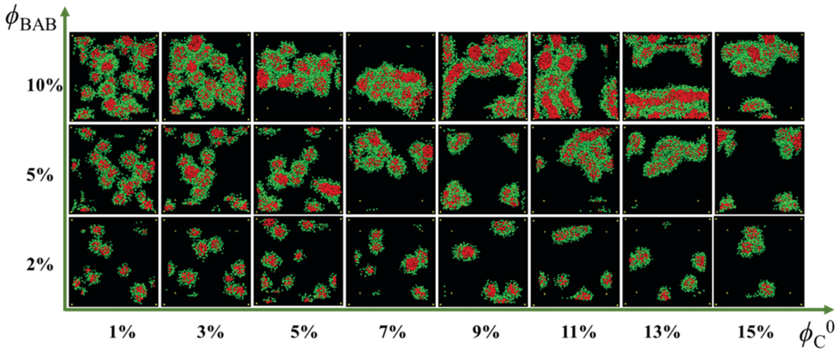

Fig. 3 The snapshots of $B_1A_3B_1$ triblock copolymer solution with addition of homopolymer C_{10}. All the interaction parameters and color codes are the same as in Fig. 1.

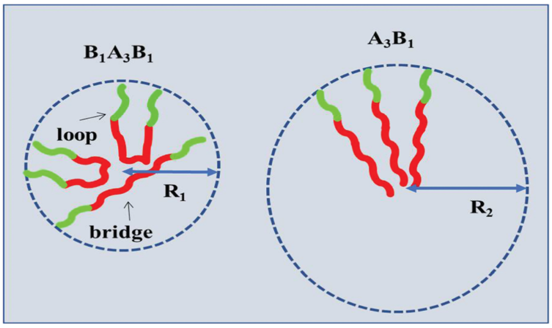

Fig. 4 The schematic conformations of a triblock copolymer (left) and a diblock copolymer (right) self-assembled into a micelle.

3.2 The mechanism of the depletion effect on the self-assembly of copolymer solutions

Early study of the effect of non-adsorbing polymers to copolymer micelles focuses on the corona part. Halperin pointed out that the presence of homopolymers results in increased screening of excluded volume interactions in corona if the corona layer is thick.[25] Therefore, the free energy variation from the corona part dominants the equilibrium structure and leads to an increase of the aggregation number, whereas the interfacial tension and molten core are not affected. This partly screening effect of excluded volume interactions in thick corona has been confirmed experimentally.[7] Our system is more like a surfactant system, the micelle shell contains in fact monolayer B beads and many solvents may still stay on the surface layer. Adding C allows exclusion of the solvents from the surface and makes B components more compact on the surface. Consequently, the average occupied area a of B beads on the micellar surface is reduced, which is confirmed by simulation results (the inset in Fig. 2). Also we found that the total volume of all micelles decreases with ϕ_c, which indicates that some solvents are excluded gradually from the micelles with addition of homopolymers. Therefore, repulsive homopolymers change the interfacial tension at the A/B interface because of the exclusion of solvents. It is in favor of minimizing incompatible micelle–homopolymer contacts and increases the micelle size.

We can study the self-assembly of copolymer solution in terms of the model proposed by Nagarajan[26] and Tanford[27] for a similar surfactant system. The free energy of each molecule in aggregated micelles f includes four parts as $f = f_{Tr} + f_{int} + f_{Head} + f_{Pack}$ (kT is unit energy). f_{Tr} is a negative constant contribution representing the transfer of a hydrophobic tail from water to the micelle core. The second term arises from the residual contact between water and the hydrophobic tail at the surface of the aggregate core, and it follows $f_{int} = \sigma \cdot a$ with σ being the interfacial energy per unit area and a being the surface area per molecule. The third term represents the repulsive interactions between head groups on the aggregate surface, which is

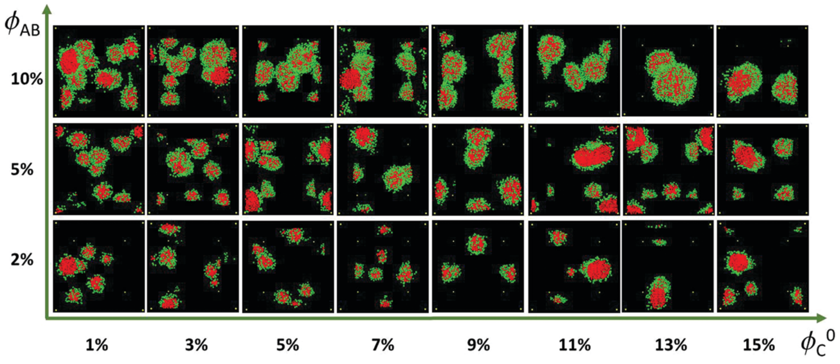

Fig. 5 The snapshots of A_3B_1 diblock copolymer solution with addition of homopolymer C_5. The interaction parameters are a_{AB} = 60, a_{AC} = 200, a_{BC} = 100, a_{AS} = 100, a_{BS} = 20, and a_{CS} = 20.

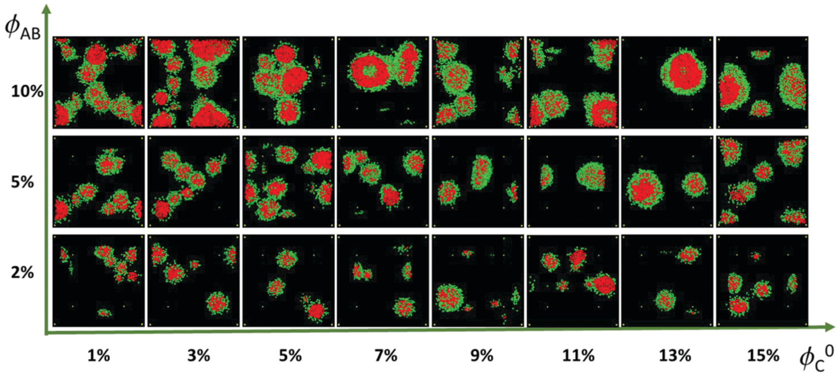

Fig. 6 The snapshots of A_3B_1 diblock copolymer solution with addition of homopolymer C_{20}. All the interaction parameters and color codes are the same as in Fig. 1.

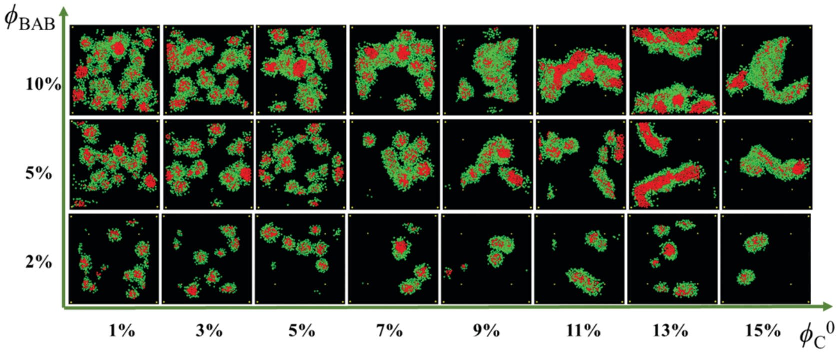

Fig. 7 The snapshots of $B_1A_3B_1$ triblock copolymer solution with addition of homopolymer C_5. All the interaction parameters and color codes are the same as in Fig. 1.

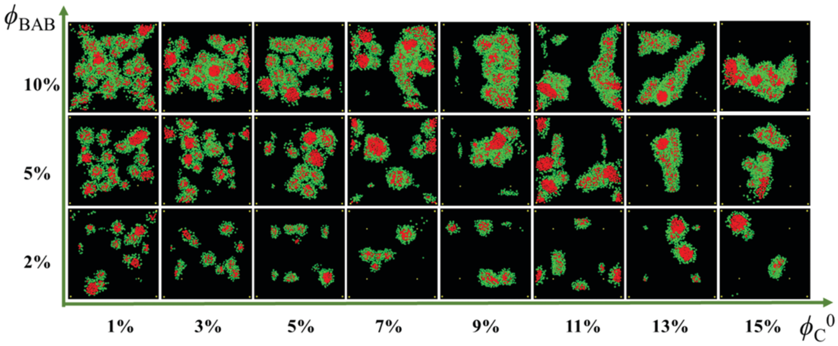

Fig. 8 The snapshots of $B_1A_3B_1$ triblock copolymer solution with addition of homopolymer C_{20}. All the interaction parameters and color codes are the same as in Fig. 1.

inversely dependent on a through $f_{\text{head}} = \alpha/a$ with repulsion parameter α. f_{Pack} is the stretching energy of tails packed in the confined core. For simplicity, we only consider AB diblock copolymers and $f_{\text{Pack}} = 3\pi^2R^2/(80Nb^2)$, here b is the monomer size, R the radius of the spherical micelle core and N the monomer (A component) number of a tail.[28]

Upon adding C, the total free energy becomes

$$f = f_{\text{Tr}} + f_{\text{int}} + f_{\text{Head}} + f_{\text{Pack}} + f_{\text{p}}. \qquad (1)$$

where f_{p} is the contribution from homopolymers. In order to consider the depletion effect we adopt the idea proposed by Safran *et al.*,[29] in which the authors investigated how the addition of non-adsorbing polymers promotes lateral contraction of the lipid layer in solution. In terms of their model, there is a depletion layer near the micellar surface. The A/B interface can be considered as a hard wall that excludes the homopolymers; the C polymers cannot penetrate inside the A-chain region. The homopolymer density is zero at the surface and

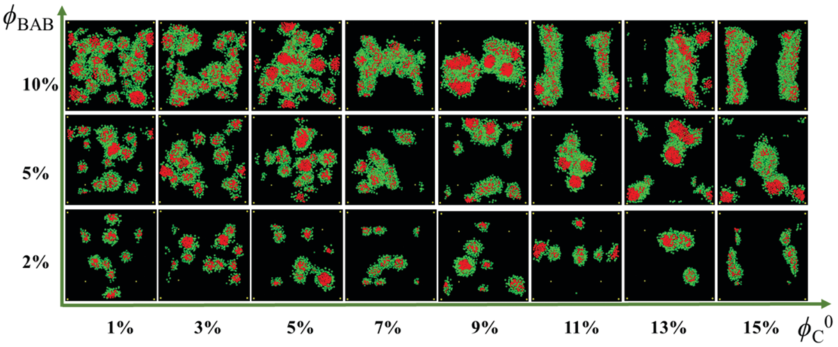

Fig. 9 The snapshots of $B_1A_3B_1$ diblock copolymer solution with addition of homopolymer C_{10}. All the interaction parameters and color codes are the same as in Fig. 1 except a_{AC} = 100.

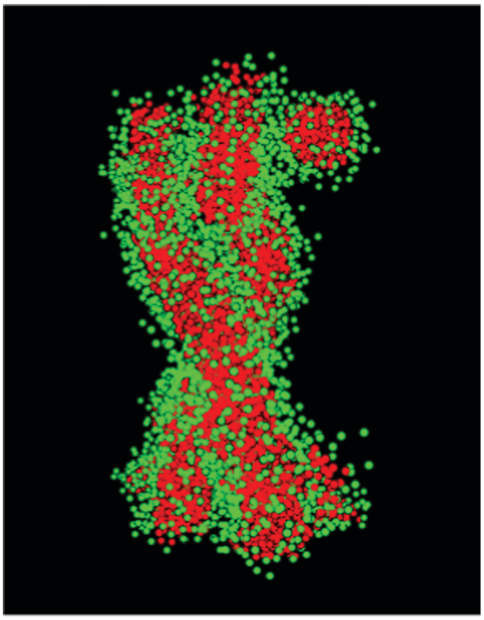

Fig. 10 The helical structure of triblock copolymer/homopolymer C_{10} complex solution with ϕ_{BAB} = 10% and ϕ_c^0 = 11%, which is an amplified picture of the correspond one in Fig. 9.

close to the bulk value far from the surface. There is still some homopolymers in contact with B-beads. We can find the number of C beads at some molecular distance from the hard wall, which represents the surface concentration of polymer monomers ϕ_{cs}. Based on a mean field argument,[29,30] ϕ_{cs} is related to the concentration ϕ_c far from the interface by $\phi_{cs} \sim 8\phi_c^2$.

The interaction between copolymers and homopolymers depends on the in-plane contact between homopolymer solutions and B-beads. Setting the interaction energy as $\beta b(\phi_{cs}/b^3)$ per copolymer molecule, the interaction is proportional to surface homopolymer concentration ϕ_{cs} adjacent to the surface of B-beads in a layer of thickness b. β is a positive constant that represents repulsive interaction of a single B block with a C polymer compared to the solvent environment. If the surface density of copolymers increases (with a larger B-bead number per unit area), the repulsive interaction of each copolymer molecule with a homopolymer will be reduced since the presence of other neighboring molecules reduces the in-plane contact of this molecule with polymer solution. Therefore, one can write the contact free energy of each molecule with polymer solution as $f_p = \beta\phi_{cs}(1 - b^2/a)/2b^2$. It can be seen that when B-beads are locally closely packed (means $a = b^2$) the polymer C cannot penetrate the B block layer and the interaction with polymer solutions vanishes. The second negative term of f_p indicates that the homopolymers tend to reduce the surface area a of each diblock copolymer molecule to avoid unfavorable contact with B blocks and lead to an effective attraction between neighboring molecules.

The volume of each A block is $v_0 = Nb^3$. Also one may have $Ra = 3v_0$ if the micelle core is approximately regard as a molten state of A beads. With the above quantities, eqn (1) is expressed as

$$f = \text{Const.} + \sigma \cdot a + \frac{\alpha}{a} + \frac{27\pi^2 Nb^4}{80a^2} + \frac{4\beta\phi_c^2\left(1 - b^2/a\right)}{b^2}. \tag{2}$$

Minimizing eqn (2) with respect to a one obtains the equilibrium equation

$$\sigma a_e - 27v_0 b/8a_e{}^2 = (\alpha - 4\beta\phi_c^2)/a_e. \tag{3}$$

Ignoring the stretching energy term (α is dominant) one gets $1/R \sim a_e \sim (\alpha/\sigma)^{1/2}(1 - 2\beta\phi_c^2/\alpha)$. The radius of micelles at equilibrium is inversely proportional to ϕ_c^2, which is in good agreement with simulation results (dots in Fig. 2). Even for triblock copolymer micelles this good linear relationship still holds. However, triblock systems show a lower slope, which should be due to the role of the conformational entropy of middle blocks. From expression (3) one can find that the equilibrium size of micelles is independent of the molecular weight of homopolymers. As mentioned previously, the dominant role of the depletion effect from homopolymers is to vary the A/B interfacial property, which is controlled by the surface homopolymer density ϕ_{cs}. Since it is mainly determined by the total amount of added C monomers, the molecular weight effect of homopolymers is expected to be unimportant here. The above statements demonstrate that the size of micelles may be precisely controlled by adding depletant polymers, which is of technical importance.

3.3 The dynamic process of micelle formation

It is worthwhile to consider the dynamic formation process of micelles in the participation of homopolymers. We indicated the structural evolution for triblock copolymer solutions ($\phi_{\mathrm{BAB}} = 5\%$) with the addition of homopolymer C_{10} ($\phi_{\mathrm{c}}^{0} = 11\%$), in which case the morphology in equilibrium is a worm-like micelle (see the ESI†). The simulation starts from a homogenous mixture followed by the rapid formation of small spherical micelles, similar to the system without C. However, this state is unstable. The dispersed micelles approach and aggregate gradually under the depletion force from homopolymers. On the other hand, homopolymers reduce the average distance between neighboring B beads on the micellar surface. The surface tension from the B-block contraction drags these copolymers in the contact region to leave and leads to micellar fusion, which results in the formation of a larger micelle. A new equilibrium is reached at which the interfacial tension is balanced by other interactions. The homopolymer-induced depletion force between different micelles cannot aggregate these particles further because of the translational entropy of large micelles.

4 Conclusions

In summary, we report the important ability of non-adsorbing homopolymers to induce the fusion of spherical amphiphilic block copolymer micelles in selective solvents. The depletion interactions influence both intermicellar and intramicellar packings. A mechanism of micelle stability is applied to make the phenomenon rational. The key role of depletants is to induce attractive force between surficial hydrophilic blocks and to reduce the surface area per molecule. Because of the constraint from the topological conformation, triblock copolymer systems display different morphological transitions with the addition of homopolymers. This study provides useful guidance on the precise control of the self-assembly structure of block copolymer solutions, which is important for their potential applications. The work with higher concentrations of homopolymers and amphiphilic copolymers is appealing. It is expected that macroscopic phase separation due to flocculation is likely to occur. Along with this phenomenon order–order transition is possible, which may exhibit a variety of interesting morphologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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