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An approach to hybrid inorganic nanoparticles in reactive PS-b-PMSMA amphiphilic copolymers

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ABSTRACT

A series of well-defined amphiphilic poly(styrene)-block-poly 3-(trimethoxysilyl) propyl methacrylate (PS-b-PMSMA) copolymers with controlled molecular weight and block length were prepared by the atom transfer free radical polymerization. The cadmium sulfide (CdS) nanoparticles were fabricated in the spherical micelles self-assembled from these prepared PS-b-PMSMA copolymers. Then, the CdS/PS-b-PMSMA films were obtained by spin coating the CdS/PS-b-PMSMA solution on silicon wafer. The experimental results showed the addition of Cu(II) could decrease the value of polydispersity index for the prepared copolymers. Nuclear magnetic resonance and Fourier transform infrared spectra showed the synthesis of PS-b-PMSMA copolymer. The average roughness and mean square roughness of the prepared CdS/PS-b-PMSMA films obtained from the atomic force microscopy analysis were 3.0–3.4 nm and 1.7–2.0 nm, respectively, indicating the excellent surface planarity. On the other hand, the ratio of block length between PS and PMSMA had a great influence on the micelle size. The larger ratio of PS to PMSMA block length resulted in the larger size of micelles and CdS nanoparticles that caused a red-shift of ultraviolet–visible and photoluminescence spectra. The red-shift of spectra was explained by the quantum confinement effect associated with the tiny size of the CdS nanoparticles.

1. Introduction

The hybrid materials based on cadmium sulfide (CdS) have been studied intensively due to their high potentials for various applications in the areas of optical materials [1,2], electronic materials [3,4], optoelectronic materials [5–8], and biological materials [9–11]. However, the aggregation of nanosized CdS in these hybrid materials often limited their application or reduces the performance. To overcome this problem, various polymers, glasses, ceramics and organic capping agents were used to improve the stability of nanoparticles and reduce the surface defects [12–15]. Recently, the amphiphilic block copolymers have been used in the preparation of CdS [13,16,17] and the other semiconductor nanoparticles [18–21]. The reaction of particle formation was confined within the cavity of the micelles self-assembled from amphiphilic block copolymers, and growth of the particle beyond the dimensions of the cavity was inhibited. Therefore, the size of particles could be well controlled. In addition, the surface properties of obtained nanoparticles could be modified by changing the different copolymers.

In recent years, a polymerization approach, atom transfer free radical polymerization (ATRP) has been considered as a versatile and powerful tool for the preparation of homopolymers and copolymers with predetermined molecular weights and narrow molecular weight distributions. The ATRP technique offered a way to form well-defined and predictable multicomponent polymer structure. Up to now, ATRP have been applied to the synthesis of well-defined macromolecular architecture such as amphiphilic random, gradient, star, and block copolymers [22–30]. Chen and his co-workers synthesized the reactive block copolymers poly(ethylene oxide)-b-poly(3-(trimethoxysilyl)propyl methacrylate) (PEO-b-PMSMA) by ATRP of 3-(trimethoxysilyl)propyl methacrylate (MSMA) with CuBr/N,N,N′,N″,N″-pentamethyl-diethylenetriamine as catalyst and poly(ethylene oxide)–bromide (PEO–Br) as a macroinitiator in anisole [31]. Further, they applied the amphiphilic block copolymers poly(ethylene oxide)-block-poly [3-(trimethoxysilyl)propyl methacrylate] (PEO-b-PMSMA) to synthesize the organic/inorganic hybrid materials. It has been found that different morphologies of

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micelles, such as spheres, rods, lamellae, and vesicles, could be prepared at different water contents [32,33]. Eisenberg and his co-workers have also investigated the various morphologies of aggregates or micelles formed from block copolymers, especially from polystyrene-b-poly(acrylic acid) (PS-b-PAA) [34–37] and polystyrene-b-poly(ethylene oxide) (PS-b-PEO) [38]. Various morphologies, such as spheres, cylinder, rods, lamellae, and vesicles, have been prepared. In addition, many factors were found to influence the resulting morphologies, including the copolymer composition and concentration [39], the nature of the common solvent [35], the type and concentration of added ions [40], and others [41]. Moreover, they applied these morphologically tunable copolymer aggregates to the synthesis of hybrid materials CdS/PS-b-PAA [42] and CdS/PEO-b-PS-b-PAA [43] and found that the block length of copolymers and copolymer concentration in solution had a great influence on the CdS particle size [42]. Other block copolymers, such as poly(styrene-b-2-vinylpyridine) (PS-b-P2VP) [44,45], poly(-ethylene glycol)-b-poly(2-N,N-dimethylaminoerthyl methacrylate) (PEG-b-PAMA) [13], and poly(acrylic acid)-b-poly(n-butyl acrylate) (PAA-b-PnBA) [46], have also been used for the preparation of CdS/copolymers hybrid materials in the literature.

MSMA is a reactive monomer that is an important silane coupling agent widely used in the preparation of organic/inorganic hybrid nanomaterials. Besides, various morphologies of aggregates or micelles formed from the PMSMA-based amphiphilic block copolymers have been reported [31–33]. However, as to our best knowledge the PMSMA-based copolymers have not found to be used to synthesize the CdS/copolymers hybrid materials in the literature. In addition, although the previous investigations on hybrid materials of CdS/copolymers have also shown that the many amphiphilic block copolymers, such as PS-b-PAA, PS-b-PEO, PS-b-P2VP, PEG-b-PAMA, and PAA-b-PnBA, were appropriate to produce the CdS/copolymers hybrid materials [13,34–47]. However, the effects of block length of hydrophilic and hydrophobic segments and ratio of Cu(II)/Cu(I) on the microstructure of block copolymer, micelle morphology, CdS particle size, optical and optoelectronic properties have not been fully explored.

In the present work, a series of poly(styrene)-block-poly 3-(trimethoxysilyl)propyl methacrylate (PS-b-PMSMA) copolymers with different molecular weight and narrow molecular weight distributions via ATRP were synthesized. The chemical structure and morphology and luminescence properties of the prepared CdS/PS-b-PMSMA nanocomposite films were examined. The effects of Cu(II)/Cu(I) and block length of PS and PMSMA on the polydispersity index (PDI), micelle morphology, CdS particle size, optical and optoelectronic properties were also investigated.

2. Experimental

2.1. Materials

3-(Trimethoxysilyl)propyl methacrylate (MSMA, 98%, Aldrich), Styrene (Fluka, >99%), Methyl 2-bromopropionate (Aldrich, 98%), Copper(I) bromide (CuBr, Aldrich 99.999%), Copper(II) bromide ($CuBr_2$, 99.999%, Aldrich), N,N,N′,N′,N″-pentamethyl diethylenetriamine (PMDETA, 99% Aldrich), Anhydrous tetrahydrofuran (THF, 99.9%, Acros), Anhydrous anisole (Aldrich, 99.7%), Cadmiumnitrat-4-hydrat ($Cd(NO_3)_2 \cdot 4H_2O$, 99%. Acros), Sodium sulfide ($NaS \cdot 9H_2O$, Acros) and Dimethyl sulfoxide (DMF, TEDIA) were used as received for the preparation of CdS/PS-b-PMSMA nanocomposite thin films.

2.2. Preparation of polystyrene macroinitiator

The synthesis of CdS/PS-b-PMSMA nanocomposite films was carried out according to the scheme shown in Fig. 1. The general procedures for the preparation of amphiphilic block copolymers PS-b-PMSMA are as follows. The desired amount of molar ratio of styrene monomer to initiator, CuBr, $CuBr_2$, and PMDETA were added to a dried three-fold flask and the solution was stirred to form the Cu complex. Then the certain amount of initiator, methyl 2-bromopropionate was added to the reaction mixture. All of the processes were operated in a nitrogen dried box. The reaction flask was put in oil bath at 110 °C to obtain the PS macroinitiator for 2–3 h. The prepared PS macroinitiator was dissolved in THF and then the ionic-exchange resin was added until the solution became light green or transparent. After that, the solution was filtered through a column of alumina. Then, the THF was removed from the solution by evaporation. The PS macroinitiator was then precipitated into H_2O/MeOH solution. The precipitation procedure was repeated two more times. The final product was dried under vacuum overnight.

2.3. Preparation of PS-b-PMSMA

The desired amount of molar ratio of MSMA monomer to PS macroinitiator, CuBr, $CuBr_2$, and PMDETA, e.g. M:I:Cu(I):Cu(II):L = 90:1:1:0.5:1, were added to a dried three-fold flask and the solution was stirred to form the Cu complex. Then, the flask was placed into an oil bath at 90 °C for 3–7 h until the formation of the copolymer with the desired molecular weight. Table 1 listed the various reaction conditions for the preparation of (PS)n-b-(PMSMA)m copolymers.

2.4. Preparation of CdS/PS-b-PMSMA thin films

In the presence of PS-b-PMSMA copolymers in anhydrous anisole, the desired amount of 0.05 M aqueous $Cd(NO_3)_2$ was added and stirred vigorously to obtain the stable micelles self-assembled from Cd^{2+}/PS-b-PMASMA copolymers. Then, stoichiometric amount of 0.05 M aqueous Na_2S was added to the reaction mixture and stirred for 7 h to obtain the CdS/PS-b-PMASMA nanocomposite. The resulting material was a colloidal solution of CdS isolated in the micelles. After that, the solution was coated on quartz or silicon wafer to measure the characteristics of the solid phase specimens. Table 2 listed the size of micelles and CdS nanoparticles and the corresponding absorption edge wavelengths (λ_{edge}) and wavelength of maximum absorbance (λ_{max}) obtained under different ratios of PS to PMSMA block length.

2.5. Characterization

The molecular weight of the prepared polymer was determined with a gel permeation chromatography (GPC) equipped with a Schambeck SFD GmbH Model RI2000 refractive index detector. The calibration was created by injecting polystyrene standard diluted to 0.5 wt% in THF (l ml/min) at 40 °C. The range of detected molecular weight was between 400 and 400,000. FTIR spectra of the nanocomposite films were obtained on a KBr pellet using a Jasco model FTIR 410 spectrometer. The morphology of micelles and fracture surface of the prepared nanocomposite films were examined on a Hitachi H-2400 scanning electron microscope (SEM). ^1H NMR spectra of the prepared copolymers were performed by a Jeol EX-400 spectrometer. The deuterated solvent, chloroform-d was used for obtaining the spectra. The AFM data was performed in tapping mode on a Nanoscope DI III multimode AFM. The root mean square roughness (R_q) and average roughness (R_a) of the prepared films were obtained from the 2D and 3D diagrams. UV–visible absorption and photoluminescence (PL) spectra were recorded on a Jasco model UV/Vis/NIR V-570 spectrophotometer and a Hitachi F-4500 luminescence spectrophotometer, respectively. Photoelectron (XPS) spectrum was obtained using a VG Microscan MT-500 ESCA system with the primary excitation source