

Supplementary data

Materials

Three block copolymers poly(ethylene oxide)-*b*-Poly(2-vinylpyridine) (PEO-*b*-P2VP) with the molecular weights of 14500-*b*-13500 □ 2600-*b*-1500 □ 5900-*b*-26400 and the molecular weight distributions Mw/Mn of 1.11, 1.07, 1.08, respectively were purchased from Polymer Source, Inc. Potassium persulfate (K₂S₂O₈) of analytical purity was recrystallized from deionized water.

Micelles formed by the complexation between PEO-*b*-P2VPH⁺ block copolymers and K₂S₂O₈.

The block copolymer was dissolved in pH 1.3, 2.0, 3.0 aqueous solutions respectively. The micelle solution was prepared by adding K₂S₂O₈ (in H₂O) dropwise to the solutions of the block copolymer under ultrasound. The final concentration of the copolymer is 1.0 mg/mL. The molar ratio of the pyridine units of the copolymer to K₂S₂O₈ was fixed at 1:1.

PEO-*b*-P2VP micelles formed in aqueous water at pH>6.0

The block copolymer PEO₃₂₉-*b*-P2VP₁₂₈ (the subscript is the average number of the repeat units) was dissolved in THF at the concentration of 1.0 mg/mL. The THF solution of the copolymer was dialyzed against deionized water for 3 days to form the copolymer micelles in the selective solvent (water).

Iodimetric titration

Iodimetric titration was conducted according to the standard procedures described in the text book of Analytical Chemistry.

The preparation of the micelles at higher pH

We carried out the micellization at higher pH. It was found that when the pH is 2.0, the mixing with K₂S₂O₈ under the identical conditions leads to the micellization of the block copolymer PEO₃₂₉-*b*-P2VP₁₂₈. The resultant micelles can dissociate by increasing the temperature of the aqueous solution, and the critical temperature for the dissociation is about 50°C, being higher than that of the micelles formed at pH 1.3. However, when the pH is 3.0, no micelles can be formed.

In the solution at pH of 1.3, [H⁺]=0.05 M. In this case, the concentration of the copolymer is 1.0 mg/mL and the concentration of pyridine groups is 0.0046 M. It is expected that at such a low pH, all the pyridine groups are protonated. This makes our understanding of the mechanism for the micellization easy. In the solutions at pH of 2 and 3, the concentrations of proton are about 0.01 and 0.001, respectively. In these cases, there may be some pyridine units that are free from the protonation. The existence of the un-protonated pyridine units should have a complicated effect on the behavior of the block copolymer or the resultant micelles when the pH is 2.0. Further studies on the effect of the pH are needed.