

Hybrid Polymeric Micelles Based on Poly(styrene-*b*-2-vinyl-1-methylpyridinium iodide-*b*-ethylene oxide) and Tungstate

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Poly(styrene-*b*-2-vinyl-1-methylpyridinium iodide-*b*-ethylene oxide) (PS-PVMP-PEO) was synthesized by quaternizing poly(2-vinyl pyridine) block of poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) with iodomethane. Then, PS-PVMP-PEO/tungstate hybrid micelles were prepared by binding tungstate to the PVMP block at neutral pH in aqueous solutions. The hybrid micelles were characterized by various techniques like dynamic light scattering, scanning electron microscopy, transmission electron microscopy, and zeta-potential measurements. It was found that the PS-PVMP-PEO/tungstate hybrid micelles have a spherical structure with a hydrodynamic diameter ranging from 80 to 120 nm depending on the amount of the incorporated tungstate.

KEY WORDS: Triblock Copolymer / Core-Shell-Corona / Tungstate / Hybrid Micelle / Stimuli-Responsive Micelle /

Various hybrid polymeric micelles composed of organic and inorganic materials can be used as stabilizers, reservoirs, and nano-reactors for inorganic materials.^{1–6} The organic-inorganic hybrid micelles, like other types of hybrid materials,^{7–10} are also expected to show new functions which the individual organic and inorganic constituents do not have. Despite the fact that AB diblock and ABA symmetric triblock copolymers have been widely employed for fabricating organic-inorganic hybrid micelles, ABC asymmetric triblock copolymers have been rarely used.^{11–14} Recently, Gohy *et al.*^{11,12} reported that a gold salt (AuCl₄[−]) can be incorporated into core-shell-corona micelles of poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS-PVP-PEO) triblock copolymers in aqueous solution. These micelles have a central PS core, middle PVP shell, and outer PEO corona. The PVP shell is positively charged under acidic conditions^{11,12,15–18} and shows an extended conformation at pH < 5 due to the repulsion between the positively-charged polymer chains segments. The PVP shells then act as reservoirs and nano-reactors for anionic species, and thus the PS-PVP-PEO micelles can be used to prepare organic-inorganic hybrid micelles.^{11–13}

The advantage of the PS-PVP-PEO micelles is demonstrated when they are employed as nano-reactors for the preparation of inorganic hollow nanoparticles.¹⁹ Compared to the micelles of AB diblock and ABA symmetric triblock copolymers, the PS-PVP-PEO micelles are stable even after the PVP shells are saturated with anionic precursors because the steric repulsion between the PEO coronas prevents the micelle aggregation. This is not the case of micelles of AB diblock and ABA symmetric triblock copolymers, which form micelles with a core-corona architecture, where the cores act as a template of the cavities, and the coronas act as a reservoirs and nano-reactors of the precursor of the inorganic material.^{20–23} In such systems, however, the template micelles become unstable when the precursor is incorporated into the coronas, because the

repulsion between the coronas is decreased by the incorporated precursor. This leads to the formation of aggregates in which two or more particles are bound to each other.

Although the PS-PVP-PEO micelles are useful in various aspects including the synthesis of inorganic hollow nanoparticles, they cannot incorporate the precursors into the shell domain under neutral and basic conditions since the PVP blocks are deprotonated and shrunk. Therefore, the use of the PS-PVP-PEO micelles are limited to acidic condition (pH < 5) for such purposes.

In this study, we have synthesized poly(styrene-*b*-2-vinyl-1-methylpyridinium iodide-*b*-ethylene oxide) (PS-PVMP-PEO) by quaternizing the PVP block of PS-PVP-PEO with iodomethane. The difference between PS-PVMP-PEO and PS-PVP-PEO is that the PVMP block in the former is positively ionized at any pH while the PVP block in the latter is ionized only under acidic condition. Therefore, the PS-PVMP-PEO micelles are expected to overcome the drawback of the PS-PVP-PEO micelles: they can incorporate precursors and other chemical species into the PVMP shell domain at any pH. This advantage will open wider applications for PS-PVMP-PEO. For example, it will be possible to use the micelles as a nano-container and a nano-carrier as well as a nano-reactor under wider pH condition. Thus, we prepared micelles of PS-PVMP-PEO in aqueous solutions under neutral pH condition, and prepared the PS-PVMP-PEO/tungstate hybrid micelles. Both PS-PVMP-PEO micelles and the PS-PVMP-PEO/tungstate hybrid micelles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), and zeta-potential measurements.

EXPERIMENTAL

Materials

PS-PVP-PEO (Polymer Source Inc.) was used as obtained.

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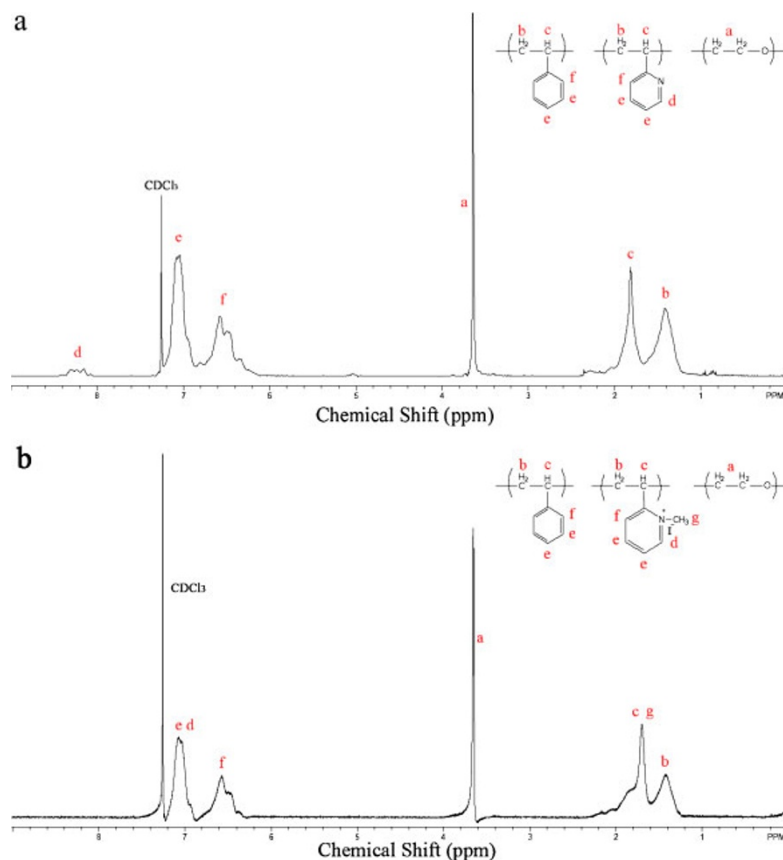


Figure 1. NMR spectra of (a) PS-PVP-PEO-1 and (b) PS-PVMP-PEO-1.

We employed two samples of PS-PVP-PEO with different PS, PVP, and PEO block lengths. One has the molecular weights of PS (45000), PVP (16000), and PEO (8500), and the other has the molecular weights of PS (20100), PVP (14200), and PEO (26000). We denote the former as PS-PVP-PEO-1 and the latter as PS-PVP-PEO-2. Iodomethane (CH_3I), sodium tungstate (Na_2WO_4), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and methanol were purchased from Wako Pure Chemicals and used without purification. Phosphotungstic acid hydrate ($\text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot x\text{H}_2\text{O}$) was obtained from Alfa Aesar and used as received.

Quaternization of the PVP block of PS-PVP-PEO

A certain amount of PS-PVP-PEO was put in a round flask and dissolved in the mixture of THF and methanol (1:1 v/v). Then a specific amount of iodomethane was added into the solution. After stirring for 2 d at room temperature, the solution was refluxed for 8 h. The polymer was precipitated by pouring the mixture into a large amount of cooled hexane. The product, PS-PVMP-PEO polymer, was dried under vacuum. The obtained polymers are denoted as PS-PVMP-PEO-1 and PS-PVMP-PEO-2.

The extent of quaternization of the PVP block was examined by NMR. The NMR spectra for both PS-PVP-PEO-1 and PS-PVMP-PEO-1 with the detailed assignment for the individual

resonance peaks are shown in Figure 1. The peaks around 6.3–7.2 ppm are attributed to the phenyl protons in the PS block and pyridyl protons in the PVP block. The peak at 3.6 ppm is assigned to the methylene group of the PEO block. The peaks around 1.4–1.8 ppm are attributed to the methylene protons of the PS and PVP backbones. It is known that the peaks around 8.2 ppm belong to the α -proton in the pyridyl ring. Comparison of the two spectra shows that the proton peaks around 8.2 ppm are almost lost in the spectrum of PS-PVMP-PEO-1. This fact indicates that almost all the PVP units were converted to PVMP. Similar results were obtained for PS-PVP-PEO-2 and PS-PVMP-PEO-2 (see supporting information). It should be noted here that there is no other significant change in the NMR spectra. We can conclude that there is no degradation of the copolymer during the quaternization.

Preparation of PS-PVMP-PEO Micelles

The PS-PVMP-PEO polymer was first dissolved in DMF at the initial concentration of 1 wt%. After the polymer was completely dissolved, water was added dropwise (1 wt% per minute) to the solution with vigorous stirring until the water content reached 15 wt%. To get the final polymer concentration of 0.5 wt%, more water had to be added to the solution. The solution was then dialyzed against water to obtain the micellar solution. This solution was diluted to a concentration

of 1 gL^{-1} as the stock solution with the pH around 7. The micellar solutions were characterized without further adjustment of pH and ionic strength.

Preparation of PS-PVMP-PEO/Tungstate Hybrid Micelles

A certain amount of micelle solution was taken from the stock solution and mixed with a specific amount of sodium tungstate solution. Then the mixture was diluted to the polymer concentration of 0.08 gL^{-1} .

^1H Nuclear Magnetic Resonance (NMR) Measurements

NMR measurements were carried out with a JEOL JNM-AL300 instrument. Deuterated chloroform was used as the solvent.

Dynamic Light Scattering (DLS) Measurements

DLS was measured with an Otsuka ELS-8000 Electrophoretic Light Scattering Spectrophotometer at a fixed 90 degree scattering angle. The correlation functions were analyzed by the cumulant method to determine the diffusion coefficient (D) of the micelles. The hydrodynamic diameter (D_h) was calculated from D using the Stokes-Einstein equation:

$$D_h = \frac{k_B T}{3\pi\eta D},$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the solvent viscosity.

Zeta-Potential Measurements

Zeta-potential was calculated from the electrophoretic mobility, which was measured with an Otsuka ELS-8000 Electrophoretic Light Scattering Spectrophotometer.

Scanning Electron Microscopy (SEM)

To prepare the SEM sample, one drop of micelle solution (polymer concentration: 1 gL^{-1}) was cast on the carbon film followed by evaporation of water under air atmosphere. SEM observations were carried out with a Hitachi U1500 Electron Microscope operated at 15 kV.

Transmission Electron Microscopy (TEM)

The TEM samples were prepared by casting one drop of micelle solution (polymer concentration: 1 gL^{-1}) on a copper grid, followed by staining with phosphotungstic acid. The TEM pictures were recorded on JEOL JEM-1210 Electron Microscope at the voltage of 80 kV.

RESULTS AND DISCUSSION

Characterization of the PS-PVMP-PEO Micelles

Figure 2 shows the micelle morphology obtained by SEM measurements. The SEM images clearly show spherical particles both for PS-PVMP-PEO-1 and PS-PVMP-PEO-2. These pictures give concrete evidence for micelle formation of PS-PVMP-PEO.

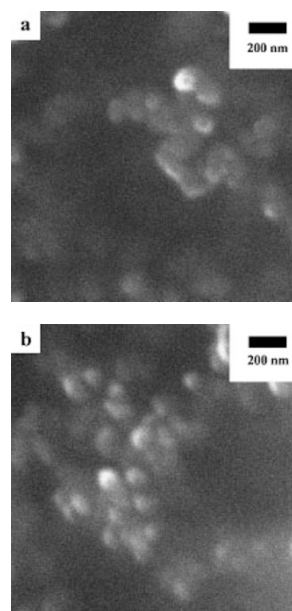


Figure 2. SEM images of (a) PS-PVMP-PEO-1 and (b) PS-PVMP-PEO-2 micelles. The sample for the SEM measurement was prepared from the solution with the polymer concentration of 1 gL^{-1} .

The hydrodynamic diameter (D_h) of the PS-PVMP-PEO micelles was measured by DLS. When the concentration of PS-PVMP-PEO-1 is higher than 0.007 gL^{-1} , we detected scattered light strong enough to make reliable analysis which yielded D_h approximately 150 nm. Below this concentration, the scattering intensity was too weak for obtaining reasonable results. For PS-PVMP-PEO-2, we obtained a reliable D_h value (approximately 120 nm) when the polymer concentration was higher than 0.04 gL^{-1} .

Critical micelle concentration (CMC) is an important parameter of polymeric micelles. However, we could not determine the CMC although we tried to estimate it by several techniques including fluorescence spectroscopy. Therefore, it is currently unclear whether the micelles have a CMC. The micelles behave like *frozen* micelles,²⁴ which have no CMC because the exchange of the unimer between the micelles and the aqueous bulk phase is quite slow (or does not occur). This can be explained by the high glass transition temperature, T_g , of PS blocks.

Figure 3 shows TEM pictures of PS-PVMP-PEO-1 and PS-PVMP-PEO-2 micelles stained with phosphotungstic acid. The dark background is due to phosphotungstic acid employed for negative staining. The white spheres indicate the PS core of the PS-PVMP-PEO micelles. It is clear from the TEM pictures that the PS cores have a spherical structure in both micelles. The averaged diameters of the PS cores are 17 nm for PS-PVMP-PEO-1 and 11 nm for PS-PVMP-PEO-2. The fact that the diameter of the PS core of the PS-PVMP-PEO-1 micelle is larger than that of PS-PVMP-PEO-2 micelle reflects the fact that the molecular weight of the PS of the former polymer is larger than that of the latter.

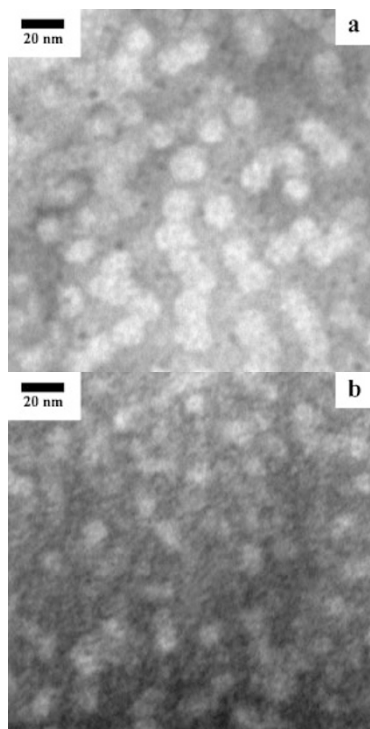


Figure 3. TEM images of (a) PS-PVMP-PEO-1 and (b) PS-PVMP-PEO-2 micelles. The micelles were stained by phosphotungstic acid.

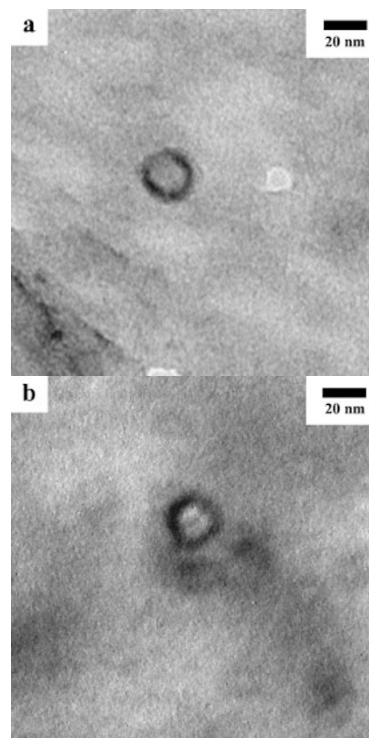


Figure 4. TEM images of (a) PS-PVMP-PEO-1/tungstate and (b) PS-PVMP-PEO-2/tungstate hybrid micelles. *DN* is equal to 100%. The concentration of PS-PVMP-PEO-1 and PS-PVMP-PEO-2 in aqueous solutions is 0.08 gL⁻¹.

Preparation of PS-PVMP-PEO/Tungstate Hybrid Micelles

We reported previously^{25,26} that some anionic species can be incorporated into the ionized PVP shell of PS-PVP-PEO micelles in acidic solutions. Therefore, we examined if anionic species can also be incorporated into the PMVP shell of PS-PVMP-PEO micelles. Tungstate ion was selected as an example of the anions, because tungstate nanoparticles have been known as a semiconductor photocatalyst. A specific amount of sodium tungstate was added into a PS-PVMP-PEO micelle solution. To show the amount of added tungstate ion we define an apparent degree of neutralization (*DN*) as follows:

$$DN(\%) = \frac{\text{amount of tungstate ion (mol)}}{\text{amount of VMP units (mol)}} \times 100,$$

where VMP stands for 2-vinyl-1-methylpyridinium ion. According to this definition, *DN* = 100% means that all of the cationic sites of the PVMP are occupied by tungstate ions under the condition that all the added tungstate ions are bound to the PMVP block. Figure 4 presents the TEM pictures of the PS-PVMP-PEO micelles after tungstate ion is incorporated. We can see a dark periphery around a white sphere in both pictures. The dark periphery is the tungstate-loaded PVMP shell and the white sphere is the glassy PS core. These pictures clearly show that tungstate ions are effectively bound to the PVMP shell to give PS-PVMP-PEO/tungstate hybrid micelles.

We also measured zeta-potential to confirm the binding of tungstate ions to the PVMP shell of the micelle. Since the PS-PVMP-PEO micelle particles have a positive charge while a

tungstate ion has a negative charge, it can be expected that the zeta-potential of the PS-PVMP-PEO micelle particles is positive, and decreases with increasing amount of the bound tungstate ion. Figure 5 shows the zeta-potential of PS-PVMP-PEO micelle as a function of *DN* (*i.e.*, the amount of the added tungstate ion). When *DN* was increased to 100%, the zeta-potential was almost zero. It indicates that almost all charge of the PVMP was cancelled by anionic tungstate ions. This fact also demonstrates that tungstate ions are well bound to the PVMP shell of the PS-PVMP-PEO polymeric micelle. It should be noted here that PS-PVMP-PEO-1 and PS-PVMP-PEO-2 show different behavior in the change of zeta-potential and that the zeta-potential does not linearly change with the total concentration of tungstate in both systems. According to the theory of interfacial double layer, zeta-potential is the potential difference between the dispersion medium and the stationary layer of the fluid around the dispersed particle. In micellar solutions, the zeta-potential will be affected by the factors which change the electrical stability of the system. In the present case, the two polymeric micelles have different particle size as well as different chain-length of positive PVMP shell. The extent of shrinkage of the micelles might be different when tungstate was added. Therefore, it seems possible that the two polymers show different behavior in the change of the zeta-potential. The non-linear change of the zeta-potential can be ascribed to the two reasons: (i) The size of micelle was changed by the addition of tungstate, as mentioned, and (ii) The amount of sorbed tungstate did not linearly increase with the

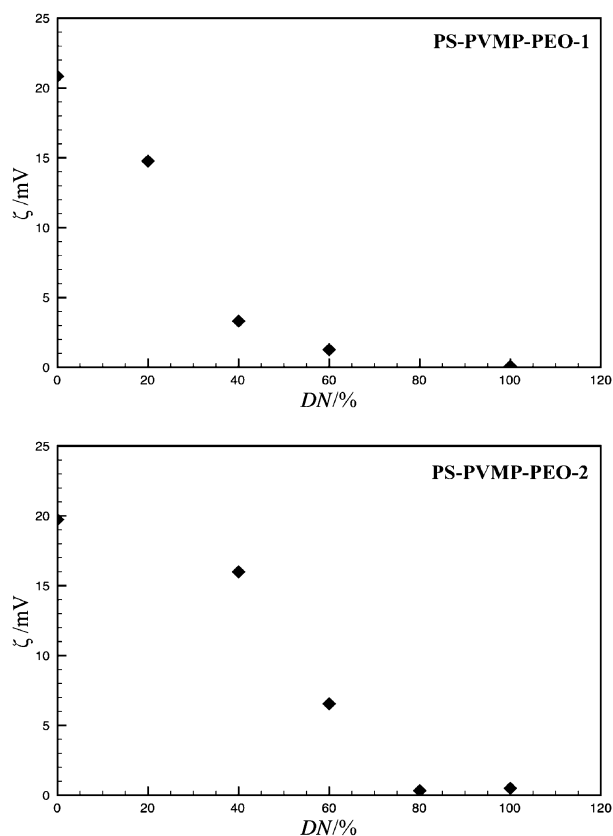


Figure 5. Change in the zeta-potential of PS-PVMP-PEO/tungstate hybrid micelles as a function of DN .

increase in the amount of added tungstate. The similar non-linear change of the zeta-potential was also observed for other systems.^{27,28}

It is expected, as in the case of PS-PVP-PEO,¹³ that the PS-PVMP-PEO micelles undergo a size change with the increasing amount of bound tungstate. Since the stimuli-responsive nature of polymeric micelles has attracted much attention in recent decades, the size change was investigated by DLS measurements. Figure 6 shows the dependence of the hydrodynamic diameter of PS-PVMP-PEO-1 micelle on DN . The hydrodynamic diameter keeps decreasing with increasing DN , and becomes constant when DN is higher than 100% (in this representation values of $DN > 100\%$ mean that there are unbound tungstate ions in the solution). This change in the size can be ascribed to the conformational change in the PVMP blocks. When $DN = 0$, the PVMP block is positively charged, so that it takes an extended conformation due to the electrostatic repulsion between the positive charges. As the tungstate ion is bound to the PVMP block, the positive charge of the polymer is cancelled by the negative charge of the tungstate ion, leading to the conformational change from extended to shrunk structures. The binding of the tungstate ion is completed at $DN = 100\%$, and thereafter the conformational change of the PVMP block does not occur any more.

It should be stressed here that the binding of the counterion to the PVMP shell could be done even in a neutral pH

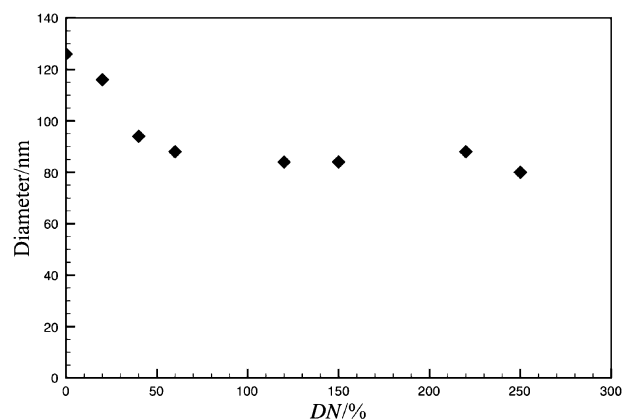


Figure 6. Change in the hydrodynamic diameter of PS-PVMP-PEO-1/tungstate hybrid micelle as a function of DN (values of $DN > 100\%$ mean that there are unbound tungstate ions in the solution).

condition. This is an advantage of PS-PVMP-PEO compared to PS-PVP-PEO—the incorporation of reactants is possible at any pH in the former whereas it is possible only in acidic conditions in the latter.

CONCLUSIONS

PS-PVMP-PEO was synthesized by quaternizing the PVP block of PS-PVP-PEO with iodomethane. The extent of quaternization of the PVP block is almost 100% as confirmed by NMR.

The micelles of PS-PVMP-PEO with PS core, PVMP shell and PEO corona were prepared in aqueous solutions by dialysis techniques. It is shown by SEM measurements that the micelles have a spherical structure. DLS measurements revealed that the hydrodynamic diameters of the PS-PVMP-PEO-1 and PS-PVMP-PEO-2 micelles are about 150 and 120 nm, respectively, at a neutral pH condition. The CMC of the micelle could not be obtained. This may be due to a frozen state of the micelles. The PS-PVMP-PEO/tungstate hybrid micelles were prepared in a neutral pH condition. TEM and zeta-potential measurements showed that tungstate anions were effectively incorporated into the PS-PVMP-PEO neat micelles to give the PS-PVMP-PEO/tungstate hybrid micelles. The incorporation of tungstate ions into the micelle caused a significant change in D_h of the micelle. The change in D_h is attributed to a conformational change in the PVMP block from an extended to a shrunk structure, which is induced by cancellation of the positive charge of the PVMP block with the negative charge of the bound tungstate ions. This stimuli-responsive nature is the main advantage of the PS-PVMP-PEO micelles.

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Electronic Supporting Information Available: NMR spectra of PS-PVP-PEO-2 and PS-PVMP-PEO-2. These materials are available via the Internet at <http://www.spsj.or.jp/c5/pj/pj.htm>

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