0.71073 Å), θ-2θ scan, $T = 298$ K, 10115 measured reflections, 9702 independent reflections ($R_{int} = 0.0339$) included in the refinement. Lorentzian, polarization, and ψ-scan absorption corrections were applied, $\mu = 2.568\ mm^{-1}$, $[\Delta/\sigma]_{max} = 0.046$, 734 parameters refined, $R1 = 0.0477$ (for 8333 reflections with $I > 2\sigma(I)$), $wR2 = 0.1231$ (on $|F^2|$). Max./min. residual peaks in the final difference map 0.794/ -0.599 e Å^{-3}. Crystals of **1** and **2** were mounted in capillaries filled with drops of the mother liquor. The structures were solved by direct methods with SHELXS 86 and refined by full-matrix least-squares techniques on F^2 using SHELXL 93. For both structures, almost all non-hydrogen atoms were refined anisotropically; the MeCN solvate and two lattice H_2O molecules of **2** were refined isotropically with occupation factors fixed at 10.76 and 10.50, respectively. All hydrogen atoms in **1** were introduced at calculated positions as riding on bonded atoms. Hydrogen atoms of the methyl groups of the acetate ligands and those of C9, C23, C24, C28, C29, C30, and C31 in **2** were introduced at calculated positions as riding on bonded atoms, the remaining hydrogen atoms were located by difference map calculations and refined isotropically; no hydrogen atoms for the H_2O and MeCN solvate molecules were included in the refinement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147434 and CCDC-147435. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Core – Shell – Corona Micelles with a Responsive Shell**

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Supramolecular assemblies formed by self-associating block copolymers have raised considerable interest in the scientific literature.[1] In most cases, amphiphilic diblock copolymers are dissolved in a solvent selective for one constituent, which results in spherical micelles that consist of a core formed by the insoluble blocks surrounded by a shell of the solvated blocks. Although ABC triblock copolymers self-organize into a wide variety of supramolecular structures in the bulk,[1] their association in selective solvents has scarcely been studied. "Three-layer" micelles were reported in water,[2] although other micelle structures can be formed in organic solvents, as demonstrated by the so-called "Janus" micelles,[3] which consist of a cross-linked polybutadiene core and a corona with a "northern" polystyrene and "southern" poly(methyl methacrylate) hemisphere. These Janus micelles have to be distinguished from three-layer micelles, because their structure is generated in the bulk and persists in solution.

Herein we report on the formation of aqueous three-layer micelles from a polystyrene-*block*-poly(2-vinyl pyridine)-*block*-poly(ethylene oxide) triblock (PS-*b*-P2VP-*b*-PEO), these micelles will be referred to as core – shell – corona (CSC) micelles. The molecular weight of each block is 20000 for PS, 14000 for P2VP, and 26000 for PEO. CSC micelles consisting of a PS core, an intermediate P2VP layer, and a PEO corona are expected to be formed. Because the water-solubility of the central P2VP block depends on the degree of ionization,[4] the CSC micelles should be pH sensitive. Structurally they are reminiscent of the so-called "onion" micelles prepared by mixing an aqueous micellar solution of PS-*b*-P2VP diblock with P2VP-*b*-PEO chains dissolved in water.[5] At pH > 10, the P2VP blocks of the two copolymers coprecipitate, and three-layer onion micelles, that consist of a PS core, a P2VP shell, and a PEO corona are formed. The effect of pH on the onion micelles is dramatically different from that on the CSC micelles, the onion micelles disintegrate into the two constituent diblocks as the pH is decreased, which is not the case for their CSC counterparts which remain intact. Moreover, the structural features of the CSC micelles can be better controlled than those of the onion micelles.

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Dynamic light scattering (DLS) was used to measure the mean hydrodynamic diameter (D_h) of the CSC micelles. Because of the glassy PS core, the micelles are expected to be kinetically frozen in water at room temperature.[6] At pH > 5, a D_h of 75.4 (± 0.5) nm and a size polydispersity (PDI) of 0.087 (± 0.017) were measured. At pH < 5, D_h and PDI were shifted to 135.2 (± 1.2) nm and 0.146 (± 0.021), respectively. The very low values of PDI must be noted, which indicates the formation of nearly monodisperse micelles. The increase in D_h at pH < 5 is consistent with the protonation of the P2VP blocks, which results in intra- and intersegmental electrostatic repulsion. The reversibility of this phenomenon has been ascertained by cycling the pH several times from basic to acidic values (Table 1). The constancy of D_h at pH > 5 is noteworthy, whereas a decrease in D_h is observed at pH < 5 as the number of cycles is increased. This effect results from the increase in the solution ionic strength because NaCl is formed with each pH-variation cycle, which decreases the strength of the electrostatic repulsion between the charged P2VP blocks.

The morphology of the CSC micelles has been observed by transmission electron microscopy (TEM). The PS and P2VP blocks have been selectively stained with RuO_4, and Figure 1a confirms that low polydispersity spherical micelles are formed. The diameter of the core plus shell (D_{CS}) has been determined from the TEM pictures and found to be ≈35 nm. Although this value is characteristic of the "dried" micelles, it should be comparable for the micelles in water at pH > 5, because the PS core and the P2VP corona are basically unswollen. TEM observations at higher magnification do not provide more detail on the internal micellar structure, that is, the core cannot be discriminated from the shell, consistent with a PS core uniformly surrounded by a dense P2VP shell. At pH < 5 an increase in D_{CS} is observed (from ≈35 to ≈50 nm; Figure 1b), in agreement with the protonation of the P2VP blocks. Moreover, Figure 1b shows the internal structure of the micelles, and allows the diameter of the PS core ($D_C \approx 20$ nm) to be measured. A diffuse P2VP layer is observed around the PS core.

The structure of the CSC micelles in the dried state has also been investigated by atomic force microscopy (AFM) in the tapping-mode. These observations complement the TEM micrographs. At pH > 5, highly regular, low polydispersity spherical micelles are observed, in agreement with DLS data and TEM observations (Figure 2a). The diameter of the CSC micelles in the dried state (D_{CSC}) has been measured ($D_{CSC} \approx 60$ nm). This value is smaller than D_h, because the PEO corona is now desolvated but it is higher than the D_{CS} value estimated by TEM because the PEO corona was not stained in Figure 1a and was thus not detected. At pH < 5 the AFM picture of the CSC micelles shows that they have characteristic dimensions (Figure 2b, $D_C \approx 30$ nm and $D_{CS} \approx$

Table 1. Changes in D_h[a] for the CSC micelles triggered by repeated pH variations.[b]

	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
D_h "acid" sample	132.6 ± 1.7	124.6 ± 0.2	120.4 ± 0.6	116.3 ± 1.5	110.1 ± 0.9
D_h "basic" sample	74.2 ± 0.5	72.6 ± 0.3	73.5 ± 1.0	75.5 ± 1.5	74.8 ± 0.7

[a] D_h given in nm. [b] An initial solution with 0.26 μmol of copolymer was prepared (D_h = 71.1 ± 1.0 nm). For each cycle, 15 μmol of HCl was added ("acid" samples), R_h was measured, then 15 μmol of NaOH was added ("basic" samples) and R_h was measured again.

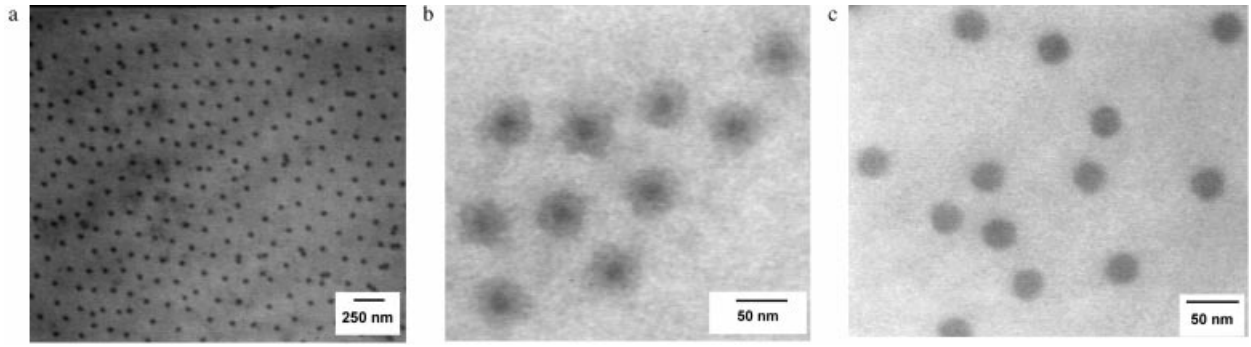

Figure 1. TEM images of the CSC micelles at pH > 5 (a), at pH < 5 (b), and after $HAuCl_4$ loading and reduction (c).

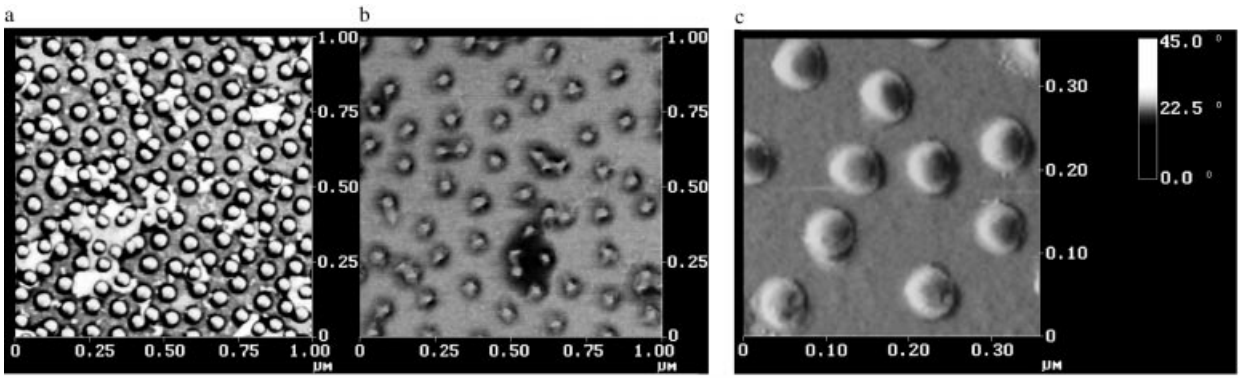

Figure 2. AFM phase-contrast pictures of the CSC micelles at pH > 5 (a), pH < 5 (b), and after $HAuCl_4$ loading and reduction (c).

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40 nm) which are in qualitative agreement with those estimated from the TEM picture (Figure 1b). The CSC micelles are observed at pH < 5 by AFM to have irregular contours. The reason might be found in the electrostatic interactions between the charged P2VP blocks and the charged substrate used, a silicon wafer with a surface oxide layer positively charged at pH < 3.8. In case of TEM observation, the substrate is neutral (Formvar), and the micelles are not significantly deformed.

Metal or semiconductor nanoparticles have raised great interest because of their unique size-dependent chemical and physical properties, which make them ideal candidates for electronic and optical nanodevices.[7] Moreover, polymer-coated metal and semiconductor nanoparticles exhibit increased stability, that results in protection against oxidation[8a] and much higher catalytic activity.[8b] Such nanoparticles can be synthesized in confined reaction vessels such as the micellar core of amphiphilic block copolymers in apolar solvents[9a,b] and in water,[9c] with the drawback that the nanoparticle size, which is fixed by the dimensions of the micellar core, can only be varied in a limited range of a few nanometers. In sharp contrast, the P2VP blocks of the CSC micelles can be used as a template for the production of metal nanoshells, the thickness of which can be tuned by the molecular weight of the P2VP block. Moreover, CSC micelles would allow the synthesis of metal or semiconductor capsules in a size range different to that of previously reported systems.[10]

The P2VP shell has been selectively loaded with $AuCl_4^-$ ions, made possible by the selective interaction of the ions with the protonated 2VP units. The excess of non-interacting $AuCl_4^-$ ions was eliminated by dialysis, followed by the reduction of Au^{3+} into Au^0 centers either by electron irradiation[9b] or by $NaBH_4$.[9c] Gold-loaded micelles have a uniform structure (Figure 1c and the AFM picture of Figure 2c). Moreover, TEM and AFM observation of a centrifugated micellar solution show that all the CSC micelles have the same gold-loading density. Finally, formation of gold nanoparticle has been monitored by UV/Vis spectroscopy. Before reduction of the gold precursor, the micellar solution is pale-yellow and an absorption is observed at 313 nm, consistent with the $HAuCl_4$ loading.[11] After reduction, the micellar solution is wine-red and the previously observed absorption disappears in favor of a broad absorption in the 400 – 600 nm range, that was assigned to the surface plasmon resonance of gold nanoparticles.[11] The broadness of this absorption indicates that individual gold particles persist in the P2VP shell and that capsules with a continuous gold wall are not formed. Further work is needed to optimize both the $HAuCl_4$ loading of the CSC micelles and the reduction conditions.

The PS(20 000)-*b*-P2VP(14 000)-*b*-PEO(26 000) triblock copolymer forms well-defined micelles. The P2VP shell can serve as a reactor for the synthesis of gold nanoparticles. Moreover, the pH-sensitive P2VP shell makes this system useful for encapsulation and/or release of active species. Finally, the hydroxyl end-group of the PEO blocks provides a unique opportunity to functionalize the CSC micelles at their periphery and to provide them with additional responsive or sensing properties.

Experimental Section

The triblock copolymer was prepared in THF at − 78 °C by sequential living anionic copolymerization of styrene and 2-vinylpyridine, initiated by secondary butyl lithium in the presence of LiCl, then termination with ethylene oxide. The terminal hydroxyl group was treated with naphthalene potassium and ethylene oxide was then added and polymerized at 0 °C. $\bar{M}_w/\bar{M}_n$ of the final triblock copolymer was 1.1. The micelles were prepared by first dissolving the copolymer (0.1 g) in a mixture of bidistilled water (0.5 g) and dimethylformamide (DMF; 4.4 g). DMF was then eliminated by dialysis against bidistilled water.

Gold nanoparticles were prepared by adding an excess of $HAuCl_4$ to the aqueous micellar solution. Unreacted $HAuCl_4$ was eliminated by dialysis of the loaded micelles against acidic water. Reduction of the gold containing anion was carried out either by electron irradiation during TEM observation[9b] or by addition of an excess of aqueous $NaBH_4$ solution (1 g L^{-1}).[9c] Unreacted $NaBH_4$ was eliminated by dialysis.

DLS measurements were performed on a Brookhaven Instruments Corp. BI-200 goniometer equipped with a BI-2030 digital correlator. The D_h and PDI of the micelles were obtained by a cumulant analysis of the experimental correlation function.

TEM pictures were recorded on a Philips CM 100 microscope equipped with a Gatan 673 CCD camera, and transferred to a computer equipped with Kontron KS 100 software. Samples were prepared by dipping a Formvar-coated copper grid into 0.2 wt % aqueous copolymer solution and contrasted by RuO_4 vapor.

AFM observations were carried out at the Centre of Microscopy of the University of Liège with a Digital Instrument Inc. Nanoscope III microscope operated at room temperature in the Tapping Mode in air. The instrument with the Extender Electronics Module provided height and phase cartography simultaneously. The samples were prepared by casting 0.004 wt % aqueous copolymer solution onto a silicon wafer covered by a 2 nm thick native silicon oxide layer.

UV/visible spectra were recorded on a Hitachi U3300 spectrometer.

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