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A Facile Approach for Preparation of Phenylphosphinic Acid-Functionalized PSt Microspheres by Emulsion Polymerization Using Amphiphilic Macro-RAFT Agent as Emulsifier

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ABSTRACT: The phenylphosphinic acid-functionalized microspheres were successfully prepared by "one-pot" emulsion polymerization of styrene/divinylbenzene with a functional macromolecular reversible addition−fragmentation chain transfer (RAFT) agent, poly(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic acid)-*block*-polystyrene (P(AOPA)-*b*-PSt), as an amphiphilic emulsifier. The monodisperse microspheres were obtained with about 300 nm of the diameters and the clear core−shell structures, while phenylphosphinic acid groups were introduced into the shell via the RAFT process. The functionalized microspheres show high ability to coordinate with Cu^{2+} or Fe^{3+}.

Introduction

In the past decades, surface-functionalized microspheres have attracted more and more attention of polymer chemists because they have a high potential for many applications.[1] Among them, it is well-known that phosphorus-containing microspheres can be used as ion-exchangers due to their good ionic coordination properties.[2−6] For the preprepared microspheres, the functionalization of surfaces can normally be achieved by grafting techniques[7−10] and chemical modifications.[11−13] For example, Alexandratos et al.[4] prepared the phosphorus-functionalized microspheres by immobilizing polyols onto cross-linked poly(vinylbenzyl chloride) and then monosubstituting with diethyl phosphate ligands; Trochimczuk[6] obtained the functionalized microspheres with phenylphosphinic acids by reacting styrene/divinylbenzene (St/DVB) resin with PCl_3 in the presence of Friedel−Crafts catalyst.

Recently, there is great interest in preparing microspheres by emulsion polymerization with polymeric surfactants[14−16] because the polymeric surfactants show obvious advantages, such as their low critical micelle concentration and low diffusion coefficient compared to that of classical low-molecular-weight surfactants. For example, Mohanty et al.[17] used amphiphilic diblock copolymers poly(styrene)-*block*-poly(styrenesulfonate) as an emulsifier to prepare electrosterically stabilized colloidal particles of different diameters between 70 and 400 nm; Chevalier and co-workers[18] reported that block copolymers poly(caprolactone)-*block*-poly(ethylene oxide) are promising nonionic macromolecular surfactants for the stabilization of emulsions due to a stronger adsorption and an increased long-term stability.

At the same time, great progress has been made in controlled/living free radical polymerization in the past few decades, such as living free radical nitroxide-mediated polymerization,[19−21] atom transfer radical polymerization,[22−24] and reversible addition−fragmentation chain transfer (RAFT)[25,26] process, which have provided a powerful tool to synthesize the block copolymer with controlled molecular weights and "well-defined" structures. Among them, RAFT polymerization is a versatile technique, which involves a fast, reversible chain-transfer process of a thiocarbonylthio compound reacting with propagating chain radicals. The process is no metal contamination in comparison with atom transfer radical polymerization and is applicable to a wide range of monomers (most monomers polymerized by free radical methods) and reaction conditions.[26]

Recently, we noticed that macro-RAFT agents have been used as stabilizers in emulsion polymerization.[27,28] Martins dos Santos and co-workers[29,30] and Charleux et al.[31] respectively synthesized poly(ethylene oxide)-based macromolecular agents and used them as stabilizers and control agents in the miniemulsion polymerization of styrene; Hawkett and co-workers reported the amphiphilic, RAFT-capped, acrylic acid−styrene diblock copolymers[32] and acrylic acid−butyl acrylate diblock copolymers[33,34] were synthesized and applied as stabilizers of emulsion polymerization; and Yan et al.[35] obtained the polymeric particles with hydrophobic cores and hydrophilic shells via emulsion polymerization of styrene using a water-soluble poly(acrylamide)-based macro-RAFT agent in aqueous solution. There is no doubt that this technique may provide a facile "one-pot" approach to prepare functionalized microspheres; however, there are no papers published on it.

In this paper, we report a facile approach for the preparation of the phenylphosphinic acid-functionalized polystyrene microspheres by "one-pot" emulsion polymerization of St/DVB in the presence of an amphiphilic functional macro-RAFT agent, poly(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic acid)-*block*-polystyrene (P(AOPA)-*b*-PSt). P(AOPA)-*b*-PSt was synthesized from RAFT polymerization of AOPA and St and used not only as emulsifier but also as macro-RAFT agent due to the structure of thiocarbonylthio moiety. In addition, P(AOPA) is a novel polymer of phosphinic acids and can be covalently anchored onto PSt microspheres by the RAFT process in emulsion polymerization, which may endow the PSt microspheres with good ionic coordination property.[4,6]

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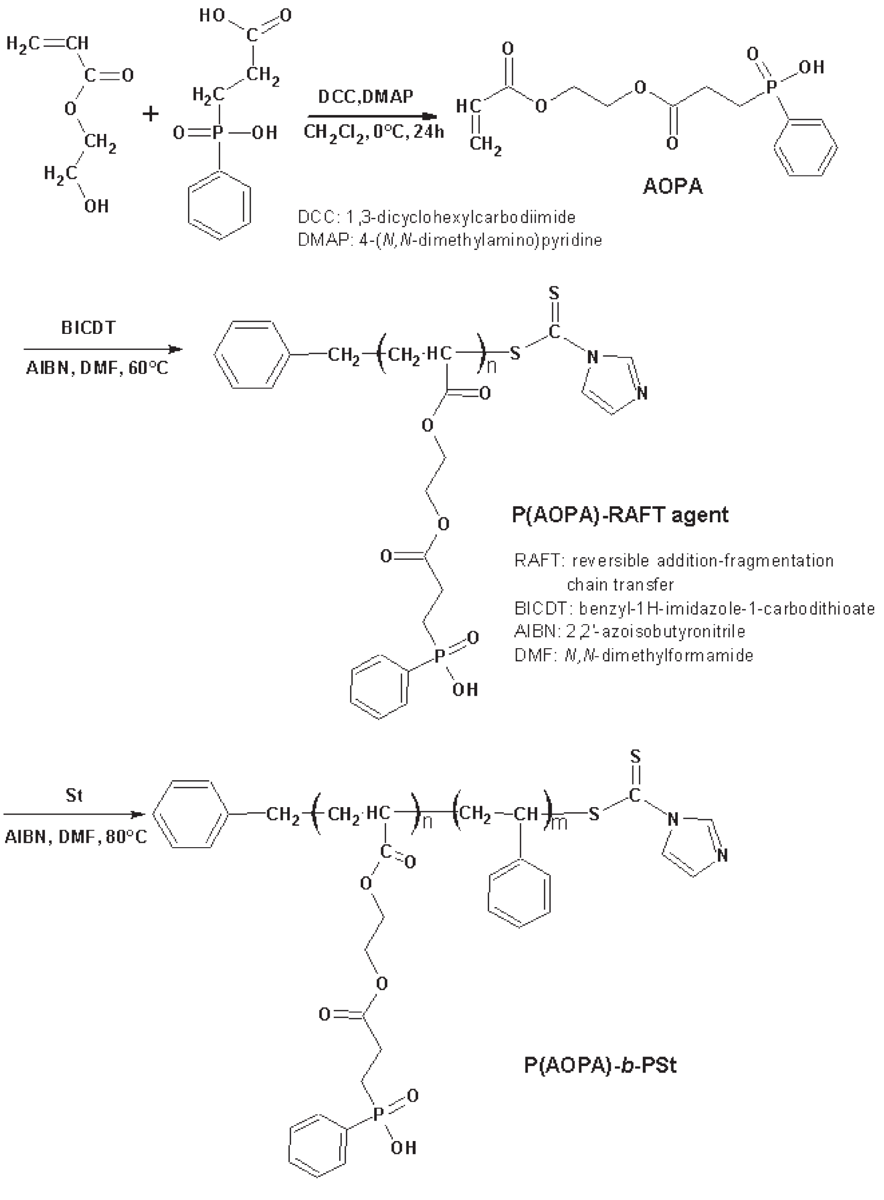
Experimental Part

Materials and Reagents. 3-[Hydroxy(phenyl)phosphoryl]propanoic acid, kindly donated by Yizheng Chemical fibers, Co. Ltd. (China), was dried for 2 days at 90 °C before use. 2-Hydroxyethyl acrylate (HEA, 98%), 1,3-dicyclohexylcarbodiimide (DCC, 99%), and 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 99%) were purchased from Alfa Aesar China (Tianjin) Co., Ltd. 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 and stored under N_2 at −20 °C prior to use. 2,2′-Azoisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd., CP) was purified by recrystallization. *N*,*N*-Dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR) and dichloromethane (CH_2Cl_2, Sinopharm Chemical Reagent Co., Ltd., AR) were dried by molecular sieves (4 Å). Benzyl 1*H*-imidazole-1-carbodithioate (BICDT) was synthesized according to a related reference.[36] All other chemical agents were used as received.

Synthesis of AOPA. A solution of 3-[hydroxy(phenyl)phosphoryl]propanoic acid (8.56 g, 40 mmol), HEA (4.64 g, 40 mmol), DCC (8.24 g, 40 mmol), and DMAP (0.1 g) in CH_2Cl_2 (80 mL) was stirred at 0−5 °C for 24 h. The reaction solution was filtered, and the solvent was evaporated under reduced pressure to give the monomer, which was purified by column chromatography on silica gel (CH_2Cl_2/CH_3OH, 20:1) to give a colorless oil (7.0 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.7-9.3$ (−OH), 7.4−7.9 ($-C_6H_5$), 5.8−6.5 ($=CH_2$ and $=CH-$), 3.2−4.4 ($O-CH_2-CH_2-O$), 2.1−2.6 ($-CH_2-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 26.6, 60.2, 62.5, 127.6, 127.8, 128.6, 128.7, 129.2, 131.3, 131.4, 132.8, 165.7, 174.0. ^{31}P NMR (162 MHz): $\delta = 44.8$.

Synthesis of P(AOPA)-*b*-PSt. P(AOPA) was first synthesized by RAFT polymerization, and the typical procedure was as follows: a stock 5 mL solution comprising AOPA (2.4 g, 7.6 mmol), BICDT (28 mg, 0.12 mmol), and AIBN (5 mg, 0.03 mmol) in DMF was prepared and was placed in an ampule. The contents were purged with argon for 10 min to eliminate the dissolved oxygen. The ampules were then flame-sealed and placed in an oil bath thermostated at 60 °C. After a preset reaction time, each ampule was cold with ice water and opened. Considering that AOPA and BICDT could be dissolved well in diethyl ether, and the polymer was not dissolved in diethyl ether

Scheme 1. Synthetic Route for the Amphiphilic Macromolecular Reversible Addition−Fragmentation Chain Transfer (RAFT) Agent, Poly-(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic acid)-*block*-polystyrene (P(AOPA)-*b*-PSt)



while it could be dissolved in methanol, the resultants were diluted with a little methanol and precipitated in 10-fold diethyl ether; the obtained polymer was dried in vacuum at 40 °C until a constant weight was obtained gravimetrically. Conversions were determined by ^{1}H NMR and gravimetric methods; both gave comparable results. P(AOPA)$_{24}$ (M_n = 8000 g/mol, PDI = 1.06, conversion = 41.2%) was obtained as macro-RAFT agent for the extension of St. The same procedure was used for the extension reaction of St, except that P(AOPA)$_{24}$ instead of BICDT was used as RAFT agent. Finally, P(AOPA)$_{24}$-*b*-PSt$_{19}$ (M_n = 9950 g/mol, PDI = 1.36) was given as the emulsifier for the emulsion polymerization.

Synthesis of Functional PSt Microspheres by Emulsion Polymerization. The microspheres were prepared via emulsion polymerization with P(AOPA)$_{24}$-*b*-PSt$_{19}$ as the emulsifier, styrene as the monomer, and divinylbenzene (DVB) as cross-linker. Ammonium persulfate (APS) was used as an initiator for the polymerization.

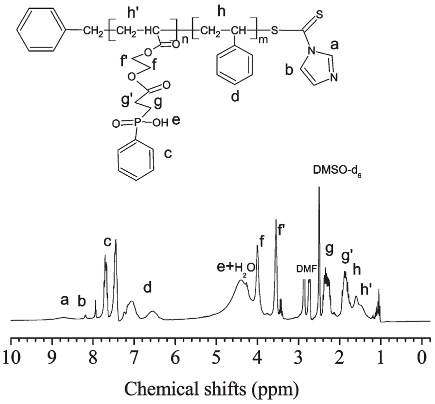


Figure 1. ^{1}H NMR spectrum of poly(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic acid)-*block*-polystyrene (P(AOPA)$_{24}$-*b*-PSt$_{19}$) in DMSO-d_6 (M_n = 9950 g/mol, PDI = 1.36).

A typical recipe for the emulsion polymerization can be described as follows: Polymerization was performed in a 100 mL three-necked reactor (usually a round-bottomed flask) immersed in a thermostated water bath and equipped with a reflux condenser (water cooling), an argon inlet, and a thermometer. Initially, 0.08 g of block copolymer was dispersed in 50 mL of distilled water under ultrasonic irradiation and purged with Ar gas for 20 min. Then, 1 g of St and 0.06 g of DVB were added under stirring, and the mixture was heated to 70 °C under Ar gas. Finally, an aqueous solution of the initiator (APS, 0.04 g dissolved in 2 mL of distilled water) was added to the mixture to start the polymerization. The polymerization was stopped after 8 h to ensure complete conversion, and the reaction mixture was slowly cooled to room temperature. Finally, the microspheres were collected by centrifugation at 15 000 rpm for 60 min and were dialyzed with ethanol for 48 h to remove unreacted monomers and free macromolecular emulsifiers. The obtained microspheres were dried in a vacuum oven at 40 °C to constant weight (0.95 g) and were stored in desiccator before use.

Coordination of PSt Microspheres with Metal Ions. 0.2 g of PSt microspheres was dispersed in dilute ionic aqueous solutions, i.e., 0.2% $FeCl_3$ aqueous solution (pH ~ 7.0) and 0.2% $CuCl_2$ aqueous solution (pH ~ 7.0) under ultrasonic irradiation. After stirring for 48 h, the coordination equilibrium might be reached, so the microspheres were collected by centrifugation at 15 000 rpm for 60 min and were dialyzed with H_2O for 48 h to remove free metal ion.

Characterization. Transmission electron microscopy (TEM) images were taken with a FEI Tecnai G20 electron microscope, using an accelerating voltage of 160 kV. 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. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) NMR spectra were obtained on a Varian INVOA-400 instrument. FT-IR spectra were recorded on a Varian-1000 at room temperature, and the solutions of polymers were dropped on KBr tablet. The molecular weights

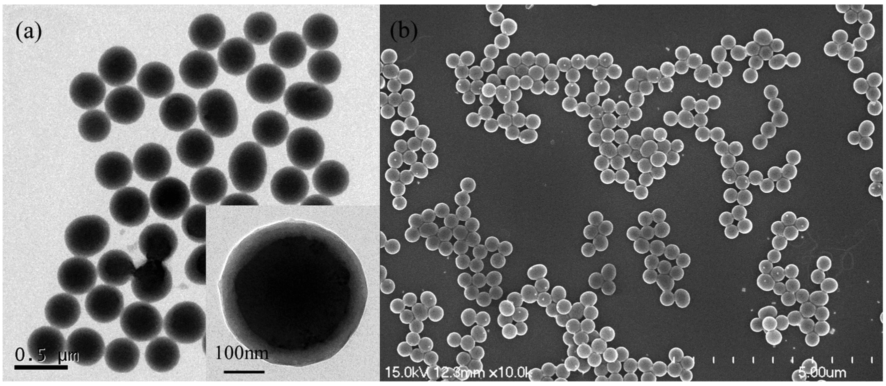


Figure 2. (a) TEM and (b) SEM spectra of PSt microspheres obtained from emulsion polymerization with the copolymer, poly(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic acid)-*block*-polystyrene (P(AOPA)$_{24}$-*b*-PSt$_{19}$) as emulsifier.

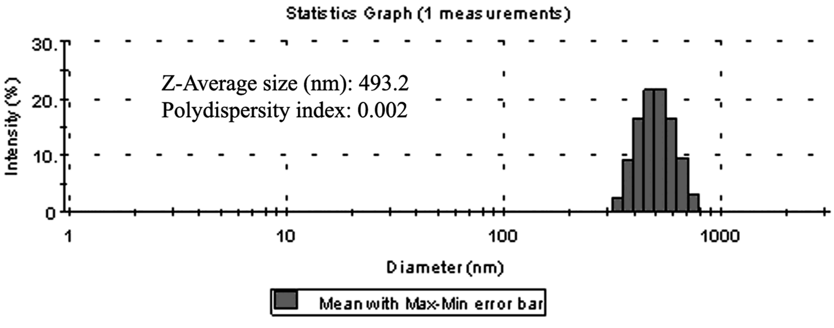


Figure 3. Particle size distribution of PSt microspheres in distilled water at the concentration of 0.16 mg/mL.

and polydispersities of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with differential refractometer with temperature control, using 500, 10^3, and 10^4 Å MZ-Gel SDplus columns with molecular weight range 100−500 000 calibrated with PS standard samples. DMF with 0.05 mol/L of LiBr was used as the eluent at a flow rate of 0.8 mL $\min^{-1}$ operated. The *Z*-average size and the polydispersity index of the micelles were measured by a Malvern HPP 5001 high-performance particle sizer (HPPS).

Results and Discussion

In this study, the novel phosphorus-containing monomer AOPA was first synthesized by esterification of 3-[hydroxy-(phenyl)phosphoryl]propanoic acid and 2-hydroxyethyl acrylate in the presence of DCC and DMAP. And then RAFT polymerization of the monomer was performed with BICDT to produce the polymer, P(AOPA). Finally, a block copolymer P(AOPA)_{24}-*b*-PSt_{19} (M_n = 9950 g/mol, PDI = 1.36) was obtained as the emulsifier via the polymerization of St using P(AOPA)_{24} (M_n = 8000 g/mol, PDI = 1.06) as macro-RAFT agent (Scheme 1). The structure of the copolymer was characterized by ^{1}H NMR spectrum (Figure 1). Besides the signal (6.3−7.3 ppm) corresponding to the protons of phenyl groups of St units, the peaks at 7.3−7.8 ppm can be clearly observed for phenyl protons of AOPA units, which indicates the successful synthesis of the copolymer. In addition, the characteristic peaks at 8.0−8.5 ppm reveal the existence of the imidazolyl group in the polymer chain.

Because of the amphiphilicity and containing the thiocarbonylthio moiety, the block copolymer can be used not only as an emulsifier but also as a macro-RAFT agent in emulsion polymerization. The emulsion polymerization of St was performed with APS as an initiator and DVB as cross-linker in the presence of amphiphilic P(AOPA)_{24}-*b*-PSt_{19} at 70 °C under Ar gas. After the polymerization, the microspheres were collected by centrifugation. The morphologies of the PSt microspheres were investigated by TEM and SEM (Figure 2). As shown in Figure 2a, the PSt microspheres possess a monodisperse diameter of about 300 nm, and the core and shell can be clearly observed. Moreover, the SEM micrograph demonstrates that the microspheres have a relatively uniform distribution (Figure 2b).

The particle sizes and size distributions were also characterized by a high-performance particle sizer (HPPS), and the results further demonstrated that the microspheres had the symmetric and very narrow size distributions (Figure 3). All the results indicate that P(AOPA)_{24}-*b*-PSt_{19} is a good macromolecular surfactant for the stabilization of emulsions.

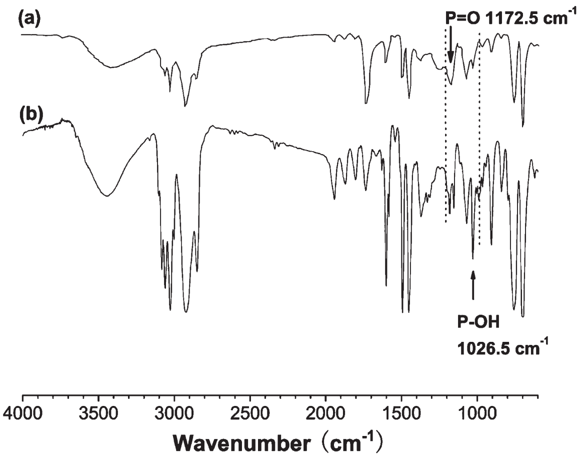
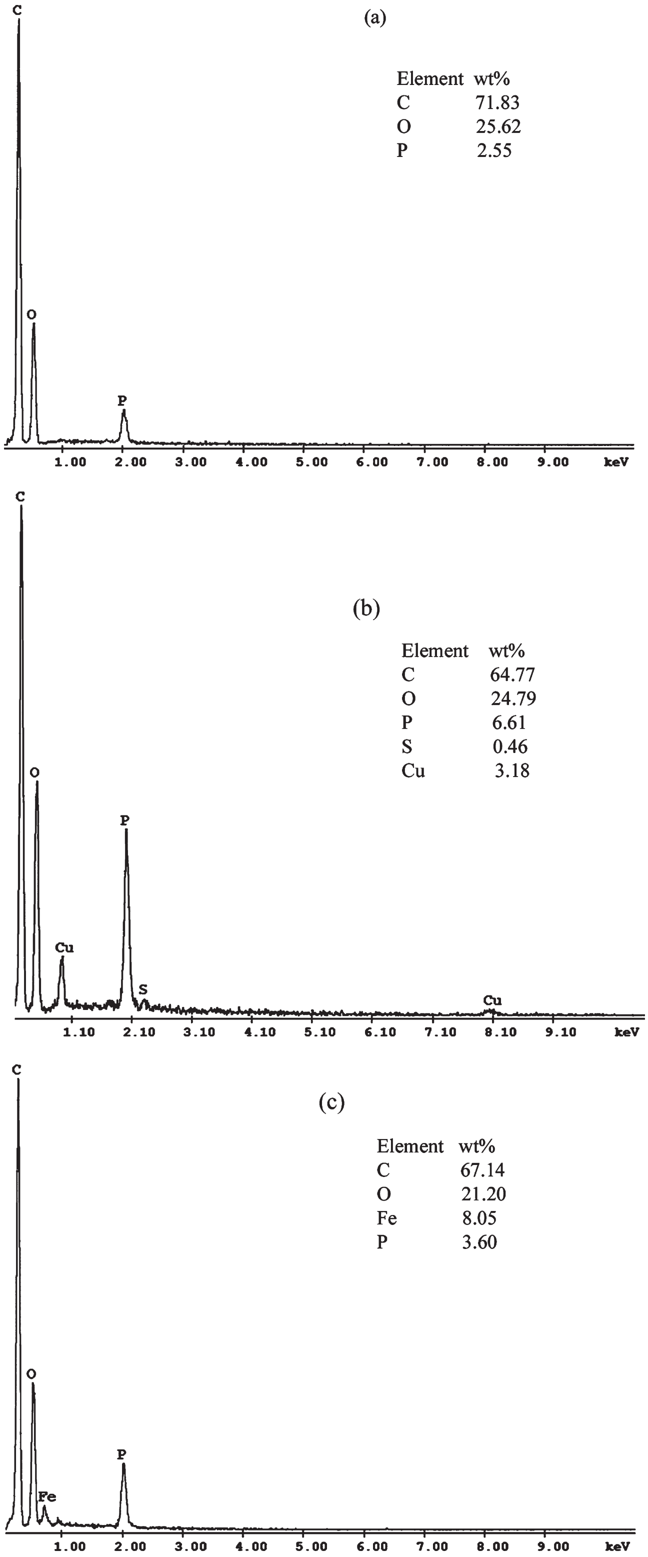


Figure 4. IR spectra of (a) poly(3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic acid)-*block*-polystyrene (P(AOPA)_{24}-*b*-PSt_{19}) and (b) functionalized PSt microspheres.

The surface chemical composition of the microspheres was characterized by FT-IR spectra (Figure 4). In comparison with P(AOPA)_{24}-*b*-PSt_{19}, the characteristic peaks at 1172.5 cm^{-1} for −P=O and at 1026.5 cm^{-1} for −P−OH are clearly observed in the spectrum of the prepared microspheres. This result indicates that the phosphinic acid groups had been successfully introduced into the shell layer of the PSt microspheres by the RAFT process in emulsion polymerization.[32,33]



(a)

Element	wt%
C	71.83
O	25.62
P	2.55

(b)

Element	wt%
C	64.77
O	24.79
P	6.61
S	0.46
Cu	3.18

(c)

Element	wt%
C	67.14
O	21.20
Fe	8.05
P	3.60

Figure 5. EDX spectra of (a) PSt microspheres, (b) PSt microsphere−Cu^{2+} complex, and (c) PSt microsphere−Fe^{3+} complex.

The resins containing variously substituted phenylphosphinic acid group have been used in ion-exchange/coordination of Cu(II), Cd(II), Ni(II), Zn(II), and Eu(III) from nitric acid solutions, and the resins with carboxyl groups in α and β positions display higher divalent metal uptake.[6] In this study, we expect that the phenylphosphinic acid groups may endow the PSt microspheres with good ionic coordination property.[4,6] In order to investigate the coordination property of the functionalized PSt microspheres, the coordination experiments were implemented with metal ions. The microspheres were first dispersed in dilute ionic aqueous solutions, i.e., 0.2% $CuCl_2$ aqueous solution and 0.2% $FeCl_3$ aqueous solution under ultrasonic irradiation. When the coordination equilibrium was reached after stirring for 48 h, the microspheres were collected by centrifugation and dialyzed with distilled water for 48 h to remove free metal ions.

The resultants were characterized by EDX analyses. In comparison with the functionalized PSt microspheres (Figure 5a), Cu and Fe elements can be clearly observed in parts b and c of Figure 5, respectively, suggesting that phenylphosphinic acid of P(AOPA) is successfully coordinated with Fe^{3+} and Cu^{2+}. According to the data of EDX spectra, the mole ratio of P/Cu and P/Fe was calculated to be 4.25 and 0.80, respectively. On the other hand, because the coordination number is 4 for Cu^{2+} and 6 for Fe^{3+}, the mole ratio of P/Cu and P/Fe should be 2 and 3, respectively, when all phosphinic acid groups were coordinated. In addition, no chlorine element can be observed in Figure 5b,c, which further demonstrates that the metal ions are coordinated with phenylphosphinic acid. Therefore, in this study, the complexations of metal ions are very high; especially for Fe^{3+}, the complexation even outreaches the full capacity, which may be attributed that some phenylphosphinic acid groups on the surfaces might be covered up to no signals in EDX spectra. The good ionic coordination property may be ascribed to the phosphoryl oxygen's greater affinity for Fe^{3+} than for H^+.[5]

Conclusion

The phenylphosphinic acid-functionalized PSt microspheres were successfully prepared by "one-pot" emulsion polymerization of St/DVB in the presence of a novel amphiphilic functional emulsifier, $P(AOPA)_{24}$-*b*-PSt_{19}. The results demonstrated that the copolymer $P(AOPA)_{24}$-*b*-PSt_{19} can be used not only as a macromolecular emulsifier but also act as a macro-RAFT agent due to containing the thiocarbonylthio moiety. The functionalized microspheres possess a monodisperse diameter of about 300 nm with the core–shell structure. It should be pointed that the phosphinic acid-functionalized PSt microspheres show high ability to coordinate with Cu^{2+} or Fe^{3+}. Therefore, we expect that the functionalized microspheres as a potential metal scavenger will be very useful for the environmental protection. To our knowledge, this is the first report to prepare surface-functionalized microspheres by "one-pot" emulsion polymerization with the functional macro-RAFT agent as amphiphilic emulsifier.

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References and Notes

(1) Kawaguchi, H. *Prog. Polym. Sci.* **2000**, *25*, 1171–1210.
(2) Murugavel, R.; Choudhury, A.; Walawalkar, M. G.; Pothiraja, R.; Rao, C. N. R. *Chem. Rev.* **2008**, *108*, 3549–3655.
(3) Trochimczuk, A. W. *React. Funct. Polym.* **2001**, *48*, 141–148.
(4) Alexandratos, S. D.; Zhu, X. P. *Macromolecules* **2005**, *38*, 5981–5986.
(5) Alexandratos, S. D.; Crick, D. W.; Quillen, D. R. *Ind. Eng. Chem. Res.* **1991**, *30*, 772–778.
(6) Trochimczuk, A. W. *React. Funct. Polym.* **2000**, *44*, 9–19.
(7) Barner, L.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2007**, *28*, 539–559.
(8) Lime, F.; Irgum, K. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1259–1265.
(9) Nebhani, L.; Sinnwell, S.; Inglis, A. J.; Stenzel, M. H.; Barner-Kowollik, C.; Barner, L. *Macromol. Rapid Commun.* **2008**, *29*, 1431–1437.
(10) Zheng, G. D.; Stover, H. D. H. *Macromolecules* **2003**, *36*, 7439–7445.
(11) Li, P.; Xu, J. J.; Wu, C. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2103–2109.
(12) Li, P.; Liu, J. H.; Yiu, H. P.; Chan, K. K. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1863–1872.
(13) Bayramoglu, G.; Arica, M. Y. *React. Funct. Polym.* **2009**, *69*, 189–196.
(14) Zhou, J. H.; Wang, L.; Ma, J. Z. *Des. Monomers Polym.* **2009**, *12*, 19–41.
(15) Sarac, A.; Senkal, B. F.; Yavuz, E.; Gursel, Y. H. *Macromol. Symp.* **2006**, *239*, 43–50.
(16) Wu, Z. T.; Zhang, Z. C. *J. Appl. Polym. Sci.* **2007**, *105*, 3492–3499.
(17) Mohanty, P. S.; Dietsch, H.; Rubatat, L.; Stradner, A.; Matsumoto, K.; Matsuoka, H.; Schurtenberger, P. *Langmuir* **2009**, *25*, 1940–1948.
(18) Chausson, M.; Fluchere, A. S.; Landreau, E.; Aguni, Y.; Chevalier, Y.; Hamaide, T.; Abdul-Malak, N.; Bonnet, I. *Int. J. Pharm.* **2008**, *362*, 153–162.
(19) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988.
(20) Keoshkerian, B.; Georges, M. K.; Boilsboissier, D. *Macromolecules* **1995**, *28*, 6381–6382.
(21) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
(22) Ge, X. G.; Wang, D. Y.; Wang, C.; Qu, M. H.; Wang, J. S.; Zhao, C. S.; Jing, X. K.; Wang, Y. Z. *Eur. Polym. J.* **2007**, *43*, 2882–2890.
(23) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721–1723.
(24) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.
(25) Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. Int. Pat. Appl. PCT/US97/12540 WO9801478; *Chem. Abstr.* **1998**, *128*, 115390.
(26) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977–6980.
(27) Cunningham, M. F. *Prog. Polym. Sci.* **2008**, *33*, 365–398.
(28) Save, M.; Guillaneuf, Y.; Gilbert, R. G. *Aust. J. Chem.* **2006**, *59*, 693–711.
(29) Martins dos Santos, A.; Le Bris, T.; Graillat, C.; D'Agosto, F.; Lansalot, M. *Macromolecules* **2009**, *42*, 946–956.
(30) Martins dos Santos, A.; Pohn, J.; Lansalot, M.; D'Agosto, F. *Macromol. Rapid Commun.* **2007**, *28*, 1325–1332.
(31) Rieger, J.; Stoffelbach, F.; Bui, C.; Alaimo, D.; Jerome, C.; Charleux, B. *Macromolecules* **2008**, *41*, 4065–4068.
(32) Ganeva, D. E.; Sprong, E.; de Bruyn, H.; Warr, G. G.; Such, C. H.; Hawkett, B. S. *Macromolecules* **2007**, *40*, 6181–6189.
(33) Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Gilbert, R. G.; Serelis, A. K.; Such, C. H.; Hawkett, B. S. *Macromolecules* **2005**, *38*, 2191–2204.
(34) Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243–9245.
(35) Ji, J.; Yan, L.; Xie, D. *J. Polym. Sci., Part A: Polym. Chem* **2008**, *46*, 3098–3107.
(36) Wang, Y. Q.; Ge, Z. M.; Hou, X. L.; Cheng, T. M.; Li, R. T. *Synthesis* **2004**, 675–678.