

Dependence of Size and Morphology on Shear Flow for PS-based Amphiphilic Block Copolymer Micelles in Aqueous Solution*

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Abstract This contribution focuses on the impact of shear flow on size and nanostructure of PS-based amphiphilic block copolymer (BC) micelles by varying the stirring rate and copolymer composition. The results show that the vesicles formed from diblock copolymer (di-BC) of PS-*b*-PAA remain with vesicular morphology, although the average size decreases, with the increase of stirring rate. However, the multi-compartment micelles (MCMs) formed from tri-block copolymer (tri-BC) of PS-*b*-P2VP-*b*-PEO are quite intricate, in which the copolymer first self-assembles into spheres, then to clusters, to large compound micelles (LCMs), and finally back to spheres, as stirring rate increases from 100 r/min to 2200 r/min. Formation mechanism studies manifest that vesicles form simultaneously as water is added to the di-BC solution, termed as direct-assembly, and remain with vesicular structure in the flowing process. While for the PS-*b*-P2VP-*b*-PEO copolymer, spherical micelles at initial stage can further assemble into clusters and LCMs, termed as second-assembly, due to the speeding-up-aggregation of the favorable stirring. As a result, an invert V-relationship between tri-BC micelle dimension and stirring rate is observed in contrast to the non-linear decreasing curve of di-BC vesicles. It is by investigating these various amphiphilic BCs that the understanding of shear dependence of size and morphology of micelles is improved from self-assembly to second-assembly process.

Keywords Self-assembly; Shear; Size; Nanostructure; Block copolymer

INTRODUCTION

Polymeric micelles self-assembled from amphiphilic block copolymers (BCs) in aqueous solution have been extensively made in the past decades^[1–3]. These micelles can segregate into distinct nanodomains due to the high immiscibility between their hydrophobic and hydrophilic blocks^[4, 5]. The micro-separated morphologies of the BCs, as well as their facile fabrication, make them an excellent precursor for the bottom-up material preparation^[6–10]. They spontaneously self-assemble to fundamental nanostructures with a high level of precision and integrating in order to achieve various functions such as catalysis, stimulus, bio-sensor, and drug delivery^[11–16]. Researches in nanomaterials have been increasingly focused on self-assembles, with their structures well-defined in two or three-dimensional nanopatterns otherwise inaccessible by lithographic processes^[17–19].

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The inherent ability of the BCs to form rich nanostructures arises from their covalent linkage of the copolymer segments, which possess their own distinct chemical and physical properties. The different fragments in amphiphilic BCs contribute to both types of macromolecular interactions in aqueous solution to form micelles for one of the blocks forming core or aggregating as a result of association of the insoluble blocks^[20]. Through careful design and selection of BCs and the assembly conditions to take advantage of these factors and their interplay, the designer may tune the nanostructures and properties according to the tailor made structure aim at a broader range of applications^[21, 22].

PS-based amphiphilic BCs are widely studied both experimentally and computationally due to the strong segregation force between hydrophobic PS and the other hydrophilic blocks^[23–26]. For example, Geng and his colleagues studied the cooperative self-assembly of PS-*b*-PAA and PS-*b*-P4VP diblock copolymers in DMF/H₂O mixtures and found that the mixture of the two copolymers self-assembled cooperatively into vesicles, instead of the spheres if used individually^[27]. To target desired structures, great efforts have been devoted to exploit the conditions of self-assembling to create PS-based hierarchical structures. The specific morphologies of the final micelles, such as spheres, rods, fibers, toroids, vesicles, lamellae, bicontinuous structures, large compound micelles (LCMs), and many others, are resulted from a balance between three contributions to the free energy, including core-chain stretching, corona-chain repulsion, and interfacial energy^[28].

Self-assembly process in solution is somewhat complex, as the compatibility of individual blocks with the prevailing solvent also becomes the influence factors. Factors influencing the final assembly structure include the compatibility between the two blocks described as the system composition and ambient conditions where the assembly takes place^[29]. System compositions, such as content of water, nature of solvent, presence of additives, and composition of the copolymer have been widely studied^[30–32]. External controls, such as UV irradiation, electricity, temperature and shear, are preferred for their easy manipulation, simple instrument and little interference^[33–37]. Typically, effect of shear flow on the phase behavior of amphiphilic systems, including block copolymers, surfactants, and liquid crystals, has attracted researchers for its important role in both basic research and practical application^[38]. However, most of these studies focus on the direct self-assembly process and lack an overview of the effect of stirring on the morphologies from different self-assembly mechanisms^[39, 40].

In this work, effects of shear flow (stirring) on the size and morphology of the micelles of two PS-based BCs in aqueous solution were investigated, *e.g.* vesicles directly assembled from PS-*b*-PAA and large-sized compound micelles (LCMs) second-assembled by PS-*b*-P2VP-*b*-PEO. The results were characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), and Marlvern Nanosizer. The di-BC micelles remain with vesicular morphology with the increase of stirring rate although their sizes decrease. However, the multi-compartment micelles (MCMs) from PS-*b*-P2VP-*b*-PEO transit from spheres to micellar clusters, to large compound micelles (LCMs), and finally back to spheres, as stirring rate increases from 100 r/min to 2200 r/min. We speculate that this is due to the different dependences of micelle formation on the stirring rate. Vesicles are formed *via* direct-assembly as water is added to the BC solution and very stable in the whole stirring process. While for the tri-BC system, spherical micelles can further assemble into clusters and LCMs, termed as second-assembly, due to the orthokinetic micelle aggregation at favorable stirring rates. At high stirring rate, the intense stirring destroys the entanglement of LCMs and leads to the formation of spheres. As a result, an invert V-relationship between micelle dimension and stirring rate is observed. Our results complement the comprehension of shear dependence of size and morphology of micelles from self-assembly to second-assembly process.

EXPERIMENTAL

Sample Preparation

The block copolymers in this work, PS(15000)-*b*-PAA(1600) and PS(75000)-*b*-P2VP(21000)-*b*-PEO(16500) (the numbers indicate the molecular weights of the blocks) were purchased from Polymer Source Canada and used as received. The copolymer (0.01 g) was first dissolved in a 1 mL of common solvent (dioxane for di-BC and THF for tri-BC) in a cone-like vial. The solution was left to stir overnight at different rates depending on

experimental requirement. Afterwards, 15.0 wt% deionized water was added dropwise to the solution under continuous stirring to induce the self-assembly of the copolymer. The resulting micellar solution was sealed and stirred at the same stirring rate for 96 h. Then 4–5 fold excess of water was added to the solution to kinetically lock the micelle morphologies. Finally, the mixture was dialyzed in dialysis tubes with distilled water for a few days to remove the solvent.

Transmission Electron Microscopy (TEM)

In order to characterize the morphologies of micelles, regular TEM was executed on a JEOL JEM-1011 transmission electron microscope with an acceleration voltage of 100 kV. A drop of the micelle solution was transited onto a TEM copper grid and the excess solution was blotted away with filter paper. The samples were allowed to dry in atmosphere and at room temperature for 1 day before TEM observation.

Size Distribution Measurement

To investigate the size changes of the vesicular micelles, dynamic light scattering (DLS) experiments were conducted on a Multi-angle Light Scattering (MALS) instrument equipped with a digital correlator (QELS 690 nm) at 90°. Water was first filtered with a 0.22 μm Millipore filter into a clean scintillation vial. Then the stock micelle solutions were filtered through a 450 nm Millipore filter before transferring to the vial. All the DLS measurements were carried out at 90° scattering angle and at room temperature.

Due to the characterization limitation, DLS is not applicable for calculating the size distribution of large-sized PS-*b*-P2VP-*b*-PEO micelles. Instead, the average size was measured on a Marlvern Nanosizer Nano-ZS 90 instrument. The dialyzed stock micelle solution was distilled into a scintillation vial and all the measurements were carried out at 90° scattering angle and at room temperature.

RESULTS AND DISCUSSION

Impact of Stirring Rate on the Micelles of Di-BC of PS-*b*-PAA

The self-assembled micellar morphology of the PS-*b*-PAA copolymer was examined with TEM. Figure 1 gives the typical images for the system with 1 wt% copolymer and 15 wt% water concentration in dioxane at different stirring rates. These TEM images show that the center of the micelles is brighter than the periphery, indicating that they are all vesicular morphologies. The vesicles seem to be aggregated at low stirring rate of 100 r/min (Fig. 1a), and then disperse and become smaller with the increase of stirring rate (Figs. 1b–1d). However, the vesicle membrane thickness values are quite similar with *ca.* 20 nm, which phenomenon was also proposed by Liu and his colleagues in a PS-*b*-PAA/P(S-*co*-MAA) system, where the vesicle size increased with increasing initial polymer concentration, but the membrane thickness remained constant^[28].

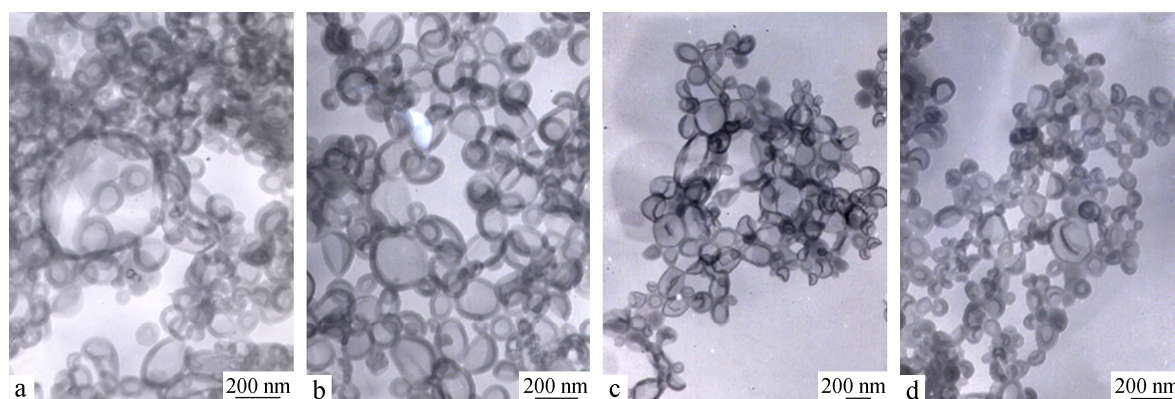


Fig. 1 Micellar morphologies characterized by TEM of PS-*b*-PAA diblock copolymer at different stirring rates: (a) 100 r/min, (b) 500 r/min, (c) 900 r/min, (d) 1600 r/min

The size distribution of vesicles was investigated by dynamic light scattering experiment, as shown in Fig. 2. The hydrodynamic radius (R_h) peak at 100 r/min is broad in a wide range of 50–1300 nm (Fig. 2a). Then with the increase of stirring rate, R_h peak drops significantly to around 190 nm at 500 r/min (Fig. 2b). As the stirring rate continues to grow, R_h decreases to around 110 nm (Fig. 2c) at 900 r/min, and finally to around 90 nm at 1600 r/min (Fig. 2d). It is evident that the size of the vesicles is strongly dependent on the stirring rate at the range of 100–900 r/min, but becomes flat at high stirring range of 900–1600 r/min. In accordance, the distribution becomes uniform and narrower in order of increasing stirring rate. Combined with TEM observations, it can be concluded that when the equilibrium vesicles are formed, the stirring rate only changes the micellar size while the vesicular morphology remains constant. As an incorporation, Yu and Jiang studied a P4VP-*b*-PS-*b*-P4VP triblock copolymer in dioxane/water and found that the size of resulting toroids decreased with the increase of stirring rate but the toroidal structure was maintained^[41].

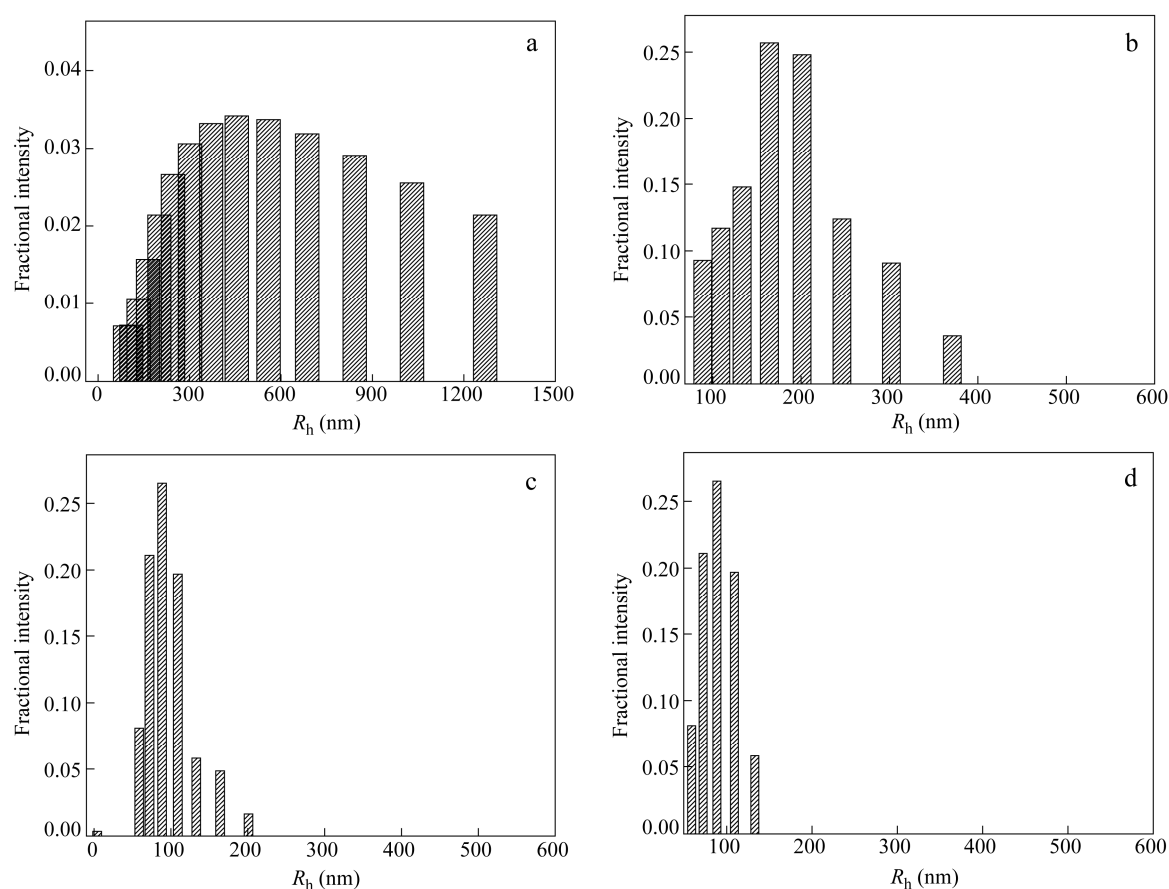


Fig. 2 Hydrodynamic radius (R_h) distribution of the vesicle changes with the stirring rates: (a) 100 r/min, (b) 500 r/min, (c) 900 r/min, (d) 1600 r/min

In order to study the formation mechanism of the vesicles, aliquots were extracted from solutions at different stages and then added with excess of water. In this case, the formation process can be speculated by quenching the intermediate structures. We found that the formation of vesicles at all the stirring rates was quite similar and just referred at 500 r/min as an example. Spheres at the initial stage can be considered as the precursors of the vesicles (Fig. 3a). Then the spheres are swollen and the PS-core chains begin to dissociate. As time passed, the spheres may become adhesive contacts and fuse, collapse, and then break in the center to form the vesicular nanostructure (Fig. 3b). Due to the equilibrium structure of vesicle^[30], no further assembling takes place in the following process, *e.g.* the vesicle is directly self-assembled from the di-BC molecules (Fig. 3c).

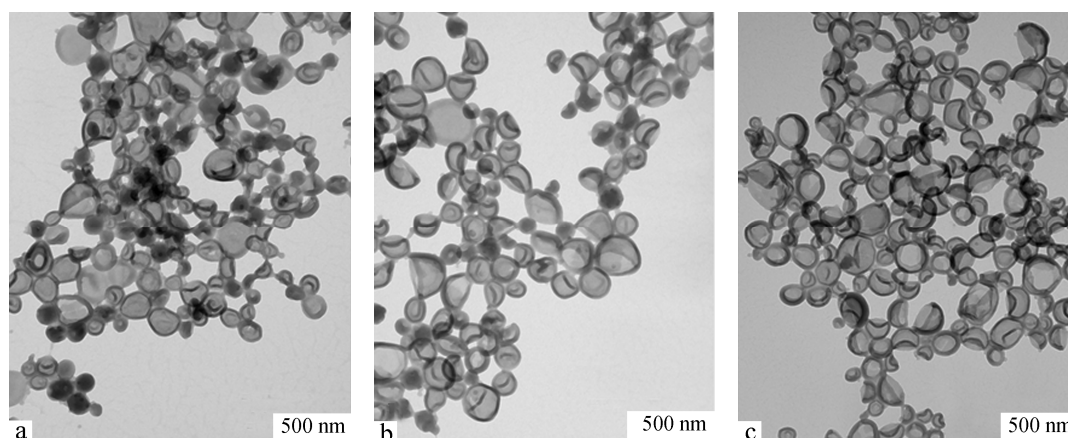


Fig. 3 TEM images of the formation of the vesicles by PS-*b*-PAA diblock copolymer in dioxane/water at 500 r/min: (a) 0 min, (b) 5 min, (c) 10 min

Effect of Shear Flow on MCMs of Triblock Copolymer of PS-*b*-P2VP-*b*-PEO

In contrary, the tri-BC shows another morphological evolution. Figure 4 presents the TEM images of the structures obtained by PS(75000)-*b*-P2VP(21000)-*b*-PEO(16500) copolymer at various stirring rates. This copolymer first self-assembles into spheres at the stirring rate of 100 r/min (Fig. 4a). For this PS-*b*-P2VP-*b*-PEO triblock copolymer, micelles are consisted with PS (red), P2VP (blue) and PEO (turquoise) as cores, shells and coronas, respectively^[42], as shown in the schematic image in Fig. 4(a). As the stirring rate increases to 500 r/min, clusters aggregated with spherical micelles begin to form (Fig. 4b). Then at 900 r/min, large-sized MCMs with spheres aligned perpendicularly to the shuttle-like contour are observed (Fig. 4c). By further increasing the stirring rate to 1500 r/min, LCMs with disk-segments are found as shown in Fig. 4(d). However, the LCMs almost disappear at the stirring rate of 2200 r/min. Instead, small spheres become the dominant morphology in Fig. 4(e).

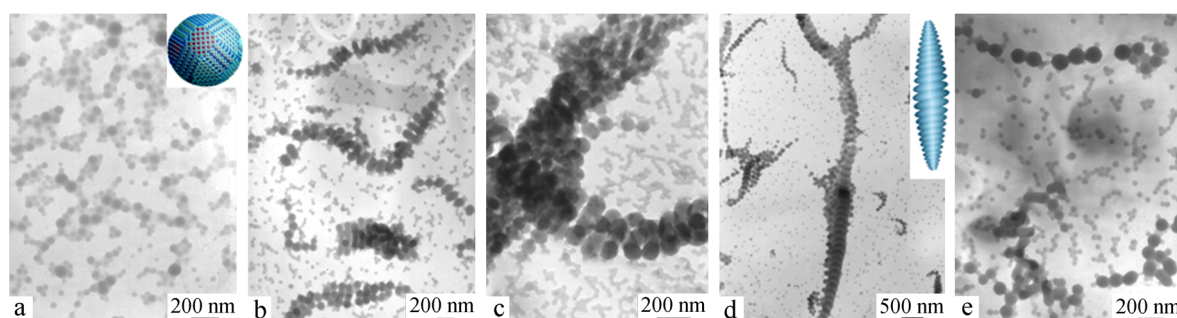


Fig. 4 Morphologies formed from PS-*b*-P2VP-*b*-PEO copolymer at various stirring rates: (a) 100 r/min, (b) 500 r/min, (c) 900 r/min, (d) 1600 r/min, (e) 2200 r/min (The schematic images inserted in (a) and (d) designating the spheres and LCMs, respectively.)

The MCMs for the tri-BC first aggregate to LCMs but finally evolve back to spheres, indicating that a critical shear rate, at which the micelles reach their maximum dimension, exist due to the competitive interplay between the shear flow and the interfacial tension of the micelles^[43]. Spheres self-assembled at low stirring rate are with high interfacial tension and more likely to aggregate to form large micelles in order to reduce interfacial energy. Meanwhile, a shear flow tends to bring polymer molecules and polysomes clusters closely associate and thereby speeds up the aggregation kinetics of sticky species, known as “orthokinetic” aggregation and usually appears in solutions of sticky moieties^[44]. Below the critical stirring rate, stirring is favorable for the formation of LCMs, which is a second-assembly process of the spheres. When above the critical rate, the intense shearing

force overwhelms the hydrophobic interaction between the micelle and the solvent and then takes the dominant role in the system. The large-sized micelles will fracture and are dissolved into small spheres with the diameters quite similar to the spherical micelles at low stirring rate.

Different Size Dependence on Stirring Rate in Vesicles and LCMs

To provide an overview of the impact of shear on the micelles of vesicles and MCMs, the change in average size as a function of stirring rate is illustrated in Fig. 5. For the vesicles of PS-*b*-PAA, the average size shows a nonlinear relationship with the increase of stirring rate (Fig. 5a). R_h decreases sharply from 510 nm to 184 nm as the stirring rate increases from 100 r/min to 500 r/min, and then slightly changes from 110 nm to 89 nm in the regime from 900 nm to 2200 nm. For LCMs of tri-BC, the size change is quite different (Fig. 5b), where an invert V-shape curve is observed compared with vesicles. The average size calculated from the Nanosizer first increases from 190 nm to 2.6 μm , reaching the maximum dimension at around 1500 r/min, and then decreases to 274 nm in the order of increasing stirring rate.

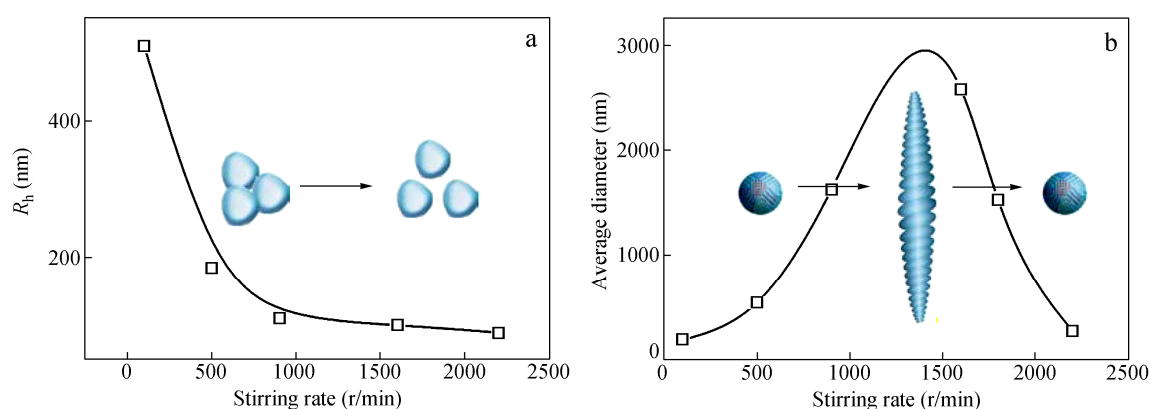


Fig. 5 Size dependence on stirring rate in (a) vesicles and (b) LCMs

The distinct size dependence on stirring rate for vesicles and MCMs is attributed to their different formation mechanisms. The vesicles are formed *via* the direct self-assembly of the PS-*b*-PAA copolymer. As water is added to the copolymer solution, the spheres are formed and then transformed into vesicles in a very short time. Once the vesicles are uniformly dispersed in the solution, increase of stirring rate provides little influence on the size of the micelles due to the stable structure of vesicles^[45]. As a result, R_h decreases significantly at the first stage of 100–900 r/min and then becomes flat in the following regime from 900 r/min to 2200 r/min. In this case, stirring might only play the role in the distribution of the micelles, reducing the contact and the adhesion of the vesicles. In the whole process, the other system magnitudes, such as polymer concentration, nature of solvent and temperature, remain constant. Consequently, the configuration of the vesicle at different stirring rates keeps constant, which results in the constant membrane thickness.

For the case of tri-BC of PS-*b*-P2VP-*b*-PEO, LCMs are formed from the second-assembly of spherical micelles, as discussed in the part of “effect of shear flow on MCMs of triblock copolymer of PS-*b*-P2VP-*b*-PEO”. Under the critical stirring rate, shear flow is appreciated for the formation of LCMs. Then as the shear rate increases, the large micellar aggregates are destroyed under the power of intensive shear stresses, leading to the re-formation of spherical micelles. Note that the secondary self-assembly process is seldom reported in the self-assembly process due to the hydrophilic effect of spherical micelles and the equilibrium structure of vesicles. For most of PS-based BCs, their sizes might change due to the morphological changes, but not due to the formation mechanisms. By comparison with the two curves and combined with TEM images, it is clear that the different roles of the stirring played in the formation mechanism of vesicles and MCMs give rise to the different size dependence on stirring rate for the two categories of micelles.

CONCLUSIONS

This work contributes to study the effects of stirring rate on the size and morphology of the micelles of two PS-based BCs in aqueous solution. The vesicles directly self-assembled from PS-*b*-PAA remain with vesicular morphology as the stirring rate increases from 100 r/min to 2200 r/min, although their sizes decrease significantly. In comparison, micellar sizes of tri-BC of PS-*b*-P2VP-*b*-PEO show an invert V-shape relationship with the stirring rate. The difference of size dependence on stirring is resulted from the formation mechanism of the micelles. Vesicles are formed *via* direct-assembly as water is added to the BC solution and are very stable in the whole stirring-conducted range. Stirring might only play the role in dispersing the vesicles, reducing contact and adhesion of the vesicles, and making a decrease in the average R_h . LCMs are formed as a coalescent result of the shear flow and the interfacial tension of the micelles. The existence of the critical stirring makes the spheres first fuse to form LCMs. With the execution of high stirring rate on the LCMs, the intense force destroys the entanglement of the chains and leads to the disassembly of LCMs. The results are characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), and Malvern Nanosizer. Our work expands the toolbox of block copolymer morphological control on self-assembly and offers an improved understanding of shear flow on micelles from different self-assembly processes, *i.e.* direct-assembly and second-assembly.

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