Communication

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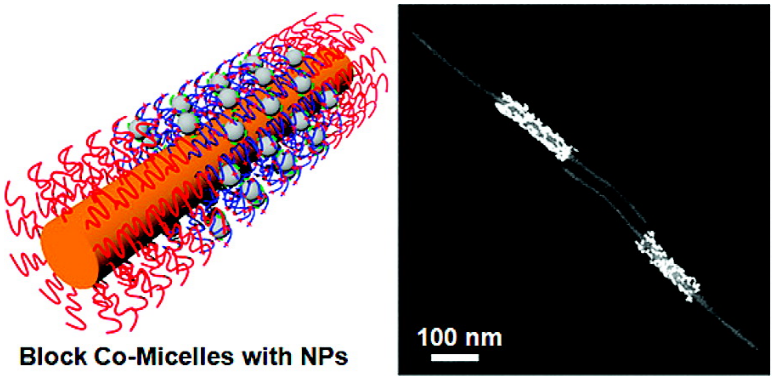

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Cylindrical Block Co-Micelles with Spatially Selective Functionalization by Nanoparticles

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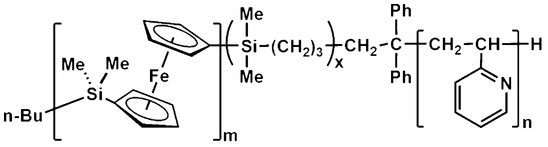
Amphiphilic block copolymers with two immiscible segments can self-assemble in selective solvents to form well-defined micellar aggregates, such as spheres, cylinders, and more complex architectures.[1−3] Interest in these types of supramolecular materials is largely stimulated by their potential applications in nanotechnology and medicine.[4−9] Cylindrical block copolymer micelles with an inherently high aspect ratio are of particular interest. Examples of their utility include applications as additives for the enhancement of the toughness of epoxy resin,[6] as templates for the mineralization of hydroxyapatite,[8] as materials for flow-intensive drug delivery,[10] and as nanoscopic etch resists.[11] As the aspect ratio of the cylindrical micelles is a key factor that influences their properties, the ability to control the length of cylindrical micelles represents an important challenge. The ability to create more complex cylindrical micellar architectures with selective functionalization is also of intense interest.[12−16]

In a recent paper,[17] we reported an unprecedented process in which crystalline-coil polyferrocenylsilane (PFS) block copolymers undergo a living supramolecular polymerization to form cylindrical micelles with a PFS core in selective solvents for the organic coblock. The process is apparently driven by epitaxial crystallization of the core-forming PFS block[18] and is initiated by short cylindrical PFS block copolymer "seed" micelles. Consistent with the living nature of the process, the ends of the cylindrical micelles remain active to the addition of further PFS block copolymer after all the initial chains in the solution have been consumed during micellization. The length of the micelles can therefore be controlled by adding different amounts of additional PFS block copolymer unimers in small amounts of a common solvent to a preformed *n*-alkane solution of the cylindrical micelle seeds. When the composition of the added additional polymer is different from that used to prepare the preformed micelles, the resulting cylindrical micelles were shown to possess a B−A−B "block co-micelle" structure. The central A block consists of the pre-existing "seed" micelles and the terminal B blocks are composed of the added second copolymer. To date, our work in this area has been limited to PFS block copolymers with nonpolar coblocks such as polyisoprene and polysiloxanes and has involved the use of nonpolar *n*-alkanes as selective solvents. In this Communication we report that the living supramolecular polymerization approach to yield cylindrical block co-micelles can be extended to hydrophilic coblocks and the use of polar media. We also demonstrate the selective patterning of the resulting block co-micelles with nanoparticles (NPs) to yield new types of nanomaterials with selective functionalization.

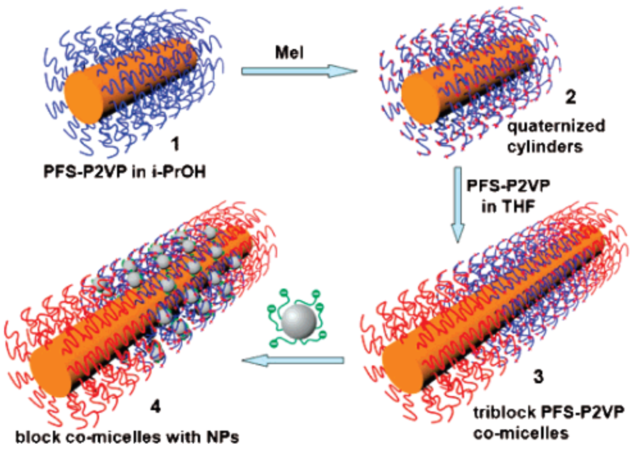
In this work we utilized a recently prepared new class of PFS block copolymers, PFS-P2VP (P2VP = poly(2-vinylpyridine)) with a semicrystalline hydrophobic ferrocenyldimethylsilane block and a hydrophilic organic coblock.[19]



PFS-P2VP

The representative example, PFS_{17}-$P2VP_{170}$ (m = 17, n = 170) was employed in this work. Dissolution of this polymer in the selective solvent 2-propanol (*i*-PrOH) gave rise to cylinders that contain a core of PFS and a corona of P2VP. The average diameter of the core was ca. 10 nm by TEM, and the length of these cylinders ranged from 3 to 10 μm.[19] We prepared cylinders with a positively charged coronal block (**2**) from preformed cylindrical micelles (**1**) by quaternization of the P2VP corona by addition of MeI to the micelle solution in isopropanol (Scheme 1). After 24 h, hexanes was added to precipitate the micelles. The product micelles (**2**) were isolated and further purified by dissolution in *i*-PrOH followed by precipitation and washing with hexanes. This cycle was repeated three more times, and the isolated solid **2** was dried under vacuum overnight. We estimated the overall degree of quaternization to be ca. 21% by comparing the integrated ^{1}H NMR signals (in MeOH-d_4) of the methyl groups and pyridinium units.

Scheme 1



Shortened seed micelles in *i*-PrOH (ca. 150 nm by TEM, Figure 1A) were prepared from quaternized **2** by sonication. To grow B−A−B triblock co-micelles, a 100 μL THF solution of PFS_{17}-$P2VP_{170}$ (10 mg/mL) was added to a 1 mL aliquot of this micelle solution (0.5 mg/mL). The supramolecular self-assembly process

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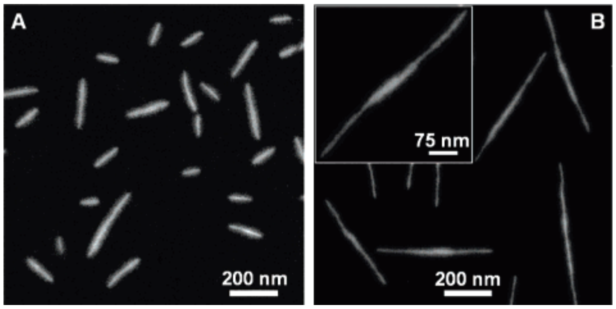

Figure 1. Dark-field TEM images show shortened quaternized PFS_{17}-$P2VP_{170}$ micelles (A) and block co-micelles after adding regular PFS_{17}-$P2VP_{170}$ (B).

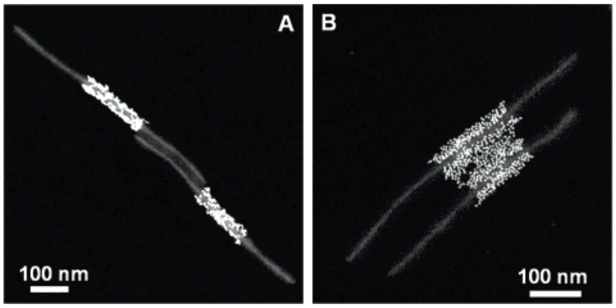

Figure 2. Dark-field TEM images show block co-micelles with the central block functionalized with Au nanoparticles (A) and PbS quantum dots (B).

was monitored using 90° dynamic light scattering (DLS). The apparent hydrodynamic radius (R_h) of the micelles increased gradually from 73 nm (seed micelles) and reached a constant value (97 nm) after 24 h.

Clear evidence for the increase in micelle length was revealed by dark-field TEM analysis (Figure 1). In a dark-field image, components containing heavy elements scatter more electrons and appear bright against the dark carbon film background. After quaternization the cylinders **2** shown after sonication in Figure 1A are wider than those of original PFS_{17}-$P2VP_{170}$ micelles **1** (ca. 17 vs 10 nm).[19] This is presumably due to the presence of iodide anions in the corona of **2** compared to **1** where the corona has no electron-dense atoms present. For similar reasons, after the addition of unquaternized PFS-P2VP to **2**, one can clearly see B−A−B triblock structures (**3**) formed with a wider central segment, flanked by two narrower terminal blocks (Figure 1B, inset). The corona chains along the terminal blocks consist of regular unquaternized P2VP that is invisible against the PFS core. Therefore the terminal blocks appear to be thinner than the central segment.

We explored the use of electrostatic interactions to selectively bind negatively charged nanoparticles to the positively charged coronal pyridinium units of the central A block of **3** to afford the composite structures **4**. Gold NPs stabilized with mercaptoacetic acid were prepared as a deep purple aqueous solution via a modified literature procedure.[20,21] The pH of the solution was adjusted to ca. 8 using $Me_4N^+[OH]^-$. Deionized water was then added to the solution of micelles **3** (H_2O/*i*-PrOH = 1:1 (v/v)) followed by the solution of Au NPs. The resulting solution was light purple, suggesting that no large Au aggregates had formed. The products were characterized by TEM. Shown in Figure 2A is a dark-field TEM image of the micelle−Au−NP composite (**4**). One can clearly see that the Au NPs are exclusively located on the central A block. No unattached NPs were observed on the carbon film.

To illustrate the generality of this electrostatic NP attachment approach, we also prepared PFS-P2VP block co-micelles functionalized with PbS quantum dots. We have demonstrated previously that the oleic acid ligands on the surface of PbS quantum dots[22] can be replaced by polymer ligands including poly(acrylic acid) (PAA).[23] An aqueous PbS-PAA suspension (pH 8) was added to the micelle solution following a similar procedure to that used for Au NPs. It is clear that PbS quantum dots are also selectively located along the central A block leaving terminal B blocks with uncharged coronas free of NPs (Figure 2B).

In summary, we have prepared a new type of cylindrical micelle architecture with an A−B−A triblock structure bearing spatially controlled coronal charge. This was achieved by extending the living supramolecular polymerization approach to block copolymers with hydrophilic blocks and to polar solvents. Electrostatic interactions can be used to selectively functionalize the new nanomaterials with Au and PbS NPs in a spatially selective manner to afford novel composite structures **4**. We are currently exploring the extension of this approach to related architectures and applications of these novel structures as functional nanomaterials. For example, the selective patterning of cylindrical nanostructures with magnetic or catalytically active NPs may provide access to novel methods for the induction of micelle organization and motility and would be of broad interest.

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Supporting Information Available: Experimental details for the synthetic work. This material is available free of charge via the Internet at http://pubs.acs.org.

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