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# Metallo-Supramolecular Block Copolymer Micelles[†]

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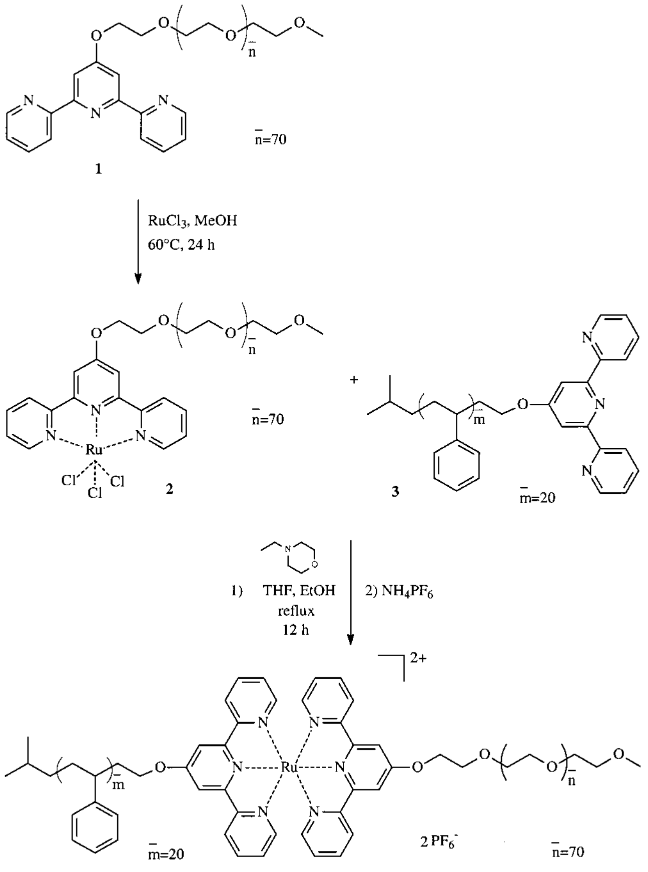
Amphiphilic block copolymers are usually prepared by sequential copolymerization of at least two monomers. Polymerization techniques such as living anionic, living cationic, and controlled radical polymerizations are able to produce amphiphilic block copolymers with predetermined molecular weight and narrow molecular weight distributions.[1] In such amphiphilic block copolymers, covalent bonds are formed between the different blocks.

Very recently, we have developed a new strategy toward block copolymer architectures that arises from a combination of supramolecular chemistry and polymer chemistry.[2] In this respect, a metal−ligand complex is used as a supramolecular linker between the hydrophobic and hydrophilic blocks of the amphiphilic block copolymers, giving rise to a metallo-supramolecular block copolymer. More precisely, monochelic polymers end-capped with the 2,2′:6′,2″-terpyridine ligand can be selectively complexed with specific transition metal ions and then subsequently reacted with other terpyridine-terminated polymer blocks via self-assembly processes. Compared to “classical” covalent block copolymers, metallo-supramolecular block copolymers offer many advantages. Besides the formation via self-organization processes, the reversibility of the supramolecular bond allows a larger control over the fine-tuning of the material properties. Moreover, the presence of a metal complex in the copolymer structure introduces additional electrochemical, photochemical, and redox properties that are not observed in the covalent counterpart.[3] Finally, the presence of active metal complexes in micellar systems could be very interesting for applications in supported catalysis as well as in nanotechnology.

This communication aims at reporting on the formation of micelles from a metallo-supramolecular polystyrene-*block*-poly(ethylene oxide) diblock copolymer. This copolymer was prepared via self-organization of the α-methoxy-*ω*-(2,2′:6′,2″-terpyridinyl)oxypoly(ethylene oxide)ruthenium(III) complex (**2**) and *ω*-(2,2′:6′,2″-terpyridine)oxypoly(styrene) (**3**) (see Scheme 1) and will be designated by the acronym PS$_{20}$-[Ru]-PEO$_{70}$, the number in the subscript being the degree of polymerization of each block. The polymeric precursors of **2** and **3** have been synthesized by living anionic polymerization processes and have a polydispersity lower than 1.1.

**Scheme 1. Synthetic Pathway to the Metallo-Supramolecular PS$_{20}$-[Ru]-PEO$_{70}$ Diblock Copolymer**



**PS$_{20}$-[Ru]-PEO$_{70}$**

Ruthenium ions were selected due to their ability to form mono-complexes by the reaction of equimolar amounts of RuCl$_3$ with terpyridine moieties.[4] The synthesis and complete characterization of **1**, **2**, and **3** were reported elsewhere.[5] Different methods were utilized proving the exclusive formation of the corresponding mono-complex **2**, such as NMR spectroscopy, UV/vis spectroscopy, and MALDI−TOF mass spectrometry. **3** was then added to **2** in a refluxing tetrahydrofuran: ethanol mixture (3:7 v/v) in the presence of a catalytic amount of *N*-ethylmorpholine. Under these conditions, ethanol is oxidized and Ru(III) is reduced to Ru(II), and a bis(terpyridine)Ru(II) complex is formed.[6] This reaction allows the complete formation of the expected PS$_{20}$-[Ru]-PEO$_{70}$ diblock copolymer (Scheme 1), as shown by NMR, SEC, and UV/vis spectroscopy.[7]

Amphiphilic block copolymers dissolved in a selective solvent of one constituent generally yield micelles that consist of a core formed by the insoluble blocks surrounded by a shell of the solvated blocks.[8] Although it contains a major hydrophilic PEO block, the PS$_{20}$-[Ru]-PEO$_{70}$ amphiphilic diblock was not readily soluble in water. Therefore, the preparation method previously introduced by Eisenberg et al. for “crew-cut” micelles was applied.[9] This involves first the dissolution of the PS$_{20}$-[Ru]-PEO$_{70}$ diblock in a common solvent for both blocks (*N*,*N*-dimethylformamide, DMF), and then a

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[†] In Memory of Carlos van den Anker, whose tragic death is a big loss to our laboratory.

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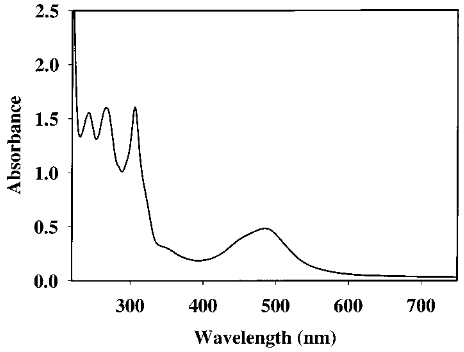


**Figure 1.** UV/vis spectrum of the $PS_{20}$-[Ru]-$PEO_{70}$ micelles in water.

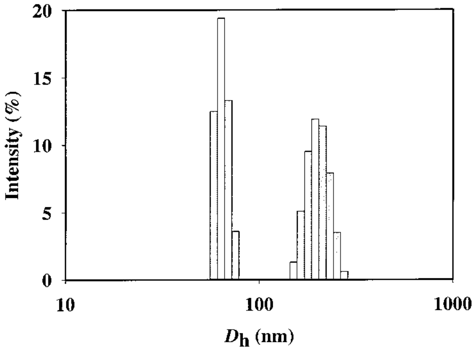


**Figure 2.** CONTIN size distribution of the $PS_{20}$-[Ru]-$PEO_{70}$ micelles in water.

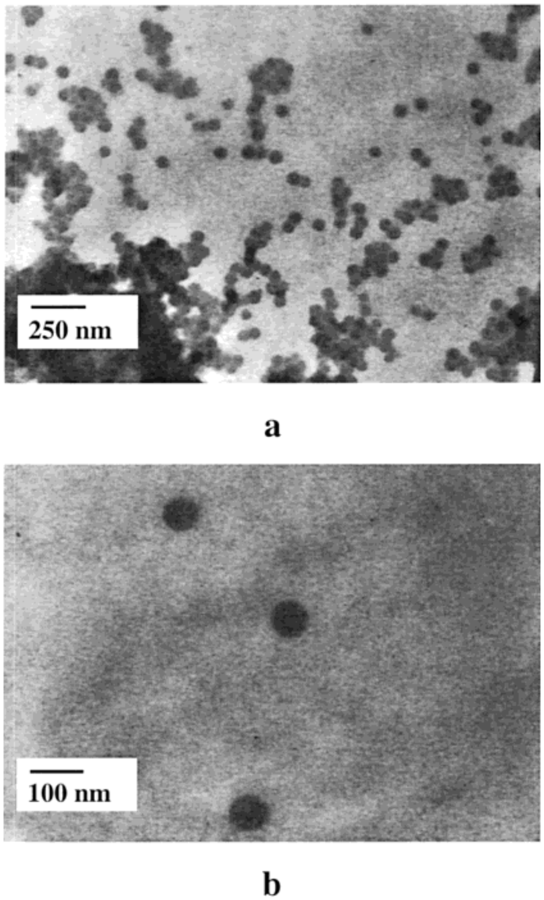


**Figure 3.** TEM pictures of the $PS_{20}$-[Ru]-$PEO_{70}$ micelles in water (without staining).

precipitant, water, is added to induce aggregation of the insoluble PS block. Subsequently, DMF is eliminated and the PS core is deswelled. Therefore, the final micelles are not at the thermodynamic equilibrium in pure water but are rather a kinetically frozen picture of a thermodynamic equilibrium state in the initial DMF/water mixture.[9] In our experiments, the micelles were prepared by dissolving 0.1 g of $PS_{20}$-[Ru]-$PEO_{70}$ in 5 mL of DMF. 5 mL of water was added dropwise, and DMF was subsequently eliminated by dialysis against pure water (Spectra-Por dialysis bag with cutoff 6000−8000 Da). The final aqueous micellar solution ($c = 0.5$ g/L) was opalescent, indicating the presence of micelles or aggregates and showed a bright red-orange color which is a characteristic feature of the bis(terpyridine)ruthenium(II) complex. The UV/vis spectrum of the metallo-supramolecular micelles, recorded on a Perkin-Elmer Lambda 45 apparatus, is shown in Figure 1. The metal-to-ligand charge-transfer (MLCT) band at ca. 490 nm is a clear indication of the stability of the bis(terpyridine)ruthenium(II) complex in water.

The association behavior of the $PS_{20}$-[Ru]-$PEO_{70}$ diblock was studied by dynamic light scattering (DLS) using a Malvern 4700C apparatus equipped with a Malvern 7032 digital correlator and an Ion Laser Technology argon laser operating at 488 nm. Although the $PS_{20}$-[Ru]-$PEO_{70}$ micelles are absorbing at 488 nm, a significant scattered light intensity was measured at this wavelength. The hydrodynamic diameter ($D_h$), the polydispersity index (PDI), and the CONTIN size distribution of the micelles were obtained by analysis of the experimental intensity correlation function as described elsewhere.[10] The mean $D_h$ for the micelles was found to be 150 ± 11 nm, and a broad PDI of 0.4 ± 0.02 was observed. Figure 2 shows the CONTIN histogram of the micelles formed by the $PS_{20}$-[Ru]-$PEO_{70}$ sample. Two different populations are observed: the first one is nearly monodisperse with $D_h$ at 65 ± 4 nm, and the second one is quite polydisperse with $D_h$ at 202 ± 37 nm. The size of the first population fits to classical block copolymer micelles with a spherical morphology while the second one has to be attributed to another type of aggregates. The equilibrium between these two populations has been studied by varying the copolymer concentration from 0.5 to 0.005 g/L. The diluted solution was equilibrated for 2 days before measurement. A CONTIN analysis of the diluted solution did not show any significant change in the partitioning between the two populations, in agreement with a very slow or even inexistent exchange process between primary micelles and aggregates.[11] These results have to be compared to previous reports on covalently bonded PS-*b*-PEO diblocks. Riess et al. have shown that the degree of association and the apparent molecular weight of the PS-*b*-PEO micelles in water increased with increasing copolymer molecular weight and decreasing PEO content.[12] Khan et al. showed by transmission electron microscopy that two populations of spherical micelles were observed in aqueous solutions of PS-*b*-PEO diblocks.[13] Two populations of micelles, with $D_h$ at 40 and 150 nm, were also detected by Xu et al. by light scattering in similar samples. The smaller population was attributed to regular micelles while the larger population was believed to consist of loose micellar clusters.[14] These results are in good agreement with our observations. On the other hand, Eisenberg et al. studied aqueous crew-cut micelles formed by very asymmetric PS-*b*-PEO diblocks containing a major PS block.[15] A wide variety of morphologies was observed ranging from spheres, rods, lamellae, vesicles, and large compound micelles.

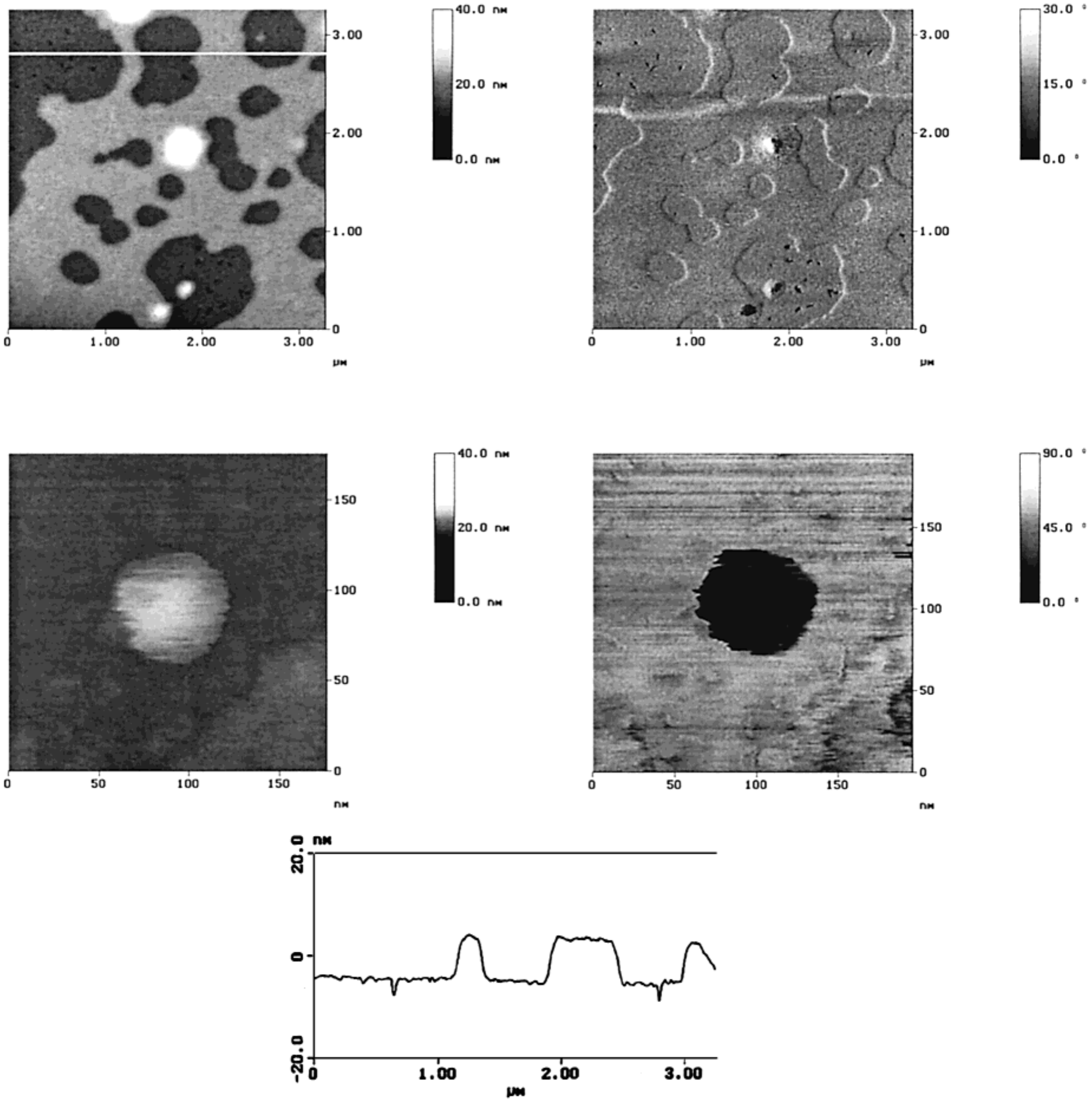


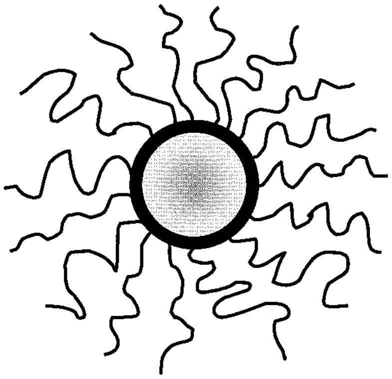
**Figure 4.** AFM pictures for the $PS_{20}$-[Ru]-$PEO_{70}$ micelles in water (left, height contrast; right, phase contrast; bottom, section indicated by a white line in the top left height image). Top: multilayer film of micelles. Middle: single micelle.

Obviously, the $PS_{20}$-[Ru]-$PEO_{70}$ diblock should be compared to the covalent systems previously studied in refs 12−14, although it has been prepared by Eisenberg's method.

To obtain more details about micellar morphology, transmission electron microscopy (TEM) observations have been carried out using a Philips CM 100 operating at a voltage of 100 kV. TEM photomicrographs were directly recorded with a Gatan 673 CCD camera. Data were transferred to a computer equipped with the Kontron KS 100 software. Samples were prepared by drop-casting the aqueous micellar solution onto Formvar-coated copper TEM grid. No contrasting agent was needed to visualize the micelles due to the presence of the ruthenium metal ions in the metallo-supramolecular block copolymer. Figure 3 shows that spherical micelles are formed in the $PS_{20}$-[Ru]-$PEO_{70}$ sample. These micelles are rather uniform in size but have a strong tendency to aggregate into large structures (Figure 3a). The mean diameter of these micelles is in good agreement with the light scattering data. Figure 3b shows a higher magnification image of the individual micelles. A very uniform contrast is observed within each $PS_{20}$-[Ru]-$PEO_{70}$ micelle.

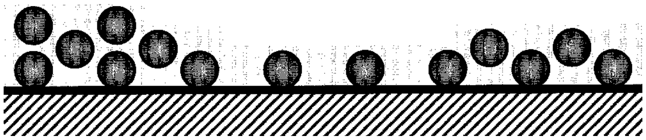
Finally, the $PS_{20}$-[Ru]-$PEO_{70}$ micelles have been dropcasted on a mica surface and studied by atomic force microscopy (AFM). AFM images were recorded with a Digital Instruments Nanoscope IIIa operated in air with the Tapping Mode. The microscope was equipped with the Extender Electronic Module that provided height and phase cartography simultaneously. Figure 4 shows the situation observed when the initial micellar aqueous solution ($c = 0.5$ g/L) was deposited on mica. Obviously, the mica surface is completely covered by $PS_{20}$-[Ru]-$PEO_{70}$ micelles (top images). The bare mica substrate was not observed. A noncontinuous micelle layer (light gray in top-right image) is observed on top of a first continuous micelle layer (dark gray in top-right image). Three layers of micelles have been also observed in this sample (data not shown). The height of one micelle layer has been measured from the steps from one layer to the other and was to be approximately 9 nm. Moreover, no individual micelle can be distinguished within the layers. No phase contrast difference has been observed

**Scheme 2. Schematic Representation of PS$_{20}$-[Ru]-PEO$_{70}$ Micelles in Water$^a$**



$^a$ A PS core in gray is surrounded by bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes in thick black and a PEO corona.

**Scheme 3. Possible Arrangement of the PS$_{20}$-[Ru]-PEO$_{70}$ Micelles Deposited on Mica$^a$**



$^a$ Dark gray spheres: PS cores; merged PEO corona in light gray.

between the different layers, indicating that they are formed of the same material (top left image in Figure 4). This suggests that the micelles are merging together inside each layer and that the PEO blocks act as a glue to stick the PS core together. The very small height of the micellar layer compared to the size of the solvated individual micelles suggests that the PEO blocks collapse as depicted in Scheme 3. However, individual PS$_{20}$-[Ru]-PEO$_{70}$ micelles have been observed together with aggregates on mica when the initial micellar solution was diluted 100 times (Figure 4, middle images). The size of the micelles measured by AFM is of the same order as the results obtained by DLS and TEM. As was previously observed by DLS, further dilution of the initial micellar solution did not lead to the complete dissociation of the aggregates of micelles. The driving force responsible for this aggregation is still not yet understood. Electrostatic interactions between bis(terpyridine)ruthenium and/or PF$_6^-$ counterions could play an important role in the collapse of the PEO blocks.

In conclusion, this preliminary report demonstrates that metallo-supramolecular amphiphilic block copolymers can be successfully utilized for the formation of aqueous micelles. The used metal−ligand complex was found to be stable under the experimental conditions used for micelle preparation and characterization. The primary micelles have a strong tendency to aggregate into larger structures. Although these results are in qualitative agreement with previous reports on the covalent bound counterparts, the presence of metal ions, as well as their associated counterions, introduces additional attractive and/or repulsive electrostatic interactions at the interface between the two immiscible blocks. In this respect, the influence of the transition metal−ligand complex on the micellar characteristic features is under current investigation.

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