In-Situ Polymerization at the Interfaces of Micelles: A "Grafting From" Method to Prepare Micelles with Mixed Coronal Chains

Kaiqiang Chen,[‡] Dehai Liang,[§] Jia Tian,[‡] Linqi Shi,[†] and Hanying Zhao*[,‡]

Key Laboratory of Functional Polymer Materials, Ministry of Education, Department of Chemistry, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, P. R. China and Department of Polymer Science and Engineering, Peking University, Beijing, 100871, P. R. China

Received: April 14, 2008; Revised Manuscript Received: July 24, 2008

Herein we describe a new strategy for producing micelles with mixed coronal chains. This method involves attachment of an atom transfer radical polymerization (ATRP) initiator at the interface of a micelle and preparation of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brushes at the interface by a "grafting from" method. Poly(ethylene glycol)-*block*-polystyrene (PEG-*b*-PS) diblock copolymer was achieved by ATRP. After the sulfonation reaction PS blocks were partly sulfonated. In aqueous solution at low pH the sulfonated block copolymer self-assembled into micelles with PS cores and PEG coronae and sodium 4-styrenesulfonate groups were distributed at the interfaces of the micelles. An ATRP initiator consisting of a quaternary ammonium salt moiety and a 2-bromo-2-methyl propionate moiety was ion exchanged onto the interface of the micelle. ATRP of DMAEMA was initiated at the interface, and micelles with PEG/PDMAEMA mixed coronal chains were prepared by ATRP. The structures of the micelles were characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), and zeta potential measurements. The size and morphology of the micelles were controlled by pH in aqueous solution. At high pH, PDMAEMA brushes collapse, forming nanodomains on the surface of the micelles. PDMAEMA brushes in the coronae of the micelles could be used as a template for preparation of gold nanoparticles.

1. Introduction

It is well known that a block copolymer in a selective solvent, i.e., a good solvent for one block but a nonsolvent for the other, will form micelles. The insoluble blocks are incorporated into a dense core of the micelle, and the soluble blocks form a corona. Self-assembly of block copolymers in the selective solvents can produce a broad range of intricate nanostructures such as spheres (spherical micelles), cylinders (cylindrical micelles), vesicles, etc. These complex nanostructures have found applications in the fields of nanotechnology,[1] biotechnology,[2] and drug delivery.[3] In recent years, many complex micelles self-assembled by block copolymers have been reported. One of typical example is micelles with mixed coronal chains formed by two different block copolymers.[4,5] Generally, hydrogen bonding plays an important role in the preparation of block copolymer micelles with mixed coronal chains. Hu and Liu introduced hydrogen bonding between two diblock copolymers and prepared micelles with mixed coronal chains.[4] Gohy and co-workers prepared mixed micelles with segregated coronal chains by mixing two triblock copolymers B−C−D and E−F−E with C and F blocks poly(2-vinylpyridine) (P2VP) and poly(acrylic acid) (PAA).[6] The driving force for formation of micelles is the hydrogen bonding between P2VP blocks and PAA blocks. Besides hydrogen bonding the cross-linking of block copolymers was also used to prepare micelles with mixed coronal chains.[7,8] For example Hui and co-workers described a one-step approach to prepare core-stabilized polymeric micelles with polystyrene/poly(ethylene oxide) (PS/PEO) as the mixed shell and cross-linked P2VP chains as the core by directly cross-linking P2VP blocks in a common solvent of PEO-*b*-P2VP and PS-*b*-P2VP.[7]

Triblock copolymers can also self-assemble into micelles consisting of a homogeneous core surrounded by two different types of coronal chains. The coronal chains can distribute randomly on the surface of the core or make a "half−half" distribution,[9] where the micelles in the latter case are also known as Janus micelles. Janus micelles reported by Müller and co-workers were obtained via cross-linking the microphases of the middle block of a triblock copolymer in bulk state and then dissolving in a solvent.

In a previous paper we reported an approach to control the morphology and functionality of micelles.[10] In the approach ATRP initiators were introduced to the interfaces of micelles, and the micelles with comb−coil coronal chains were prepared by in-situ polymerization. In this paper we report a new method to prepare micelles with mixed coronae chains by in-situ polymerization at the interfaces of micelles. Diblock copolymer micelles with ATRP initiators ion bound to the interfaces of micelles were prepared in aqueous solution. Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brushes were prepared by a "grafting from" method. After in-situ polymerization, micelles with PDMAEMA/poly(ethylene glycol) (PDMAEMA/PEG) mixed coronal chains were obtained. Our research provided a new method to prepare micelles with mixed coronal chains, and the micelles prepared in this method had very defined structure.

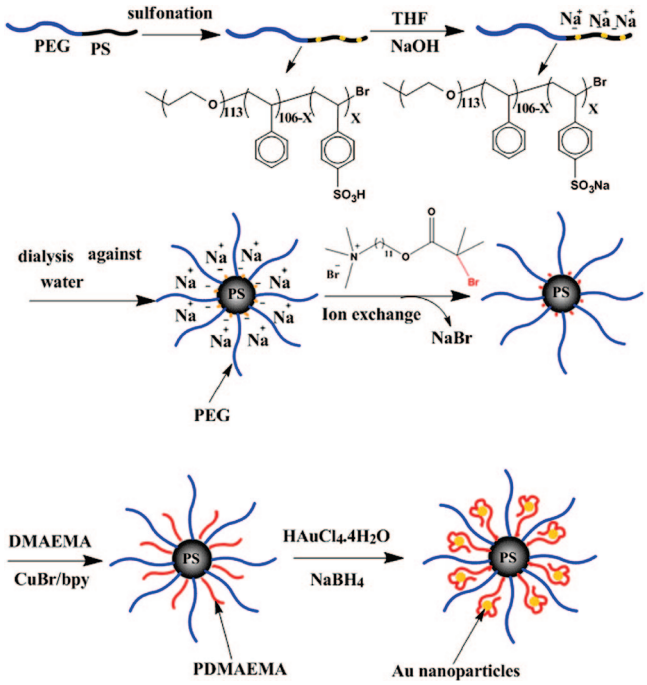
2. Results and Discussions

The overall experiment is illustrated in Scheme 1. In this study a macroinitiator was prepared by reaction of 2-bromo-2-

* To whom correspondence should be addressed. Phone: 86-22-23498703. E-mail: hyzhao@nankai.edu.cn.
‡ Department of Chemistry, Nankai University.
† Institute of Polymer Chemistry, Nankai University.
§ Department of Polymer Science and Engineering, Peking University.

10.1021/jp803216s CCC: $40.75
Published on Web 09/13/2008

SCHEME 1: Schematic Representation for Preparation of Micelles with PDMAEMA/PEG Mixed Coronal Chains by In-Situ ATRP at the Interfaces of Micelles



methylpropionyl bromide and hydroxyl groups at the end of poly(ethylene glycol) monomethyl ether ($CH_3O-PEG-OH$) chains. The average degree of polymerization (DP_n) of the macroinitiator determined by ^1H NMR is 113 (Supporting Information). The macroinitiator was used to initiate successive ATRP of styrene. A PEG-*b*-PS diblock copolymer was prepared by ATRP. According to ^1H NMR results the average DP_n of PS block is 106 (Supporting Information). The diblock copolymer, designated as PEG_{113}-*b*-PS_{106}, was composed of one hydrophilic PEG block and one hydrophobic PS block. According to gel permeation chromatography (GPC) results the apparent molecular weight (M_n) and molecular weight distribution of the diblock copolymer are 16K and 1.13, respectively. Sulfonation of PS blocks was conducted in dichloroethane in the presence of acetyl sulfate. The degree of sulfonation is 3.23 mol %, as determined by elemental analysis.

PEG-*b*-PS diblock copolymer (0.1 g) was dissolved in 30 mL of THF following addition of 1 mL of NaOH solution (8 mM). Micelles with the hydrophilic sodium 4-styrenesulfonate groups at the interfaces were obtained after the block copolymer solution was dialyzed against doubly distilled water for 2 days to remove THF and NaOH. The structure and dimensions of the micelles were studied by direct observations with transmission electron microscopy (TEM). A TEM image of the micelles is shown in Figure 1. The TEM specimen was not stained, so the well-solvated PEG coronae and PS cores are not directly visible. The contrast on the TEM image was attributed to the hydrophilic sodium 4-styrenesulfonate groups located at the interfaces of micelles (Scheme 1). From the TEM image it could be calculated that the diameter of the spherical micelles ranges from 30 to 80 nm with an average value of 50 nm. In previous research it was found that ionomers, i.e., hydrophobic polymer chains with only a few mole percent ionic groups on the backbone, are able to form polymer colloid particles in aqueous solutions.[11] In water, the hydrophobic chains collapse and form the core part of particles while the ionic groups stay on the surface. It is the ionic groups that stabilize the colloid particles.

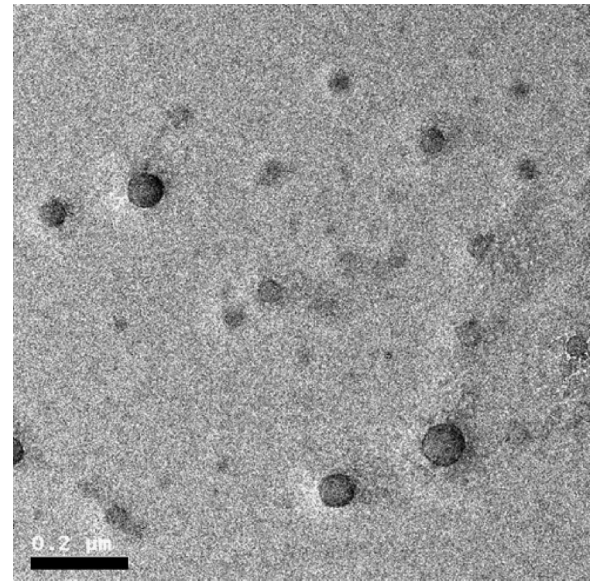


Figure 1. TEM image of micelles formed by sulfonated PEG−PS diblock copolymer. The TEM specimen was not stained, and the contrast was due to the sodium 4-styrenesulfonate groups at the interfaces of micelles. The scale bar represents 0.2 μm.

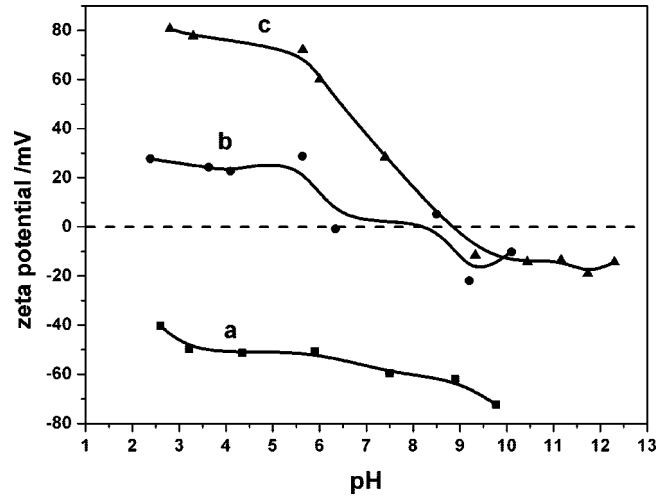


Figure 2. Zeta potential versus pH curves for micelles formed by sulfonated PEG-*b*-PS diblock copolymer (a), micelles after introduction of ammonium ATRP initiator at the interfaces (b), and micelles after in-situ ATRP of DMAEMA (c).

In this research, upon addition of the sulfonated PEG−PS diblock copolymer solution into water, hydrophobic PS blocks collapse and self-assemble into the cores of micelles and hydrophilic PEG blocks form the shells. The sodium 4-styrenesulfonate groups on PS blocks are hydrophilic and distribute at the interfaces (Scheme 1). This can be proved by the results of aqueous electrophoresis measurements. A plot of zeta potentials vs pH of the micellar solution is shown as curve a in Figure 2. Negative zeta potentials are observed at all pH values, which indicate that the micelles are negatively charged and the hydrophilic sodium 4-styrenesulfonate groups are located at the interfaces. The block copolymer micelles are stabilized by negative charges at the interfaces of micelles as well as solvated PEG coronae.

Ammonium ATRP initiator 11′-(*N,N,N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate was ion exchanged onto the interfaces of micelles (Scheme 1). Upon addition of the ATRP initiator into the micellar solution, the

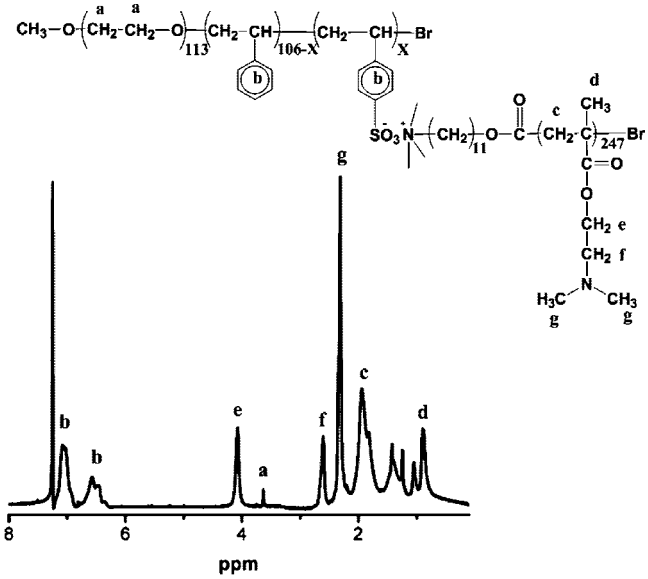


Figure 3. ^{1}H NMR spectrum of PEG-*b*-(PS-*g*-PDMAEMA) in $CDCCl_3$. The repeating unit number of PDMAEMA is 247.

zeta potentials of micelles changed from negative to zero at pH 6.3 (curve b in Figure 2), which means the negatively charged micelles were neutralized by positively charged ATRP initiator.

The in-situ ATRP of DMAEMA at the interfaces of micelles was conducted in aqueous solution. With the growth of PDMAEMA chains at the interfaces, micelles with PS cores and PEG/PDMAEMA mixed coronae were prepared (Scheme 1). In ATRP of DMAEMA, CuBr catalyst and 2,2′-bipyridine (bpy) are both water soluble. Thus, polymerization of DMAEMA will be in the aqueous phase. After 2 days of dialysis of the micellar solution against doubly distilled water, the catalyst, ligand, and excess monomer were removed from the solution and the micelles with PDMAEMA and PEG mixed coronal chains obtained (Scheme 1). After freeze drying, the micelles were dissolved in deuterated chloroform and a solution of PEG-*b*-(PS-*g*-PDMAEMA) polymer was obtained. The structure and ^{1}H NMR spectrum of a polymer is shown in Figure 3. The chemical shift appearing at 2.6 ppm (signal *f*) was attributed to the methylene protons ($-C\mathbf{H}_2-N(CH_3)_2$) on the tertiary amine. Signal *g* at 2.33 ppm is assigned to the methyl protons connecting to the nitrogen atom of DMAEMA, and signal *a* at 3.6 ppm was attributed to the methylene protons on PEG units ($-C\mathbf{H}_2-C\mathbf{H}_2-O-$). On the basis of elemental analysis and ^{1}H NMR results the DP_n value of PDMAEMA was obtained (Supporting Information). In this study micelles with two different PDMAEMA chain lengths were prepared, one with a DP_n of 50 and the other with a DP_n of 247. The polymers are referred to as PEG_{113}-*b*-(PS_{106}-*g*-$PDMAEMA_{50}$) and PEG_{113}-*b*-(PS_{106}-*g*-$PDMAEMA_{247}$), respectively. According to GPC results, the apparent molecular weights and molecular weight distributions of PEG_{113}-*b*-(PS_{106}-*g*-$PDMAEMA_{50}$) and PEG_{113}-*b*-(PS_{106}-*g*-$PDMAEMA_{247}$) are 23K, 1.22 and 51K, 1.38.

PDMAEMA is a pH-sensitive polymer in aqueous solution. Under acidic conditions, the amine groups on the side chains of PDMAEMA are protonated. Subsequent addition of NaOH solution to the PDMAEMA solution deprotonates the side amine groups and makes the polymer hydrophobic.[12] Therefore, at low pH values, PDMAEMA chains are positively charged and the micelles with mixed coronal chains exhibit positive zeta potentials as shown by curve c in Figure 2. With increasing pH in the solution, PDMAEMA chains are gradually deprotonated and the zeta potential value of the micelles decreases.

Figure 4a and 4b shows TEM images of micelles with the PS cores and PEG/PDMAEMA mixed coronae prepared at pH values of 4.0 and 9.2. The DP_n value of PDMAEMA is 50. The specimens for TEM observation were stained by OsO_4, so on the TEM images the dark phases represented PDMAEMA domains. In Figure 4a the PDMAEMA shells on the surface of micelles were observed. In Figure 4b PDMAEMA chains form nanodomains on micelles. The different morphologies observed at different pH values can be explained according to the theory of mixed polymer brushes.[13−16] Mixed polymer brushes are binary polymer brushes composed of two incompatible polymer chains grafted to a solid substrate. The solvent has a significant effect on the morphologies of mixed polymer brushes. If the solvent is a good solvent for both components, two possible morphologies are formed to avoid unfavorable interactions. The two tethered chains segregate perpendicular to the substrate, forming the layered morphology of the polymer film, or the two polymer chains self-assemble laterally into two-dimensional surface structures. If the solvent is bad for one component, this polymer will form nanodomains.[14] In this study, PDMAEMA is immiscible with PEG and the mixed coronal chains can be treated as mixed homopolymer brushes grafted to the surface of PS core in which PEG chains were tethered to the PS core by a covalent bond and PDMAEMA chains were tethered by an ionic bond. Mixed polymer brushes can be switched between different surface energetic states by applying external stimuli. At pH 4.0, water is a good solvent for protonated PDMAEMA chains and PEG chains, uniform layers of PDMAEMA and PEG were formed around the PS core after drying micelles from the solution. Because of strong unfavorable interaction between protonated PDMAEMA and PS core, the PEG component is enriched near the PS core and PDMAEMA chains occupy the top of the brush. Thus, in Figure 4a a uniform PDMAEMA shell was observed on the surface of a micelle. For the micelles prepared at pH 9.2, the hydrophobic PDMAEMA chains collapse from the solution, forming PDMAEMA nanodomains on the surface of micelles, and the solvated PEG chains stabilize the micelles. After drying, PDMAEMA nanodomains on the surfaces of micelles were created (Figure 4b). The structure of the micelles was illustrated in Scheme 2a.

It was found that the size of the micelles prepared at pH 4.0 ranged from 130 to 160 nm. However, for the micelles prepared at pH 9.2 the size ranged from 50 to 80 nm, which is smaller than the micelles prepared at pH 4.0. At a low pH, the protonated PDMAEMA chains are extended due to the electrostatic repulsions and uniform layers of PDMAEMA and PEG were formed with the PEG component enriched near the PS core. In Figure 4a the white phases inside the black shells represent both PS cores and PEG layers, so the size of micelles prepared at a low pH is bigger. At a high pH the PDMAEMA chains were deprotonated and collapsed from the solution onto the interfaces of micelles, so the size of the micelle is smaller (Figure 4b). In Figure 4b dark nanosized domains on micelles could be observed. The dark domains are stained PDMAEMA phases, and the white domains with no contrast are PEG phases. The insert in Figure 4b is a magnified TEM image of micelles prepared at pH 9.2. From the image it was calculated that the lengths of the PDMAEMA domains are in the range between 28 and 35 nm and the widths are between 10 and 15 nm.

Figure 4c shows a TEM image of the micelles with long PDMAEMA chain prepared at pH 9.2. The average DP_n of PDMAEMA brushes is 247. On the image the PS core

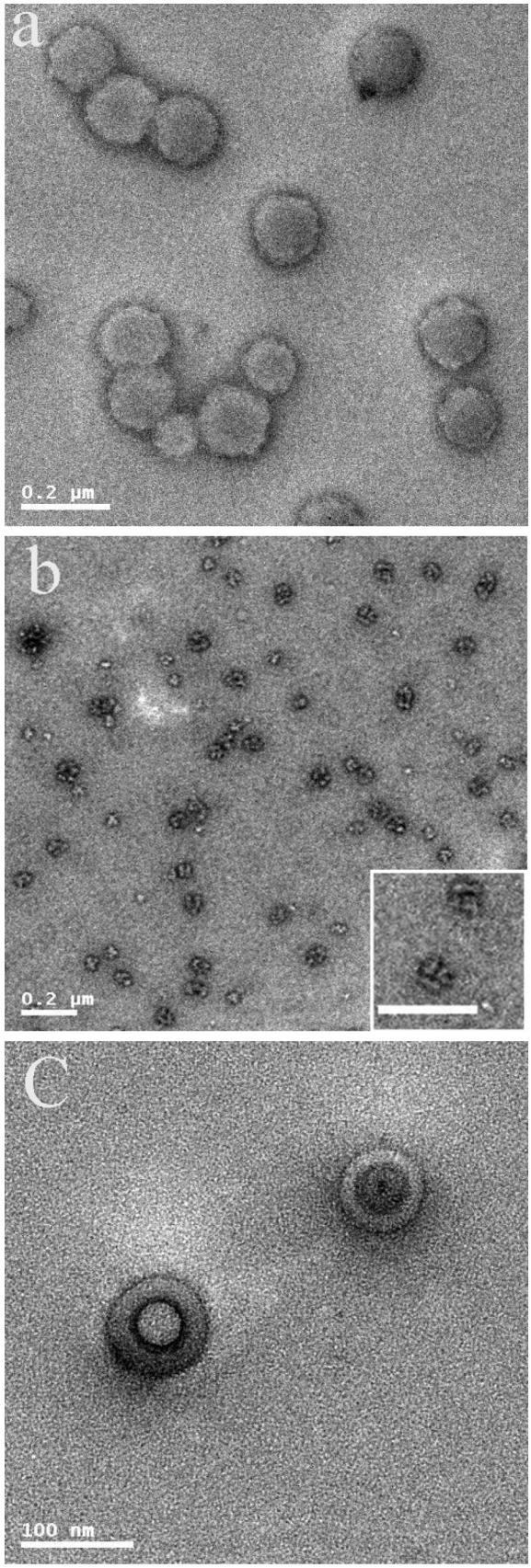
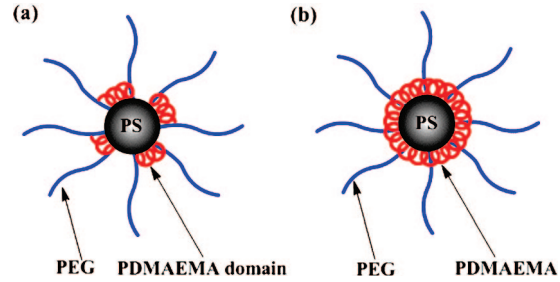


Figure 4. TEM images of the micelles with PS cores and PEG/PDMAEMA mixed coronae prepared at pH 4.0 (a) and 9.2 (b). The number-average degree of polymerization (DP_n) of PDMAEMA is 50. The insert in image b is a magnified TEM image showing PDMAEMA nanodomains on micelles. The scale bar in the insert is 200 nm. (c) TEM image of micelles with long PDMAEMA chain (DP_n 247) prepared at pH 9.2. All TEM specimens were stained by OsO_4.

SCHEME 2: (a) Schematic Representation for Micelles with (a) Short[a] and (b) Long[b] PDMAEMA Chains



[a] In aqueous solution at pH 9.2 PDMAEMA chains collapse, forming separated nanosized PDMAEMA domains on the surface of the PS core. [b] Continuous PDMAEMA nanodomains were formed on the surface of PS core in an aqueous solution at pH 9.2.

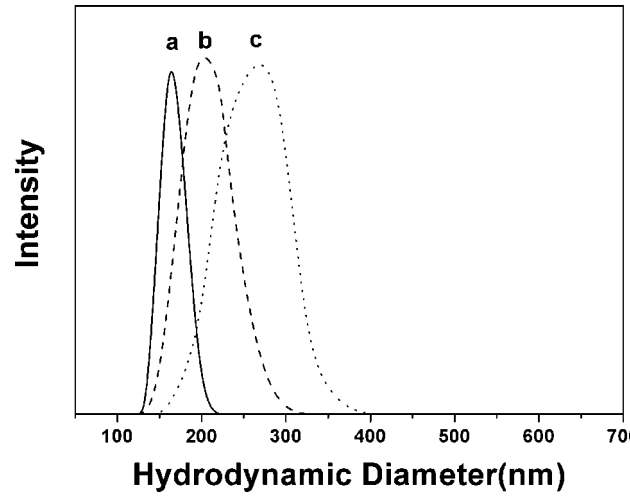


Figure 5. Size distribution of the micelles formed by partly sulfonated PEG_{113}-*b*-PS_{106} diblock copolymer in an aqueous solution at pH 5.6 (a), and size distributions of micelles with PS cores and PDMAEMA/PEG mixed coronae prepared in aqueous solutions at pH 9.2 (b) and 4.0 (c).

surrounded by condensed PDMAEMA phase can be observed. At a high pH PDMAEMA chains collapse, forming nanosized domains on the surface of micelles. With the increase of PDMAEMA chain length the size of the PDMAEMA domain increases, and finally, continuous PDMAEMA domains were formed around the PS core. The structure of the micelles is illustrated in Scheme 2b.

The size distributions of the micelles before and after polymerization of DMAEMA were determined by dynamic light scattering (DLS), and the results are shown in Figure 5. After in-situ ATRP of DMAEMA at the interface, the average hydrodynamic diameter (D_h) of the micelles significantly increases. The pH of the solution exerts an influence on the size of the micelles with mixed coronae. At pH 9.2 the average hydrodynamic diameter is 214 nm; however, it increases to 272 nm at pH 4.0, indicating that the average size of the micelles increases with decreasing pH in the solution. At pH 4.0 PDMAEMA chains are protonated and positively charged. The PDMAEMA chains are highly stretched due to the electrostatic repulsions, which results in an apparent larger size. At pH 9.2 the PDMAEMA chains are deprotonated and the hydrophobic chains collapse from the solution onto the surface of the PS core, so the apparent size is smaller.

PDMAEMA domains could be used as the nanoreactors to generate gold nanoparticles.[17] Synthesis of gold nanoparticles

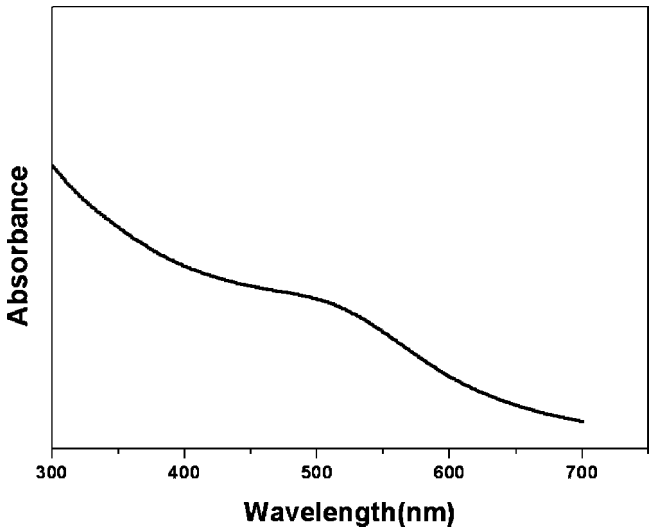


Figure 6. UV−vis spectrum of gold nanoparticles prepared in PDMAEMA brushes on micelles at a Au/N molar ratio of 1:4.

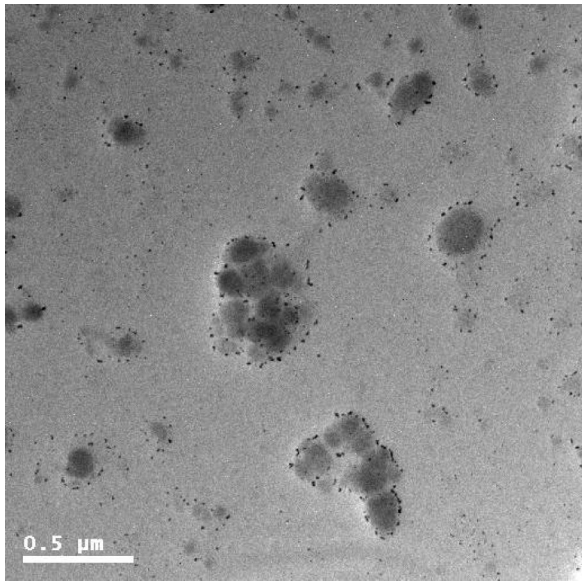


Figure 7. TEM image of micelles with gold nanoparticles prepared in PDMAEMA brushes at a Au/N molar ratio of 1:4.

incorporated in PDMAEMA brushes on micelles was carried out in aqueous solution by reduction of hydrogen tetrachloroaureate ($HAuCl_4 \cdot 4H_2O$) at room temperature. Upon addition of $NaBH_4$ the micellar solution became light orange-red immediately. Figure 6 shows the UV−vis spectrum of the gold nanoparticles prepared at a Au/N molar ratio of 1:4. The resonance plasmon of gold nanoparticles appears as a shoulder at about 510 nm, which means the average size of the nanoparticles is less than 10 nm.[18] Figure 7 is a TEM image of the micelles with gold nanoparticles. In the image 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. The average size of the gold nanoparticles is 8 nm. It is worth noting that in the TEM image aggregations of micelles were observed, which means the stability of micelles is decreased after preparation of gold nanoparticles in the PDMAEMA brushes. This can be explained by the fact that the micelles with mixed corona chains were originally stabilized by PEG and PDMAEMA chains; however, after preparation of gold nanoparticles some PDMAEMA chains were used to stabilize the gold nanoparticles, so the stability of micelles was decreased and aggregations of micelles were observed.

3. Conclusions

In summary, we prepared micelles with PDMAEMA and PEG mixed coronal chains using a "grafting from" method. Diblock copolymer micelles with ATRP initiators at the interfaces were prepared in aqueous solution, and after in-situ polymerization micelles with mixed coronal chains were prepared. Micelles with mixed coronae have different morphologies at different pH values. At low pH PDMAEMA brushes were protonated and the PDMAEMA chains stretched out into the solution, and at high pH PDMAEMA collapsed from the solution, forming nanosized domains on the surface of the PS core. PDMAEMA brushes in the coronae of micelles could be used as a template for preparation of gold nanoparticles. Micelles with gold nanoparticles on the surface could find potential applications in catalysis of chemical reactions and protein separation.

4. Experimental Section

Materials. Poly(ethylene glycol) monomethyl ether (CH_3O−PEG−OH, $M_n = 5000$) was purchased from Fluka. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (Acros, 99%) was dried over CaH_2 and distilled under reduced pressure. Styrene (Tian Jin Institute of Chemical Agents) was purified by washing with aqueous solution of NaOH and water, drying over $MgSO_4$, and then distilling under reduced pressure. CuBr (Sinopharm Chemical Reagent Co., Ltd.) was purified by stirring in glacial acetic acid. After filtration, it was washed with alcohol and ethyl ether and then dried in vacuum. 2,2′-Bipyridine (bpy) (Sinopharm Chemical Reagent Co., Ltd.), *N*,*N*,*N*′,*N*′,*N*′-pentmethyldiethylenetriamine (PMDETA) (Aldrich, 99%), 2-bromo-2-methylpropionyl bromide (Aldrich, 98%), 11-bromo-1-undecanol (Aldrich, 98%), and triethylamine (TEA) (Aldrich, 99%) were used as received. All solvents were distilled before use.

Preparation of PEG Macroinitiator (PEG-Br). CH_3O−PEG−OH (15.0 g) was dissolved in 180 mL of toluene. After azeotropic distillation of 30 mL of toluene at reduced pressure to remove traces of water, TEA (0.834 mL) was added and the solution was cooled to 27 °C. 2-Bromoisobutyryl bromide (0.074 mL) was added into the solution dropwise, and the reaction mixture was stirred at 40 °C for 2 days. The solution was filtered, 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, dissolved in water at pH 8−9, and then extracted with dichloromethane. The organic layers were collected and dried over $MgSO_4$. After removal of the solvent under reduced pressure purified macroinitiator PEG-Br was obtained. 400 MHz ^{1}H NMR ($CDCl_3$), δ ppm: 4.28 (t, 2H); 3.59 (m, 402H); 3.33 (s, 3H); 1.89 (s, 6H).

Preparation of PEG-*b*-PS Diblock Copolymer. PEG-*b*-PS was synthesized by ATRP of styrene using PEG-Br as the initiator. CuBr (23 mg) and PMDETA (100 μL) were dissolved in 0.6 mL of styrene in a 25 mL two-neck flask and degassed with three freeze−pump−thaw cycles. A mixture of 0.8 g of PEG-Br initiator and 1.0 mL of styrene were transferred into the solution through a syringe. The light-green mixture was degassed with two freeze−pump−thaw cycles and stirred at 105 °C for 4 h under nitrogen atmosphere. The resulting polymer was dissolved in THF, purified through a basic alumina column, and then precipitated into a 6-fold excess of hexane. Extraction of the diblock copolymer with water and cyclohexane was

carried out in order to remove PEG and PS homopolymers. The diblock copolymer was dried under vacuum at 35 °C for 2 days.

Preparation of Sulfonated PEG-*b*-PS. The sulfonated PEG-*b*-PS was prepared according to previous literature based on a two-step reaction.[19,20] (1) Acetyl sulfate preparation: Acetic anhydride (0.32 mL) was added to 1.65 mL of 1,2-dichloroethane. Sulfuric acid (98%, 0.175 mL) was added to the solution at 0 °C, and a clear solution was obtained. (2) Sulfonation reaction: PEG_{113}-*b*-PS_{106} (1 g) was dissolved in 10 mL of 1,2-dichloroethane, and a solution of acetyl sulfate in 1,2-dichloroethane was added to the polymer solution. The solution was stirred at 50 °C for 2 h. Finally, 10 mL of 2-propanol was added to stop the reaction. The polymer was isolated by rotary evaporation, washed for 2 h in boiling water, filtered, and vaccuum dried at 50 °C for 5 days. The degree of sulfonation was determined to be about 3.23 mol % based on elemental analysis.

Preparation of ATRP Initiator 11′-(*N*,*N*,*N*-Trimethylammonium Bromide)undecyl-2-bromo-2-methyl Propionate. ATRP initiator 11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate was synthesized using a procedure similar to that reported in the literature,[21] and details can be found in our previous publications.[22,23]

Preparation of PEG-*b*-PS Micelles with ATRP Initiator at the Interfaces. Sulfonated PEG-*b*-PS diblock copolymer (0.1 g) was dissolved in 30 mL of THF following addition of 1 mL of NaOH solution (8 mM). Micelles with the ionic groups at the interfaces were obtained after the block copolymer solution was dialyzed against doubly distilled water for 2 days. After dialysis 3.7 mg of ATRP initiator 11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate was added to the above micellar solution and the solution was dialyzed against doubly distilled water for 2 days to remove excess ATRP Initiator.

In-Situ ATRP of DMAEMA at the Interfaces of Micelles. In a 25 mL flask the micellar solution was purged with nitrogen gas for 30 min. In another flask 3.7 mg of CuBr and 11.6 mg of bpy were dissolved in 2 mL of doubly distilled water. After being degassed with three freeze−pump−thaw cycles, the micellar solution and 0.4 mL of DMAEMA monomer were transferred into the catalyst solution. The red-brown mixture was stirred at 30 °C for 15 h. The resulting micellar solution was dialyzed against doubly distilled water for 2 days to remove the catalyst, ligand, and excess monomer.

Characterization. ^{1}H NMR spectra were recorded on a Varian 300 spectrometer. ATRP initiator was measured in deuterated DMSO; PEG macroinitiator, PEG-*b*-PS, and PEG-*b*-(PS-*g*-PDMAEMA) were measured in deuterated chloroform. The apparent molecular weight and molecular weight distributions were determined with a gel permeation chromatograph (GPC) equipped with a Waters 717 autosampler, Waters 1525 HPLC pump, three Waters UltraStyragel columns with 5K−600K, 500−30K, and 100−10K molecular ranges, and a Waters 2414 Refractive Index Detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Molecular weights were calibrated on PS standards. Transmission electron microscopy (TEM) observations were carried out on a Tecnai G2 20 S-TWIN electron microscope equipped with a model 794 CCD camera (512 × 512). The zeta potential values of the micelles were determined on a Brookheaven ZetaPALS (Brookheaven Instrument, USA) at 25 °C. The instrument utilizes phase analysis light scattering to provide an average over multiple particles. Doubly distilled water was used as the background electrolyte for zeta potential measurements, and the pH was adjusted with 0.1 M NaOH and HCl solutions. Dynamic light scattering (DLS) was performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm. Micelle solutions were measured at a scattering angle of 90° at 25 °C. The UV−vis spectrum of gold nanoparticles was collected on a Shimazu UV−vis spectrophotometer (UV-2550).

Acknowledgment. This project was supported by the National Natural Science Foundation of China (NSFC) under Contracts 20574037 and 20774046 and the Science and Technology Committee of Tianjin under contract no. 05YFJMJC06700.

Supporting Information Available: ^{1}H NMR spectra of the macroinitiator and diblock copolymers and more TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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JP803216S