Electronic Supplementary Information for

Stability enhancement of ZnTPPS in acidic aqueous solutions by polymeric micelles

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Experimental Section

Materials

Poly(ethylene glycol) monomethyl ether (CH_3O-PEG_{114}-OH) (M_n=5000 g/mol and polydispersity index PDI = 1.05) was purchased from Fluka. CuCl and 4-vinyl pyridine were purchased from Aldrich and purified according to ref. 1. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized according to ref.1. The water used in this study was purified with a Millipore Mill-Q system (>18 MΩ). Other reagents were used as received without further purification.

Preparation of the Macroinitiator PEG-Br.

The macroinitiator PEG_{114}-Br was synthesized according to ref. 2. The typical procedure to prepare PEG_{114}-Br was introduced as follows. 25.0 g CH_3O-PEG_{114}-OH was dissolved in 300 mL toluene in a 500 mL three-neck flask. After azeotropic distillation of about 60 mL toluene at

reduced pressure to remove traces of water, 1.2 mL triethylamine was added and the solution mixture was cooled down to 0 °C. Then 1.2 mL 2-bromoisobutyryl bromide was added via a syringe over 1 hour, and the reaction mixture was stirred overnight at room temperature. The solution was treated with charcoal, which was subsequently removed by filtration, and most of the toluene was removed by rotary evaporation prior to precipitation into a 10-fold excess of cold ether. The crude polymer was dried under vacuum, then dissolved in water at pH 8-9, and then extracted with CH_2Cl_2. The organic layer was collected and dried over $MgSO_4$, and the purified PEG_{114}-Br was isolated after the evaporation of the solvents under vacuum.

Synthesis of PEG-*b*-P4VP.

PEG-*b*-P4VP was synthesized by ATRP of 4-vinyl pyridine using PEG-Br as macroinitiator. 5.0 g PEG_{114}-Br was added to a reaction flask and then 6 ml solvent mixture of butanone and 2-propanol (7:3 by volume) was added. The sample was first stirred and then degassed under nitrogen purge. Subsequently, 0.15 g CuCl and 0.35 g Me_6TREN catalysts were introduced into the reaction flask. Then 10.0 g 4-vinyl pyridine was added into the flask and degassed under nitrogen purge again. Polymerization was performed at 40ºC for 4 hours and the monomer conversion in 4 hours is over 75%. The block copolymer PEG-*b*-P4VP was purified by first passing through an Al_2O_3 column to remove the

copper catalyst and then deposited in cold ether. The powder of PEG-*b*-P4VP was dried in a vacuum oven at 30ºC.

^{1}HNMR Characterization.

The ^{1}HNMR spectra of the polymers in $CDCl_3$ shown in Fig. S1 were recorded on a Bruker AV300 spectrometer. The composition of PEG-*b*-P4VP is determined by the ratio of the total area of peaks b and c to peak a and the degree of polymerization (DP) of P4VP is determined to be 90. The M_n of the block copolymer is calculated to be 1.4×10^4 g/mol.

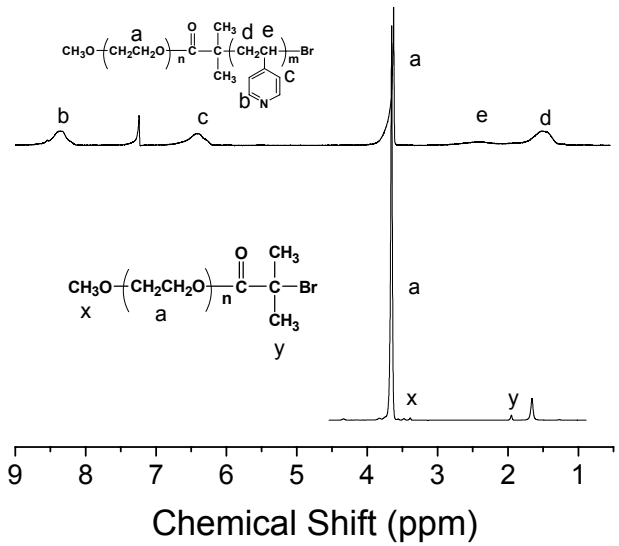

Fig. S1 ^{1}H NMR spectra of PEG_{114}-Br and PEG_{114}-*b*-$P4VP_{90}$ in $CDCl_3$.

Gel Permeation Chromatography (GPC).

PEG_{114}-Br and PEG_{114}-*b*-$P4VP_{90}$ were characterized by a Waters 600E GPC system, with DMF as the eluent and narrowly distributed polystyrene as the calibration standard. The GPC traces for PEG_{114}-Br

and PEG_{114}-*b*-$P4VP_{90}$ in DMF are shown in Fig. S2. The polydispersity index (PDI) of PEG_{114}-Br and PEG_{114}-*b*-$P4VP_{90}$ measured by GPC is 1.03 and 1.23, respectively. The weight-averaged molecular weight (M_w) of the block copolymer is calculated to be 1.8×10^4 g/mol by $M_w = M_n \times$ PDI.

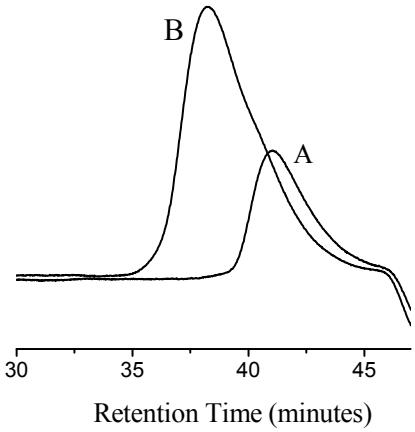

Fig. S2 GPC traces for PEG_{114}-Br (A) and PEG_{114}-*b*-$P4VP_{90}$ (B)

Dynamic light scattering (DLS).

Fig. S3 shows the DLS profile of PEG_{114}-*b*-$P4VP_{90}$ micelles without ZnTPPS at pH 9.0, where the micelle solutions have the same polymer concentration of 0.033 mg/mL with that of complex micelles solutions of PEG_{114}-*b*-$P4VP_{90}$ and ZnTPPS where R = 10. The result shows that the micelles have a mean hydrodynamic diameter of 96 nm, which is smaller than that of the complex micelles of PEG_{114}-*b*-$P4VP_{90}$ and ZnTPPS.

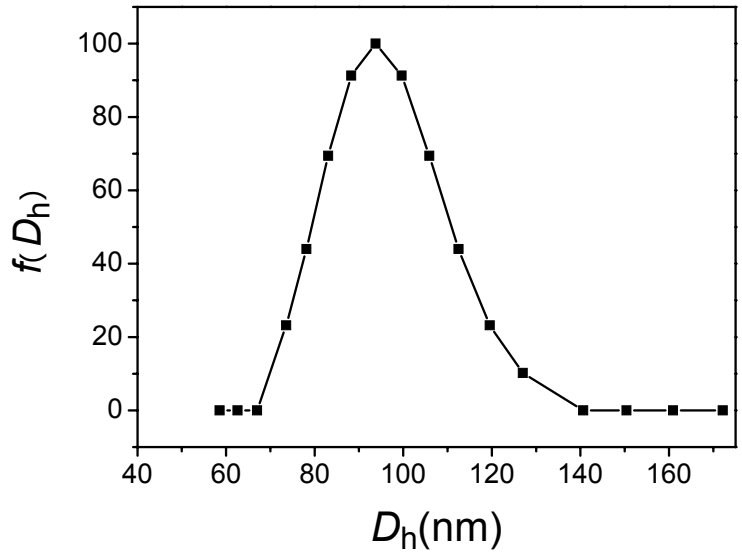

Fig. S3 DLS profile of micelles of PEG_{114}-*b*-$P4VP_{90}$ without ZnTPPS at pH 9.0. The DLS measurements were performed at the scattering angle of 90^{o} at room temperature.

References

1. J. H. Xia, X. Zhang, and K. Matyjaszewski, *Macromolecules*, 1999, 32*,* 3531.

2. (a) S. Y. Liu, J. V. M. Weaver, M. Save, and S. P. Armes, *Langmuir*, 2002, **18***,* 8350.

(b) W. Q. Zhang, L. Q. Shi, L. C. Gao, Y. L. An, G. Y. Li, K. Wu, and Z. Liu, *Macromolecules,* 2005, **38**, 899.