Preparation and Characterization of Poly[acrylamide-*co*-3-(acryloylamino)propyldodecyldimethylammonium bromide]/Polyoxometalate Composite Microspheres

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ABSTRACT: Surfmer [3-(acryloylamino)propyl]dodecyldimethyl ammonium bromide (APDDAB) was synthesized and characterized. On the basis of the reverse emulsion polymerization technique, poly[acrylamide-*co*-3-(acryloylamino)propyldodecyldimethylammonium bromide] [P(AM-*co*-APDDAB)] copolymer microgels were obtained with the copolymerization of acrylamide and APDDAB. The P(AM-*co*-APDDAB)/polyoxotungstates composite microspheres were prepared with the ion-exchange reaction of the P(AM-*co*-APDDAB) microgels with phosphotungstic acid ($H_3PW_{12}O_{40}$). The morphologies and components of the composite microspheres were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, thermogravimetric analysis, and Fourier transform infrared spectroscopy. The results indicate that the P(AM-*co*-APDDAB)/$PW_{12}O_{40}$ composite microspheres all had a core–shell structure. For the composite microspheres, the hydrogel P(AM-*co*-APDDAB) was dominantly located in the core, and the complexes of $PW_{12}O_{40}^{3-}$ with APDDAB were mainly located in the surface; these features made the composite microspheres amphiphilic and provided for potential catalysis in a two-phase reaction. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 509–516, 2011

Key words: copolymers; metal–polymer complexes; microgels; polyamides; surfactants

INTRODUCTION

Microgels have recently attracted considerable attention from the scientific community because of their potential applications in various fields, such as in controlled drug-delivery systems,[1–5] enzyme[6] and cell[7] immobilization, and separation technology.[8] The applications of microgels in these fields are based on their diversified functions. For example, poly(*N*-isopropylacrylamide) microgels are used in drug delivery because they exhibit a lower critical solution temperature, around 33°C, and are biocompatible. Ionically responsive poly(acrylic acid) microgels and poly(methacrylic acid) are widely used in functional microvalves[9] and environmentally responsive sensors[10–12] because these hydrogels, with weakly acidic or weakly basic pendent groups, exhibit reversible changes in volume as the pH of the surrounding medium is altered.[13,14] More recently, our group developed a microgel template method to fabricate microspheric composite materials with core–shell structures. With poly(*N*-isopropylacrylamide-*co*-acrylic acid), poly(*N*-isopropylacrylamide-*co*-methacrylic acid), polyacrylamide (PAM), and poly(*N*-isopropylacrylamide) microgels as templates, several interesting polymeric composite microspheres with core–shell structures have been successfully synthesized.[15–18] On the basis of microgels with core–shell structures, these materials could be used as microreactors when the shell was composed of a layer of catalysts. For these kinds of materials, the core, composed of hydrogels, is similar to the core of a water-in-oil emulsion droplet in the storage of the water-soluble substance, and the amphiphilic shell is analogous to a phase-transfer catalyst layer located at the interface of a water-in-oil emulsion droplet. Therefore, this kind of material could potentially be used as a catalytic material in a liquid–liquid diphase reaction. Compared with the emulsion used in a diphase reaction, this kind of material is easily separated from the reactive system. Therefore, the construction of this kind of material is significant to overcome some disadvantages of traditional phase-transfer catalysts. To obtain composite

microspheres with a phase-transfer catalyst on the surface, the introduction of polymerizable surfactants on the surface of microgels may be considered because these reactive surfactants can copolymerize with the main monomer and become covalently bound to form an integral polymeric material.[19,20] Naturally, two factors are very important for the preparation of the desired composite microspheres. First, the reactivity of the surfactant should be well fitted to the reactivity of the other monomers engaged so that the desired copolymer can be obtained. Second, to use an inverse emulsion polymerization, polymerizable surfactants should have the polymerizable group located at the end of the hydrophilic group to copolymerize with other water-soluble monomers in the aqueous phase.

On the basis of the aforementioned considerations, we report herein a structural composite material, a microgel with a copolymer of acrylamide (AM) and [3-(acryloylamino)propyl]dodecyldimethyl ammonium bromide (APDDAB) as the core and complexes of APDDAB and polyoxotungstates as the shell. The copolymer microgels as the core were first synthesized by inverse emulsion polymerization, and then, the moieties of alkyl quaternary ammonium on the surface of the microgels reacted with phosphotungstic acid to form the complexes of APDDAB and polyoxotungstates by ionic exchange. The microgel core was suitable for storing the water-soluble H_2O_2, and the amphiphilic quaternary ammonium polyoxometalate in the shell was a potential catalyst to be used in H_2O_2-based catalytic oxidation in an organic medium. The remarkable features of the composite microspheres were that both the catalyst and aqueous phase could be simultaneously separated from the reactive system. Yamada and coworkers[21–23] prepared a series of hydrogel composite materials via poly({[3-(acrylolylamino) propyl]dodecyldimethylammonium nitrate}-co-(N-isopropylacrylamide)$_{12}$) crosslinked by polyoxotungstates. Additionally, these materials were efficient catalysts for the oxidation of alkenes, amines, and sulfides. However, these materials were bulk materials. To our knowledge, much less has been reported on microgel composite materials with amphiphilic quaternary ammonium polyoxometalate. In the light of the protocol mentioned previously, the results described herein are used as an example for constructing these kinds of materials.

EXPERIMENTAL

Materials

APDDAB was prepared according to procedures described in the literature.[15] The monomer AM was purified by recrystallization in acetone and dried *in vacuo*. The initiator ammonium persulfate, the crosslinker N,N′-methylenebisacrylamide, the promoter N,N,N′,N′-tetramethyl ethylenediamine, phos-

photungstic acid ($H_3PW_{12}O_{40}$), cyclohexane, and acetone were of analytical grade. All of these chemicals were used without further purification. The water used in the experiment was doubly distilled.

Preparation of the poly[acrylamide-co-3-(acryloyl-amino)propyldodecyldimethylammonium bromide] [P(AM-co-APDDAB)] microgels

A typical process for the preparation of P(AM-co-0.5% APDDAB) microgels is as follows. A-250 mL, three-necked boiling flask was equipped with a mechanical stirrer, a nitrogen inlet, and a Hirsch funnel. To the flask was added 100 mL of cyclohexane containing 0.52 g of Span-80 (Sorbitan monooleate). The mixture was stirred vigorously under a nitrogen atmosphere until the surfactant was uniformly dispersed. After that, 1.2 g of AM, APDDAB (0.5 wt %, APDDAB/APDDAB+AM), 0.06 g of N,N′-methylenebisacrylamide, and 1 mL of ammonium persulfate solution (216 mg/mL in the aqueous phase) were dissolved in 6 mL of double-distilled water. Then, the resulting mixture was added to the flask via the funnel, and the mixture was stirred continuously under a nitrogen atmosphere. The reaction was initiated by the addition of 1 mL of the promoter N,N,N′,N′-tetramethyl ethylenediamine solution (50 mg/mL). The reaction was conducted under stirring (800 rpm) at 20°C for 4 h. The P(AM-co-0.5% APDDAB) microgels were collected by filtration, washed alternatively with double-distilled water and acetone several times to remove the unreacted monomer and other impurities, and dried at room temperature. P(AM-co-1.0% APDDAB), P(AM-co-1.5% APDDAB), and P(AM-co-2.0% APDDAB) were obtained by similar processes.

Preparation of the P(AM-co-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres

The P(AM-co-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres were prepared with an ion-exchange reaction between $H_3PW_{12}O_{40}$ and APDDAB loaded on the P(AM-co-APDDAB) microspheres. The typical procedure was as follows. A given amount of P(AM-co-0.5% APDDAB) microgels was suspended in 10 mL of an $H_3PW_{12}O_{40}$ aqueous solution, and then, the suspension was placed at 20°C for a week. The P(AM-co-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres were obtained after the composite microspheres were successively washed with water and acetone several times. The same procedure was used to prepare P(AM-co-1.0% APDDAB)/PW$_{12}$O$_{40}$, P(AM-co-1.5% APDDAB)/PW$_{12}$O$_{40}$, and P(AM-co-2.0% APD-DAB)/PW$_{12}$O$_{40}$ composite microspheres. The amount of P(AM-co-APDDAB) microgels, the concentration of $H_3PW_{12}O_{40}$, and the names of the respective products are listed in Table I.

TABLE I
Conditions for the Preparation of the Composite Microspheres

	P(AM-*co*-0.5% APDDAB)/ PW$_{12}$O$_{40}$	P(AM-*co*-1.0% APDDAB)/ PW$_{12}$O$_{40}$	P(AM-*co*-1.5% APDDAB)/ PW$_{12}$O$_{40}$	P(AM-*co*-2.0% APDDAB)/ PW$_{12}$O$_{40}$
Amount of copolymer microgel (g)	0.20	0.20	0.20	0.20
Concentration of PW$_{12}$O$_{40}^{3-}$ in 10 mL of water (g)	0.0034	0.0069	0.0103	0.0138

Characterization

The morphologies of the P(AM-*co*-APDDAB) microgels and the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres were examined with a Philips scanning electron microscope (Philips-FEI, Holand) at an accelerating voltage of 20 kV, and the samples were coated with a thin layer of gold before measurement. The elements in the samples were probed by an energy-dispersive X-ray spectroscopy (EDX) attached to a Hitachi S-570 electron microscope (Hiyach Ltd, Kanda Neribeicho, Chiyoda-ku, Tokyo, Japan). The IR spectra were recorded on an AVTAR360 Nicolet (Thermo Fisher Scientific Inc, Madison, Wisconsin, USA) Fourier transform infrared (FTIR) spectrometer with KBr pellets. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA-7 (PerkinElmer, Inc., Woodland, California, USA) instrument. The composite powders were heated to 750°C in air at a scan rate of 20°C/min.

RESULTS AND DISCUSSION

Morphologies of the P(AM-*co*-APDDAB) microspheres

Scanning electron microscopy (SEM) images of the P(AM-*co*-APDDAB) microgels are shown in Figure 1. The results indicate that the surface of the P(AM-*co*-APDDAB) microgels in the dry state were smooth. The average diameter was about 50 μm, and their sizes were fairly uniform. Additionally, the internal structure of the microgel shown in Figure 1 (insert) indicates that the microgel had a core–shell structure. The freeze-dried P(AM-*co*-APDDAB) microgels shown in Figure 2 indicate that the microgels were spongelike structures with a diameter between 70 and 80 μm, and the pore size obviously decreased with amount of APDDAB in the copolymer microgels. The pore sizes for P(AM-*co*-0.5% APDDAB), P(AM-*co*-1.0% APDDAB), P(AM-*co*-1.5% APDDAB), and P(AM-*co*-2.0% APDDAB) were 1.6–3.0 μm, 1–2.5 μm, less than 2 μm, and less than 1.0 μm, respectively. The difference in the surface morphologies between the dried microgel and the freeze-dried sample was reported and explained.[13] In the water-swollen state, water in the bigger pores of hydrogels and the small pores composed of polymeric networks was instantaneously solidified, as the water-swollen microgels were treated by liquid nitrogen quenching. The solidified water in all pores of hydrogels was sublimated during freeze-drying. As a result, the freeze-dried microgels with spongelike structures could form. However, when the water-swollen microgels were treated with acetone to dehydrate, the hydrogen bonds between the water
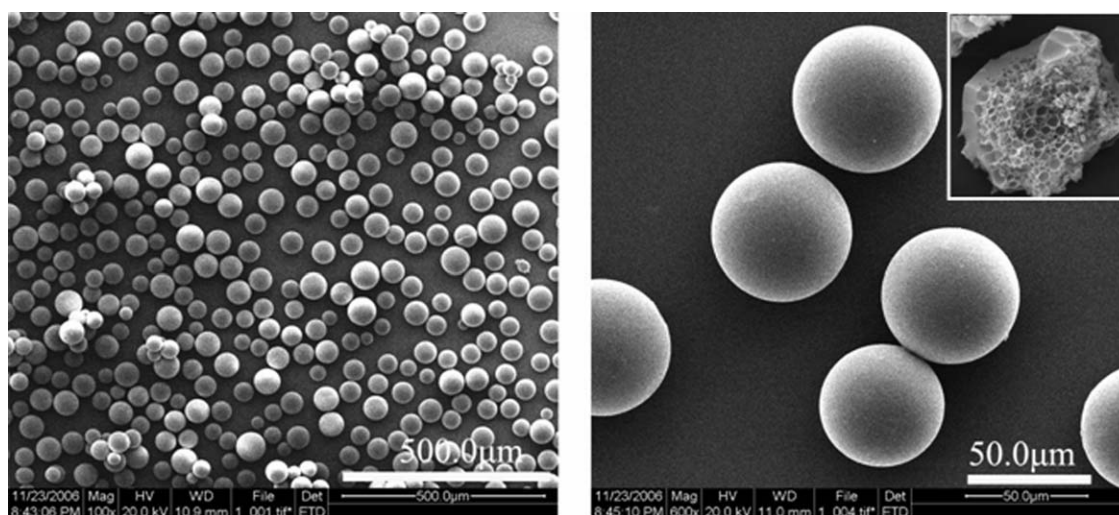

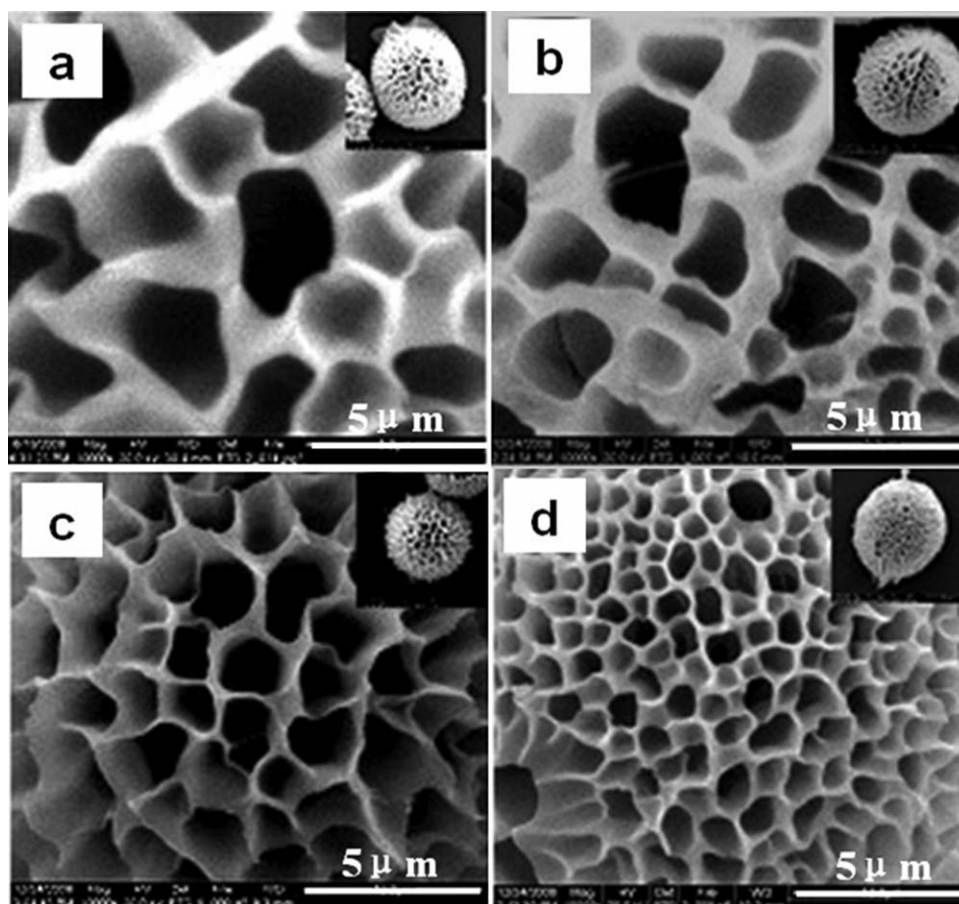**Figure 1** Typical SEM images of the P(AM-*co*-APDDAB) microgels.

Figure 2 SEM images of the freeze-dried P(AM-*co*-APDDAB) microgels. Amount of APDDAB: (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 wt %.

molecules and the polar groups of polymeric chains in the microgels weakened, and the hydrogen bonds among the polar groups of the polymeric chains could simultaneously form. As a result, all of the polymeric chains in the microgels simultaneously shrank, and the surface of the dried microgels became smooth (as shown in Fig. 1). From the previous explanation, the difference in the surface morphologies and the swelling degrees, ranging from 140 to 160% in Figures 1 and 2, could be understood.

As to the obvious decrease in the pore size with the amount of APDDAB in the P(AM-*co*-APDDAB) microgels, it was related to the presence of APDDAB in the microgels. Our previous study indicated that APDDAB was analogous to a typical surfactant because of the formation of aggregation in an aqueous solution.[17] In this experiment, P(AM-*co*-APD-DAB) microgels were formed in the reverse emulsion. It was reasonable that the APDDAB molecules as surfactants oriented themselves at the interface of oil and water. In this case, the polymerizable groups, acryloylamino groups, were located at the water phase, and dodecyl groups were inclined to the oil phase; this not only enhanced microphase separation

at the surface of the droplets but also increased the amount of copolymers of APDDAB and AM at the surface of the microgels. Consequently, the pores originating from the microphase separation became denser, and the more moieties of the hydrophobic dodecyl groups at the surface of the microgels led to a decrease in the water swelling degree of the microgels. In light of these explanations, the obvious decrease in the pore size with amount of APDDAB in the P(AM-*co*-APDDAB) microgels could be understood. Some evidence regarding the greater amount of copolymers of APDDAB and AM at the surface of the microgels is offered in the next section.

Morphologies of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres

Figure 3 shows typical SEM images of the P(AM-*co*-0.5% APDDAB)/PW$_{12}$O$_{40}$ composite microspheres and their enlarged surface structures. As shown in the enlarged pictures, the diameter of the composite microspheres was about 50 μm, and their surfaces were smooth. However, the corresponding freeze-dried composite microspheres shown in Figure 4
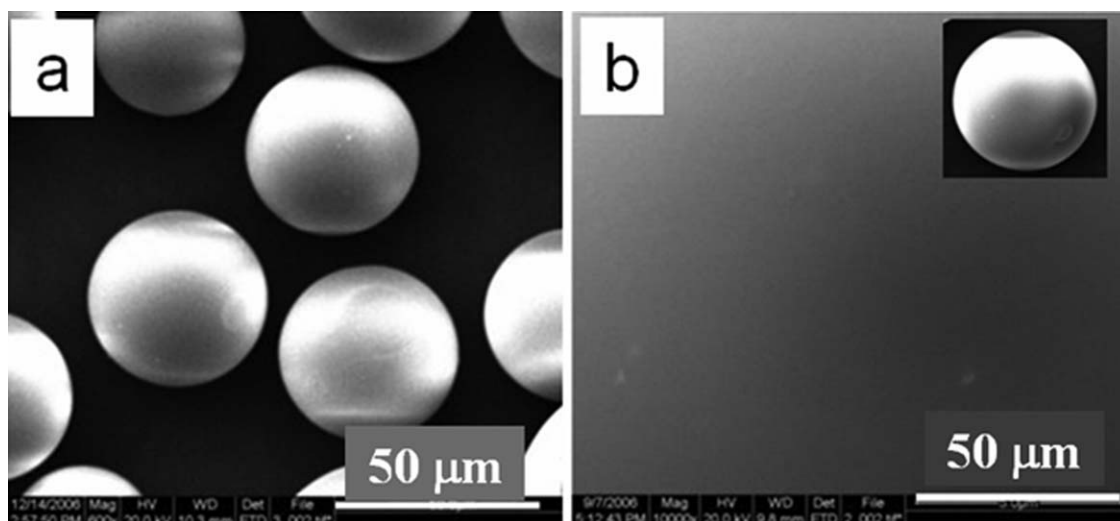
Figure 3 SEM images of the P(AM-*co*-0.5% APDDAB)/PW$_{12}$O$_{40}$ microspheres.

were spongelike structures, and their pore size decreased obviously with the amount of APDDAB in the microgels. Compared with the corresponding P(AM-*co*-APDDAB) shown in Figure 2, the pore sizes of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite

microspheres were smaller because the alkyl quaternary ammonium moieties in the copolymer of P(AM-*co*-APDDAB) crosslinked by PW$_{12}$O$_{40}^{3-}$ made the swelling degree of the composite microspheres decrease. Naturally, it was easy to understand that
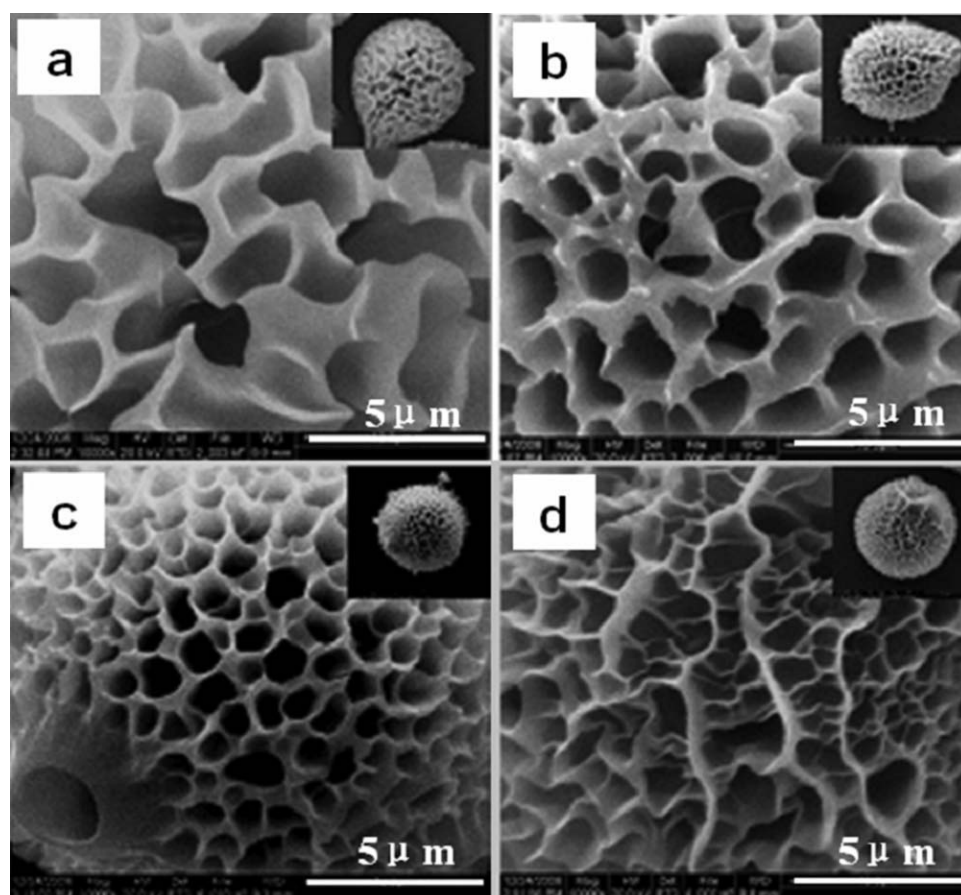

Figure 4 SEM images of the freeze-dried P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres. Amount of APDDAB: (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 wt %.
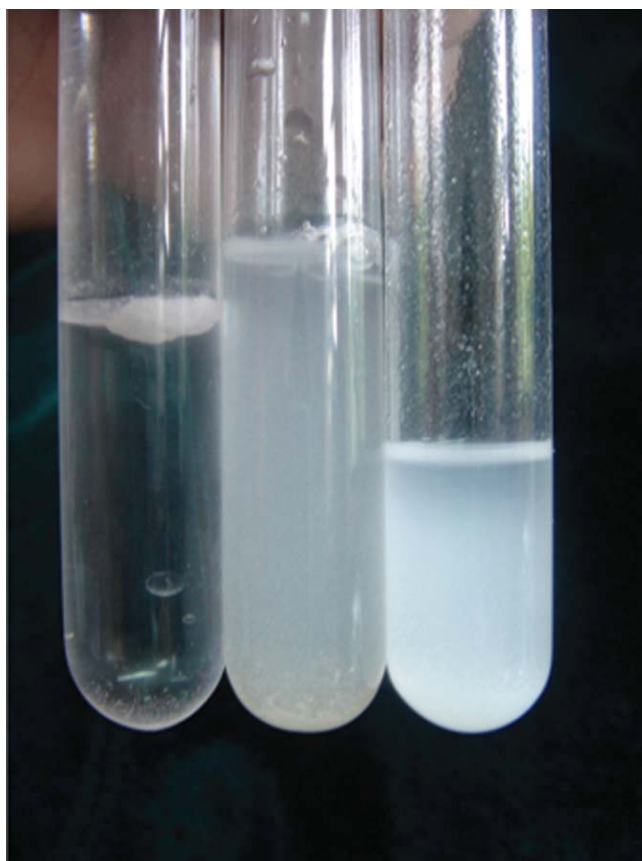
Figure 5 Photos of P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ added to water (middle), in cyclohexane (right), and PAM microspheres floated in cyclohexane (left). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the porous size decreased with increasing APDDAB in the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres. Notably, the diameter of P(AM-*co*-0.5% APD-DAB)/PW$_{12}$O$_{40}$ was similar to that of P(AM-*co*-0.5% APDDAB). Although there were crosslinkings of PW$_{12}$O$_{40}^{3-}$ in P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$, the crosslinkings only occurred at surface because of the crosslinked alkyl quaternary ammonium moieties located at the surface of P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$.

The previous observations denoted that the loading amount of PW$_{12}$O$_{40}^{3-}$ and the porous size of the composite microspheres could be controlled by the alteration of the amount of APDDAB in polymerization. Crosslinking between PW$_{12}$O$_{40}^{3-}$ with alkyl quaternary ammonium cations of grafted polymers has been reported.[21–23] The resultant product was essential for crosslinking the polymers through phosphotungstates and an amphiphilic, crosslinked, and supramolecular insoluble complex. The materials reported in the literature were bulk (nonstructured) materials; however, the material we prepared presented a core–shell structure. The amphiphilic microsphere material in structure was more similar to a

micelle. Therefore, the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microsphere was more suitable for use in phase-transfer catalysis. For a P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microsphere used in phase-transfer catalysis, one could expect that both the phase-transfer catalyst and aqueous phase (even product with polarity) could be simultaneously separated from a reaction system. So, the method for the preparation of this material offers an example for the construction of some materials to be used in phase-transfer catalysis.

The P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres were amphiphilic, which was verified by the observations shown in Figure 5. The composite microspheres could be stably suspended in both water and cyclohexane. PAM microspheres with hydrophilicity, however, floated in cyclohexane; this implied that APDDAB made the P(AM-*co*-APD-DAB)/PW$_{12}$O$_{40}$ microspheres amphiphilic, and the APDDAB alkyl chains on the surface of the composite microsphere could alter the orientation with a change in the polarity of the medium. This nature was favorable for the suspension of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres in an oil/water diphase. Both APDDAB and PW$_{12}$O$_{40}^{3-}$ mainly distributed to the surface of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres, which was proven by some experiments discussed in the next section.

Analysis of the components of the P(AM-*co*-APD-DAB)/PW$_{12}$O$_{40}$ composite microspheres

Techniques including FTIR, EDX, and TGA were used for the characterization of the P(AM-*co*-APD-DAB)/PW$_{12}$O$_{40}$ composite microspheres. The results obtained from these characterizations are as follows.

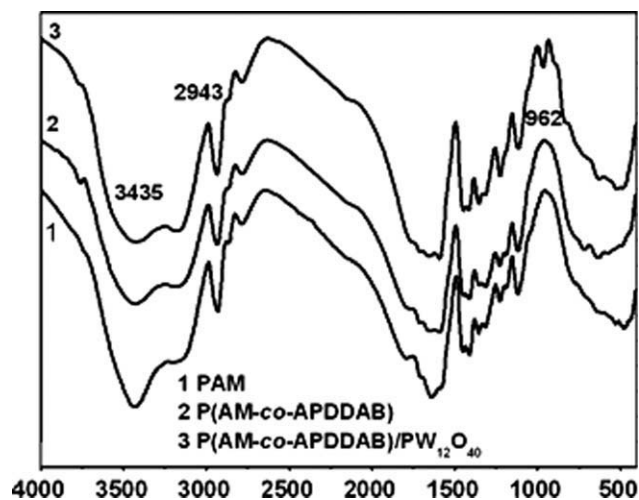Figure 6 shows the typical FTIR spectra of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres, PAM

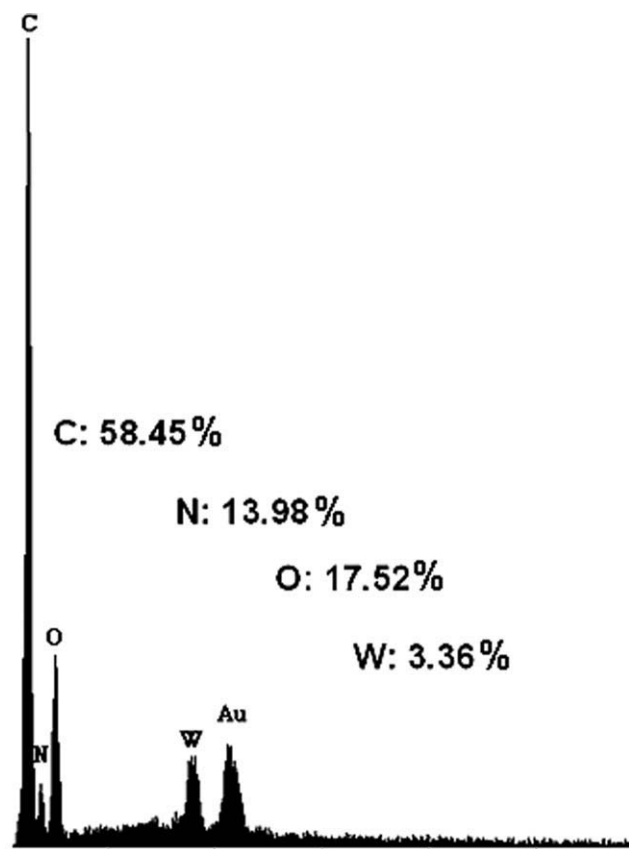**Figure 6** IR spectra of PAM, P(AM-*co*-APDDAB), and P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$.

Figure 7 EDX of P(AM-*co*-2.0% APDDAB)/PW$_{12}$O$_{40}$.

microgels, and P(AM-*co*-APDDAB) microspheres. The characteristic peaks were at 1658 cm^{-1} (C=O), 2943 cm^{-1} (CH$_2$), and 3500–3300 cm^{-1} (NH), which confirmed that PAM existed in the composite materials. The spectra were consistent with those in the literature.[13] Peaks at 3180 cm^{-1} (N—H in the secondary amide), 1580 cm^{-1} (N—H in the secondary amide), and 1780 cm^{-1} (C=O) appeared. These changes indicated that APDDAB existed in the composite microspheres.

The set of peaks at 1080, 990, 893, and 813 cm^{-1} were related to the asymmetric stretching of the P—O bond, the asymmetric stretching of the W—O bond, and the symmetric and asymmetric stretching of the W—O—W bridge, respectively. The peaks at 1080, 893, and 813 cm^{-1} were almost unchanged, but the peak at 990 cm^{-1} was redshifted to 962 cm^{-1} (W=O); this indicating that the chemical interaction of W=O in PW$_{12}$O$_{40}^{3-}$ with APDDAB occurred in the composite microspheres and the Keggin structure of PW$_{12}$O$_{40}^{3-}$ remained. These were in perfect agreement with the FTIR data reported by Prasad et al.[24]

To obtain information on the elements of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microsphere, EDX analysis was carried out. The typical result is shown in Figure 7. The obvious characteris-

tic peaks for C, N, O, and W elements, originating from the composite microspheres, were found; this indicated that PW$_{12}$O$_{40}^{3-}$ was incorporated in the P(AM-*co*-APDDAB). From the semiquantitative data by EDX, the PW$_{12}$O$_{40}^{3-}$ content on the surface of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microsphere with different amounts of APDDAB were calculated. Amounts of 1.9, 2.6, 3.3, and 5.2% of PW$_{12}$O$_{40}^{3-}$ were, respectively, present in P(AM-*co*-0.5% APDDAB)/PW$_{12}$O$_{40}$, P(AM-*co*-1.0% APDDAB)/PW$_{12}$O$_{40}$, P(AM-*co*-1.5% APDDAB)/PW$_{12}$O$_{40}$, and P(AM-*co*-2.0% APDDAB)/PW$_{12}$O$_{40}$. These data reflect the contents of the elements at the surface of the composite microspheres.

TGA is useful for determining the content of inorganic components in organic–inorganic composite materials. Herein, the results of the P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$ composite microspheres with different amounts of APDDAB are shown in Figure 8. The thermogravimetric curve of the composite microspheres was very similar to that of the synthesized PAM/APDDAB–PWA composite microspheres reported in literature.[15] The 10% weight losses before 200°C for the determined samples were attributed to the removal of physically absorbed water. From 200 to 560°C, the weight loss was ascribed to the decomposition of the organic components. The residue rates for the four samples were 3.5, 4.3, 5.8, and 9.8%, respectively. Generally, the residue composition of PW$_{12}$O$_{40}^{3-}$ after calcinations was a mixture of P$_2$O$_5$ and WO$_3$. According to this fact, amounts of PW$_{12}$O$_{40}^{3-}$ calculated from the residue rates for P(AM-*co*-0.5% APDDAB)/PW$_{12}$O$_{40}$, P(AM-*co*-1.0% APDDAB)/PW$_{12}$O$_{40}$, P(AM-*co*-1.5% APDDAB)/PW$_{12}$O$_{40}$, and P(AM-*co*-2.0% APDDAB)/PW$_{12}$O$_{40}$ were 2.3, 2.9, 3.5, and 5.3%, respectively. The corresponding data calculated from EDX, 1.9, 2.6, 3.3, and 5.2%, respectively, were close to the data mentioned
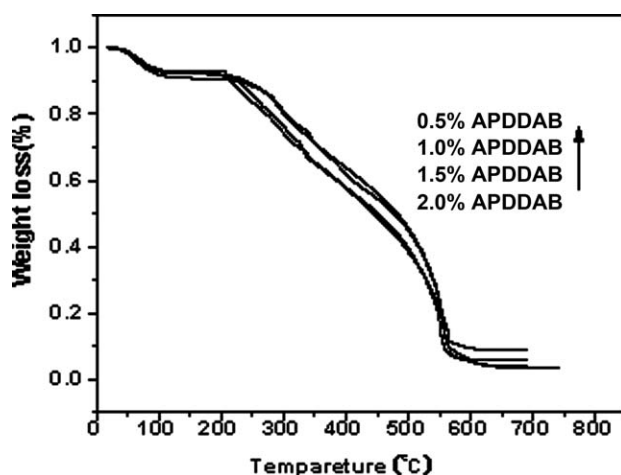

Figure 8 TGA of P(AM-*co*-APDDAB)/PW$_{12}$O$_{40}$.

previously; this indicated that $PW_{12}O_{40}^{3-}$ was mainly located at the surface of the composite microspheres. Interestingly, from these data, the distribution of components in the composite microspheres could be obtained. It has been reported that there is an interaction between $PW_{12}O_{40}^{3-}$ and PAM;[25,26] this implied that there was an interaction between $PW_{12}O_{40}^{3-}$ and segments of AM in the P(AM-*co*-APDDAB)/$PW_{12}O_{40}$ composite microspheres. However, the electrostatic interaction between APDDAB and $PW_{12}O_{40}^{3-}$ in the P(AM-*co*-APDDAB)/$PW_{12}O_{40}$ composite microspheres was dominant.[21–23] With regard to the aforementioned conclusion that $PW_{12}O_{40}^{3-}$ was mainly located at the surface of the composite microsphere, we speculated that APDDAB in the P(AM-*co*-APDDAB) microgels was mainly distributed at the surface. So, the composite microspheres had a core–shell structure and amphiphilic features, which are useful in phase-transfer catalysis.

CONCLUSIONS

We reported a method for preparing microgels (P(AM-*co*-APDDAB) with the copolymerization of AM and the polymerizable surfactant APDDAB in a reverse emulsion. Additionally, P(AM-*co*-APDDAB)/$PW_{12}O_{40}$ composite microspheres were prepared through the interaction between the alkyl quaternary ammonium groups in the microgels [P(AM-*co*-APDDAB)] and $PW_{12}O_{40}^{3-}$ in the $H_3PW_{12}O_{40}$ solution. The composite microspheres were amphiphilic, and the moieties with surface activity (alkyl quaternary ammonium) and the component with potential catalysis ($PW_{12}O_{40}^{3-}$) were mainly located on the surface of the composite microspheres. This structural feature was similar to that of the micelle phase-transfer catalyst. The protocol regarding the preparation of the composite microspheres reported here offers an example for constructing easily separated microspheres for potential use in diphase reactions.

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