

Suspension polymerization stabilized by triblock copolymer with CdS nanoparticles

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ABSTRACT

In this paper, a new method to prepare polymer colloid particles stabilized by triblock copolymer with CdS nanoparticles was described. Poly(ethylene glycol-*block*-styrene-*block*-2-(dimethylamino) ethyl methacrylate) (PEG-*b*-PS-*b*-PDMAEMA) triblock copolymer was synthesized by sequential ATRP method. Micelles with CdS nanoparticles in the corona were prepared by “in situ” reaction of hydrogen sulfide with cadmium ion clusters in the corona of the micelles. The size of the CdS nanoparticles is affected by molar ratio of DMAEMA to cadmium ions and polymer concentration in the solution. When introduced into o/w emulsion the micelles reassemble on the surface of styrene oil droplets. PS colloid particles stabilized by triblock copolymer with CdS nanoparticles were achieved by suspension polymerization. TEM image indicates that CdS nanoparticles locate at the surface of the PS colloid particles.

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1. Introduction

In the past decades, preparation of semiconductor nanoparticles or clusters has been intensively studied because of their unique optical and electronic properties [1,2]. CdS nanoparticle is one of the most intensively investigated semiconducting nanoparticles [3]. CdS nanoparticles have been synthesized on many kinds of templates such as polymers [4–6], zeolites, etc. [7]. Because in the nanocomposites, polymeric materials not only act as stabilizers, but also promote the processability, solubility, and control of the growth of nanoparticles; various synthetic methods based on polymeric materials have been developed during the past decade [8–13]. Recently, many people have prepared CdS nanoparticles in micelles formed by amphiphilic block copolymer [14–25]. Control of the location of the CdS nanoparticles within micelles is very important for a variety of applications. In most cases, a micelle core can be regarded as a nano-sized reactor, and core embedded nanoparticles can be synthesized via an appropriate reaction [24]. However, in some cases, the location of the nanoparticles in the corona region (corona-embedded nanoparticles) is desired as well [25]. The location of the nanoparticles in a micelle is determined by solvent, the metal precursor type, the reaction conditions and the interaction between the ions and the polymer chains [26].

Recently, another interesting research area is the use of particles to stabilize emulsions as it gains the advantage over conventional

emulsions and can find numerous practical applications [27,28]. An emulsion stabilized by particles instead of surfactant molecules is called Pickering emulsion [29]. In a Pickering emulsion, the nanometer or micrometer-sized particles are strongly adsorbed at the liquid–liquid interface, and the Gibbs-free energy to remove one particle away from the interface is significantly higher than that of surfactants in conventional emulsion [30]. In addition, Pickering emulsion provides novel and simple template for the self-assembly of microparticles or even nanoparticles [31–33]. In Pickering emulsion, the reduction of the interfacial energy depends on the size of particles. For smaller nanoparticles, the reduction of the interfacial energy is smaller and the assembly is less stable than for larger ones. In fact, no stabilization was observed when particles with diameters less than 1.6 nm were used in a mixture of oil and water [32]. However, if nanoparticles are embedded in polymer micelles, extra interfacial energy will be gained via interaction between polymer chains and fluids, and stable Pickering emulsion can be prepared. In previous papers we reported preparation of colloid particles stabilized by clay layers with polymer brushes [34,35]. The target of this research is to develop a new method to prepare polymer colloid particles stabilized by triblock copolymer with CdS semiconducting nanoparticles.

Poly(ethylene glycol-*block*-styrene-*block*-2-(dimethylamino) ethyl methacrylate) (PEG-*b*-PS-*b*-PDMAEMA) triblock copolymer was synthesized by sequential ATRP method (Scheme 1). The preparation of micelles with corona-embedded CdS nanoparticles follows the method reported by Hanying Zhao and coworkers [24,25]. In such a triblock copolymer micelle, the core is composed of collapsed PS blocks and the shell is composed of PEG blocks and CdS nanoparticles are protected by PDMAEMA chains (Scheme 2).

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pressure to remove traces of water, triethylamine (0.830 mL) was added, and the solution was cooled to 0 °C. 2-Bromoisobutryl bromide (0.074 mL) was added 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 10-fold of cold ether. The crude polymer was dried under vacuum, dissolved in water at pH 8–9, and then extracted with dichloromethane. The organic layer was collected, dried over MgSO₄. After removal of the solvent under reduced pressure the purified macroinitiator was obtained.

2.3. Preparation of PEG-*b*-PS diblock copolymer (PEG-Br)

PEG-*b*-PS was synthesized by bulk ATRP of styrene using PEG-Br as the initiator. CuBr (0.057 g) and PMDETA (167 μL) were dissolved in 0.8 mL styrene in a 25 mL two-neck flask and degassed with three freeze–pump–thaw cycles. PEG-Br initiator (2 g) dissolved in 4 mL of styrene was transferred into the solution through a syringe. The mixture was then degassed with another two freeze–pump–thaw cycles and stirred at 110 °C for 4 h under nitrogen atmosphere. The resulting polymer was dissolved in tetrahydrofuran (THF) and Cu²⁺ was removed by an alumina column. The block copolymer was obtained by precipitating the solution into 6-fold of hexane. In order to remove PEG and PS homopolymers from the block copolymer, extractions of the diblock copolymer with water and cyclohexane were carried out.

2.4. Preparation of PEG-*b*-PS-*b*-PDMAEMA triblock copolymer

CuBr (5 mg) and PMDETA (15 μL) were dissolved in 0.5 mL of *o*-dichlorobenzene. After degassed with three freeze–pump–thaw cycles, PEG-*b*-PS initiator (0.5 g) dissolved in a mixture of 0.22 mL DMAEMA and 0.7 mL dichlorobenzene was transferred into the solution through a syringe. The mixture was then degassed with another two freeze–pump–thaw cycles and stirred in an oil bath at 90 °C for 16 h. The resulting triblock copolymer was purified through an alumina column and the solvent was removed by rotary evaporation.

2.5. Preparation of corona-embedded CdS nanoparticles

PEG-*b*-PS-*b*-PDMAEMA triblock copolymer was dissolved in 5 mL of THF at varying concentration under vigorous stirring for 0.5 h. Cadmium acetate dihydrate in 0.5 mL of a mixture of methanol and THF (1:2 v/v) was added into the polymer solution under stirring at room temperature, and a light-blue solution was achieved indicating that the compound micelles were formed in the solution [24]. A micelle solution with corona-embedded CdS nanoparticles was achieved by dropping 1 mL of PEG-*b*-PS-*b*-PDMAEMA-Cd²⁺ complex solution into 20 mL of doubly distilled water at pH 5.6, followed by bubbling H₂S gas through the micelle solution for 10 min. The resulting yellow stable CdS colloidal solutions were characterized after 24 h of aging because the CdS nanoparticle dispersion exhibits a minor change in size within the first 24 h, after which it is stable for a long time.

2.6. Suspension polymerization of styrene

After removal of THF in the micellar solution under reduced pressure, a mixture of AIBN (1 mg), styrene monomer (1.1 mL) and divinylbenzene (30 μL) was added into the micellar solution (10 mL). The mixture stirred at 75 °C for 4 h under nitrogen atmosphere.

2.7. Characterization

¹H NMR spectra were recorded on a Varian 300 spectrometer. All the samples were measured in deuterated chloroform. The apparent molecular weight and molecular weight distributions were determined on a gel permeation chromatograph (GPC) equipped with a Waters 717 autosampler, Waters 1525 HPLC pump, three Waters UltraStyragel columns with 5–600K, 500–30K, and 100–10K molecular ranges, and a Waters 2414 Refractive Index Detector. THF was used as eluent at a flow rate of 1.0 mL/min. Molecular weights were calibrated on PS standards. Transmission electron microscopy (TEM) observations were made on a Tecnai G2 20 S-TWIN electron microscope equipped with a Model 794 CCD camera (512 × 512). UV–vis absorption spectroscopy was performed on a Shimadzu UV–vis spectrophotometer (UV-2401PC) by scanning the solution in a 1 cm quartz cell. The scanning range was from 190 nm to 700 nm. Absorption from the solvent was subtracted from each spectrum. A Zeta PALS zetameter (Brookhaven Instrument Corp., NJ) was used for the measurements of zeta potential. Four measurements were taken to obtain an average value for each data point, with each measurement consisting of 15 iterations of the fitting routine to obtain a more accurate reading of the phase signal. Dynamic light scattering (DLS) was performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 514 nm at a scattering angle of 90°.

3. Results and discussion

PEG-*b*-PS-*b*-PDMAEMA triblock copolymer was synthesized by sequential ATRP (Scheme 1). Fig. 1 is ¹H NMR spectrum of PEG-*b*-PS-*b*-PDMAEMA copolymer. The sharp single peak at 3.64 ppm is attributed to the methylene protons of PEG. Peaks at 7.14 ppm and 6.69 ppm are phenyl protons of styrene repeating units. The peaks at 4.09 ppm, 2.62 ppm are characteristic of the protons on methylene groups in DMAEMA repeating units, and the peak at 2.33 ppm is assigned to the methyl protons connecting to the nitrogen atom. According to ¹H NMR result, it can be calculated that the molar ratio of three components is 104: 33:113 (styrene:DMAEMA:EG). This sample is indicated as PEG₁₁₃-*b*-PS₁₀₄-*b*-PDMAEMA₃₃. Apparent molecular weight (*M_n*) and molecular weight distribution determined by GPC were 22K and 1.26, respectively.

Upon addition of cadmium ions into a solution of the triblock polymer in THF, a solvent for the three blocks, salt-induced micelle forms due to complexation of Cd²⁺ with DMAEMA units [24].

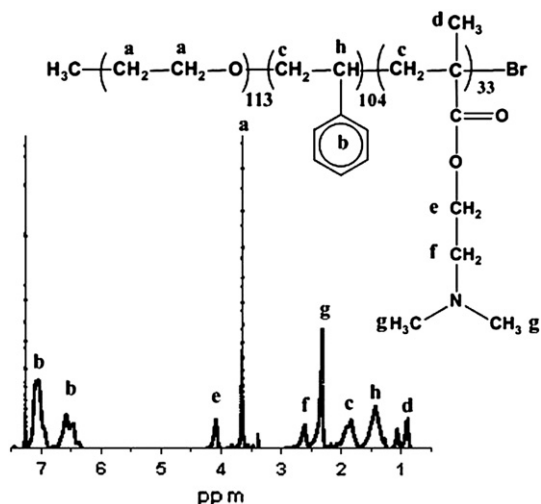


Fig. 1. ¹H NMR spectrum of PEG-*b*-PS-*b*-PDMAEMA triblock copolymer in CDCl₃.

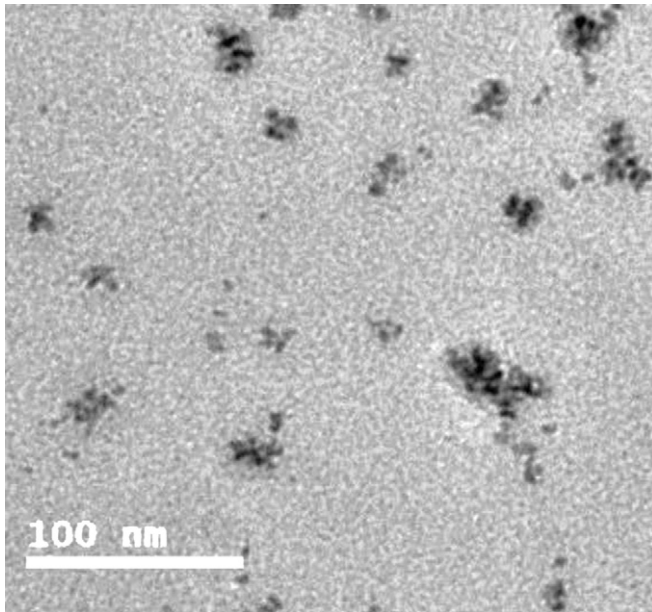


Fig. 2. A TEM image of corona-embedded CdS nanoparticle prepared by dropping 1 mL THF solution of PEG-*b*-PS-*b*-PDMAEMA-Cd²⁺ into 20 mL of water at a pH value of 5.6 followed by introducing H₂S gas. The concentration of PEG-*b*-PS-*b*-PDMAEMA in THF is 5 g/L and the molar ratio of DMAEMA to Cd²⁺ is 1:0.5.

Micelles with corona-embedded CdS nanoparticles were prepared by dropping 1 mL THF solution of salt-induced compound micelles into 20 mL of water at a pH value of 5.6, followed by introducing H₂S gas. A TEM image of micelles with corona-embedded CdS nanoparticles is shown in Fig. 2. The core of micelle is composed of collapsed PS blocks and the corona is composed of PEG blocks, PDMAEMA blocks and CdS nanoparticles. Because the TEM specimen was not stained, on the image only CdS nanoparticles with an average diameter of 3–6 nm in the corona of micelles can be observed. The diameter of the micelles in aqueous solution ranges from 20 nm to 40 nm. DLS result indicates that the dynamic diameter of the micelles lies in the range between 30 nm and 70 nm (Fig. 3). Because the micelles were in “drying” state in TEM measurements, the size determined by TEM is smaller than the value measured by DLS.

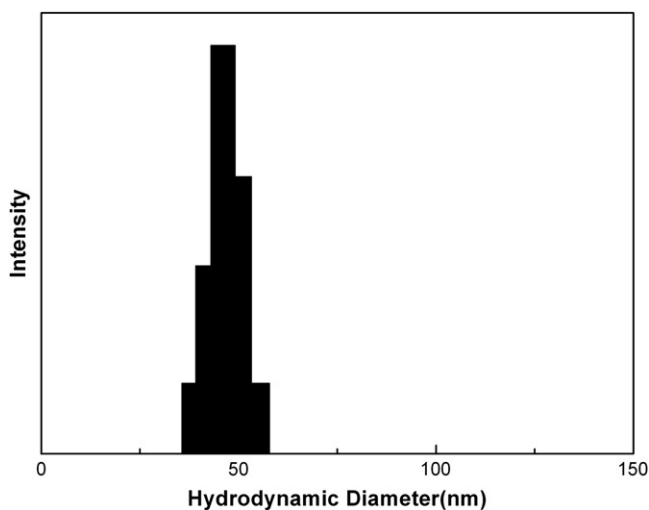


Fig. 3. Size distribution of triblock copolymer micelles with corona-embedded CdS nanoparticles. Micelles were prepared by dropping 1 mL THF solution of PEG-*b*-PS-*b*-PDMAEMA-Cd²⁺ into 20 mL of water at a pH value of 5.6 followed by introducing H₂S gas. The concentration of PEG-*b*-PS-*b*-PDMAEMA in THF is 5 g/L and the molar ratio of DMAEMA to Cd²⁺ is 1:0.5.

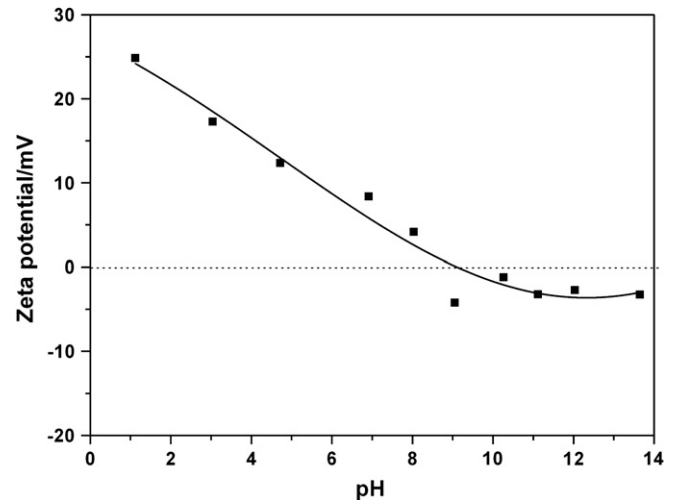


Fig. 4. A plot of zeta-potential values of micelles with corona-embedded CdS nanoparticles as a function of pH values in aqueous solution. Micelles were prepared by dropping 1 mL THF solution of PEG-*b*-PS-*b*-PDMAEMA-Cd²⁺ into 20 mL of water at a pH value of 5.6 followed by introducing H₂S gas. The concentration of PEG-*b*-PS-*b*-PDMAEMA in THF is 5 g/L and the molar ratio of DMAEMA to Cd²⁺ is 1:0.5.

In the micelles with corona-embedded CdS nanoparticles in water, a part of DMAEMA units form complex with CdS nanoparticles, and others are free DMAEMA units. The free DMAEMA units and PEG blocks stabilize the micelles. PDMAEMA is a pH sensitive polymer. Under acidic condition, the amine groups on DMAEMA units are protonated, causing the polymer to be hydrophilic. The subsequent addition of base deprotonates the amine groups. So pH value of the solution exerts an important effect on the micelles. Fig. 4 shows a plot of zeta potential of the micelles vs. pH values in aqueous solution. At low pH values zeta potentials of micelles keep positive, which means in the micelles free DMAEMA units are protonated. The increase of the pH value in solution deprotonates the amine groups and results in a decrease of the zeta-potential values. The isoelectric point of the micelles was at approximately pH 9.1.

UV–vis absorption spectroscopy is one of the most frequently used methods to determine the size of CdS nanoparticles. The absorption edge (λ_e) calculated from absorption spectra can be converted into CdS particle size using Henglein’s empirical curve [36,37]. Curves A, B, and C in Fig. 5 are three UV–vis absorption spectra of nanoparticles prepared at different molar ratios of

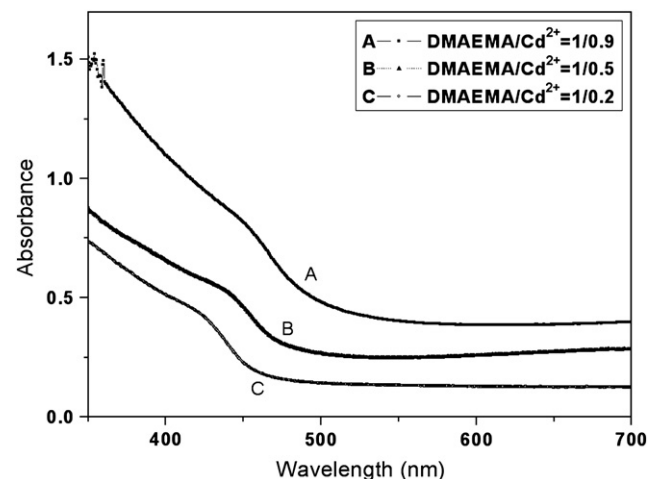


Fig. 5. UV–vis absorption spectra of CdS nanoparticles at different molar ratios of DMAEMA to Cd²⁺. The concentration of the block copolymer in THF is 5 g/L. The plots are shifted vertically for clarity.

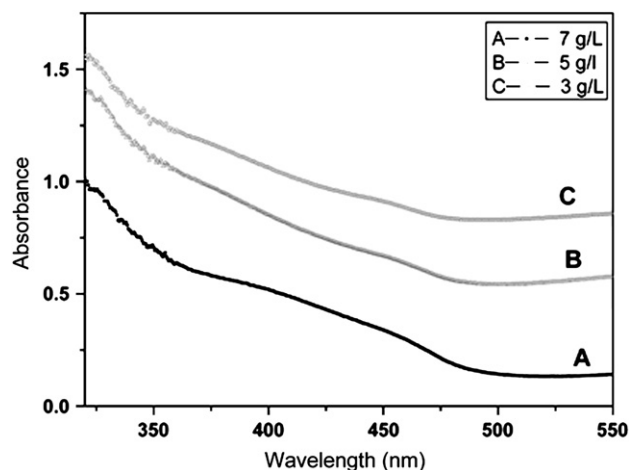


Fig. 6. UV-vis absorption spectra of CdS nanoparticles prepared by dropping 1 mL THF solution of PEG-*b*-PS-PDMAEMA-Cd²⁺ solution with various concentrations into 20 mL of water, followed by introduction of H₂S gas. The molar ratio of DMAEMA units to Cd²⁺ is kept at 1:0.5.

DMAEMA to cadmium ions. When the molar ratio is 1:0.2, the absorption edge is at about 460 nm corresponding to particle diameter of 3.85 nm. However, when the ratio reaches 1:0.5 and 1:0.9, the absorption edge red-shifts to 480 nm and 497 nm, which corresponds to particle diameters of 4.64 nm and 6.14 nm, respectively. This result indicates that the larger nanoparticles can be prepared at lower molar ratio of DMAEMA to cadmium ions. This trend keeps consistent with the result reported by Bronstein et al. [15].

The concentration of triblock copolymer in THF plays an important role in controlling the size of CdS nanoparticles. Fig. 6 shows UV-vis absorption spectra of CdS nanoparticles embedded in the corona of micelles in aqueous solution. The molar ratio of DMAEMA units to cadmium ions was kept constant (1:0.5). It is noted that when the concentrations of the block copolymer are 7 g/L, 5 g/L and 3 g/L, the absorption edges are at 495 nm, 485 nm and 480 nm, which means smaller nanoparticles can be prepared at lower polymer concentration. This can be explained by the fact that in the experiments the molar ratio of DMAEMA units to cadmium ions was kept constant, at higher triblock copolymer concentrations there will be more chances for CdS to grow into larger particles in the corona of the micelles.

An emulsion stabilized by solid particles instead of surfactant molecules is called Pickering emulsion. The solid particles can be latex particles, inorganic particles (including silica particles, clay particles, etc.), semiconducting nanoparticles, or even polymer micelles. Fujii and coworkers used shell-cross-linked micelles as pH responsive particulate emulsifiers and found that these micelles produced relatively fine o/w emulsions [38]. Here preparation of PS colloid particles stabilized by triblock copolymer with CdS nanoparticles was reported.

Upon addition of styrene oil droplets into aqueous solution of micelles, triblock copolymer micelles with corona-embedded CdS nanoparticles will reassemble at the interface between oil and water. PS blocks interpenetrate into oil phase, and PEG blocks interpenetrate into aqueous phase. In the meanwhile, CdS nanoparticles protected by DMAEMA units stay at the interface (Scheme 2). Fig. 7 shows a TEM image of the emulsion after evaporation of styrene monomer and water. Many rings composed of dark CdS dots can be observed on the image, which indicate that the CdS nanoparticles with triblock copolymer chains are located at the interface between oil and water. The size of the nanoparticles is still in the range between 3 nm and 6 nm indicating that the nanoparticles are kept stable at the interface and no aggregation can be observed.

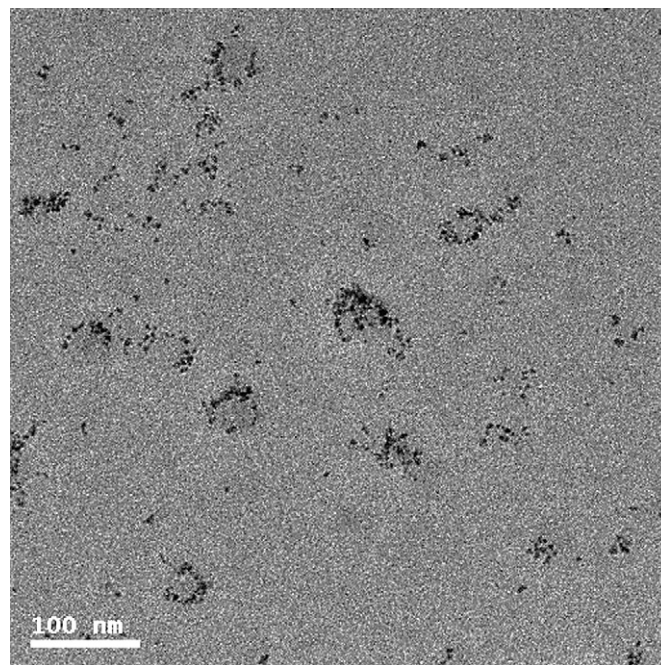


Fig. 7. A TEM image of dry rings composed of triblock copolymer and CdS nanoparticles at the interface of oil and water after evaporation of water and styrene. After removal of THF under reduced pressure, 1.1 mL of styrene monomer was added into 10 mL of micellar solution.

One of the goals of this research is to prepare colloid particles with nanoparticles and functional polymer chains on the surface. In previous literatures, nanoparticles on the surface of colloid particles were prepared within the charged polymer brushes [39–41]. These immobilized metal nanoparticles find practical applications such as catalysis, sensors, drug delivery and protein adsorption. Pickering suspension polymerization stabilized by triblock

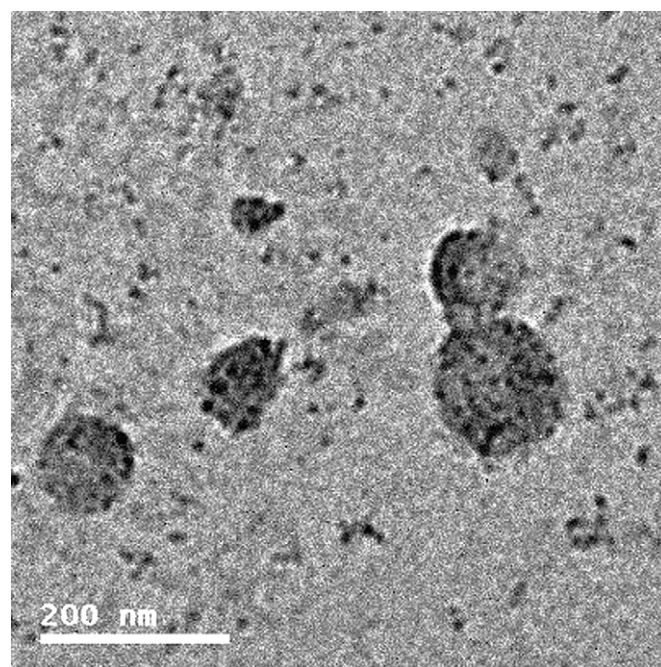


Fig. 8. A TEM image of PS colloid particles stabilized by PEG-*b*-PS-*b*-PDMAEMA triblock copolymer with CdS nanoparticles. After removal of THF in the micellar solution under reduced pressure, a mixture of AIBN (1 mg), styrene monomer (1.1 mL) and divinylbenzene (30 μ L) was added into the micellar solution (10 mL). The mixture was stirred at 75 °C for 4 h under nitrogen atmosphere.

copolymer with nanoparticles provides a new method to prepare colloid particles with nanoparticles on the surface. PS colloid particles were prepared by Pickering suspension polymerization. Styrene monomer, DVB cross-linker, and AIBN initiator were added into the aqueous solution of micelles with corona-embedded CdS nanoparticles. The polymerization was conducted at 75 °C for 4 h. Fig. 8 shows a TEM image of PS colloid particles. The diameter of the PS colloid particles ranges from 80 nm to 180 nm. On the image, CdS nanoparticles located on the surface of PS colloid particles can be observed. As we discussed above, upon addition of styrene oil droplets into aqueous solution of micelles, triblock copolymer micelles reassemble at liquid–liquid interface. At the interface, PS blocks interpenetrate into oil phase, and PEG blocks interpenetrate into aqueous phase (Scheme 2). After polymerization, PS blocks of the triblock copolymer still keep interpenetration into PS colloid particles, and PEG blocks into aqueous phase. Because PDMAEMA blocks are bounded to CdS nanoparticles, nanoparticles stay at the surface of colloid particles.

4. Conclusions

In summary, we have successfully prepared micelles with corona-embedded CdS nanoparticles based on complex formation between DMAEMA units and cadmium ions. Upon addition of styrene droplets into the micellar solution, the micelles with CdS nanoparticles tend to locate and reassemble at the interface between oil and water. PS colloid particles stabilized by triblock copolymer with CdS nanoparticles were prepared by suspension polymerization. CdS nanoparticles locate on the surface of PS colloid particles.

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