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Synthesis of surface-functionalized polystyrene sub-micron spheres using novel amphiphilic comonomer

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ABSTRACT

A facile "one-pot" emulsion polymerization is reported to prepare surface-functionalized sub-micron spheres using novel amphiphilic comonomer as the reactive emulsifier. Specifically, amphiphilic 3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl) phosphinic sodium (AEOPS) was used not only as a comonomer, but also as a good emulsifier for the polymerization due to the relatively long chain of amphiphilic structure. Nearly monodisperse polystyrene sub-micron spheres with tunable sizes and zeta potentials were obtained. The phosphinic group-functionalized surfaces were demonstrated by the use of these particles to remove heavy metal ions (such as Cd^{2+}, Pb^{2+}) from water with a high efficiency.

1. Introduction

Surface-functionalized polymeric colloidal particles from nanoscopic [1] to micron [2] sizes represent an important class of materials that have attracted widespread interests in various fields, such as drug delivery [3], photonic crystals [4,5], colloidal assembly [6], templated synthesis of functional materials [7], and many more. The particle surfaces are normally functionalized by grafting [8–11] or derivatization reactions [12–14]. For example, Lime et al. [11] performed hydrobromination of residual vinyl groups on divinylbenzene polymer particles, and then grafted the polymers by atom transfer radical surface graft polymerization of glycidyl methacrylate; Bayramoglu and Arica [14] obtained poly(2-hydroxyethyl methacrylate/ethylenglycol dimethacrylate) microsphers containing surface-anchored sulfonic acid via the successive reactions:the microspheres were first prepared via suspension polymerization; after activation of the surface hydroxyl by bromination, surface-initiated atom transfer radical polymerization of glycidyl methacrylate was conducted; and then the epoxy groups of comb polymer was converted into sulfonic acid groups with reaction of sodium sulfite.

In order to eliminate the tedious and complicated reaction steps often involved with such surface functionalization approaches, there have been great interests in search of "one-pot" emulsion polymerization using reactive surfactants [15–17]. Recently there are some literatures about one pot synthesis of amphiphilic block copolymer latex [18–27]. Lefay et al. [27] prepared polystyrene or poly(methyl methacrylate/n-butyl acrylate) microspheres using amphiphilic gradient poly(styrene-*co*-acrylic acid) copolymer as emulsion polymerization stabilizer, and Mohanty et al. [22] studied electrosterically stabilized colloidal particles of different diameters between 70 nm and 400 nm by amphiphilic diblock copolymers poly(styrene)-block-poly(styrene sulfonate) as an emulsifier. In our previous work, a "one-pot" emulsion polymerization was used to prepare functionalized poly(styrene/divinylbenzene) (St/DVB) with poly(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl (phenyl)phosphinic acid)-*b*-polystyrene as an amphiphilic emulsifier [24]. However, it always requires complex reactions to synthesize the amphiphilic block copolymer for the "one-pot" emulsion polymerization.

We also notice that some polymeric microspheres were prepared by emulsion polymerization of styrene with other vinyl monomers [28–31], such as methacrylate acid [32,33], sodium styrene sulfonate [34], and etc. For example, Blom et al. [28] performed the emulsion polymerization of n-butyl acrylate in the presence of a polymerizable sulfobetaine monomer; Ramos et al. [29] investigated 2-(methacryloyloxy)ethyl] trimethyl ammonium chloride and vinylbenzyl trimethyl ammonium chloride as ionic comonomers in the emulsion polymerization of styrene. However, the colloid stability was relatively bad from these kinds of emulsion polymerizations, as shown by the high amounts of coagulum produced (4.2–38.1%) [29,35].

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In this paper, we design and synthesize a new amphiphilic functional monomer, 3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl) phosphinic sodium (AEOPS), which has a relatively long chain of amphiphilic structure that may be expected to stabilize the polymeric colloid better. Then we perform the emulsion polymerization with AEOPS to investigate its efficacy as emulsifier, while phosphinic group of AEOPS is covalently anchored onto PSt sub-micron spheres during the polymerization process, and endows the PSt sub-micron spheres with a good ionic coordination property [36–41]. As a result, nearly monodisperse polystyrene sub-micron spheres with tunable sizes and zeta potentials could be obtained, and the phosphinic group-functionalized surfaces were demonstrated by the use of these particles to remove toxic heavy metal cations from water with a high efficiency.

2. Experimental section

2.1. Materials and reagents

3-[hydroxy(phenyl)phosphoryl]propanoic acid, kindly donated by Sinopec Yizheng Chemical fibers, Co. Ltd., was dried for 24 h at 80 °C before use. 2-Hydroxyethyl acrylate (Alfa Aesar China (Tianjin) Co., Ltd., 97.0%) was distilled under reduced pressure prior to use. AEOPS was synthesized according to a modified literature method [42] (see Supporting Information). St (Sinopharm Chemical Reagent Co., Ltd., CP) was washed with a 5% sodium hydroxide aqueous solution and then with deionized water until neutralization, and after being dried with anhydrous sodium sulfate overnight, it was distilled under reduced pressure, stored under N_2 at -20 °C prior to use. All other chemical agents were used as received.

2.2. Synthesis of functional PSt sub-micron spheres by emulsion polymerization

The sub-micron spheres were prepared via emulsion polymerization with AEOPS as the emulsifier and comonomer, styrene as the monomer, DVB as the cross-linker and ammonium persulfate (APS) as the initiator. A typical procedure for the emulsion polymerization can be described as follows: Polymerization was performed in a 150 mL one-necked round-bottomed flask. Initially, 0.1 g of AEOPS was dissolved in 80 mL of distilled water, then, 1 g of St and 0.02 g of DVB were added under stirring. The mixture was dispersed under ultrasonic irradiation (75 W, 40 kHz) for ~2 min at room temperature (~22.0 °C), and purged with Argon gas for 20 min to get rid of the oxygen. After it was heated to 70 °C, an aqueous solution of the initiator (APS, 0.04 g dissolved in 2 mL of distilled water) was added to the mixture. After the polymerization was conducted for 24 h to ensure complete conversion, and the reaction mixture was slowly cooled to room temperature. Finally, the latex particles diluted in water by 1:40 (v/v) for the measurements of Z-average size and zeta potentials.

In addition, the emulsion polymerizations with the different recipe were also carried out: the concentration of AEOPS was changed from 0.30 g/L to 7.32 g/L to investigate the influence on the size of microspheres at 12.5 g/L of St concentration; and the concentrations of AEOPS (12.5 g/L) and monomer (250 g/L) were successfully used to obtain the high solid content (~24.6%).

2.3. Coordination of PSt sub-micron spheres with metal ions

0.145 g of PSt sub-micron spheres were dispersed in distilled water (10 ml) under ultrasonic irradiation, and then dialyzed (MWCO = 3500) in a dilute ionic aqueous solutions, i.e. 4.00 mmol/L $Pb(NO_3)_2$ aqueous solution (PH~7.0) or $CdCl_2$ aqueous solution (PH~7.0). 0.50 mL of the solution was removed to record the atomic absorption spectra at some pre-set interval times. Before the atomic absorption spectra of the samples were recorded, calibration curves of Pb^{2+} and Cd^{2+} were constructed.

2.4. Characterization

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Varian INVOA-400 instrument. Fourier transform infrared (FT-IR) spectra were recorded on a Varian-1000 spectrometer. The Z-average size and the polydispersity index of the particles were measured by a Malvern HPP5001 high-performance particle sizer (HPPS). Transmission electron microscopy (TEM) images were taken with a FEI Tecnai G20 electron microscope, using an accelerating voltage of 160 kV. The nanocarrier solution (~5 μl) was put on 400 mesh Ultrathin Type-A TEM Grid (Ted Pella, Redding, CA) and immediately wicked dry by kimwipes, and then imaged directly under TEM. Energy-dispersive X-ray (EDX) analysis was carried out by a Hitachi S570 scanning electron microscope equipped with an EDAX-PV 9100 energy dispersion X-ray fluorescence analyzer. The zeta potential measurements were conducted on a Malvern Zetasizer NanoZS system with irradiation from a 632.8 nm He–Ne laser. The critical micelle concentration (CMC) was determined using pyrene as a fluorescence probe, and the fluorescence spectra were recorded using FLS920 fluorescence spectrometer with the excitation wavelength of 335 nm while the emission fluorescence at 373 and 384 nm were monitored. The sorption of Pb^{2+} or Cd^{2+} was measured for PSt sub-micron spheres using atomic absorption spectrometry (DUO-220, Varian of America). Surface tension measurements of AEOPS aqueous solution were carried out by du Nouy Ring method using a JK99C automatic surface tensiometer and a platinum ring (Shanghai Zhongchen Co., China). The stock solutions were prepared by dissolving the AEOPS into deionized water and then a series of AEOPS aqueous solutions with different concentrations were obtained by diluting the stock solution with deionized water. The obtained values were checked through measurement of the surface tension of deionized water.

3. Results and discussion

In this study, the amphiphilic monomer AEOPS was synthesized by the esterification of 3-[hydroxy(phenyl)phosphoryl]propanoic acid and 2-hydroxyethyl acrylate in the presence of DCC and DMAP. The structure of AEOPS was confirmed by ^{1}H NMR spectrum (Fig. 1a). The characteristic peaks at $\delta = 7.4$–7.8 ppm ($-C_6H_5$) and 5.8–6.4 ppm ($-CH{=}CH_2$) indicate the successful synthesis of AEOPS. The amphiphilicity of the AEOPS monomer was determined by measuring its critical micelle concentration (CMC) using pyrene as a fluorescence probe: the concentration of monomer was varied from 1.0×10^{-4} to 1.0×10^{-2} g/L while the concentration of pyrene was fixed at 0.6 μM, and the CMC was estimated as the cross-point when extrapolating the intensity ratio I_{373}/I_{384} at low and high concentration regions. The CMC of AEOPS is determined to be 1.211×10^{-3} g/L (Fig. 1b). In addition, surface tension measurements were also carried out in AEOPS aqueous solutions (Fig. S1, see Supporting Information). The surface tension shows a decreasing tendency with increasing concentration of AEOPS, especially at $\sim 10^{-3}$ g/L of the concentration, which is very close to the CMC value from the method of fluorescence spectra.

The emulsion polymerization of St/DVB was performed with AEOPS as the emulsifier and comonomer. After the polymerization, the solid content was collected by centrifugation. The morphology of the PSt sub-micron spheres was revealed by TEM. As shown in Fig. 2A: the as-produced PSt particles are spherical and monodisperse with a diameter of about 200 nm, and the outer shell and

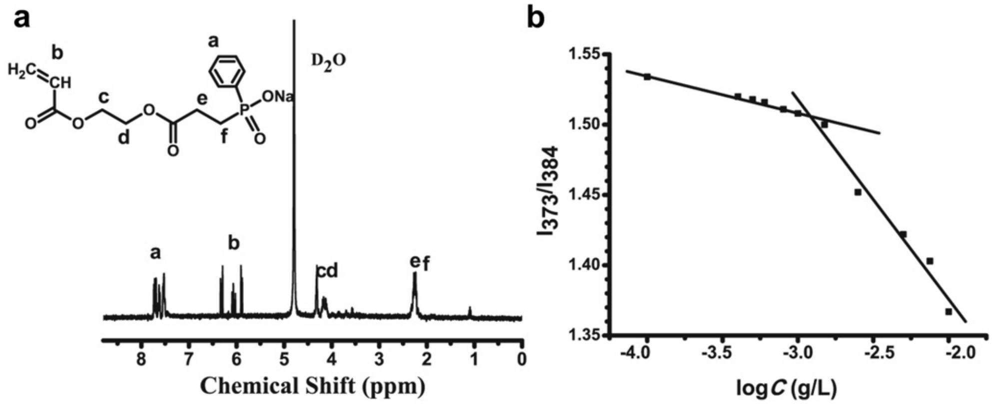

Fig. 1. (a) ^1H NMR spectrum (400 MHz, D_2O) of AEOPS at a low concentration and (b) The fluorescence intensity ratio I_{373}/I_{384} of pyrene as a function of AEOPS concentration.

core are clearly observed. The particle sizes and size distributions further demonstrate that the sub-micron spheres have a symmetric and very narrow size distribution. The single peak is positioned at 247 nm, which agrees very well with TEM observations; the small polydispersity index further suggests that there is no aggregation in the dispersion of the sub-micron spheres (Fig. 2B). For PSt microspheres from emulsion polymerization with high solid content (24.6%), there are still a single peak and a small polydispersity index for particle size distributions (Fig. S2, see Supporting Information), which suggest the successful emulsion polymerization with high solid content. All the results indicate that AEOPS can be used as an emulsifier to stabilize the emulsions in substitution of surfactants, which may be associated with the amphiphilic structure of AEOPS.

The surface structures of the sub-micron spheres were characterized by FT-IR spectra (Fig. 2C). In comparison with AEOPS (Fig. 2C, trace a), the characteristic peaks at 1192 cm^{-1} ($-P{=}O$), 1026 cm^{-1} ($-P-O$) and 1620 ($-C{=}O$) occur for the functional PSt sub-micron spheres, while the peak at 998 cm^{-1} ($-C{=}C$) disappears (Fig. 2C, trace b). The zeta potential measurement was also implemented for the characterization of the surface function of PSt sub-micron spheres. Fig. 2D shows the PSt sub-micron spheres have a zeta potential of −26.0 mV which should be ascribed to the anchored phosphinic group. These results unambiguously show that the PSt sub-micron spheres are functionalized by phosphinic groups of AEOPS, which may be covalently anchored onto PSt sub-micron spheres by the copolymerization process.

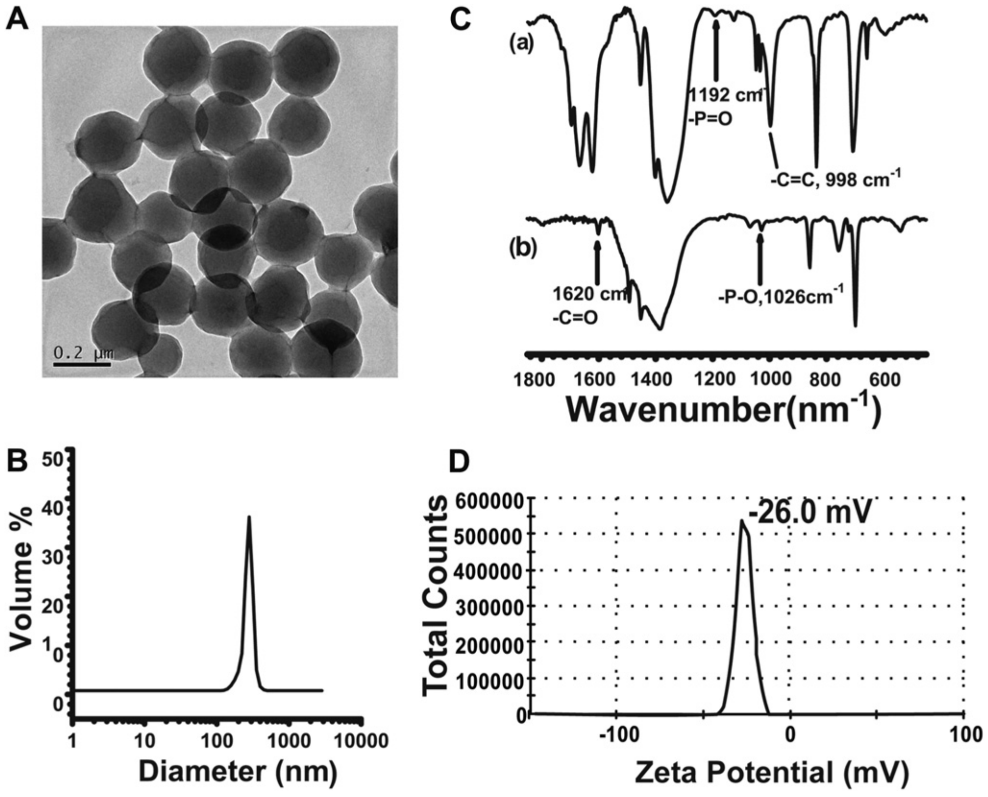

Fig. 2. (A) TEM image and (B) particle size distribution of PSt sub-micron spheres obtained from emulsion polymerization with AEOPS as emulsifier with the concentration of 1.22 g/L (i.e. [AEOPS] = 1.22 g/L): Z-average size = 247 nm, polydispersity index = 0.042; (C) IR spectra of (a) AEOPS and (b) functional PSt sub-micron spheres; and (D) The zeta potential distribution curve for PSt sub-micron spheres ([AEOPS] = 1.22 g/L).

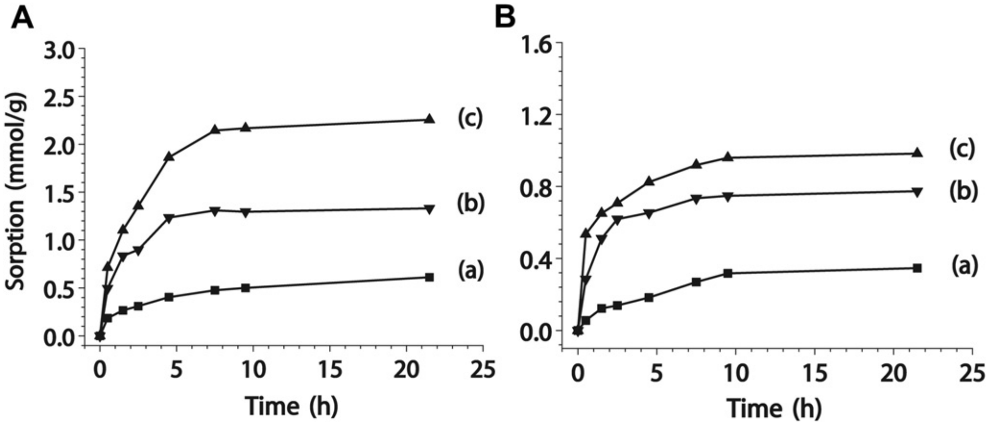

Fig. 3. The sorption of (A) Cd^{2+} and (B) Pb^{2+}as a function of the time for the PSt sub-micron spheres with the zeta potential: (a) −26.0 mV, (b) −51.3 mV, and (c) −70.7 mV.

Expectedly, the size and the zeta potential of the sub-micron spheres are tunable by the concentration of AEOPS used in the emulsion polymerizations. The more AEOPS in the polymerization will lead to the smaller size like conventional emulsion polymerization (Fig. S3, see Supporting Information); whereas, at relatively high concentration of AEOPS, the size of the final particles would become larger (Fig. S4, see Supporting Information), which may be attributed that some emulsifiers might be entrapped into the micelle at relatively high concentration, thereby combining some water into the micelle to enlarge the sizes. In addition, the more negative zeta potential of the sub-micron spheres could be obtained with larger concentration of AEOPS in the polymerization (Fig. S5, see Supporting Information). To quantitatively examine the degree of surface functionalization, we tested the ionic coordination property of the as-prepared PSt sub-micron spheres. Specifically, the PSt sub-micron spheres were treated with dilute solution of heavy metal ions, such as Cd^{2+} and Pb^{2+}. Those heavy metal ions are known as environmental hazards that cause long-term risk to the ecosystem and humans. The sorption of the metal ions as a function of the time was depicted in Fig. 3 for PSt sub-micron

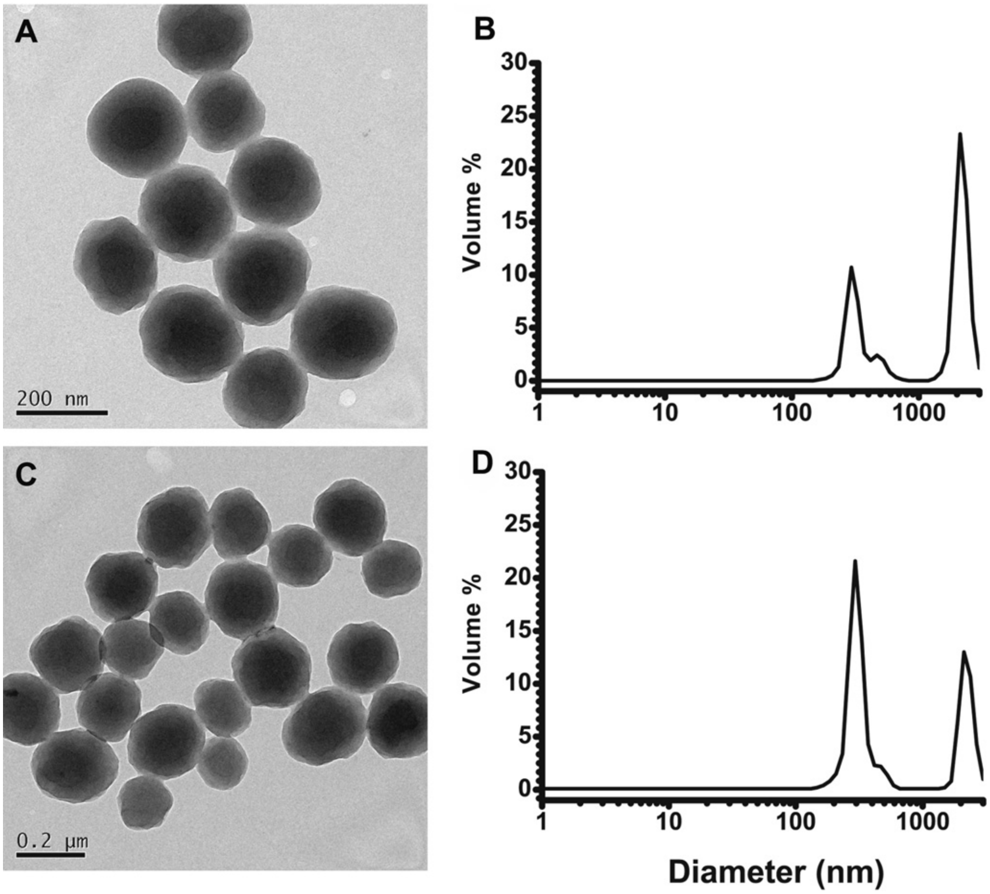

Fig. 4. TEM images and size distributions of PSt sub-micron sphere–Cd^{2+} complex (A, B) and PSt sub-micron sphere–Pb^{2+} complex (C, D). All the PSt sub-micron spheres before ion coordination have a zeta potential of −26.0 mV.

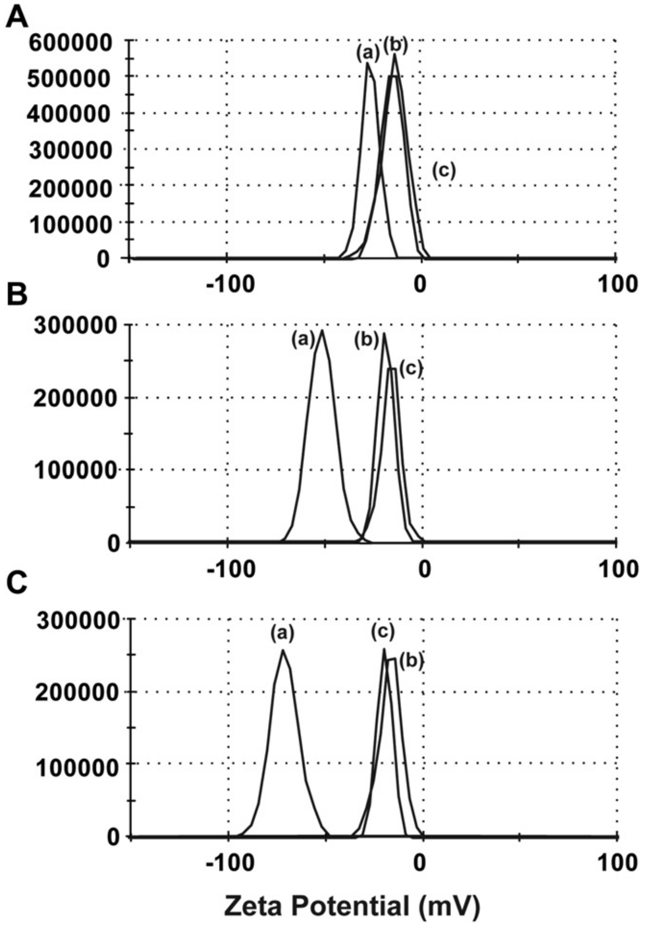

Fig. 5. The zeta potential distribution curves for the original PSt sub-micron spheres : −26.0 mV (A, trace a), −51.3 mV (B, trace a), and −70.7 mV (C, trace a); PSt sub-micron sphere–Cd^{2+} complex : −16.2 mV (A, trace b), −16.5 mV (B, trace b), and −19.2 mV (C, trace b); and PSt sub-micron sphere–Pb^{2+} complex : −16.8 mV (A, trace c), −16.6 mV (B, trace c), and −19.5 mV (C, trace c).

spheres with the different zeta potentials. The sorption of Cd^{2+} and Pb^{2+} can reach the maximum capacity of 0.612 mmol/g and 0.346 mmol/g within 600 min for PSt sub-micron spheres with the zeta potential of −26.0 mV, respectively (Fig. 3A, trace a and 3B, trace a). The difference of sorption capacity between Cd^{2+} and Pb^{2+} may be ascribed to the different charge density because the electrostatic interaction is essential for the ion sorption in this study: for the smaller volume of Cd^{2+}, there is a relatively larger charge density, which may lead to the larger sorption capacity. Interestingly, the maximum ion sorption capacity of the PSt sub-micron spheres is tunable when their zeta potentials vary (Fig. 3). For instance, when the zeta potential is changed to −70.7 mV, the maximum ion sorption capacity of the PSt microsphere reaches 2.255 mmol/g for Cd^{2+}, and 0.982 mmol/g for Pb^{2+} ions, respectively (Fig. 3A, trace c and 3B, trace c). These values are markedly larger than the reported numbers of functionalized PSt sub-micron spheres prepared by other surface functionalization approaches: 0.054 mmol/g for Cd^{2+} reported by Trochimczuk [40]; or 0.152 mmol/g for Pb^{2+} and 0.274 mmol/g for Cd^{2+}, respectively, reported by Liu et al. [43]. The difference between the sorption capacities should be ascribed to the different surface-functionalized methods: Trochimczuk [40] obtained the functionalized sub-micron spheres with phenylphosphinic acids by reacting styrene/divinylbenzene (St/DVB) resin with PCl_3 in the presence of Friedel–Crafts catalyst; and Liu et al. [43] grafted chitosan onto amine-functionalized magnetite nanoparticles via Schiff base bonds. Our results indicate that the surface-functionalized PSt sub-micron spheres prepared by the "one-pot" emulsion polymerization process with the reactive amphiphilic comonomer not only have a tunable surface function density, but also are significantly more efficient in removing heavy metal ions pollution from water.

The presences of Pb^{2+} and Cd^{2+} on the surface of the PSt sub-micron spheres are further confirmed by EDX spectra (Fig. S6, see Supporting Information). The morphologies and size distributions of PSt sub-micron sphere–Pb^{2+} and Cd^{2+} complexes were characterized by TEM and HPPS, respectively. In comparison with PSt sub-micron spheres before coordination with the metal ions (Fig. 2A), the complexes have the similar core–shell structure (Fig. 4A and C). At the same time, it should be noticed that the complexes have the multi-peaks in the size distribution (Fig. 4B and D), which suggests that some inter-particle aggregates occurred when the PSt sub-micron spheres are coordinated with Pb^{2+} and Cd^{2+}, respectively.

In order to further understand the difference of ion sorption capacities, we studied the zeta potential of the PSt sub-micron sphere–ion complexes. The zeta potential is a measure of the number of charges per particle surface, and it can be used to assign the change of the surface charge created by anions and cations. The PSt sub-micron spheres ([AEOPS] = 1.22 g/L) has a zeta potential of −26.0 mV (Fig. 5A, trace a) due to the anchored phosphinic group, and after it coordinated with Cd^{2+} and Pb^{2+}, the zeta potentials is expectedly increased to −16.2 mV (Fig. 5A, trace b) and −16.4 mV (Fig. 5A, trace c), respectively. Surprisingly, we obtained essentially the same zeta potential for ion-bound PSt sub-micron spheres even though their initial zeta potentials vary greatly before ion coordination, as an example shown in Fig. 5. The results further showed the PSt sub-micron spheres with different initial zeta potential would have a different cation sorption capacity: the more negative zeta potential, the higher capacity.

4. Conclusion

In summary, we report a facile approach to prepare surface-functionalized polystyrene sub-micron spheres by "one-pot" emulsion polymerization using novel amphiphilic comonomer as an emulsifier. The functional comonomer has a long chain of amphiphilic structure. The resultants were characterized by ^1H NMR, FT-IR, TEM, HPPS, EDX, zeta potential and fluorescence spectra. The results show that AEOPS could be used not only as a comonomer due to the acrylate structure, but also as a good emulsifier with the CMC of 1.211×10^{-3} g/L. The core–shell structured, surface-functionalized PSt sub-micron spheres were shown to have a monodisperse diameter with tunable sizes ($d \sim 10^2$ nm) and zeta potentials by changing the concentration of AEOPS used in the emulsion polymerizations, and the phosphinic groups are covalently anchored onto PSt sub-micron spheres during the polymerization process. The surface-functionalized polymer particles coordinate well with Pb^{2+} or Cd^{2+} to form the aggregates with the larger sizes and polydispersities, and the sorption capacity of the sub-micron spheres is increased with the more negative zeta potentials. This property may be used for the removal of heavy metal ions from wastewater. We expect that a similar concept should be generically applicable to the emulsion polymerizations using other similar functional amphiphilic monomers. As such, this surfactant-free approach enables the control of both the particle sizes and particle surface functions with unlimited choice of particle compositions.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.polymer.2012.05.058.

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