Molecular Architecture Effect on Self-Assembled Nanostructures of a Linear-Dendritic Rod Triblock Copolymer in Solution

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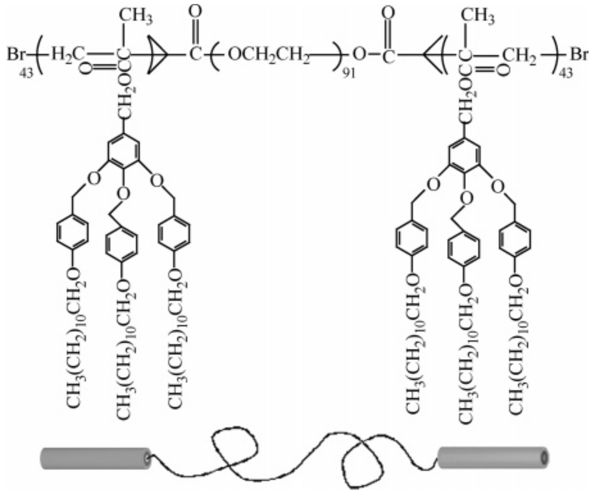
Block copolymers have been one of the most important topics in polymer chemistry and physics for the last two decades.[1] In a dilute solution with a selective solvent for one block, a block copolymer may self-assemble into different nanostructured objects, each of which comprises a dense insoluble core and an outer less dense shell of the soluble segment.[2] To control the structure of an block copolymer self-assembly in solution, one must manipulate the balance among the interfacial energy, repulsion of soluble blocks in shells, and the entropy penalty of insoluble blocks packed in cores.[3] For a block copolymer with a given chemical structure, it has been demonstrated that adjusting the composition of the block copolymer and solution conditions can effectively change the self-assembly morphology.[4] On the other hand, block copolymers with novel chemical structures and molecular architectures are highly desired, of which the self-assembly behaviors are suspected to be new and interesting.[5]

With abundant experimental results reported on flexible block copolymers solution self-assembly, only a few examples of rod−coil or semirod−coil block copolymers in selective solvents have been investigated.[6] Compared to flexible chains that will be significantly stretched, rodlike blocks lose much less entropy when they are packed in micelle cores. Therefore, rod−coil copolymers are conceived to possibly have different self-assembly behaviors from conventional block copolymers. We report here the synthesis and solution self-assembly of a triblock copolymer containing two hydrophobic blocks that were monodendron-jacketed polymethacrylate (PDMA) obtained by polymerization of a generation 1 (G1) Percec-type dendritic methacrylate[7] and a middle hydrophilic flexible block of poly(ethylene glycol) (PEG). Compared with conventional polymers with polymethacrylate (PMA) backbones, PDMA is more rigid due to the steric hindrance imposed by the bulky dendritic side groups attached to each repeating unit.[7,8] Therefore, we consider our G1 dendronized PDMA blocks to be semirigid. We have investigated the self-assembly behavior of the resultant triblock copolymer in a solvent mixture of THF and water using the water-adding method.[9] In addition to the spherical and cylindrical micelles, twisted cylindrical micelles were found to form helices at sufficient high water content, which were able to aggregate and become super-helices and super-rings like "olive crowns". Our experimental results reveal that block copolymers comprising dendronized blocks and triblock architecture could pave the way for the next level of complexity in materials synthesis.

Scheme 1. Chemical Structure and Schematic Representation of the Triblock Copolymer



The triblock copolymer of PDMA-*b*-PEG-*b*-PDMA was prepared as described in the Supporting Information. The chemical structure and schematic representation of this copolymer are shown in Scheme 1. The gel permeation chromatography (GPC) analysis gave a number-average molecular weight (M_n) of 62 900 and a relatively narrow polydispersity of 1.19 for the copolymer. The M_n of the copolymer (94 200 g/mol) and the total DP for the PDMA (86) calculated from ^{1}H NMR measurements were always larger than the GPC measurements. This reflected that the dendritic polymer took a compact molecular shape in solution and the hydrodynamic volume of the copolymer was smaller compared to that of the linear PSt standard with the same molecular weight.

We preliminarily characterized the bulk properties of the resultant PDMA$_{43}$−PEG$_{91}$−PDMA$_{43}$ by using DSC (differential scanning calorimetry) and WAXS (wide-angle X-ray scattering). It is known that the homo-PEG with M_n of 4000 g/mol possesses a melting temperature around 60 °C,[10] and the homo-PDMA exhibits a hexagonal columnar liquid crystalline (LC) phase (Φ_H) below 90 °C.[11] However, for the entire temperature range from −50 to +150 °C, no latent heat corresponding to phase transitions of the PEG and PDMA blocks was detected for the copolymer during the DSC cooling and heating scans. Only a glass transition was observed at T_g of 44.7 °C. The WAXS experiments demonstrated an amorphous halo at high $2\theta \sim 20°$, with the halo maximum presenting a d spacing of 0.45 nm, indicating a molten state of the PEG. At low 2θ around 2.264°, a single strong diffraction peak was observed. However, the absence of the higher order diffraction in the low 2θ region indicated no long-range ordered Φ_H phase of the PDMA blocks. The d spacing of 3.9 nm corresponding to the low angle diffraction was close to that of (110) found in the homo-PDMA Φ_H phase.[11,12] We speculated that the PEG and PDMA blocks were partially miscible, and the copolymer thus lacked long-range ordered

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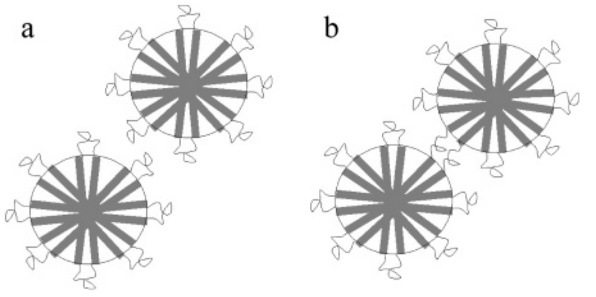

Figure 1. Schematic representation of core−shell nanostructures formed by a self-assembly of the linear−dendritic rod triblock copolymer: (a) core-fringe; (b) bridge.

microphase separation structure in bulk state. In this case, both the crystallization of PEG and the LC transformation of PDMA became difficult. Moreover, the T_g of the copolymer decreased significantly compared with 52 °C for the homo-PDMA.[13]

With the amphiphilic nature of the triblock copolymer, the PEG and PDMA blocks could be phase separated in a solvent mixture containing water. The self-assembly of the copolymer micelles brought about the hydrophobic cores of PDMA and the hydrophilic shells of PEG. As illustrated in Figure 1, the triblock copolymer may pack the PDMA blocks in the same micelle with the middle PEG blocks looped in the shell, leading to a core-fringe structure (Figure 1a). It is also possible that the two PDMA blocks of a copolymer molecule insert into different cores, leaving the PEG block as a bridge connecting neighboring micelles (Figure 1b). Both the spherical and cylindrical micelles of the triblock copolymer were observed after sufficient amount of water was added into the THF solution of the triblock copolymer. We found that the micelle structures were water content dependent. At a water content below 10 wt %, the copolymer solution remained transparent. Further adding water gave a bluish solution, implying the occurrence of self-assembly. The copolymer self-assembled into spherical (Figure 2a) and cylindrical (Figure 2b) micelles when the water content fell to 10−20 and 20−40 wt %, respectively. Interestingly, as the water content went higher than 40 wt %, in addition to the cylinders, another two typical aggregates, i.e., super-helices (Figure 2c) and super-rings (Figure 2d) appeared, with the lateral dimensions much larger than those of the spherical and cylindrical micelles.

As evidenced in Figure 2a, the spherical micelles are well separated. This indicates that each copolymer molecule prefers packing the two PDMA blocks in the same sphere, forming core-fringe structure. The dynamic light scattering (DLS) experiment revealed that the spherical micelles in solution possessed a hydrodynamic radius (R_h) of 18 nm with a narrow size distribution ($\mu/\Gamma^2 = 0.02$). After complete removal of solvent, the diameter of dried spheres measured by TEM was approximately 30 nm. Compared with the micelles in solution, the dimension of the dried micelles was only slightly decreased, indicating that the semirigid PDMA blocks helped to avoid drastic collapse of the micelles during drying, and thus retained the micelle shape formed in solution. For the homo-PDMA in Φ_H phase, the projection of each repeating unit on the chain (rod) axis is nearly 0.25 nm.[11] Assuming that the conformation of the PDMA blocks in the micelle core is similar to that in the Φ_H phase, we estimated the chain length of the PDMA block with DP of 43 to be 11 nm. Therefore, the spherical micelles in dry state should have a diameter of the PDMA cores of approximately 22 nm, and a PEG shell thickness of nearly 4 nm.

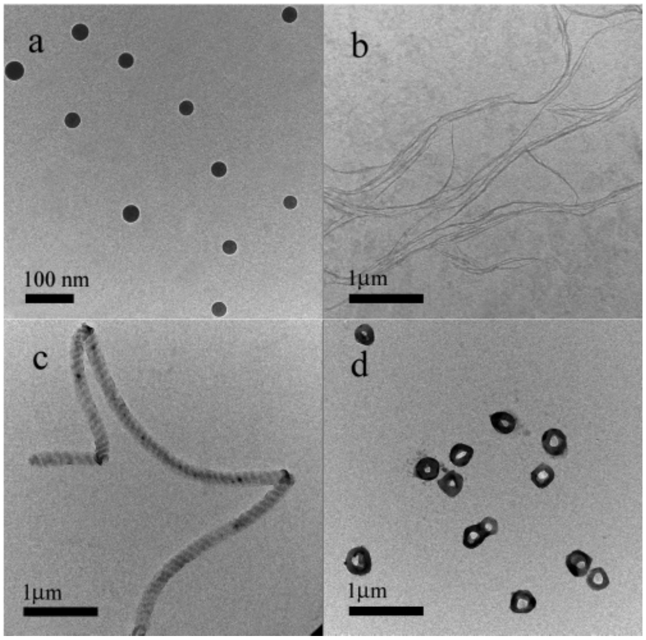

Figure 2. TEM images of the micelles and aggregates assembled by the triblock copolymer in THF/water solution, with the water contents of 20 (a), 30 (b), 45 (c), and 50 wt % (d), respectively.

Figure 2b shows that the cylindrical micelles formed at a water content of 30 wt % tend to aggregate paralleled to be bundles. Therefore, in addition to the core-fringe structure, the triblock architecture could also lead to the bridging of PEG chains between micelles, as represented in Figure 1b. The diameter measured from the individual dried cylindrical micelles was approximately 33 nm under TEM. Compared with that of the spherical micelles, the diameter of the cylinders was slightly increased. From a geometric point of view, the transformation from spherical to cylindrical micelles of the triblock copolymer may be due to the decreasing of the average interface area occupied by per PEG loop.[14] Recently, Wu et al. have reported that for a coil−rod diblock copolymer of poly(styrene-*block*-(2,5-bis[4-methoxyphenyl]oxycarbonyl)styrene) forming spherical micelles in dilute solution, the cores with the insoluble rodlike blocks may contain more than 50% solvent in the highly packed state.[15] In our case, we speculated that the micelle cores were also swollen by the solvent mixture. With increasing the water content, the solvent mixture became poorer for the semirigid PDMA blocks, and the micelle cores were packed more densely, leading to the average interface area per PEG loop decreased. Therefore, the PEG loops were more stretched in the direction perpendicular to the interface due to the repulsion from neighboring loops.

One may expect that further increasing the water content gives the formation of lamellae and/or vesicles, as reported by Eisenberg et al.[16] However, in this research, when the water content exceeded 40 wt %, large aggregates of super-helices and super-rings appeared (see Figure 2, parts c and d) with a coexistence of the cylindrical micelles (see Figure 3). The super-helices possessed a diameter of around 100 nm and a pitch length of approximately 50 nm; and their contour

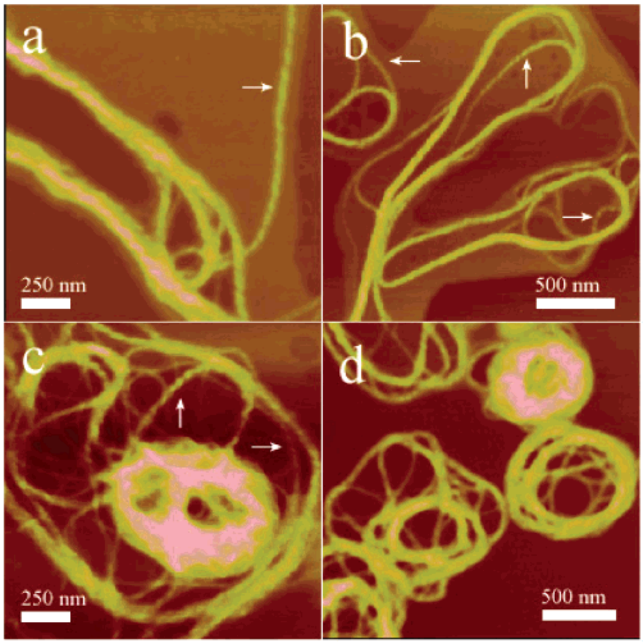

Figure 3. AFM images of the twisted cylinders and their aggregates of the triblock copolymer. The water content of the THF/water mixture was 45 wt %: (a and b) super-helices; (c and d) super-rings.

length could reach several tens of micrometers. For the super-rings, the ring widths and diameters were approximately 100 nm and 350–400 nm, respectively. We utilized AFM to explore the detail structures of the cylinders and the large aggregates absorbed and dried on fresh mica surface. As pointed by the arrows in Figure 3, the single cylinders with the diameter of 33 nm are in fact spirally twisted toward helices, with a well-defined pitch length of about 50 nm that is identical to that of super-helices. Moreover, the AFM experiments clearly revealed that both the super-helices and the "olive crowns"-like super-rings were resulted from the aggregation of the twisted cylinders.

The helical superstructures due to the self-assembly of our triblock copolymer in solution look similar to that found in the rod–coil copolymer of polystyrene-*b*-polyisocyanopeptide.[17,18] Such tertiary chiral architectures in synthetic block copolymers obtained in solutions are believed to be tightly related to their secondary structures with chirality.[18] Despite the fact that the studied copolymer lacks well-defined chiral center in its primary structure, both right- and left-handed helices can be observed as evidenced in Figure 2c and Figure 3, which are similar to that described by Sommerdijk et al.[19] One possible reason is that the Percec type dendronized PDMA blocks may carry nonnegligible tacticity.[18] Although the ATRP method usually leads to an atactic polymer, the bulky G1 pendant groups can provide a significant steric hindrance during polymerization of the monomers, which may assist the PDMA backbones adopting isotactic and/or syndiotactic configuration. If it is the case, there are chiral, although not homochiral structures along the PDMA chains. Particularly, those stereogenic centers close to the segment linkages may well give rise to a helical bias of the interface of the cylindrical micelles. Moreover, it is known that the Percec type dendritic groups (and also the polymers) may form supramolecular helical structures containing a mixture of left and right-handed helices in condensed state.[20] Recently, it has been demonstrated that the helicity of these supramolecular structures is also created and maintained in solvophobic solution and a single helical direction can be selected by a stereocenter.[21] We expect that the THF/water mixture may provide a solvophobic solvent for our triblock copolymer, which help to retain the helical conformation of the PDMA blocks that can further induce the formation of the spirally twisted cylinders. In addition, we consider that the triblock architecture may also facilitate the formation of the morphological chirality. When forming the core-fringe structure, the macroconformation of the triblock copolymer can be referred as once-folded chain, wherein the fold is composed of the PEG blocks. In this sense, the self-assembly of our triblock copolymer is analogous to the chain-folding crystallization of linear polymers. It is well-known that achiral crystalline polymers, e.g., polyethylene (PE), are able to form twisted lamellae.[22] Keith and Padden have proposed a general mechanical model to explain the lamellar twisting of polymer crystals on the basis of unbalanced surface stress.[23] Structure investigation has revealed that the PE chains within the crystalline core are tilted with respect to the lamellar surface normal. The chain tilting induced surface stresses probably arises from differences in fold conformations on opposite sides of the lamella, resulting in an overall twisting of the entire lamella. In this study, the cylinders should become ribbonlike at high water contents (otherwise, we could not detect the helical structures as shown in Figure 3). When the semirigid PDMA go naturally tilted to the interface that is more or less flattened, the stress, similar to that existing in chain-folding lamellar surface of PE, would be imposed on the shells through the PEG loops (the folds). Since the solvent-swollen PDMA cores are soft, we expect that a small unbalanced stress can help the twisting of the cylinders.

Figure 3 tells that the twisted cylinders can aggregate to form the super-helices and super-rings. For a twisted ribbonlike cylinder, its one side was compressed, but the other side (the outer side) was expended. The expended interface may make a triblock chain easier to be unfolded, namely, to have one PDMA semirod remaining in the core and the other dangling in solution. Furthermore, the dangling blocks can insert into other micelles, giving rise to bundles of the twisted cylinders. As a result, the expended interfaces of neighboring cylindrical micelles stuck together, and therefore, the twisted cylinders and the super-helices shared the same pitch length. The super-helices and super-rings are composed of different numbers of cylinders (see Figure 3), indicating that the observed aggregates are kinetically trapped rather than equilibrium in solution.

The super-helices are easy to form loops or crossed over with each other (see Figure 3a and 3b), which act as a transient state for the super-ring formation. Figure 4a–d present a series of SEM images obtained at different time of the solution under vigorous mechanical stirring at a water content of 50 wt %. Initially, the super-helices coexisted with many cylindrical micelles, and the number of super-helices increased with time. As shown in Figure 4a (time of 18 h), the super-helices were bended and crossed over with each other, with a diameter ranging from 80 to 100 nm. After 24 h, disfigured super-rings attached on super-helices were observed (Figure 4b for 24 h and Figure 4c for 40 h). This implied that some midsections of the looped or curved super-helices fused with each other when they

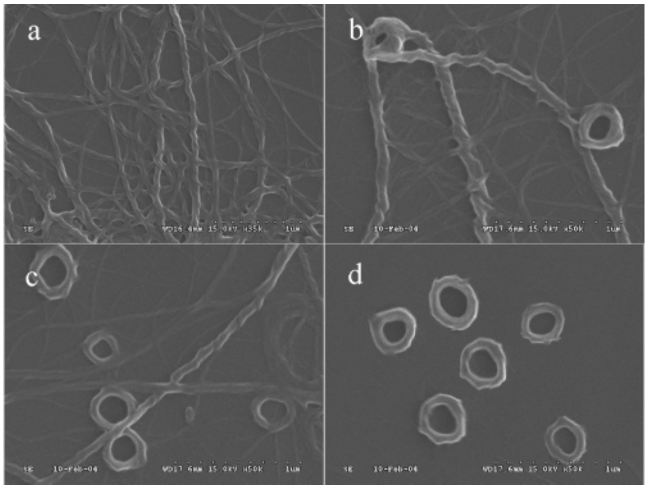

Figure 4. Aggregate morphologies at different time stages observed by SEM with 50 wt % water content of THF/water mixture: (a) 18 h; (b) 24 h; (c) 40 h; (d) 48 h.

met, resulting into super-rings.[24] The rings became more regular with increasing time. After 48 h, the well-defined ring-shaped aggregates with an average width of 100 nm were formed (Figure 4d). The super-rings would remain dominant in morphology after 120 h. The formation of super-ring structures therefore helps the micelles to eliminate the cylinder end caps,[25] which favors the free energy decrease of the aggregates.

In summary, we have successfully synthesized a novel amphiphilic triblock copolymer via ATRP, which is a combination of a hydrophilic linear PEG middle block and two hydrophobic dendritic polymethacrylate that are semirigid. The self-assembly morphology of the triblock copolymer induced by changing water content in the binary solvent mixture (THF/water) was investigated. When the water content was 10−20 wt %, the triblock copolymer self-assembled into spherical micelles with the core-fringe structure; when it was 20−40 wt %, cylindrical micelles were formed, which could aggregate to be bundles. When the water content was increased higher than 40 wt %, although the triblock copolymer did not possess a well-defined chiral center in the primary structure, cylindrical micelles became twisted helices. As the building blocks, the twisted cylindrical micelles further aggregated to form super-helices and super-rings. We anticipate that such a system presents an opportunity to create nanostructured materials. In term of the potential applications, the structures of the self-assemblies and aggregates may provide templates to fabricate nanocomposites (for example, the PEG blocks in the shells may form a complex with a wide range of metal ions). The research is currently ongoing in our laboratory.

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Supporting Information Available: Text giving the complete experimental procedure, a scheme outlining the synthetic route of the triblock copolymer $PDMA_{43}$-*b*-PEG_{91}-*b*-$PDMA_{43}$, and figures showing some experimental results of GPC, ^{1}H NMR, DSC, WAXS, and DLS. This material is available free of charge via the Internet at http://pubs.acs.org.

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