Supporting Information

In-situ Polymerization at the Interfaces of Micelles: A "Grafting From" Method to Prepare Micelles with Mixed Coronae

Kaiqiang Chen, Dehai liang, Jia Tian, Linqi Shi, Hanying Zhao

Macroinitiator PEG-Br

The apparent molecular weight (M_n) and molecular weight distribution of PEG-Br determined by GPC were 5K and 1.01, respectively. Figure S1 shows the ^{1}H NMR spectrum of the PEG-Br macroinitiator. Signal *a* at 3.4 ppm is attributed to the protons at the terminal methyl group (-CH_3). Signal *b* at 3.6 ppm is attributed to the methylene protons of PEG units (-CH_2-CH_2-O-). Signal *d* at 1.9 ppm is associated with the methyl protons on 2-bromoisobutyryl groups (-C(Br)-CH_3). The area ratio of signal a to signal *d* is 1/2, which means the esterification of the terminal –OH groups was conducted completely. Based on the area ratio of signal b to signal a, the number average degree of polymerization (DP_n) of PEG is determined to be 113 (Equation1).

$$\frac{I_b}{I_a} = \frac{4DP_{PEG}}{3} \quad \textbf{(1)}$$

Where, I_a and I_b are the integral area of signal *a* and signal *b* respectively, DP_{PEG} is the number average degree of polymerization of PEG., the number of methylene protons on per repeating unit is 4 and the number of methyl protons on terminal groups (signal *a* at 3.4 ppm) is 3.

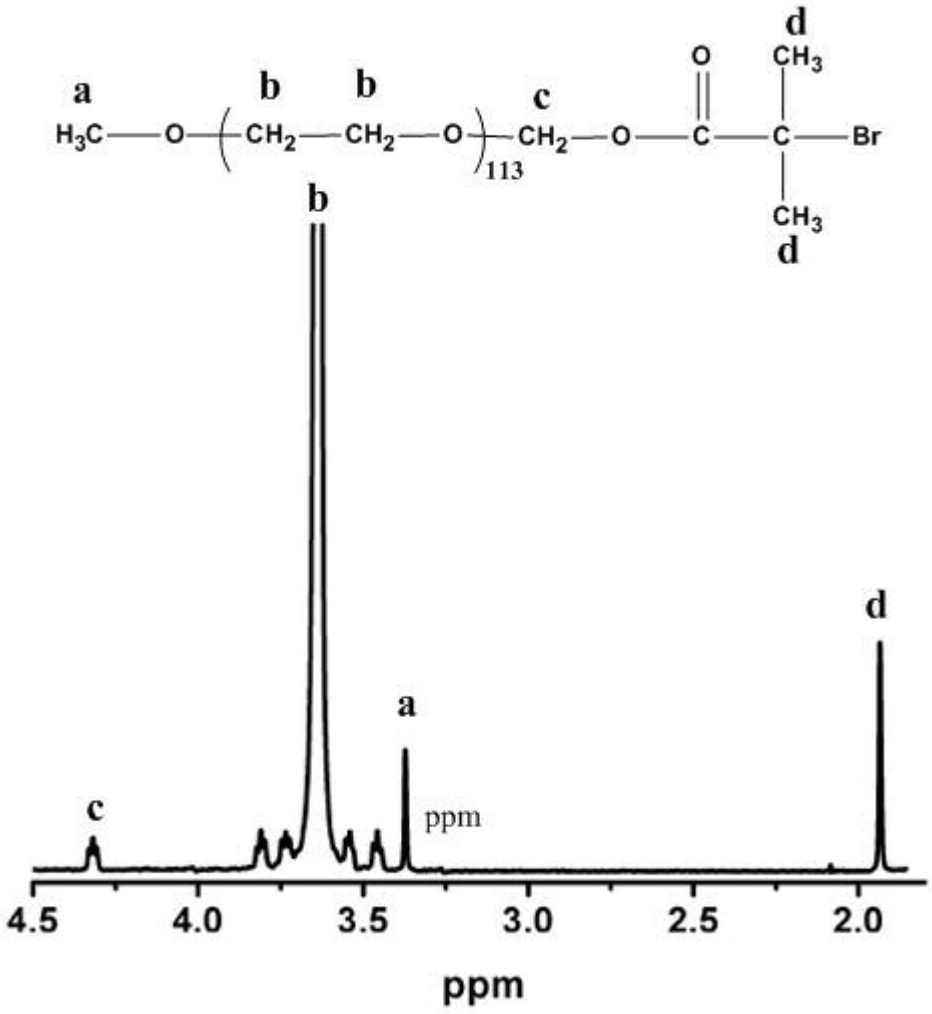

Figure S1. ^{1}H NMR spectrum of PEG-Br macroinitiator in $CDCl_3$.

PEG-b-PS diblock copolymer

According to GPC, the apparent molecular weight (M*n*) and molecular weight distribution of PEG-b-PS were 16K, 1.08, respectively. Figure S2 is the ^{1}H NMR spectrum of PEG-*b*-PS block copolymer. Signal *b* at 3.6 ppm is attributed to the methylene protons of PEG units (-CH_2-CH_2-O-). Signal *e* at 7.14 ppm and 6.69 ppm is attributed to phenyl protons on styrene repeating units. According to the area ratio of signa *b* to signa *e*, the DP_n value of PS is determined to be 106 (Equation 2).

$$\frac{I_e}{I_b} = \frac{5DP_{PS}}{113 \times 4} \qquad (2)$$

where I_e and I_b are the integral area of signal e and signal b respectively, DP_{PS} is the number average degree of polymerization of PS, the number of methylene protons on per PEG repeating unit is 4, the DP_n value of PEG is 113, and the number of phenyl protons on per PS repeating unit is 5.

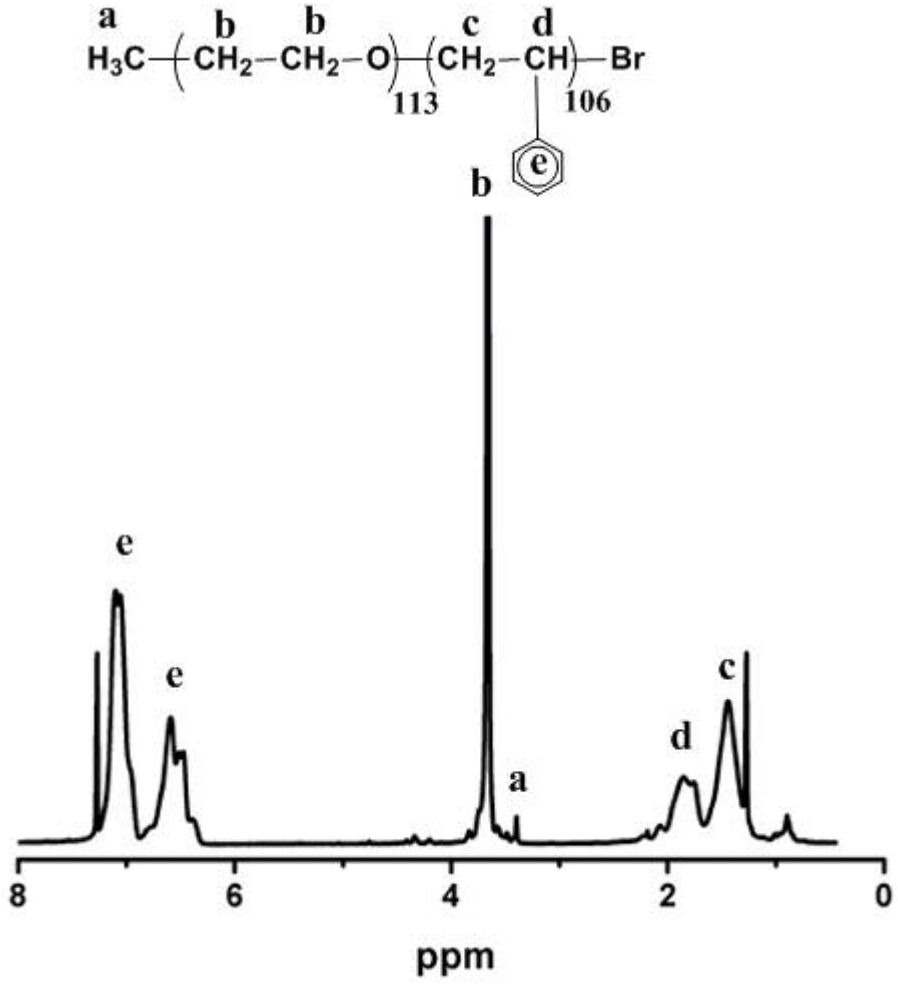

Figure S2. ^{1}H NMR spectrum of PEG-*b*-PS diblock copolymer in $CDCl_3$.

Sulphonated PEG-b-PS

Based on element analysis result the content of sulfur was determined to be 0.64 wt%, and thus

the degree of sulfonation of PS block was calculated to be 3.31 mol%.

In-situ ATRP of DMAEMA at the interface of micelles

According to GPC, the apparent molecular weight (M*n*) and the molecular weight distribution of PEG_{113}-*b*-(PS_{106}-g-$PDMAEMA_{50}$) were 23K and 1.22, respectively; the apparent molecular weight (M*n*) and the molecular weight distribution of PEG_{113}-*b*-(PS_{106}-g-$PDMAEMA_{247}$) were 51K and 1.38, respectively.

The structure and ^{1}H NMR spectrum of the polymer are shown in Figure S3. Signal *a* at 3.6 ppm was attributed to the methylene protons on PEG units (–C**H**$_2$–C**H**$_2$–O-). The chemical shift appeared at 2.6 ppm (signal *f*) was attributed to the methylene protons (–C**H**$_2$–N$(CH_3)_2$) on the tertiary amine. Signal *g* at 2.33 ppm is assigned to the methyl protons connecting to the nitrogen atom of DMAEMA. The number average degree of polymerization (DP_n) of PDMAEMA was calculated base on the area ratio of signal *a* to signal *g* by Equation 3.

$$\frac{I_g}{I_a} = \frac{106 \times 3.31\% \times 6DP_{PDMAEMA}}{113 \times 4} \quad \textbf{(3)}$$

Where, I_g and I_a are the integral area of signal g and signal a respectively, $DP_{PDMAEMA}$ is the number average degree of polymerization of PDMAEMA, the number average degree of polymerization of PS is 106, the degree of sulfonation of PS block is 3.31%, the number of methyl protons connecting to the nitrogen atom of DMAEMA is 6, the number of methylene protons on per PEG repeating unit is 4, and the number average degree of polymerization of PEG. is 113.

In this study, micelles with two different PDMAEMA chain lengths were prepared, one with DP_n of 50 and the other with DP_n of 247. The polymers were referred to as PEG_{113}-*b*-(PS_{106}-g-$PDMAEMA_{50}$) and PEG_{113}-*b*-(PS_{106}-g-$PDMAEMA_{247}$), respectively.

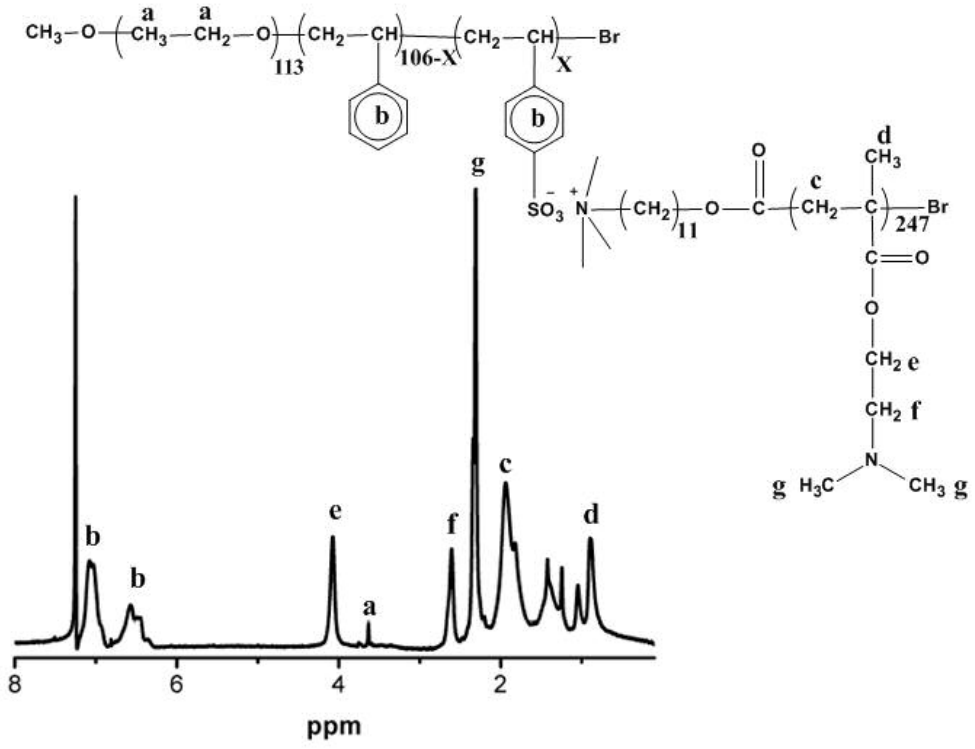

Figure S3. ^{1}H NMR spectrum of PEG-*b*-(PS-g-PDMAEMA) in $CDCCl_3$.

Figure S4 shows two TEM images of the micelles with gold nanoparticles. The preparation of gold nanoparticles in PDMAEMA brushes was carried out in aqueous solution by reduction of hydrogen tetrachloroaureate ($HAuCl_4.4H_2O$) at room temperature. In the images, the gold nanoparticles around the micelles could be observed, which proves that PDMAEMA brushes were synthesized on PS cores and gold nanoparticles were prepared in PDMAEMA brushes.

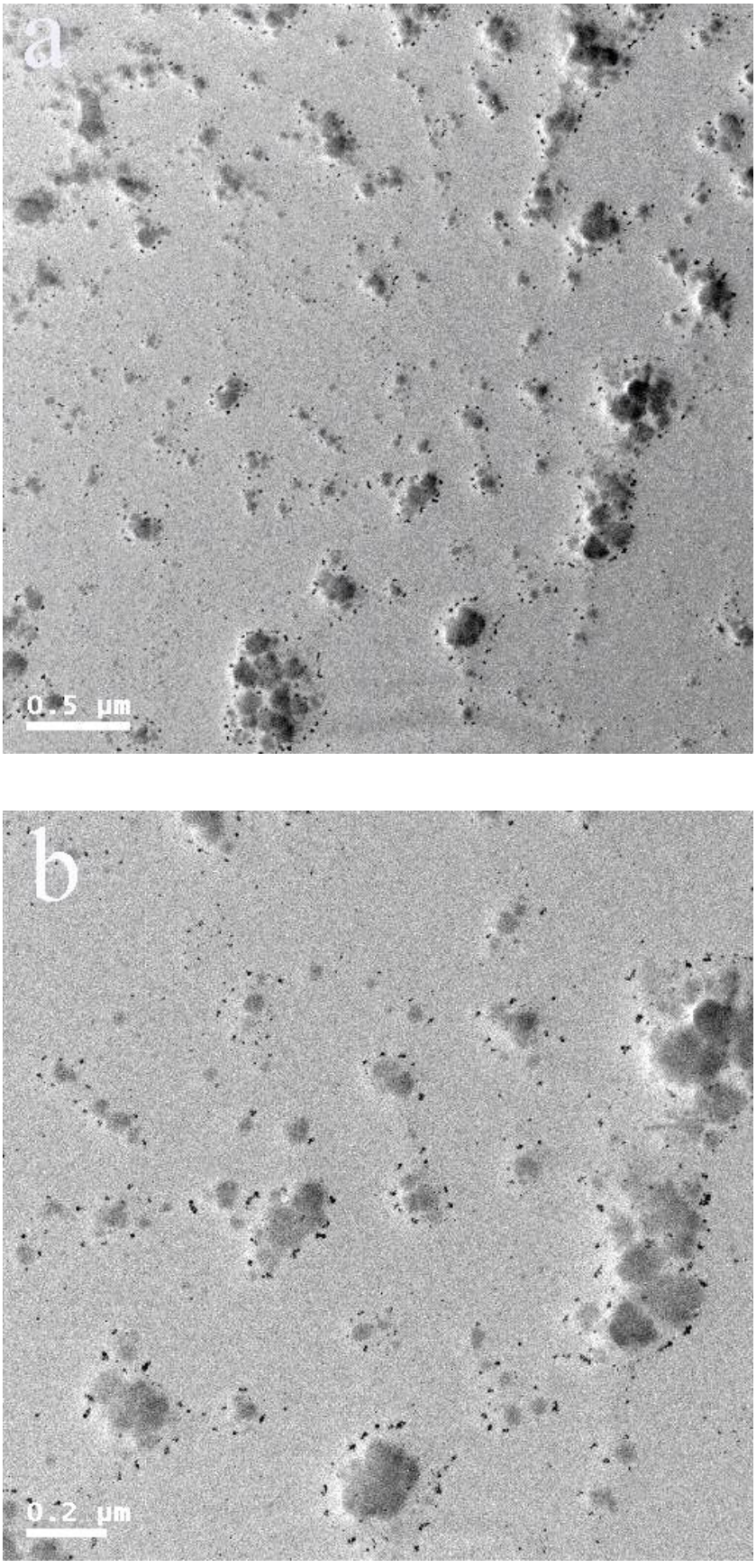

Figure S4. Two TEM images of micelles at different magnification show gold nanoparticles were prepared in PDMAEMA brushes at Au/N molar ratio of 1:4.