

Electronic Supplementary Information (ESI) for

Effective oxidation protection of polymer micelles for copper nanoparticles in water

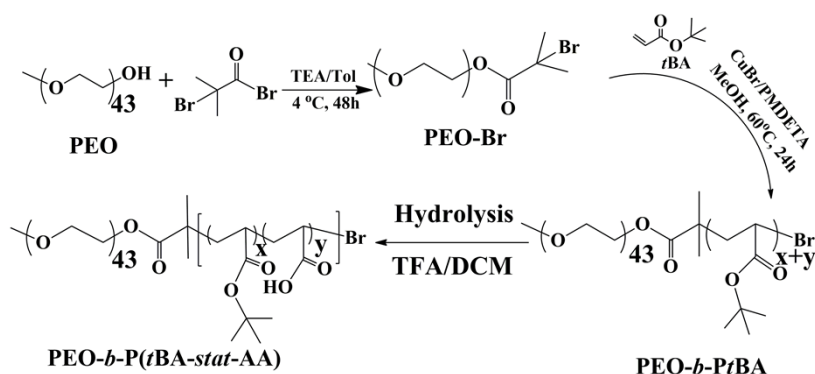
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Scheme S1 The structure of chlorophyll and chloroplast. The hydrophobic chain of chlorophyll is inserted in the membrane of (I) chloroplast and (II) thylakoid.



Scheme S2 Synthetic route to PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) block copolymer.



Scheme S3 Michael addition reaction between thiazolidine-2,4-dione and styrene using Cu nanoparticles as the catalyst dispersed in THF at 25°C.

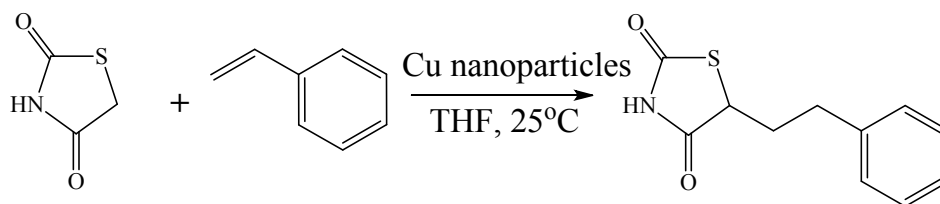


Fig. S1 GPC traces of PEO₄₃-*b*-PtBA₂₀ diblock copolymer in DMF.

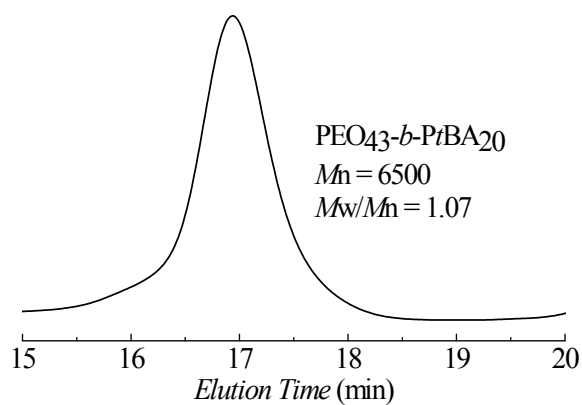
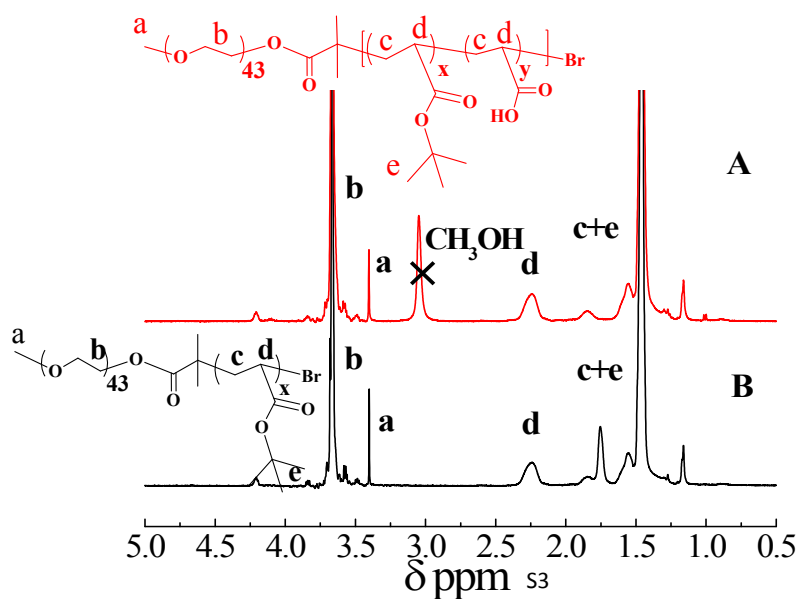


Fig. S2 ¹H NMR spectra of (A) PEO₄₃-*b*-P(BA₁₈-*stat*-AA₂) diblock copolymer and (B) PEO₄₃-*b*-PtBA₂₀ diblock copolymer in CDCl₃.



Determination of the block copolymer composition:

In the ^1H NMR spectra (Fig. S2), peaks a and b belong to PEO, peak d and peak c+e belong to PtBA. The degrees of polymerization were calculated according to the following procedures.

In Table S1, a_b , a_d and a_{c+e} are the areas of peaks b, d and c+e in Fig. S2. x and y are the degrees of polymerization of PtBA and PAA, respectively. A represents the copolymer $\text{PEO}_{43}\text{-}b\text{-PtBA}_x$. B corresponds to $\text{PEO}_{43}\text{-}b\text{-P}(t\text{BA}_x\text{-stat-AA}_y)$.

Table S1. The integration areas of different peaks and the degrees of polymerization of different copolymers.

Polymer	Solvent	a_b	a_d	a_{c+e}	x	y
A	CDCl_3	170	20.4	219.3	20	
B	CDCl_3	170	19.6	201.9	18	2

A: according to peak d: $x = \frac{20.4}{170} \times \frac{43 \times 4 - 2}{1} = 20.4 \approx 20$

according to peak c+e: $x = \frac{219.3}{170} \times \frac{43 \times 4 - 2}{9 + 2} = 19.9 \approx 20$

B: according to peaks d and c+e:

$$x + y = 20$$

$$2y + (2 + 9)x = 201.9$$

$$x = 18.1 \approx 18$$

$$y = 1.6 \approx 2$$

Fig. S3 (A) CMC measurement of the PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) block copolymer micelles. Fluorescence emission spectrum of pyrene at 383.1 nm is a function of the copolymer concentration in pure water at 25 °C. This experiment confirmed the CMC of the copolymer is 39.8 μg mL⁻¹. (B) Fluorescence emission spectrum of pyrene from 350 nm to 500 nm.

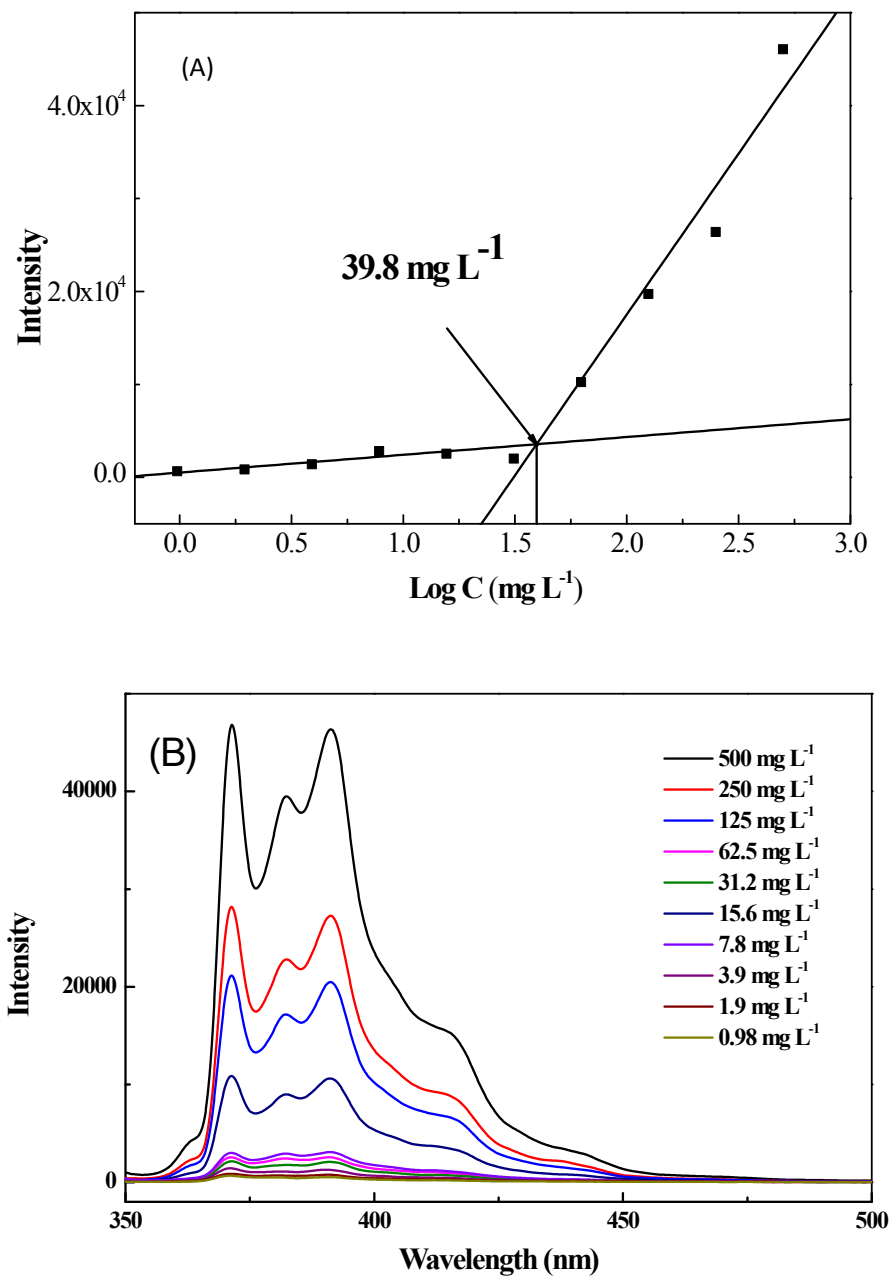


Fig. S4 (A) Intensity and (B) number-averaged size distribution of polymer micelles before and after deposition of copper determined by DLS in water.

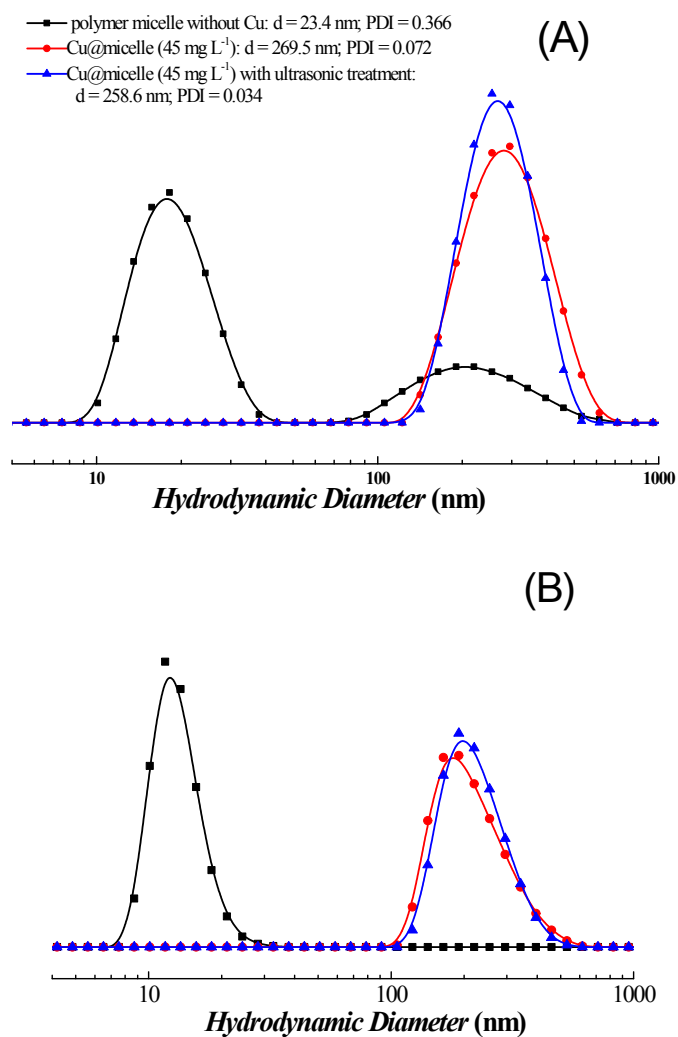
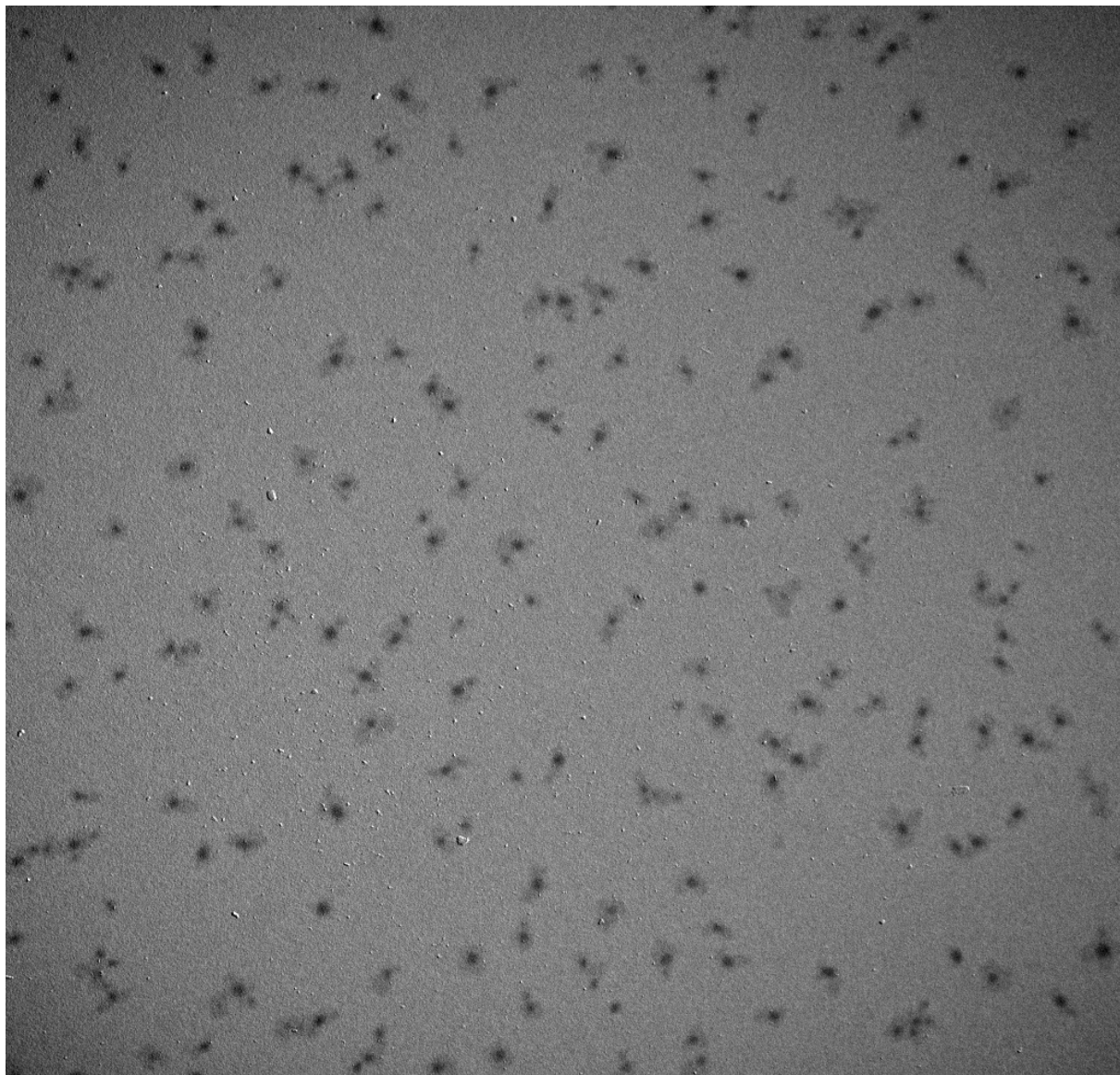


Fig. S5 TEM images of copper nanoparticles protected by PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) micelles. The concentration of copper after reduction is 45 μg mL⁻¹. The corona-core structure is clear.



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500 nm

HV=80.0kV

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Fig. S6 TEM images of copper nanoparticles protected by PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) micelles. The concentration of copper after reduction is 76 μg mL⁻¹. Compared with Fig. S5, the corona-core structure is not clear.

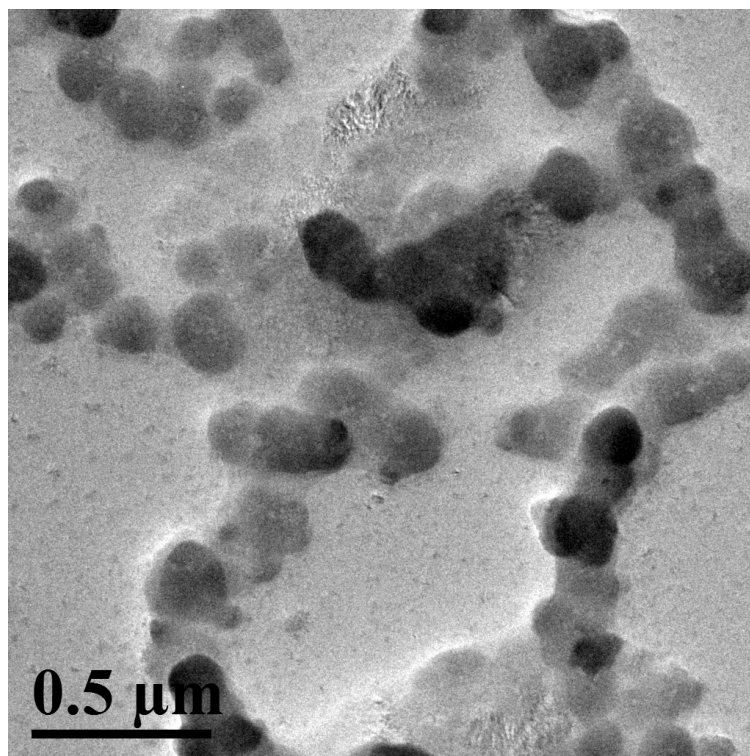


Fig. S7 Correlation coefficient and PDI data of polymer micelle (a) in water; (b) in water/THF mixture for 1 min and (c) 1 h. The data in (c) is not reliable due to the high PDI.

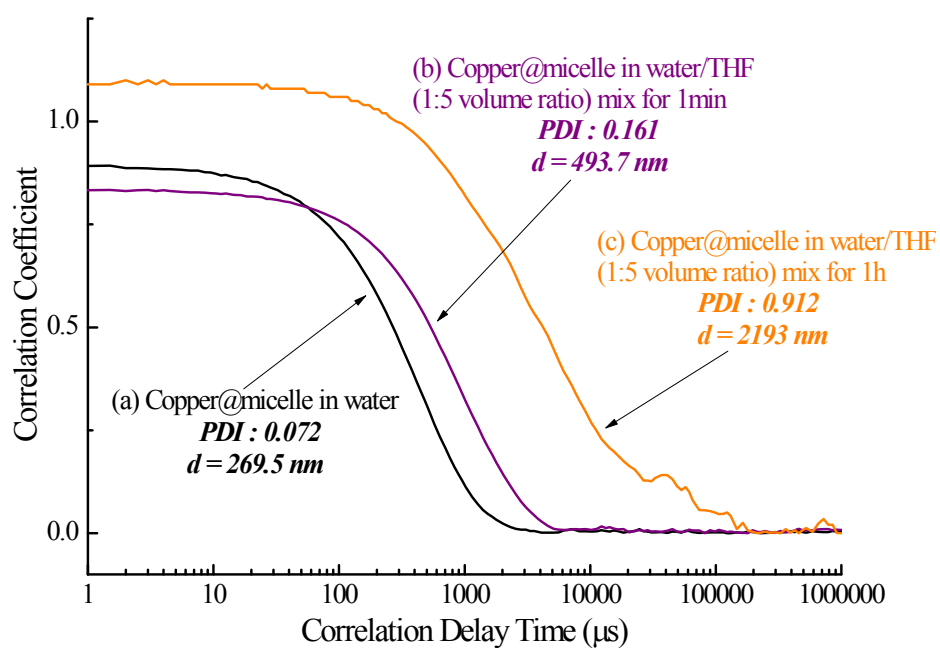


Fig. S8 Conversion of Michael addition reaction between thiazolidine-2,4-dione and styrene using different copper catalysts.

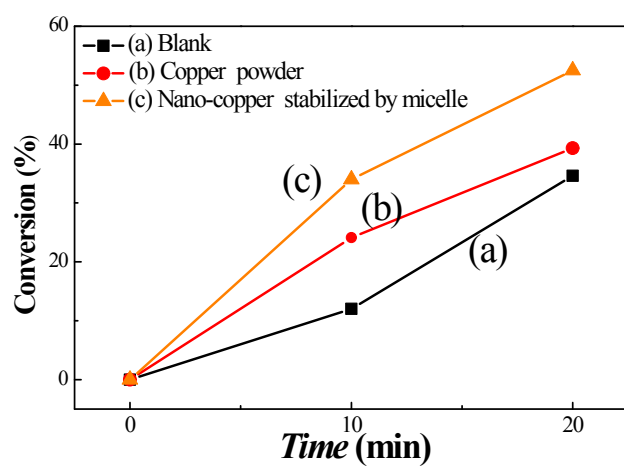
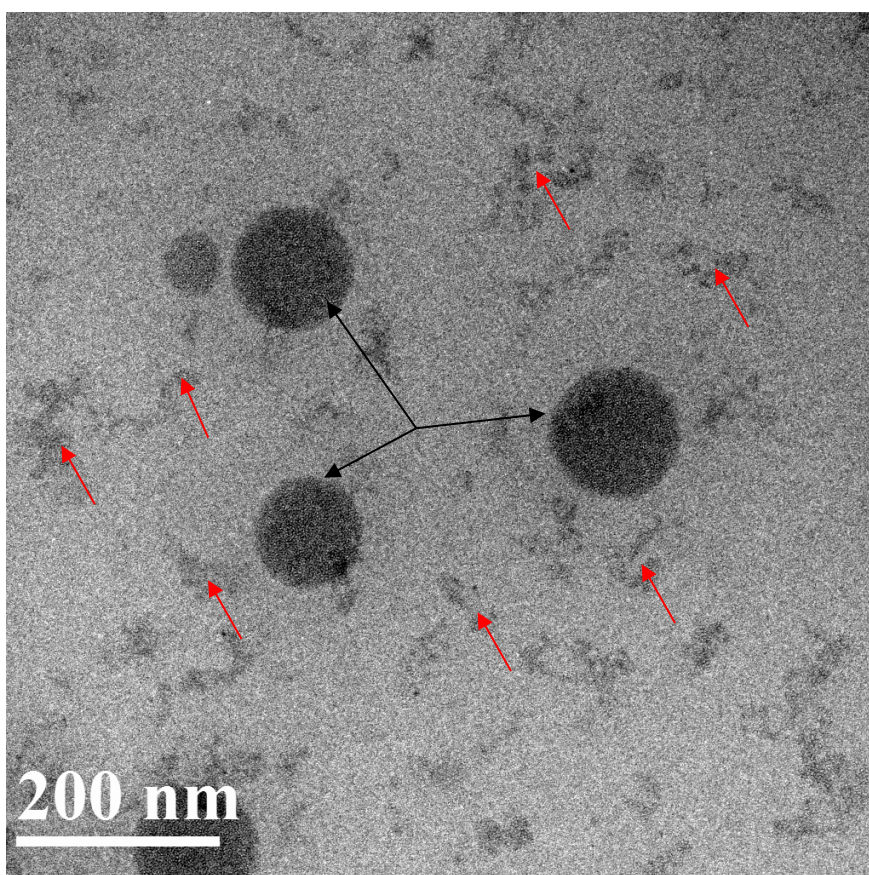


Fig. S9 TEM image of copper@micelle dissolved in THF. Black arrows: copper nanoparticles; Red arrows: polymer aggregations.



Experimental Section

Materials. Polyethylene glycol monomethylether (MeO-PEO-OH; $M_n = 1900$) was purchased from Alfa Aesar and dried azeotropically by using anhydrous toluene to remove traces of water. *t*-Butyl acrylate (*t*BA) monomer was obtained from Tokyo Chemical Industry Co., Ltd. A silica column was used to remove the inhibitor before use. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 98%), triethylamine, copper(II) bromide (CuBr_2 , 99.9%), styrene and thiazolidine-2,4-dione were purchased from Aladdin Chemistry, Co. Dimethyl formamide (DMF), 2-bromoisobutyryl bromide, copper(I) bromide (CuBr , 99.9%) and other reagents were used as received. Dialysis tubing with molecular weight cutoff from 8000 to 14000 was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Characterization. DMF GPC. Gel permeation chromatography (GPC) analysis was carried out with a Waters Breeze 1525 GPC analysis system with two PL mix-D columns, using DMF with 0.5 M LiBr as eluent at a flow rate of 1.0 mL/min at 35 °C. The copolymer was dissolved in DMF and filtered prior to analysis.

¹H NMR Spectra. ¹H NMR Spectra were recorded using a Bruker AV 400 MHz spectrometer at ambient temperature using CDCl_3 as solvents.

DLS Studies. Zetasizer Nano series instrument (Malvern Instruments ZS 90) equipped with a multipurpose autotitrator (MPT-2) was used to conduct the studies. DLS studies of aqueous polymer vesicles and micelles were carried out at a fixed scattering angle of 90°. Each reported measurement was conducted three runs. The diameter of the vesicles and micelles in our research were measured using dynamic light scattering by quoting Stokes–Einstein equation ($D =$

$kT/(3\pi\eta D_h)$).

TEM images were obtained using a JEM 2100 electron microscope operating at an acceleration voltage of 200 kV. To prepare TEM samples, 10 μL of diluted aqueous particle solution was placed on a copper grid coated with thin films of carbon. The water droplet was removed by evaporation under ambient conditions.

The fluorescence study was carried out at an emission wavelength of 372.1 nm and an excitation wavelength of 334 nm using pyrene as the fluorescence probe. The fluorescence spectroscopy is purchased from Thermo Fisher (LF-1202002).

The UV-vis absorption spectra of aqueous polymer solution and copper nanoparticles were acquired using a UV-759S spectroscopy (UV-759S, Q/YXL270, Shanghai Precision & Scientific Instrument Co., Ltd) to monitor the UV absorption changing of the solution.

X-ray photoelectron spectroscopy (XPS) spectrum was conducted to test the existence of copper nanoparticles. The copper nanoparticle solution was diluted at ambient temperature to 50 $\mu\text{g}/\text{mL}$ and dropped (10 μL) onto a silica wafer ($1\times 1\text{ cm}^2$) and dried at room temperature. The silica wafer was washed with acetone for 4 times before sample preparing. The XPS spectroscopy is purchased from Thermo Scientific Escalab 250Xi.

Synthesis of PEO₄₃-Br macroinitiator. PEO-Br macroinitiator were prepared by the reaction of 2-bromoisobutyryl bromide with MeO-PEO-OH in the presence of triethylamine according to a previously reported method.^{1,2} MeO-PEO₄₃-OH (10.0 g, 5.3 mmol) was dissolved in toluene (250 mL) in the flask in the oil bath at 135 °C and traces of water were removed by azeotropic distillation. The flask was cooled to room temperature and then placed in an ice-water bath.

Triethylamine (2.0 mL) was added into the flask. 2-Bromoisobutyryl bromide (1.90 mL, 15.0 mmol) in anhydrous toluene (20 mL) was subsequently added to the flask at a rate of approximately one drop every 10 s. After 40 h, the precipitated byproducts were removed by filtration. The organic solution was removed by rotary evaporation. The crude products were dissolved in dichloromethane (50 mL) and then mixed with pure water (50 mL) by vigorously stirring to remove the byproducts. The water phase was then extracted by dichloromethane twice. The combined organic solution was then further washed with 1.0 M HCl (50 mL) and 1.0 M NaOH (50 mL) aqueous solution and dried over anhydrous MgSO₄. The crude product was dissolved in dichloromethane (10.0 mL) and then precipitated in 500 mL of diethyl ether twice. Yield: 75%.

Synthesis of PEO₄₃-*b*-PtBA₂₀ block copolymer by ATRP. PEO₄₃-*b*-PtBA₂₀ was synthesized by ATRP in methanol using PEO-Br as macroinitiator, Cu(I)Br as the catalyst and PMDETA as the ligand. The molar ratio of PEO-Br: Cu(I)Br: PMDETA was 1: 1: 2. In a flask with a magnetic flea and a rubber septum, PEO-Br (0.50 g, 0.25 mmol) and PMDETA (0.043 g, 0.25 mmol) were dissolved in 3.0 mL methanol. Then *t*BA (0.63 g, 0.005 mol) was added into the flask. The solution was deoxygenated using an Argon sparge for 30 min before adding Cu(I)Br (0.036 g, 0.25 mmol). The polymerization was conducted under an Argon atmosphere at 60 °C for 24 h. On exposure to air the green solution turned to blue, indicating the produce of inactive Cu(II) complex. The copolymer was dissolved in dichloromethane and then passed through a silica column to remove the copper catalyst. Solvent and trace of residual monomer were removed under vacuum. GPC trace: see Fig. S1. ¹H NMR spectrum: see Fig. S2.

Preparation of PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) copolymer. Firstly, PEO₄₃-*b*-P(*t*BA₂₀) copolymer was dissolved in dichloromethane. TFA was then added with a TFA: *t*BA molar ratio of 2:1. After 0.5 h, the solution was concentrated with rotary evaporation and then dried under vacuum for 24 h to obtain the PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) copolymer. ¹H NMR spectrum: see Fig. S2.

Self-assembly of PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) into micelles. PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) copolymer (24.0 mg) was firstly dissolved in THF. Then water was added at a rate of approximately one drop every 2 s with vigorous stirring. After 2 h of stirring, the organic solvent was removed via dialysis against water for 48 h.

Preparation of copper nanoparticles stabilized by polymer micelles. The aqueous PEO₄₃-*b*-P(*t*BA₁₈-*stat*-AA₂) micelle solution (1.0 mg/mL; 10 mL) was mixed with CuCl₂ solution (2.0 mg/mL; 0.3 mL). After gently stirring for 30 min at room temperature, the solid NaBH₄ (3.0 mg) was then quickly added to the micelle solution. The solution immediately became yellow after adding NaBH₄. After 6 h of reduction, the solution was further purified by dialysis against water for 20 h and the final pH is ~ 7.

Catalytic activity of copper nanoparticles for Michael addition reaction.

In a typical experiment, the mixture of copper nanoparticles (2 μg), thiazolidine-2,4-dione (1.0 mmol) and styrene compound (1.0 mmol) in THF (2 mL) were mixed at room temperature. UV-vis spectra was conducted to record the intensity change of the peak from 300 nm to 550 nm in 20

mins.

Catalytic activity of copper nanoparticles in Michael addition reaction.

The conversions of reactants were evaluated by UV-vis spectroscopy. In the presence of copper nanoparticles protected by polymer micelles (Fig. 2), the maximum conversion of styrene can reach 53% after 20 min. (Fig. S8), which is nearly one time higher than that in the absence of micelle-protected copper nanoparticles (34%, Fig. S8).

The bulk copper powder without micelle stabilization also has catalytic property (Fig. S8) compared with the blank one. However, the catalytic property is worse than the micelle-protected copper nanoparticles because both styrene and thiazolidine-2,4-dione can diffuse into micelle to interact with nano-copper in THF, providing more surface area and finally leading to a better catalytic activity than bulk powders. This diffusion hypothesis can be further confirmed by the correlation function and the PDI data before and after THF added into the solution in Fig. S7. From the figure, we can see that the PDI data become higher (from 0.072 to 0.912) which means the devastation of the micelle system. As shown in the TEM images in Fig. S6, the core-shell structure (Fig. 2) were destroyed after the copper@micelle was dissolved in water/THF solution for one hour.

References

1. H. Lu, L. Fan, Q. Liu, J. Wei, T. Ren and J. Du, *Polym. Chem.*, 2012, **3**, 2217-2227.
2. T. B. Ren, Q. M. Liu, H. Lu, H. M. Liu, X. Zhang and J. Z. Du, *J. Mater. Chem.*, 2012, **22**, 12329-12338.