Macromolecules **2002,** *35,* 7427−7435

Covalent vs Metallo-supramolecular Block Copolymer Micelles

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Received March 25, 2002; Revised Manuscript Received June 7, 2002

ABSTRACT: An amphiphilic metallo-supramolecular polystyrene-*block*-poly(ethylene oxide) diblock copolymer containing a bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex (PS_{20}-[Ru]-PEO_{70}) as a supramolecular connection between the two constituting blocks has been compared to the covalently bonded counterpart (PS_{22}-*b*-PEO_{70}). The two different copolymers have been used to prepare kinetically frozen aqueous micelles that consist of a glassy polystyrene core surrounded by a poly(ethylene oxide) corona. The micelles have been characterized by dynamic light scattering (DLS). In the case of the PS_{22}-*b*-PEO_{70} copolymer, micelles with a hydrodynamic diameter (D_h) of 18 nm are observed while stable micelles with a D_h of 65 nm and larger aggregates are formed for the PS_{20}-[Ru]-PEO_{70} sample. Addition of different salts during the initial stage of micelle formation has a deep effect on the final micellar characteristic features, which are now similar to the ones of the covalent system. This effect is attributed to a decreased electrostatic repulsion between the charged bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes which are present at the interface between the immiscible polystyrene and poly(ethylene oxide) blocks. Furthermore, addition of different salts to solutions of the PS_{20}-[Ru]-PEO_{70} micelles, initially prepared in the absence of salt, caused a decrease of their size, although the packing of the charged bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes could not be changed in these kinetically frozen micelles. A decrease in micelle size has also been observed as temperature increases. These effects have not been observed in the covalently connected counterpart and are thought to originate from stretched poly(ethylene oxide) chain segments. A model for metallo-supramolecular micelles is tentatively proposed that takes into account the experimental observations.

Introduction

Metallo-supramolecular block copolymers, which arise from a combination of metallo-supramolecular and polymer chemistry, pave the way toward novel types of functional nanomaterials.[1] In this respect, very interesting supramolecular assemblies have been obtained from diblock copolymers containing a polyferrocene block.[2] Another promising strategy lies in the incorporation of a ligand at the junction between the two blocks of a diblock copolymer.[3] This strategy has been successfully applied for the self-assembly of bipyridine-functionalized diblocks into hetero-arm star copolymers through the complexation of the bipyridine ligand with various metal ions[3a] and to various diblocks containing terpyridine−metal complexes.[3b−e]

Very recently, we have introduced a metal−ligand complex as a supramolecular linker between the different blocks, giving rise to a metallo-supramolecular block copolymer.[4] More precisely, e.g., monochelic polymers end-capped with a 2,2′:6′,2″-terpyridine ligand, can be selectively complexed with a wide range of transition metal ions and then subsequently reacted with other uncomplexed 2,2′:6′,2″-terpyridine-terminated polymer blocks via self-assembly processes. It has been shown that not only symmetrical “homo-complexes” with two identical ligands can be prepared.[5] Utilizing special metal ions, such as ruthenium, also unsymmetrical “hetero-complexes” consisting of two different ligands can be synthesized: e.g., two different macromolecules end-capped by the terpyridine ligand can be subsequently reacted, giving rise to a supramolecular AB diblock copolymer.[6] 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 the construction of “smart materials” with tunable properties. Moreover, the electrochemical and photochemical properties of the utilized complexes can be engineered by choosing the appropriate metal ion and counterion.[7]

Block copolymers consisting of at least two immiscible blocks are known for bulk self-organization at the 10 nanometers scale.[8] When dissolved in a selective solvent of one of the blocks, block copolymer micelles are observed that consist of a core formed by insoluble blocks surrounded by a corona of soluble blocks.[9] The micellar characteristic features (size and shape) are mainly controlled by three independent parameters: the stretching of the core-forming chains, the interfacial tension between the micellar core and the solvent, and the repulsions among chains in the corona.[10] In preliminary reports,[11] we have shown that micelles were formed in water by metallo-supramolecular amphiphilic diblock copolymers consisting of a polystyrene[11a] or a poly(ethylene-*co*-butylene)[11b] hydrophobic block and a poly(ethylene oxide) hydrophilic block with a bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex as a supramolecular connection between the two constituting blocks.

The purpose of this paper is to highlight in detail the role of the charged metal complexes on the supramolecular organization of the metallo-supramolecular copolymers. The presence of charged moieties at the

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[§] J.-F. Gohy is “Charge de Recherches” by the Belgian National Fund for Scientific Research (F.N.R.S.).

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10.1021/ma0204812 CCC: $22.00

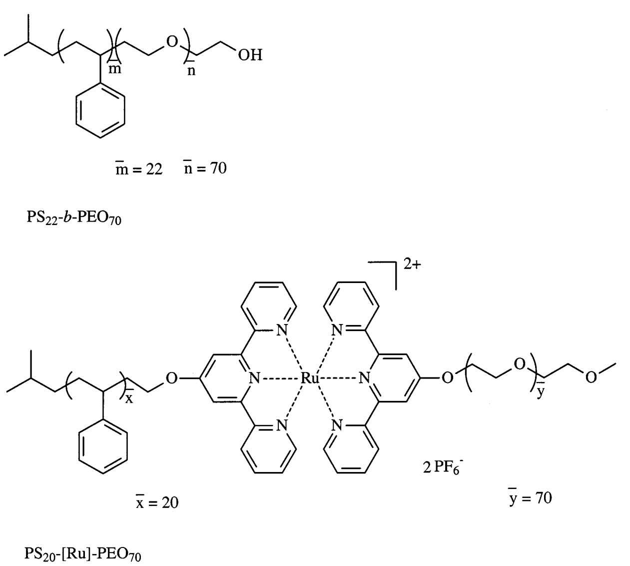

Figure 1. Structure of the two different diblock copolymers investigated in this study.

Table 1. Molecular Characteristic Features and Chemical Structure of the Two Copolymers Considered in This Study

acronym	M_n PS block	PS block polydispersity	M_n PEO block	copolymer polydispersity
PS_{22}-*b*-PEO_{70}	2200	1.15	3100	1.10
PS_{20}-[Ru]-PEO_{70}	2000	1.10	3100	1.10

interface between the two immiscible blocks is expected to strongly affect their properties as well as morphologies and therefore their phase separation. In turn, these electrostatic interactions could be screened by addition of salt. Therefore, parameters such as the ionic strength during the micelle preparation will be varied. The micellar characteristic features of the metallo-supramolecular micelles will be also compared to the ones of the covalent counterpart.

Experimental Part

Synthesis. The molecular characteristic features of the two samples considered in this study are listed in Table 1. Their chemical structure is shown in Figure 1. The covalently bonded polystyrene-*block*-poly(ethylene oxide) copolymer was prepared by sequential anionic polymerization of styrene and ethylene oxide, as described elsewhere.[12]

A terpyridine-terminated poly(ethylene oxide) was prepared as described in ref 5a. Selected analytical data for this compound are shown here: ^{1}H NMR ($CDCl_3$): $\delta = 8.68, 8.61, 8.04, 7.85, 7.34, 4.40, 3.93, 3.83-3.45, 3.38$. ^{13}C NMR ($CDCl_3$): $\delta = 166.6, 156.7, 155.6, 148.7, 136.4, 123.5, 120.9, 107.0, 72.2-67.4, 58.6$ 53.3. UV/vis (H_2O): λ_{max} (nm) = 278, 234. MALDI−TOF MS: $M_n = 3436$ g/mol. GPC (RI): $M_n = 2360$, PDI = 1.21.

This terpyridine-terminated poly(ethylene oxide) was then complexed with $RuCl_3$ to form the corresponding monocomplex (for the methodology, see ref 13). Selected analytical data for this compound are shown here: ^{1}H NMR ($CDCl_3$): $\delta = 3.92-3.46, 3.38$. UV/vis (H_2O): λ_{max} (nm) = 272, 375. MALDI−TOF MS: $M_n = 3447$ g/mol.

A terpyridine-terminated polystyrene was prepared as described in ref 6. Selected analytical data for this compound are shown here: ^{1}H NMR ($CDCl_3$): $\delta = 8.67, 8.60, 7.91, 7.83, 7.31-6.39, 4.11-3.96, 2.90, 2.66, 2.18-1.10, 0.78$. UV/vis ($CH_2Cl_2$): λ_{max} (nm) = 278, 243. MALDI−TOF MS: $M_n = 2104$ g/mol. GPC (UV): $M_n = 1850$, PDI = 1.10.

Finally, the monocomplex of the terpyridine-terminated poly(ethylene oxide) was reacted with the terpyridine-terminated polystyrene to form the expected PS_{20}-[Ru]-PEO_{70} metallo-supramolecular copolymer as described in refs 6 and 11a. Selected analytical data for this compound are shown here: ^{1}H NMR ($CDCl_3$): $\delta = 8.36, 8.26, 8.17, 7.88-7.73, 7.33-6.32, 4.74, 4.28-4.04, 3.92-3.42, 3.38, 1.72-0.60$. UV/vis ($CH_3CN$): λ_{max} (nm): 486, 305, 268. GPC (UV): $M_n = 7810$, PDI = 1.10. MALDI−TOF MS: $M_n = 5348$ g/mol.

Preparation of the Micelles. The two investigated samples, although they contain a larger hydrophilic poly(ethylene oxide) block, were not readily soluble in water. Therefore, the preparation method previously introduced by Eisenberg et al. for "crew-cut" micelles was applied.[14] First, an initial solution of each copolymer in *N*,*N*-dimethylformamide (DMF) was prepared (concentration of 1 g/L), and then water was dropwise added to induce aggregation of the insoluble polystyrene block. Subsequently, the DMF/water solution was dialyzed several times against water (Spectra-Por dialysis bags, cutoff 6000−8000 Da). The final concentration of the copolymer in pure water was set to 0.5 g/L. The ionic strength was adjusted by adding the required amount of a stock salt solution in water, and the concentration of the copolymer was then set to 0.25 g/L.

For some experiments, an aqueous salt solution was used instead of pure water for the preparation of the micelles and the subsequent dialysis (see below).

Dynamic Light Scattering (DLS). DLS measurements were performed with a Malvern 4700C apparatus equipped with a Malvern 7032 digital correlator and an Ion Laser Technology argon laser with a wavelength of 488 nm. Although the metallo-supramolecular copolymer was absorbing light at this wavelength, sufficient light was scattered to allow data with good statistics to be obtained. Each DLS data resulted from the averaging of 10 measurements. The scattering angle used for the measurements was 90°. A temperature-controlled refractive index matching bath surrounded the scattering cell.

The second-order correlation function $G_2(t)$ was measured. In the case of single-exponential decay, $G_2(t)$ can be expressed by eq 1:

$$G_2(t) = B[1 + \beta \exp(-2\Gamma t)] = B[1 + \beta|G_1(t)|^2] \qquad (1)$$

where B is the baseline, β is an optical constant that depends on the instrument, Γ is the decay rate for the process, t is time, and $G_1(t)$ is the first-order correlation function. Γ is given by

$$\Gamma = Kq^2 \qquad (2)$$

where K is the translation diffusion coefficient and q is the absolute value of the scattering vector

$$q = [4\pi n \sin(\theta/2)]/\lambda \qquad (3)$$

n is the refractive index of the solvent, θ is the diffusion angle, and λ is the wavelength of the incident light.

The diffusion coefficient extrapolated to zero concentration (K_0) for spherical particles is related to the hydrodynamic diameter, D_h, by the Stokes−Einstein equation:

$$K_0 = k_B T/3\pi\eta D_h \qquad (4)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η the viscosity of the solvent. Practically, the initial micellar solutions were diluted by adding either pure water or a salt solution with the required concentration, and K was measured at different micellar concentrations. In all the experiments, K was found to be constant whatever the concentration, in agreement with the formation of kinetically frozen micelles. Moreover, no critical micellar concentration (cmc) was detected by DLS, indicating that the cmc should be extremely low in this system, in agreement with other results obtained on frozen micelles.[10]

When aggregates of different sizes were formed in solution, the experimental correlation function depends on all the individual decay processes. In this case, the data were

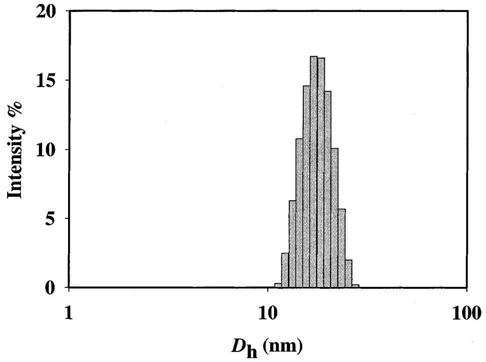

Figure 2. CONTIN size distribution histogram of the micelles formed by the PS_{22}-*b*-PEO_{70} covalently bonded copolymer in water.

analyzed by the Contin routine, a constrained regularization method program for the inverse Laplace transformation of dynamic light scattering data. The Contin program gave access to the distribution of the relaxation times in the experimental time correlation functions. The *Z*-averaged distribution of D_h was then calculated.

UV/vis Spectroscopy. The UV/vis spectra were recorded on a Perkin-Elmer Lambda 45 apparatus. The temperature of the sample was controlled with a Peltier PTP1 heating stage.

Results and Discussion

In a preliminary communication, the PS_{20}-[Ru]-PEO_{70} sample was reported to form well-defined spherical micelles in water.[11a] Moreover, the primary micelles had a strong tendency to aggregate into large structures. These micelles and aggregates were characterized by a combination of DLS, transmission electron microscopy (TEM), and atomic force microscopy (AFM). A good agreement was found between the results obtained by these three independent techniques. In TEM experiments, the PS_{20}-[Ru]-PEO_{70} micelles were characterized by a large electronic contrast due to the presence of ruthenium ions. The micelles revealed a strong tendency to form continuous layers when they were deposited on a mica surface, as shown by AFM experiments. The TEM experiments confirmed that the large aggregates were resulting from the clustering of individual micelles.

The aim of the present paper is to compare the characteristic features of the micelles formed by the metallo-supramolecular amphiphilic diblock copolymer to the ones of the covalently connected block copolymer. For that purpose, the covalent PS_{22}-*b*-PEO_{70} copolymer is thought to be a good model compound to be compared to the metallo-supramolecular counterpart. Another related concern will be the influence of the charged metal complexes on the final micellar characteristic features.

Comparison of the Micelles Formed by the Covalent and Metallo-supramolecular Copolymers. The PS_{22}-*b*-PEO_{70} copolymer was not readily soluble in water, and therefore the micellar solution was prepared by using the same procedure as the one described for the PS_{20}-[Ru]-PEO_{70} sample (see Experimental Part). The resulting aqueous micelles were characterized by DLS. The CONTIN histogram of the micelles formed by the PS_{22}-*b*-PEO_{70} sample is shown in Figure 2. A single population with a mean D_h of 18 nm is observed. The characteristic size of the micelles is in agreement with commonly reported data for block copolymer starlike micelles.[9] In sharp contrast, two populations are observed for the PS_{20}-[Ru]-PEO_{70} sample (see Figure 3a). The one with a mean D_h of 65 nm has been attributed to single micelles while the other has been assigned to aggregates of micelles.[11] The much bigger size of the metallo-supramolecular micelles compared to the covalent counterparts must be due to the presence of charged metal−ligand complexes at the interface between the PS and PEO blocks. As detailed in the last section of this contribution, these charged metal complexes are expected to modify the curvature of the PS core during the formation of the micelles and to strongly influence the conformation of the PEO chain segments in their vicinity. Moreover, the steric crowding due to the large size of the metal complex[15] is expected to have a strong influence on the characteristic features of the metallo-supramolecular micelles. Finally, the influence of the associated PF_6^- counteranions should not be neglected. These three effects result in turn in much larger micelles for the PS_{20}-[Ru]-PEO_{70} sample.

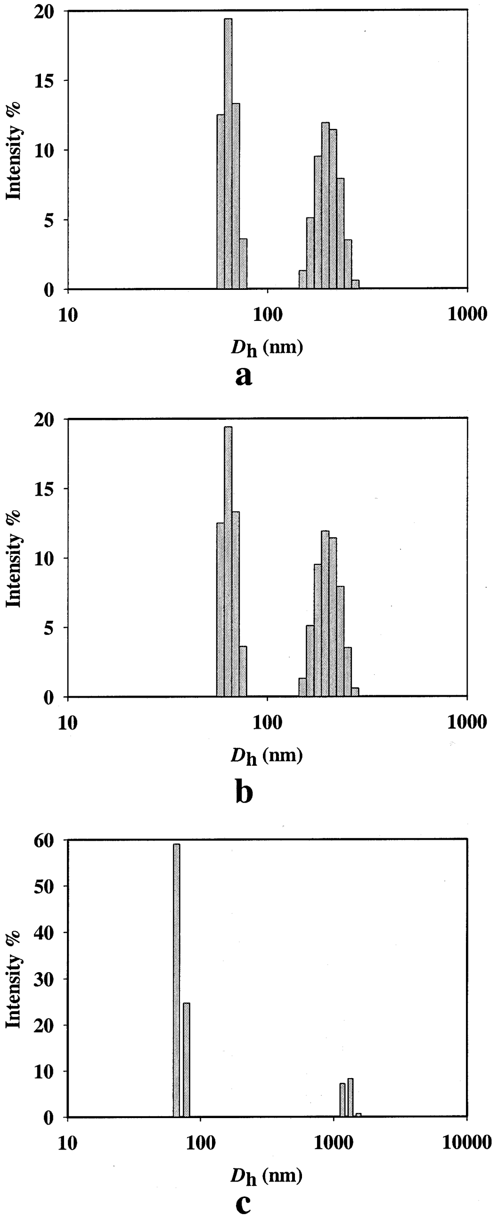

Figure 3. CONTIN size distribution histograms for the initial PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles in water with a concentration of 0.5 g/L (a); the same sample which has been diluted to 0.01 g/L (b) and the initial sample after 6 weeks of aging (c) (note the different scaling).

Another important difference between the covalent and metallo-supramolecular sample is the presence of aggregates of micelles in the latter. Nevertheless, it should be noted that aggregates of micelles have been observed in previous reports on covalent PS-*b*-PEO micelles. Indeed, Khan et al. showed by transmission electron microscopy that two populations were observed for aqueous PS-*b*-PEO micelles.[16] Two populations, with D_h at 40 and 150 nm, respectively, were also detected by Xu et al. by light scattering in similar samples. The smaller population was attributed to regular micelles while the larger one was believed to consist of loose micellar clusters.[17] However, all the previously investigated samples did contain a much higher molar percentage of styrene units. Indeed, DLS measurements on a covalent PS$_{19}$-*b*-PEO$_{49}$ sample (data not shown) revealed two populations (micelles and aggregates of micelles) in the CONTIN histogram. From these results, it seems that aggregates of micelles are observed when starting from copolymers with a larger hydrophobic block. Actually, 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 the PS molar content.[18] These bigger micelles have smaller PEO stabilizing blocks, which are less effective for the steric stabilization of the micelles. These micelles have thus a more pronounced tendency to form aggregates than the ones formed by the copolymers containing a smaller PS block. However, these copolymers are not directly comparable to the PS$_{20}$-[Ru]-PEO$_{70}$ sample, and the formation of aggregates in this sample will be discussed below.

Stability of the PS$_{20}$-[Ru]-PEO$_{70}$ Metallo-supramolecular Micelles. It is important to study the stability of the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes when they are confined near an aqueous environment. The effect of dilution and time has been investigated by DLS. Figure 3a shows the initial CONTIN size distribution measured in a freshly prepared sample. It must be noted that the results presented in Figure 3a are reproducible whenever metallo-supramolecular micelles have been prepared by the method described in the Experimental Part. Figure 3b shows the CONTIN size distribution of the same sample which has been diluted from 0.5 to 0.01 g/L and then measured immediately. The size distribution is not affected by dilution at least within a time scale of half an hour. The effect of time is illustrated in Figure 3c in which the initial micellar solution has been measured 6 weeks after preparation. The D_h of the primary micelles is not affected while the characteristic size of the aggregates is much larger, shifting from 200 nm to 1.3 μm. Moreover, some insoluble material was observed at the bottom of the glass vessel containing the micellar solution. This indicates that the large aggregates resulting from the merging of the primary micelles are growing with time to macroscopic structures. The steric stabilization of the micelles arising from the PEO block is thus not effective enough to prevent aggregation of the individual micelles over weeks or months.

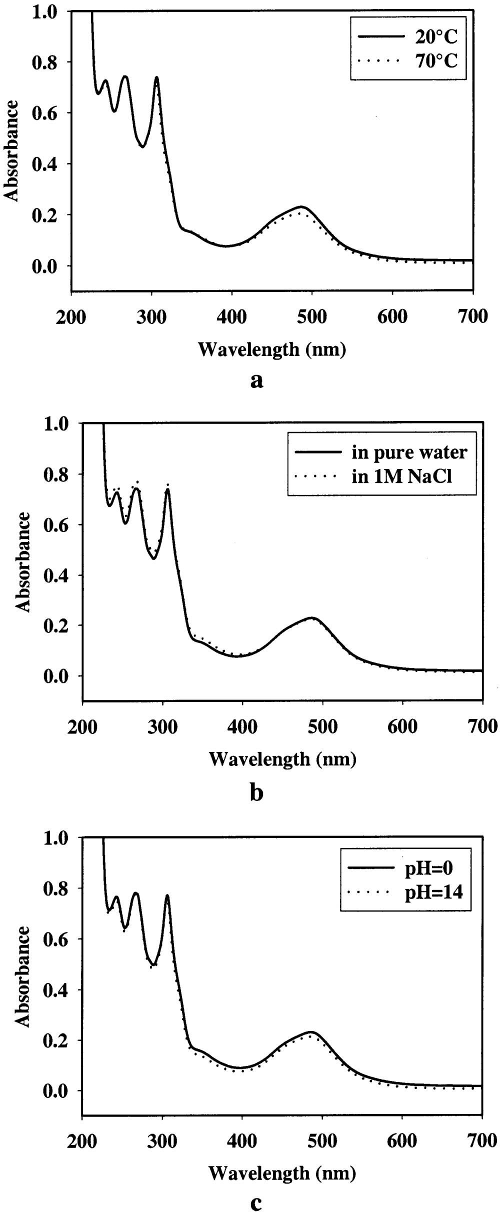

Figure 4. UV/vis spectra of PS$_{20}$-[Ru]-PEO$_{70}$ metallo-supramolecular micelles in water recorded as a function of temperature (a), NaCl concentration (b), and pH (c). For the sake of clarity, only the spectra at 20 and 70 °C have been plotted in (a) while only the spectra in pure water and at a NaCl concentration of 1 mol/L are shown in (b); the spectra at pH = 0 (HCl, 1 mol/L) and pH = 14 (NaOH, 1 mol/L) are shown in (c).

UV/vis spectroscopy is another useful technique to study the stability of the metallo-supramolecular block copolymers since the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes reveal characteristic UV/vis absorption peaks (see Figure 4). Among these absorption peaks, the broad band centered around 490 nm is of special interest since it corresponds to the metal−ligand charge transfer (MLCT) absorption of the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes.[19] The UV/vis spectra shown in Figure 4a−c are basically insensitive to temperature (a) and to salt concentration (b), at least in the investigated ranges, and to pH changes (c) over the whole range (0−14). Moreover, the intensity of the different absorption peaks does not depend on the temperature, the salt concentration, and the pH. This clearly indicates that the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes do not break apart and thus that the compositional integrity of the PS$_{20}$-[Ru]-PEO$_{70}$ metallo-supramolecular micelles is maintained. Moreover, UV/vis spectra are known to be sensitive to the degree or type of aggregation of the absorbing molecules.[20] It can be thus concluded from Figure 4 that no important change in the aggregation behavior (e.g.,

Table 2. D_h (nm) Measured for Primary Micelles Prepared in 1 mol/L Salt Solutions

NH_4PF_6	NH_4Cl	NaCl	Na_2SO_4	KCl	Na_3PO_4
23.2	24.4	22.4	21.4	22.7	24

in the aggregation number, in the micellar shape, or in the molecular architecture of the complexes) of the PS_{20}-[Ru]-PEO_{70} system is occurring as the temperature, the salt concentration, or the pH is changed. This conclusion is not surprising since the used preparation method basically leads to kinetically frozen micelles.[10] However, in the present contribution, the PS block is rather small, and the PS micellar core should have a glass transition temperature substantially lower than 100 °C.

Influence of Salt during the Preparation of PS_{20}-[Ru]-PEO_{70} Metallo-supramolecular Micelles. To study the influence of ionic strength on the packing of the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes at the PS/PEO interface during micelle formation, aqueous salt solutions have been added to the initial solution of the copolymer in *N*,*N*-dimethylformamide. Once the micelles were formed, the organic solvent was eliminated by dialysis against the same aqueous salt solution. The D_h of the primary micelles prepared in the presence of various salts is listed in Table 2. Two conclusions can be drawn from these data. First, the final D_h does not depend on the nature of the salt. It is thought that the addition of salt results in Debye screening between neighboring charged metal complex. Since the charged metal complex can be approached more closely than in pure water, the size of the micellar core is accordingly decreased (for a constant aggregation number of PS_{20}-[Ru]-PEO_{70} chains). This hypothesis will be developed in further details in the last section. The second interesting observation comes from the values of D_h which are now close to the D_h measured for the covalent PS_{22}-*b*-PEO_{70} sample. Thus, whenever the electrostatic repulsion between neighboring metal charged complexed are screened, the final micellar characteristic features are basically driven by the same factors (e.g., entropy of the core-forming chains, repulsion among coronal chain, etc.) governing the micellization of covalent block copolymers. However, it should be noted that aggregates of micelles have been observed for samples directly prepared in salt solutions.

Influence of Salt on Preformed PS_{20}-[Ru]-PEO_{70} Metallo-supramolecular Micelles. This section describes the effect of various salts on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles which have been initially prepared in pure water. The preparation method used in the present study essentially leads to kinetically frozen micelles formed of a PEO corona and a glassy PS core at the surface of which the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes are expected to be located. Therefore, a subsequent change of the ionic strength should not be able to affect the relative arrangement of the complexes whose position has been fixed during micelle preparation. However, the results plotted in Figure 5 show a pronounced effect of salt on the D_h of primary micelles. For each salt investigated, a distinct decrease of the D_h was noted. Indeed, D_h shifted from 65 to 30 nm when a concentration of 0.5 mol/L of NH_4PF_6 was reached in solution (Figure 6). Figure 5 demonstrates that the nature of the cation has basically no effect since the D_h vs salt concentration curves obtained for NaCl, NH_4Cl, and KCl are basically the same. In sharp contrast, the nature of the anion has an effect as shown by the data plotted in Figure 6. Indeed, a much more important decrease in D_h is observed whenever PF_6^- anions are used instead of Cl^- ones. The origin of this anion-specific effect is still unclear. The effect of the total ionic strength is studied in Figure 7 in which mono-, di-, and trivalent anions are compared. Since the chemical nature of the anion is varied in this experiment, it is not therefore straightforward to draw a clear conclusion from these data. Nevertheless, the larger decrease in D_h has been observed for Na_3PO_4, thus when the ionic strength was the larger. The small difference between results obtained with either Na_2SO_4 or Na_3PO_4 might be due to

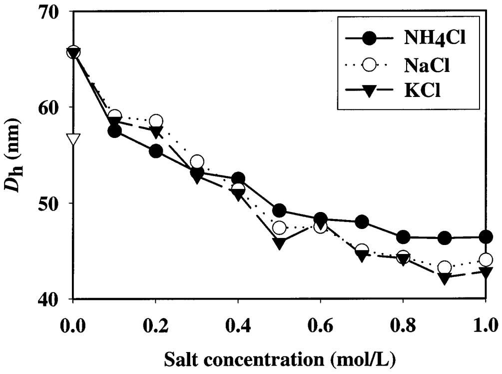

Figure 5. Addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles: effect of the salt concentration (different cations are used) on D_h of the primary micelles. The white triangle corresponds to the micelles obtained after elimination of the salt (NaCl) by dialysis.

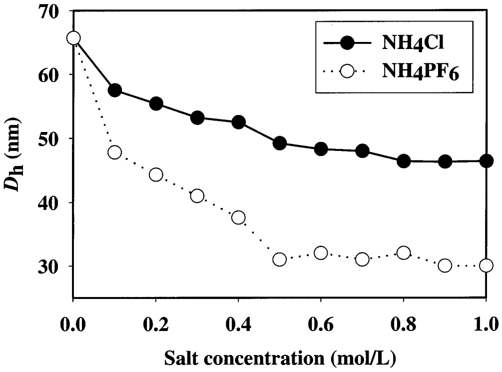

Figure 6. Addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles: effect of the salt concentration (different anions are used) on D_h of the primary micelles.

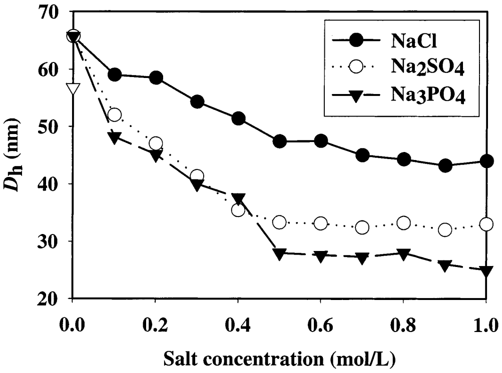

Figure 7. Addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles: effect of the total ionic strength on D_h of the primary micelles. The white triangle corresponds to the micelles obtained after elimination of the salt (NaCl) by dialysis.

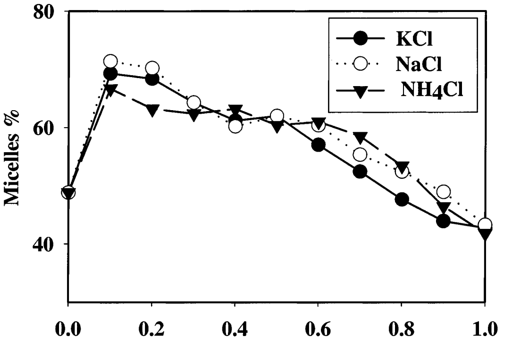

Figure 8. Addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles: effect of the salt concentration (different cations are used) on the weight percentage of primary micelles.

the ionization of Na_3PO_4, which is a weaker electrolyte, and leads to a distribution of several ionic species when dissolved in water (HPO_4^{2-}, $H_2PO_4^{-}$, ...) and accordingly to a smaller number of ions in aqueous solution.

The magnitude of these salt effects is rather unexpected for micelles containing a PEO corona and no polyelectrolyte blocks. Moreover, this effect was found to be reversible since the D_h of the metallo-supramolecular primary micelles increases when the added salt is eliminated by dialysis (see Figures 5 and 7).

For the sake of comparison, we have added these salts to micelles formed by the covalent PS_{22}-*b*-PEO_{70} counterpart, and no effect on the D_h has been observed at least in the investigated salt concentration range (up to 1 mol/L). Actually, it is known that the addition of salt causes dehydration of PEO and thus decreases its solubility.[21] In this respect, addition of salt has been reported to decrease the critical temperature of micellization of Pluronics and to change micellar characteristic features such as the aggregation number and the radius of the core.[22] Since PS_{22}-*b*-PEO_{70} micelles contain a frozen PS core, the addition of salt is not expected to markedly change their structure. However, the dehydration of the PEO corona could dramatically reduce the steric stabilization of the micelles and in turn induce flocculation. This extreme situation has not been met within the investigated salt concentration range.

Aggregates of micelles have been observed together with primary micelles whatever the added salt concentration. The evolution of the weight percentage of primary micelles vs the salt concentration has been also investigated. The results are shown in Figures 8 and 9 for some of the investigated added salts. For that purpose, the two populations in the CONTIN histograms have been integrated, and a weight percentage of micelles has been accordingly calculated. From the data reported in Figures 8 and 9, it is clear that the addition of a small amount of salt (0.1 mol/L) is breaking apart the aggregates. This effect could result from the fixing of the salt in the PEO corona that then behaves as a polyelectrolyte.[23] The further addition of salt results in an increase in the number of aggregates, in agreement with a decreased solubility of the PEO blocks in salt aqueous solution[21] and a subsequent clustering of the less stable micelles into aggregates. The characteristic size of the aggregates has been accordingly measured as a function of salt concentration and has been found to decrease first at low salt concentration and then to increase with salt concentration (Figure 10). This observation is in complete agreement with the arguments developed hereabove (at low salt concentration: screened electrostatic repulsion between "polyelectrolyte-like" micelles; at high salt concentration: decreased solubility of the micelles and further aggregation).

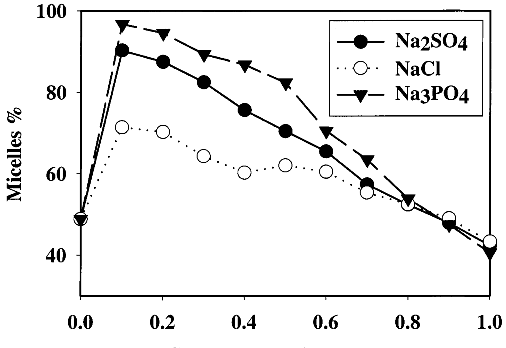

Figure 9. Addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles: effect of total ionic strength on the weight percentage of primary micelles.

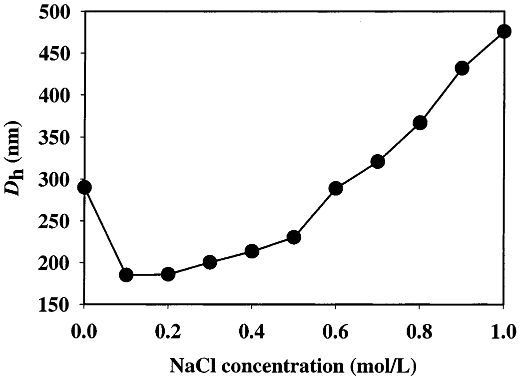

Figure 10. Addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles: effect of the NaCl concentration on D_h of the aggregates of micelles.

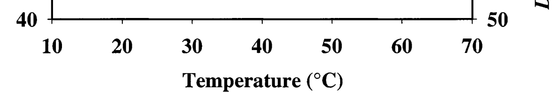

Figure 11. Effect of temperature on the D_h of PS_{20}-[Ru]-PEO_{70} primary micelles (left) and aggregates of micelles (right).

Influence of Temperature on PS_{20}-[Ru]-PEO_{70} Metallo-supramolecular Micelles. The effect of temperature on the PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles in salt-free solution has been studied in the 20−65 °C temperature range. The mean D_h of the primary micelles and the aggregates has been plotted as a function of temperature in Figure 11. The initial D_h of the primary micelles (65 nm at 20 °C) was found to decrease to 40 nm at 65 °C. The characteristic size of the aggregates of micelles was almost constant, but the percentage of micelles was decreasing with temperature

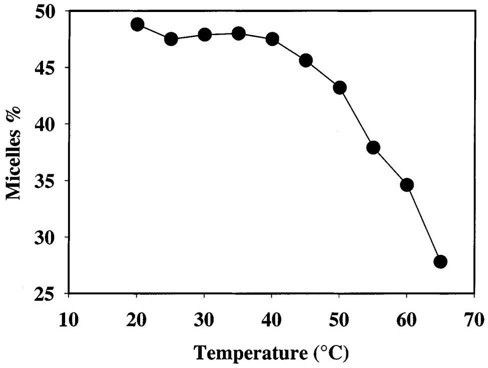

Figure 12. Effect of temperature on the weight percentage of PS_{20}-[Ru]-PEO_{70} primary micelles.

(Figure 12). These effects can be explained on the basis of a decreased solubility of the PEO blocks as temperature increases, as previously reported.[24] The PEO blocks have then a tendency to collapse on the PS core and are less effective to prevent flocculation. This results in a decreased D_h and to an increased number of aggregates as temperature increases. However, the very strong decrease of the D_h of the primary micelles should be noted.

In sharp contrast, the D_h of the PS_{22}-*b*-PEO_{70} micelles was insensitive to temperature in the investigated range. This apparent contradiction could originate from the presence of stretched "polyelectrolyte-like" PEO segments in the metallo-supramolecular micelles, as it will be discussed in the final section. Indeed, some ions can easily bind to EO units. As temperature increases, the binding constant of the ions associated with PEO blocks decreases, and the polyelectrolyte-like behavior of the PEO chains is no longer observed.

Model for the Aggregation Behavior of PS_{20}-[Ru]-PEO_{70} Metallo-supramolecular Micelles. In this section, a tentative model for the supramolecular organization of the metallo- supramolecular PS_{20}-[Ru]-PEO_{70} copolymer into aqueous micelles will be provided. This model takes into account the experimental results shown in the previous sections. The comparison of the results obtained on the metallo-supramolecular and covalent samples will be extensively used.

The proposed structure for metallo-supramolecular PS_{20}-[Ru]-PEO_{70} micelles is depicted in Figure 13. A PS core is formed which is surrounded by a PEO corona. Because of the chemical structure of the PS_{20}-[Ru]-PEO_{70} diblock copolymer, the charged bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes are located at the interface between the PS core and the PEO corona (see Figure 13). It is known that the interfacial tension between the core, the corona, and the solvent outside is an important factor in the control of the micellar characteristic features.[10] The localization of the charged metal complexes precisely at this interface is thus expected to have a strong effect. Indeed, the curvature of the PS core should decrease in order to minimize the electrostatic repulsions occurring between neighboring units. The large sizes of both bis(2,2′:6′,2″-terpyridine)-ruthenium(II) complexes and their associated PF_6^- counteranions introduce important steric crowding (see Figure 13a), which could also strongly affect the structure of the PS/PEO interface. In this respect, bigger micelles should be observed for the metallo-supramolecular diblock compared to the covalent parent compound at a constant aggregation number.

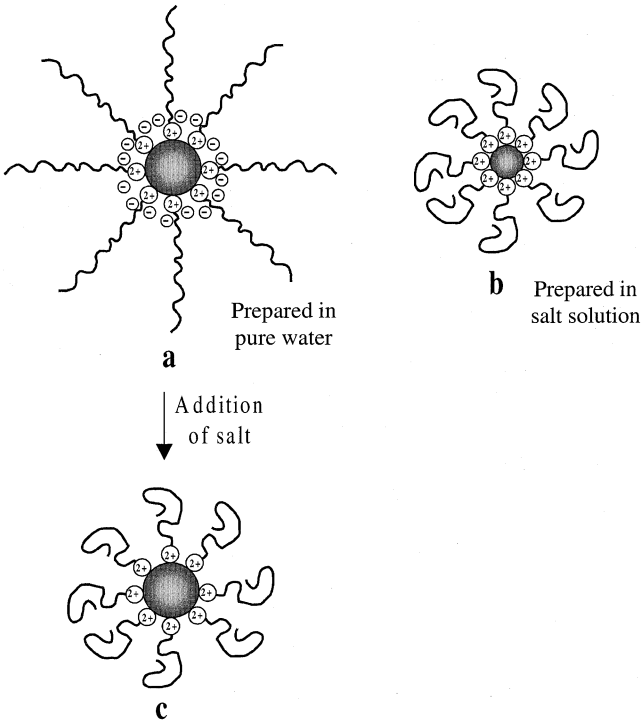

Figure 13. Schematical representation of the PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles prepared in water (a) and in a salt solution (b) and influence of the addition of salt on PS_{20}-[Ru]-PEO_{70} metallo-supramolecular micelles prepared in water (c). PS core in gray, open circles with 2+ sign for bis(terpyridine)ruthenium(II) complexes, open circles with minus sign for PF_6^- anions. PF_6^- anions have been only drawn in (a).

The much bigger size of the metallo-supramolecular micelles compared to the covalent ones suggests that electrostatic repulsion between neighboring bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes should play a major role. If it is so, the characteristic features of the metallo-supramolecular micelles should be strongly sensitive to Debye screening effects, as it is demonstrated in the previous sections. Two important clues can be deduced from these experimental results.

First, metallo-supramolecular micelles prepared in the presence of salt (see Table 2) have a D_h (around 22–25 nm) which is now close to the one of the covalent counterpart (18 nm). These experiments clearly show that the repulsion between neighboring units plays an important role in the micellar structure. The slightly larger size of the metallo-supramolecular micelles prepared in the presence of salt can be attributed to the bulkiness of the bis(*2,2′*:6′,2″-terpyridine)ruthenium(II) complexes and their associated counteranions at the PS/PEO interface (with the condition of the same aggregation number for the covalent and metallo-supramolecular micelles). A schematical picture of metallo-supramolecular micelles prepared in the presence of a screening salt is depicted in Figure 13b.

In a second set of experiments, salt has been added to metallo-supramolecular micelles formed in pure water. As discussed earlier, these micelles are typically kinetically frozen in water. Therefore, the further addition of salt will not modify the packing of the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes at the PS/PEO interface. However, a strong effect of salt on the D_h of the metallo-supramolecular micelles was noted. The final size of the metallo-supramolecular micelles was always larger than the D_h of the covalent micelles and of the metallo-supramolecular micelles prepared in the presence of salt. These results clearly indicate that the larger size of metallo-supramolecular micelles compared to the covalent counterpart is originating not only from electrostatic repulsion between neighboring bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes but also from another phenomenon which has been tentatively attributed to the electrostatically driven stretching of PEO segments. In the first set of experiments (micelles prepared in the presence of salt), both effects cannot be discriminated. In the present contribution, the PEO chains seem to behave as polyelectrolyte blocks. This polyelectrolyte-like behavior could be due to the "entrapping" of residual NH_4PF_6 strongly associated with EO units and which would not have been removed during the dialysis step. Such a situation has been already reported for PEO-containing aqueous systems in the presence of salts[25] and is depicted in Figure 13a. The diffusion of a screening salt in the PEO corona could reduce the electrostatic repulsion and accordingly the D_h of the whole micelle, as shown in Figure 13c.

The existence of stretched PEO chain segments is in agreement with the influence of temperature on the D_h of the metallo-supramolecular micelles. Actually, an important decrease in D_h is observed when temperature is increased. Moreover, this temperature effect has not been observed for the covalent counterpart. The income of thermal energy could reduce the stretching of the PEO chains, as stated before. The D_h of the whole micelle would be accordingly decreased. However, a complete description of the system should include the contribution of hydrogen-bonded water molecules which are expected to play an important role as far as enthalpy (hydrated EO units vs hydrated cations and PF_6^- counteranions) and entropy (ordering of water molecules around EO units, cations, and PF_6^- counteranions) are considered.

The polyelectrolyte-like behavior of PEO block could also strongly influence the formation of aggregates of micelles in metallo-supramolecular block copolymer micelles. In this respect, it is well-known that polyelectrolyte chains are forming loose aggregates in salt-free solution.[26] However, these aggregates dissociate as salt is added. The situation is much more complex as far as metallo-supramolecular block copolymer micelles are concerned and could be tentatively summarized in the following way. In salt-free solution, PEO chains behave as polyelectrolyte chains due to the presence of charged metal complexes, their counterions, and small amounts of entrapped residual salt. Accordingly, PEO chains are highly stretched and aggregates are observed. Addition of a small amount of salt decreases the stretching of the PEO chains and the number of aggregates, due to Debye screening. Finally, addition of a larger amount of salt still decreases the stretching of the PEO chains but also affects their water solubility. The number and the size of the aggregates accordingly increase.

Conclusions

This paper reports on the detailed characterization of metallo-supramolecular micelles that consist of a PS core surrounded by a PEO corona. The PS and PEO blocks of the constituting diblock (PS_{20}-[Ru]-PEO_{70}) are linked together by a bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex, which is therefore located at the interface between the PS core and the PEO corona. In a first step, the stability of the noncovalent bond with time, temperature, and pH of the aqueous solution has been ascertained. Then, the micellar characteristic features of the metallo-supramolecular micelles have been compared to the ones of a covalent counterpart (PS_{22}-*b*-PEO_{70}). With the hypothesis of a constant aggregation number for metallo-supramolecular and covalent micelles, the much bigger size of the first system can be accounted for electrostatic repulsions and steric crowding between neighboring bis(2,2′:6′,2″-terpyridine)ruthenium(II) complexes and their associated PF_6^- anions at the PS/PEO interface. This effect is evidenced whenever the metallo-supramolecular micelles are prepared in the presence of a screening salt. In this case, the micellar characteristic features are similar for metallo-supramolecular and covalent micelles. Salt has been also added to kinetically frozen PS_{20}-[Ru]-PEO_{70} micelles which were initially prepared in pure water. Although the packing of the PS_{20}-[Ru]-PEO_{70} chains at the PS/PEO interface could not be changed in this case, a distinct decrease in micellar size has been noted. This effect has been tentatively attributed to the presence of stretched PEO chains, which behave as polyelectrolyte blocks. The addition of a screening salt is therefore able to reduce the electrostatic repulsion, and the stretching of these PEO chains is accordingly reduced. An increase of temperature also results in a decreased stretching of these PEO segments. These results are integrated in a tentative model for the structure of metallo-supramolecular micelles, which is submitted to debate.

Acknowledgment. The authors thank the DPI and NWO for financial support and Prof. D. Schubert (Frankfurt, Germany) for helpful comments. J.F.G. thanks the FNRS and the European Science Foundation SUPERNET program.

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MA0204812