Polymer 50 (2009) 5701–5707

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of phenylphosphinic acid-containing amphiphilic homopolymers by reversible addition-fragmentation transfer (RAFT) polymerization and its aggregation in water

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ARTICLE INFO

Article history:
Received 8 May 2009
Received in revised form
26 August 2009
Accepted 2 September 2009
Available online 6 October 2009

Keywords:
Phosphorus-containing polymer
Amphiphilic homopolymer
RAFT polymerization

ABSTRACT

A novel amphiphilic phosphorus-containing polymer was prepared by RAFT polymerization of 3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl) phosphinic acid (AOPA). The monomer was first synthesized by esterification of 3-[hydroxy(phenyl)phosphoryl]propanoic acid and 2-hydroxyethyl acrylate, and then the polymerizations were performed at 60 °C. The polymerization was well controlled, and the polymers with "well-defined" structures were successfully synthesized. The polymers can self-assemble to form the micelles in distilled water due to the special amphiphilic structure, and the shell of the micelles could be cross-linked by the coordination of phosphinic acid with cations. The property may promote the polymers to be used in the ionic exchange for the environment protection.

1. Introduction

Synthesis of polymers with functional groups is among the most significant accomplishments in polymer chemistry. The properties of polymers can be widely changed by choosing a variety of functional monomers, and the selection of polymers with particular kinds of functional groups depends on their intended applications. Recently there has been great interest in preparation of phosphorus-containing polymers, since such materials can be used as ion exchangers [1–5], adhesion to metals [6], bone and dentin [7], and flame retardants [8–10]. Using step polycondensation technique, Asrar et al. [9] synthesized the fire-retardant poly(ethylene terephthalate) by the copolymerization of ethylene glycol, terephthalic acid and 2-carboxyethyl(phenylphosphinic) acid, and Pretula and co-workers [11,12] reported the direct synthesis of poly (ethylene phosphate) based on reaction of ethylene glycol with phosphoric acid, and the kinetics and mechanism were investigated. By radical polymerization method, poly(vinylphosphonic acid) oligomers were prepared in the presence of a series of chain transfer agents, such as bromotrichloromethane, and perfluorohexyl iodide [13,14], and high-molecular weight polymers were obtained from the polymerization of vinylphosphonic acid initiated by 2,2′-azo(isobutyroic acid amidine)dihydrochloride at 80 °C [15]. In addition, some chemical modifications were used to synthesize phosphorus-containing polymers, for example, Trochimczuk prepared the functionalized phenylphosphinic acid resins by reacting St/DVB resin with PCl_3 in the presence of Friedel–Crafts catalyst [5].

At the same time, great progress has been made in controlled/living free radical polymerizations in the past few decades, such as living free radical nitroxide-mediated polymerization (NMP) [16–18], atom transfer radical polymerization (ATRP) [19–21] and reversible addition-fragmentation chain transfer (RAFT) [22,23] process. These techniques could potentially provide new ways to prepare phosphorous-containing polymers with controlled molecular weights and "well-defined" structures. However, to our knowledge, these techniques are seldom used to synthesize phosphorus-containing polymers until now. Recently Boutevin et al. [24] reported that phosphonated methacrylate was copolymerized with vinylidene chloride and methyl acrylate to prepare a phosphonated gradient terpolymer by RAFT polymerization, but the polymers need to be hydrolyzed or modified to give phosphinic acid.

In this paper, we report the synthesis of phenylphosphinic acid-containing amphiphilic homopolymers by RAFT polymerization of 3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl) phosphinic acid (AOPA), a novel phosphorus-containing monomer. Regarding amphiphilic homopolymers, Thayumanavan and co-workers [25] once reported that a styrene-based water-soluble polymer was explored for its use as a host for lipophilic substrates in aqueous medium; and Tang et al. [26] studied the self-assembling of an

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doi:10.1016/j.polymer.2009.09.074

amphiphilic polyacetylene carrying L-leucine pendants. However, to our knowledge, amphiphilic homopolymers have been less investigated until now while a wealth of efforts has been devoted to the research on amphiphilic block copolymers. In this study, the phenylphosphinic acid-containing amphiphilic homopolymers may self-assemble to micelles with good ionic coordination property in aqueous solutions. The properties of aggregation in water and coordination with cations were investigated. The resultants were characterized by ^{1}H and ^{13}P nuclear magnetic resonance (^{1}H and ^{13}P NMR) spectra, gel permeation chromatographer (GPC), Fourier transform infrared spectrometer (FT-IR), transmission electron microscopy (TEM), high performance particle sizer (HPPS), and energy-dispersive X-ray (EDX).

2. Experimental procedures

2.1. 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), 1,3-Dicyclohexylcarbodiimide (DCC, 99%) and 4-(*N*,*N*-dimethylamino) pyridine (DMAP, 99%) were purchased from Alfa Aesar China (Tianjin) Co., Ltd.. 2,2′-Azoisobutyronitrile (AIBN) was purified by recrystallization. *N*, *N*-Dimethylformamide (DMF) and dichloromethane (CH_2Cl_2) was dried by molecular sieves (4 Å). Benzyl 1H-imidazole-1-carbodithioate (BICDT) was synthesized according to the related reference [27]. All other chemical agents were used as received.

2.2. 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, $CDCl_3$): $\delta = 24.7$, 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): $\delta = 44.8$.

2.3. RAFT polymerization of AOPA

A typical procedure for RAFT polymerization of AOPA was as follows: a stock 10 mL solution comprising AOPA (4.8 g, 15.2 mmol), BICDT (56 mg, 0.24 mmol), AIBN (10 mg, 0.06 mmol) in DMF was prepared, and aliquots of 2.5 mL were placed in each ampoule. The contents were purged with argon for 10 min to eliminate the dissolved oxygen. The ampoules were then flame-sealed and placed in an oil bath thermostated at 60 °C. After a preset reaction time, each ampoule 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 diether ether 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.

The conversion (Conv. %) of polymerization was determined according to equation (1):

$$\text{Conv.\%} = (W_P - W_B)/W_M \times 100\% \tag{1}$$

where, W_P, W_B and W_M stand for the weights of the crude product, BICDT and monomer, respectively.

The same procedure was used for the extension reaction of AOPA, except that P(AOPA) instead of BICDT was used as macro-RAFT agent.

2.4. Aggregation of the polymers in water

Concerning that the coordination of phenylphosphinic acid with cations can occur with the self-assembly in water due to the amphiphilic structure, the experiments were performed as below: A solution of P(AOPA) (10 mg) in methanol (10 mL) was dialyzed with distilled water, 0.2% $FeCl_3$ aqueous solution (pH ~7.0), and 0.2% $CuCl_2$ aqueous solution (pH ~7.0) for 48 h, respectively. Regarding the coordination with Fe^{3+} and Cu^{2+}, after stirring for 48 h, the aggregations were further dialyzed with distilled water for 48 h to remove free metal ion. The morphology and component of the aggregation were characterized by TEM, HPPS, FT-IR and EDX.

2.5. Characterization

Fourier transform infrared spectrometer (FT-IR) spectra were recorded on a Varian-1000 at room temperature, and the solutions of polymers were dropped on KBr tablet. Transmission electron microscopy (TEM) images were taken with a FEI Tecnai G20 electron microscope, using an accelerating voltage of 160 kV, and the samples were prepared by placing a drop of polymer dispersion onto a carbon-coated Cu grid. 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, ^{13}C and ^{13}P NMR nuclear magnetic resonance (^{1}H, ^{13}C and ^{13}P NMR) spectra were obtained on a Varian INVOA-400 instrument. The molecular weights and polydispersities of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with differential refractometer with temperature control, using 500,10^3,10^4 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 operated. The *Z*-average size and the polydispersity index of the micelles were measured by Malvern HPP 5001 high performance particle sizer (HPPS).

3. Results and discussion

In this study, the novel phosphorus-containing monomer, AOPA was synthesized by esterification of 3-[hydroxy(phenyl)phosphoryl] propanoic acid and 2-hydroxyethyl acrylate in the presence of DCC and DMAP. The monomer was characterized by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra (Fig. 1). It is clearly seen that the characteristic peaks were well assigned to the protons of the monomer in ^{1}H NMR spectrum (Fig. 1a) and to the carbons of the monomer in ^{13}C NMR spectrum (Fig. 1b), while a peak was clearly observed at $\delta = 44.8$ ppm for phenylphosphinic acid [28] in ^{31}P NMR spectrum (Fig. 1c) that was calibrated by $(CH_3)_3PO$ ($\delta = 36.2$ ppm). The results indicated the successful synthesis of the monomer.

The polymerizations were carried out at 60 °C in the presence of BICDT, which is a good RAFT agent for methyl acrylate derivatives [23]. The polymerization results are listed in Table 1. As can be seen from Table 1, the polymers formed with controlled molecular weights and narrow polydispersities. It was also noted that the molecular weights from GPC are much higher than the theory value, which may be ascribed to the marked difference of the structures between P(AOPA) and PSt standard samples. Fig. 2 depicts Conversion and $\ln([M]_0/[M])$ as a function of time for the polymerization of AOPA. It is obvious that a linear relationship existed between $\ln([M]_0/[M])$ and polymerization time, which indicates that the polymerization is a first order reaction with respect to monomer

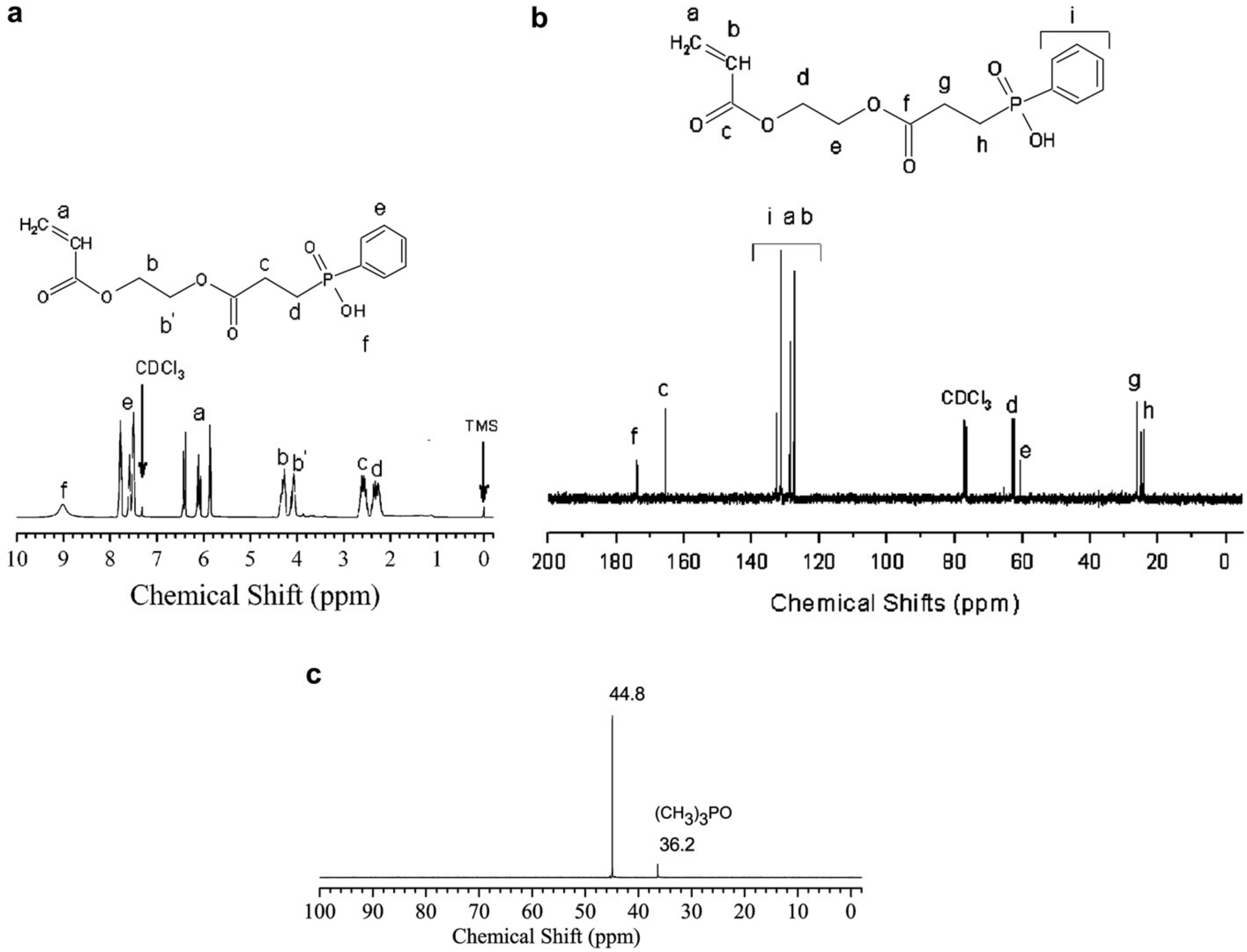

Fig. 1. (a) ^{1}H NMR (400 MHz, $CDCl_3$), (b) ^{13}C NMR (100 MHz, $CDCl_3$) and (c) ^{31}P NMR (162 MHz, $CDCl_3$) spectra of the monomer AOPA.

concentration and that the number of radicals remains constant during the polymerization. It should be explained that the polymerization was stopped at the conversion of 73% because the polymeric chain radicals may be terminated at the higher conversion [29]. Fig. 3 shows the evolution of the molecular weight and molecular weight distribution with monomer conversion for the polymerization. It can be clearly seen that the molecular weight of the polymer obtained increases linearly with conversion, and the molecular weight distributions remains narrow ($M_w/M_n < 1.20$) with monomer conversion increasing.

Typical GPC curves for different reaction times are depicted in Fig. 4. It is further demonstrated that the molecular weight distributions remains narrow with the growth of molecular weight

Table 1
The results of AOPA polymerized at 60 °C in the presence of BICDT ($[AOPA]_0$: $[BICDT]_0$: $[AIBN]_0 = 250:4:1$, $[AOPA]_0 = 1.54$ mol/L in DMF).

Entry	Time (h)	Conv.[a]	$M_{n(th)}$[b]	$M_{n(NMR)}$[c]	$M_{n(GPC)}$[d]	PDI[d]
1	5	0.35	7200	7700	20,200	1.09
2	17	0.40	8200	7800	25,100	1.06
3	38	0.56	11,400	10,300	37,600	1.15
4	50	0.61	12,400	11,800	47,400	1.14
5	72	0.73	14,800	/	51,200	1.19

[a] Determined gravimetrically, calculated according to Equation (1).

[b] Calculated by Equation: $M_{n(th)} = Conv. \times W_M/M_B + M_{m,\,B}$, where, W_M and M_B are the weight of monomer in the feed and the moles of BICDT added, respectively, and $M_{m,\,B}$ is the molar mass of BICDT.

[c] Calculated according to Equation (2).

[d] Determined by gel permeation chromatography (GPC).

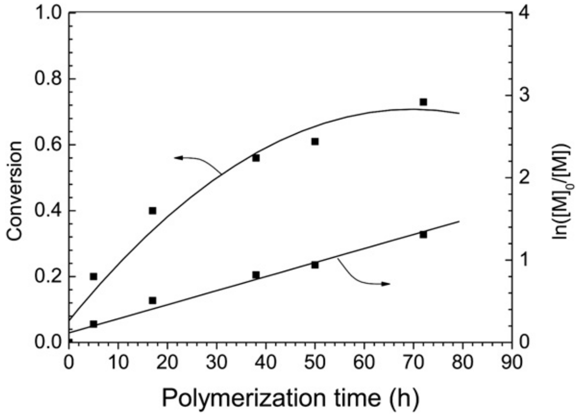

Fig. 2. Conversion and $\ln([M]_0/[M])$ as a function of time for the polymerization of AOPA.

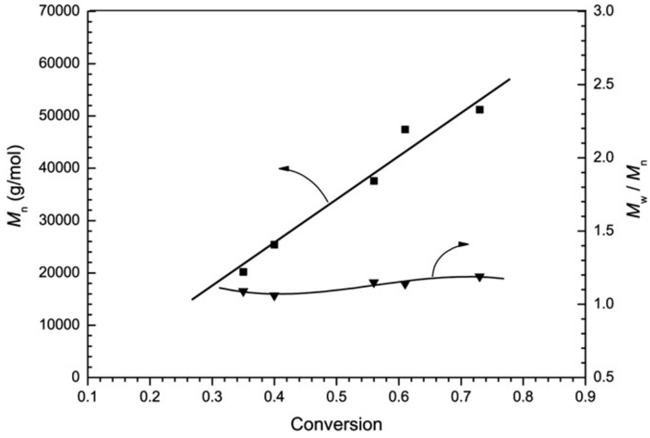

Fig. 3. Molecular weight and molecular weight distribution as a function of monomer conversion for the polymerization of AOPA.

(Fig. 4a–c). According to RAFT process, P(AOPA) with a thiocarbonylthio group can be used as a macro-RAFT agent for chain extension. The chain-extension reaction of P(AOPA) (Fig. 4a) with AOPA was carried out in DMF at 60 °C. Finally, extended P(AOPA) (Fig. 4d) was obtained at the fresh AOPA conversion of 12%. It could be observed that the peak of macro-RAFT agent (Fig. 4a) shifted higher molecular weight (Fig. 4d), and the symmetric peak was obtained, indicating all macro-RAFT agent participated in the extension of AOPA. All the evidence demonstrated that the polymerization was well controlled by RAFT agent.

The polymer structures were characterized by ^{1}H NMR and a typical ^{1}H NMR spectrum of P(AOPA) as example was shown in Fig. 5. The peaks at $\delta = 3.0$–4.5 ppm is assigned to the methylene protons of AOPA units, which does not interfere with the peaks at 2.0–2.5 ppm corresponding to –CH– of the polymer backbone [30]. In addition, the signals at $\delta = 7.8$–8.6 ppm show that the existence of imidazolyl group of BICDT in the polymer chain. Provided that each macromolecule contains one imidazolyl residue, number average molecular weight, $M_{n(NMR)}$, can be calculated according to Equation :

$$M_{n(NMR)} = \frac{312\, I_{4.0}}{4\, I_{S-CH-}} + M_{BICDT} \qquad (2)$$

where, $I_{4.0}$ is the integral values of the peaks at $\delta = 3.0$–4.5 ppm, I_{S-CH-} is the integral value of the peaks at 4.6–4.9 ppm corresponding to the proton of S–CH– [31], 312 is the molar mass of AOPA. The calculated values of molecular weight are listed in Table 1. The close agreement within a reasonable error between M_n(NMR) and M_n(th) is an additional evidence for the 'living/controlled' polymerization.

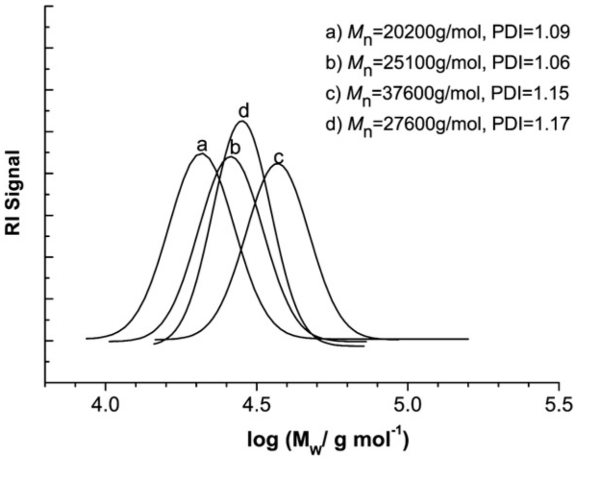

Fig. 4. GPC curves of P(AOPA) samples from the polymerizations (**a**–**c**, entries 1–3 in Table 1; and **d** for the extension of AOPA at the conversion of 12%).

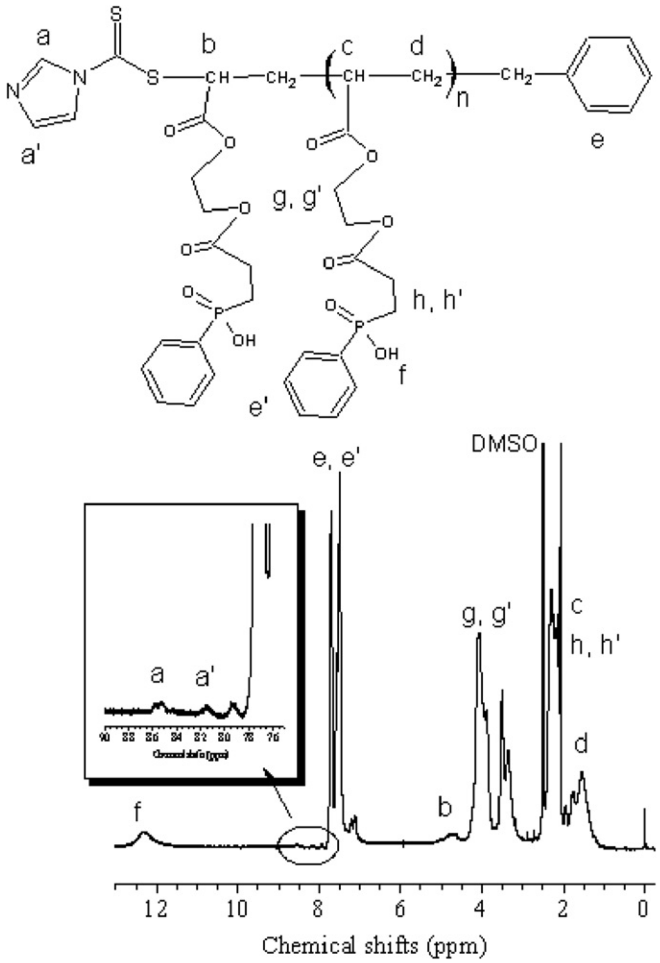

Fig. 5. ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$) of P(AOPA) (entry 2, Table 1).

It is interesting that the polymers may self-assemble to micelles in water due to the amphiphilic structure of P(AOPA). Concerning that phenylphosphinic acid can coordinate with cations while the polymers self-assembly in water, the polymer solutions were dialyzed with 0.2% $FeCl_3$ aqueous solution and 0.2% $CuCl_2$ aqueous solution respectively besides with distilled water. The morphologies of the polymers in water and cation aqueous solutions were investigated by TEM (Fig. 6). The polymers might form the micelles with the diameters of about 20 nm, and the core and outer shell could be clearly observed (inset, Fig. 6a), although the core looks apparently lighter than the shell in the overview image (overview, Fig. 6a) that may be due to the P elements riched shells of the micelles. When the polymers were dialyzed with $FeCl_3$ and $CuCl_2$ dilute aqueous solution, the shells became darker (Fig. 6b and 6c), which may be ascribed to the staining of metal ions coordination. In addition, the agglomerate of the particles was also observed in the TEM images (Fig. 6a–c) which are likely attributed to the strong hydrogen-bond interaction of the phenylphosphinic acid groups from different particles during TEM sampling.

The nanometer sizes and size distributions of the self-assembly of the polymers in H_2O medium were characterized by HPPS, and the results are represented in Fig. 7. All the samples had the symmetric distributions except for some few aggregates at the size of more than

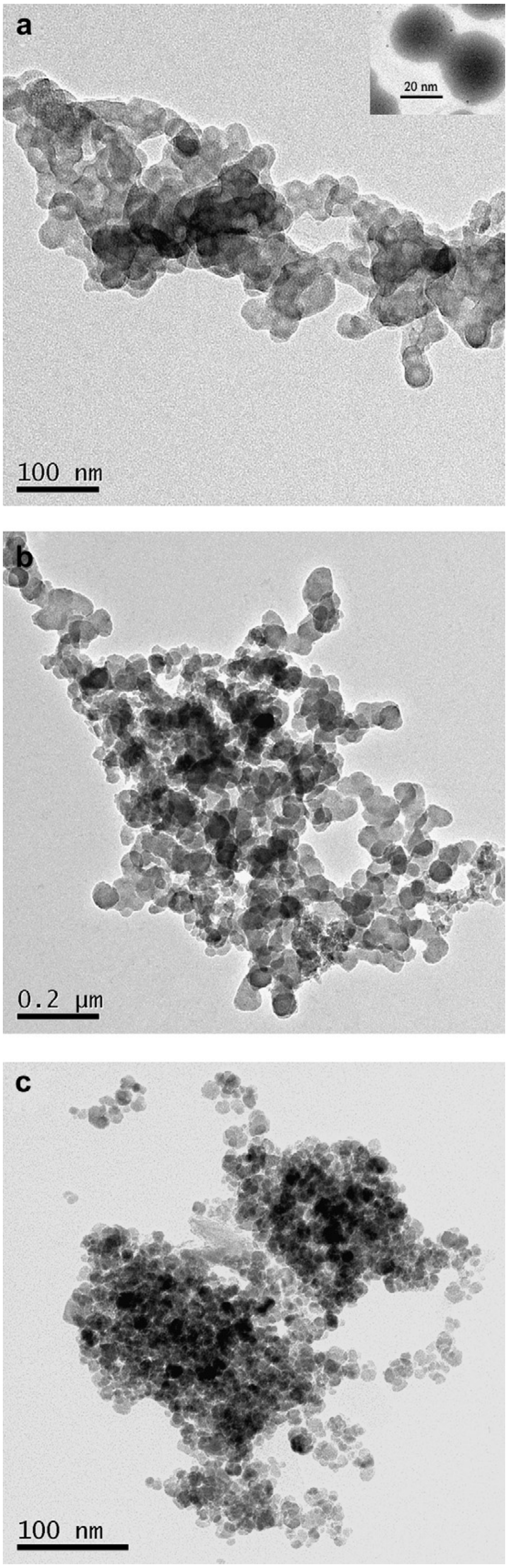

Fig. 6. TEM images of P(AOPA) (entry 2, Table 1) dialyzed by (a) distilled water, (b) 0.2% $FeCl_3$ aqueous solution, and (c) 0.2% $CuCl_2$ aqueous solution for 48 h.

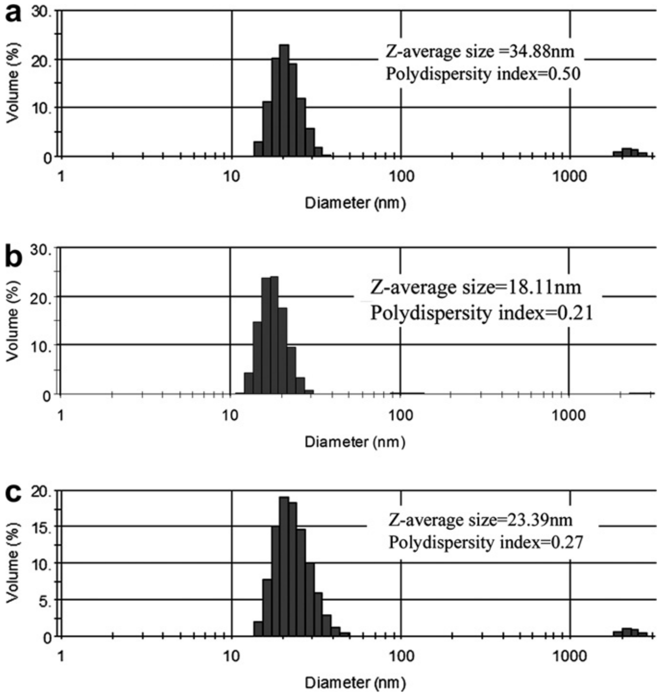

Fig. 7. Size distributions of P(AOPA) (entry 2, Table 1) in (a) distilled water, (b) 0.2% $FeCl_3$ aqueous solution, and (c) 0.2% $CuCl_2$ aqueous solution.

1000 nm, which may be attributed to the strong interaction of polymer chains due to phenylphosphinic acid. Compared with the samples dialyzed from distilled water (Fig. 7a), the polymers dialyzed with 0.2% $FeCl_3$ aqueous solutions has a smaller *Z*-average size and a narrower size distribution (Fig. 7b), the same results were obtained for the samples dialyzed from 0.2% $CuCl_2$ aqueous solution (Fig. 7c). These phenomena might be ascribed to the coordination of phenylphosphinic acid with metal ions [4,5], which may lead to tighten the micelles and form a cross-linked shell.

In order to clarify this point, the nanoparticles were collected by centrifugation at 10,000 rpm for 60 min, and were characterized by FT-IR and EDX Spectra. Fig. 8 shows FT-IR spectra of P(AOPA) samples dialyzed by distilled water, 0.2% $FeCl_3$ and 0.2% $CuCl_2$

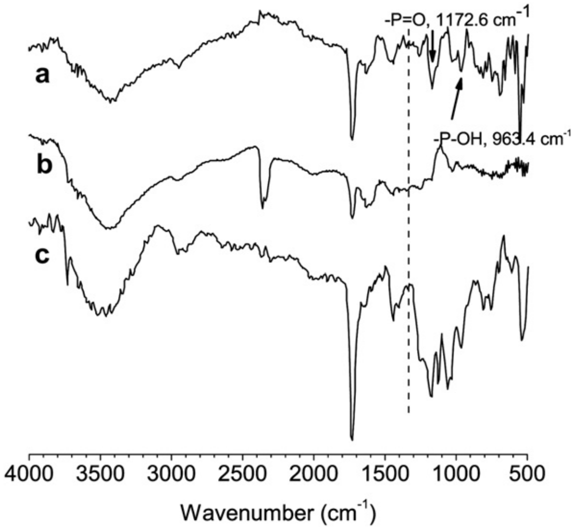

Fig. 8. IR spectra of (a) P(AOPA) (entry 2, Table 1), (b) P(AOPA)-Cu^{2+} and (c) P(AOPA)-Fe^{3+} complex.

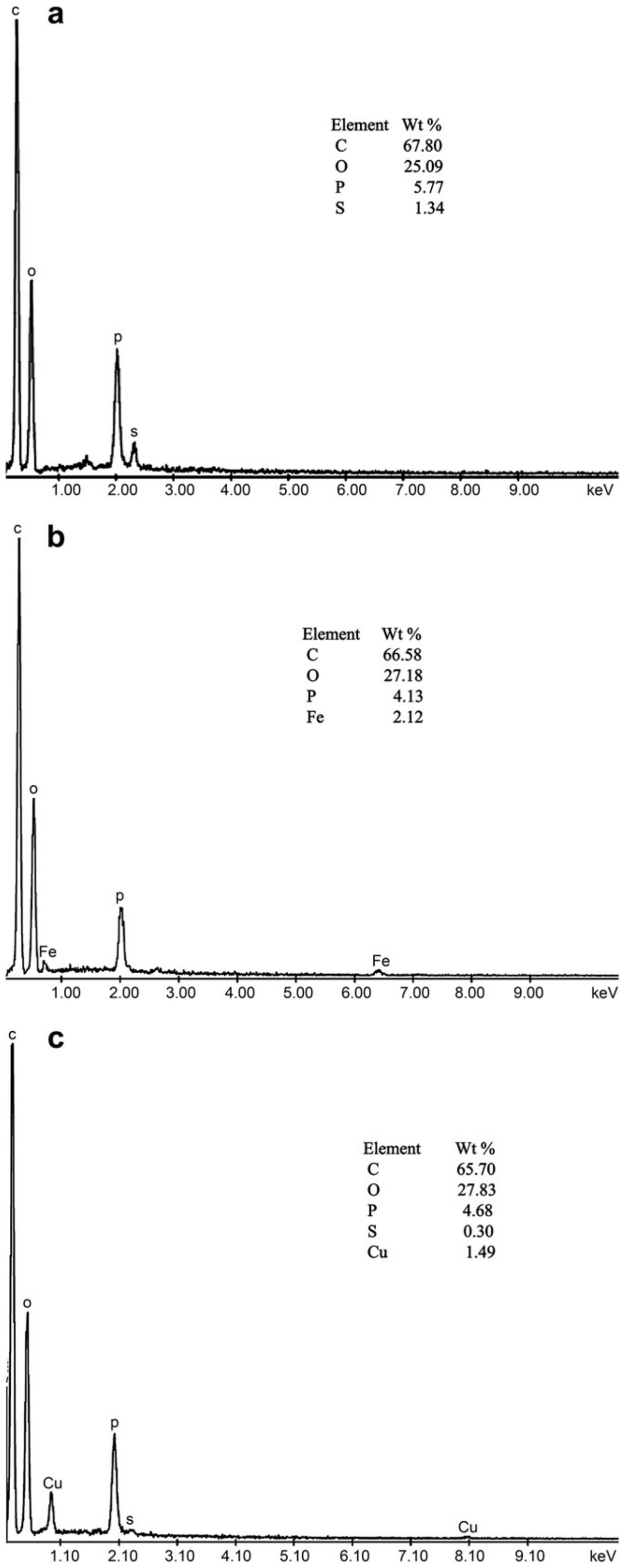

Fig. 9. EDX spectra of P(AOPA) (entry 2, Table 1) samples dialyzed with (a) distilled water, (b) 0.2% $FeCl_3$ aqueous solution, and (c) 0.2% $CuCl_2$ aqueous solution.

aqueous solution, respectively. It was noticed that the characteristic peaks at 1172.6 cm^{-1} for –P═O and at 963.4 cm^{-1} for –P–OH of P(AOPA) (Fig. 8a) were changed dramatically for the samples dialyzed by 0.2% $FeCl_3$ and 0.2% $CuCl_2$ aqueous solution (Fig. 8b and c), which should be attributed that phenylphosphinic acid coordinated with Cu^{2+} or Fe^{3+} cations.

EDX spectra were depicted in Fig. 9. In comparison to the polymer dialyzed with distilled water (Fig. 9a), Fe and Cu were clearly observed in Fig. 9b and c respectively, suggesting that phenylphosphinic acid of P(AOPA) was successfully coordinated with Fe^{3+} and Cu^{2+}. According to the data of EDX spectra, the mole ratio of P/Fe and P/Cu could be calculated as 3.5 and 6.4 respectively. On the other hand, because the coordination number is 6 for Fe^{3+} and 4 for Cu^{2+}, the mole ratio of P/Fe and P/Cu should be 3 and 2 respectively when all phosphinic acid groups have been coordinated. In comparison, in this study, the complexation of Fe is very high and almost reaches the full capacity. This is consistent with the results reported by Alexandratos et al. [4], which may be ascribed to the phosphoryl oxygen's greater affinity for Fe^{3+} than for H^+. It should be noted that the higher complexation (Fig. 9b and c), the smaller *Z*-average size (Fig. 7b and c). The results further demonstrated the micelles might coordinate with Cu^{2+} or Fe^{3+} to tighten the micelles and form the stable particles with the cross-linked shell.

4. Conclusion

A novel amphiphilic phosphorus-containing polymer, P(AOPA) was successfully prepared by RAFT polymerization of AOPA, which was first synthesized by esterification of 3-[hydroxy(phenyl) phosphoryl]propanoic acid and 2-hydroxyethyl acrylate in the presence of DCC and DMAP. The polymerizations were performed at 60 °C. The resultants were characterized by ^1H NMR, ^{13}C NMR, ^{13}P NMR, GPC, FT-IR, TEM, and EDX. The results showed that the polymerization was well controlled, and the polymers with controlled molecular weights and narrow polydispersities were successfully synthesized. The polymers can self-assemble to form the micelles with the diameters of about 20 nm in distilled water due to the special amphiphilic structure. Furthermore, the micelles might coordinate with Cu^{2+} or Fe^{3+} to form the stable particles with the cross-linked shell. The property may promote the polymers to be used in the ionic exchange for the environment protection.

Acknowledgments

We thank Natural Science Foundation of China (50903060), Natural Science Foundation of Jiangsu Province (BK2007547), Program of Innovative Research Team of Soochow University, Key Project in Science & Technology Innovation Cultivation Program of Soochow University, and Key Laboratory of Organic Chemistry of Jiangsu Province for their financial support.

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