



Preparation and characterization of magnetic composite microspheres using a free radical polymerization system consisting of DPE

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ABSTRACT

In this paper, a free radical polymerization system consisting of DPE was used to prepare magnetic composite microspheres. $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ core-shell magnetic composite microspheres have been synthesized by copolymerization of acrylic acid, methyl methacrylate and styrene using DPE as radical control agent in the presence of Fe_3O_4 nanoparticles. The structure and properties of the magnetic composite microspheres were analyzed by FTIR, ^1H NMR, SEC-MALLS, TEM, TGA, VSM and other instruments, and the formation mechanism of composite microspheres was supported by those results. It was found that the $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ microspheres were nano-size with relatively homogeneous particle size distribution, perfect sphere-shaped morphologies, superparamagnetism with a saturation magnetization of 18.430 emu/g, and high magnetic content with a value of 40%. ^1H NMR and TEM analysis indicated that at the first stage of polymerization, a DPE-containing copolymer of acrylic acid, methyl methacrylate formed and was then absorbed on the surface of Fe_3O_4 nanoparticles. Contact angle analysis indicated that the DPE-containing copolymer improved hydrophobicity of Fe_3O_4 nanoparticles through chemical absorption. In the second step polymerization, certain amount of monomers of styrene and residue methacrylate were initiated by the DPE-containing copolymer on the Fe_3O_4 nanoparticles' surface and resulted in the formation of $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ composite microspheres.

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1. Introduction

In recent years, magnetic composite microspheres consisting of a magnetic core and a polymer shell have received much attention because of their wide range of potential applications in the fields such as magnetic bioseparation, enzyme immobilization, cell isolation, nucleic acid (RNA and DNA) and protein purification, and immunoassay [1–6]. In most applications, the magnetic composite microspheres are required to possess non-toxicity, good stability, high concentration of magnetite and functional groups, and controlled morphology. Therefore, it is of crucial significance to establish a method to prepare magnetic composite microspheres not only satisfying the above-mentioned requirements but also having wide applicability.

Several methods have been developed to prepare magnetic composite microspheres, such as physical encapsulation of magnetite with polymer, emulsion or suspension polymerization in the presence of magnetic nanoparticles, and the so-called surface-initiated polymerization [7–12]. The surface-initiated polymerization strategy

is a promising candidate to achieve both high stability of polymer shell and high graft density, but it usually results in a poor control of polymer shell structures. Subsequently, two kinds of controlled radical polymerization techniques including nitroxide mediated polymerization and atom transfer radical polymerization, were successfully used in surface-initiated polymerization to prepare magnetic composite microspheres with controlled structures. For example, Chen et al. [13] reported the synthesis of polystyrene-grafted magnetite composite microspheres by nitroxide mediated polymerization method. The results showed that polystyrene with narrow molecular weight distribution was successfully grafted onto the magnetite particles. Using surface-initiated atom transfer radical polymerization, Sun et al. [12] prepared an iron oxide/polystyrene core/shell nanoparticle and Marutani et al. [14] synthesized a PMMA-coated magnetic nanoparticle. All the hybrid nanoparticles possessed well-defined, chemical bonding polymer shells. However, both the above-cited techniques have some drawbacks such as in the case of nitroxide mediated polymerization the utilization of high temperature, and the difficulties to remove the heavy metal catalyst in atom transfer radical polymerization at the end of the polymerization. Recently, it was found that the use of 1,1-diphenylethylene (DPE) in conventional free radical polymerization allows a high degree of polymer structural control [15–18]. This new method (DPE method) is

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a two-step procedure requiring in the first step the preparation of a precursor polymer in the presence of DPE. This precursor polymer is then used as active species in a second polymerization, where block copolymer formation takes place. The two steps can be carried out either sequentially and spatially separated or conducted like a one pot synthesis with consecutive addition of monomers. The DPE method possesses several advantages such as relatively low polymerization temperature (80 °C), no sensitivity to impurities in the reaction medium, and wide applicability to many monomers.

On the basis of the above information, in this work, DPE method was extended to prepare magnetic composite microspheres. Firstly, an amphiphilic precursor polymer was designed and synthesized by copolymerization of methyl methacrylate and acrylic acid in the presence of DPE. This DPE-containing amphiphilic precursor could be absorbed on the surface of magnetic nanoparticles and stabilize magnetic nanoparticles in the oil monomer. When the third monomer styrene was added to the system, the activated precursor polymer initiated styrene and residual methacrylate to polymerize on the surface of the magnetic particles, and then formed magnetic composite microspheres. The results of the current research are stated as following.

2. Experimental

2.1. Materials

Acrylic acid (AA), methyl methacrylate (MMA) and styrene (St) were distilled under reduced pressure before use. Potassium persulfate (KPS), sodium hydroxide (NaOH), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), hydrofluoric acid (HF), toluene, tetrahydrofuran (THF) and cyclohexane were all used as received. The above-mentioned materials were of analytical grade, and purchased from Tianjin kermel chem. Reagent Company. 1,1-diphenylethylene (DPE, 98%, Alfa) was used without further purification. All the reaction medium was deionized water.

2.2. Preparation of magnetic nanoparticle (Fe_3O_4)

Magnetic nanoparticles were prepared via co-precipitation of Fe^{3+} and Fe^{2+} ions in the presence of NaOH. Specifically, 11.2 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 16.3 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 200 ml of deionized water in a flask. This solution was stirred, followed by adding 3 M NaOH solution quickly at 30 °C until the mixture reached a pH around 11. After 30 min, the mixture was heated to 80 °C for 30 min. The Fe_3O_4 nanoparticles were isolated from the solution by magnetic separation and washed with deionized water until pH 7 was reached. Finally, the magnetic nanoparticles were sealed and stored at room temperature.

2.3. Preparation of magnetic composite microspheres $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$

The polymerization was carried out in a three-necked flask equipped with a stirrer, a condenser and a thermometer. Firstly, 0.05 g of DPE, 0.15 g of AA, 3 g of MMA and 30 g of water were added into reactor and stirred. When the mixture was heated to 80 °C, 10 g of KPS solution (1% w/w in water) was introduced to initiate the polymerization. After a period of time, 25.2 g of sonicated magnetic fluid (0.2 g magnetic nanoparticles in 25 g of water) was dropped into the stirred mixture and the system was allowed to polymerize for 4 h. Then polymerization was ended by cooling the mixture to room temperature, and the magnetic nanoparticles coated with precursor polymer of P(AA-MMA) formed in the

system. Subsequently, the mixture was heated to 80 °C again and 3 g of styrene was added to continue polymerization on the surface of magnetic nanoparticles. After 4 h, the mixture was cooled to room temperature and the polymerization stopped. The magnetic composite microspheres were collected by magnetic separation and then washed with acetone, cyclohexane and deionized water several times. Finally, the separated product was dried in a vacuum oven at 40 °C for 24 h.

The polymer shell P(AA-MMA-St) was cleaved from the magnetic composite microspheres according to the following procedure: 0.1 g of $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ was vigorously stirred in a flask containing 3.5 ml of toluene, 3.5 ml of 5 wt% aqueous HF solution. After 2 h, the aqueous layer was removed, and then 3.5 ml of 5% aqueous HF solution was added and stirred for another 2 h. This process was repeated five times. Then organic layer containing cleaved polymer was washed with aqueous NaHCO_3 solution and water, filtered to remove solid impurities, and dried under vacuum. At last polymer shell was obtained.

2.4. Characterization of magnetic particles

Fourier transform infrared (FTIR) spectroscopy was acquired on a TENSOR27 FTIR spectrometer (Bruker). The samples were prepared by mixing composite microspheres with KBr and pressing into a compact pellet.

^1H NMR and ^{13}C NMR spectra were recorded by INOVA-400 spectrometer (Varian), $\text{DMSO}-d_6$ and CDCl_3 as solvents, and tetramethylsilane (TMS) as internal standard.

Polymer molecular weight was determined by size-exclusion chromatography with multi-angle laser light-scattering detection (SEC-MALLS). SEC was performed using a HPLC pump (Waters 515) and a column (300 mm \times 0.8 mm, MZ-Gel SDplus 500 Å 5 μm). Column effluent was monitored sequentially with a mini-Dawn light-scattering detector (Wyatt technology, Santa, Barbara, CA, USA) and an Optilab rEX differential refractometer (Wyatt Technology). Two 25 mm high-pressure filter with 0.22 and 0.1 μm pore (Millipore) were used for on-line filtration of the mobile phase. The mobile phase was THF with a flow rate of 0.5 ml/min.

UV-vis spectrometer analysis was performed on a UV-2550 (Shimadzu) to record the absorption of the DPE-containing precursor polymer P(AA-MMA) in THF solution.

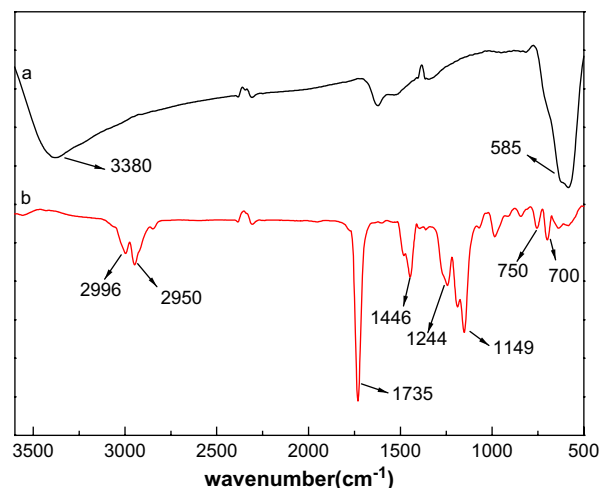


Fig. 1. Infrared spectra of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ (b).

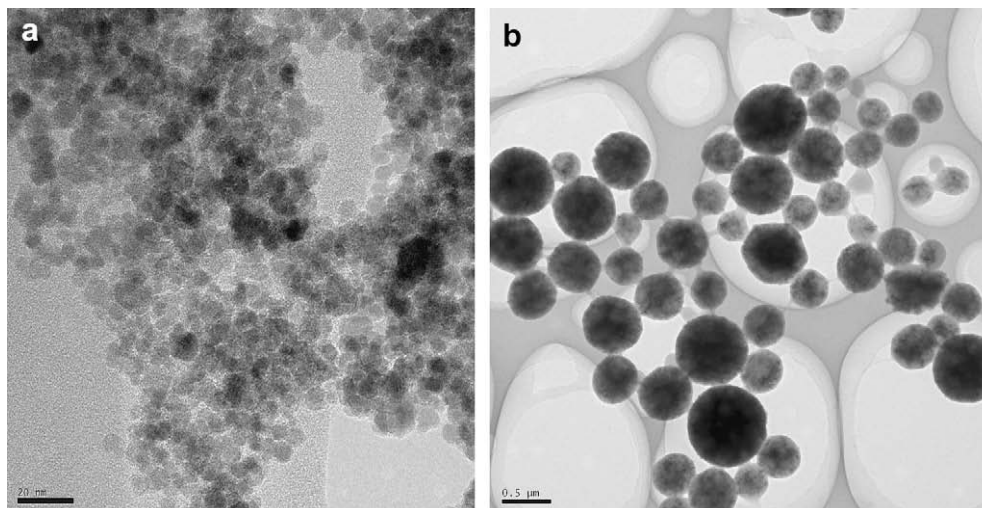


Fig. 2. The TEM images of Fe_3O_4 nanoparticles (a) $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ microspheres (b).

The microscopic morphologies of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ particles were observed in a transmission Electron Microscope (TEM, JEOL JEM-3010).

The average diameter and particle size distribution of magnetic microspheres were determined by dynamic light-scattering on a Zetasizer Nano ZS-90 (Malvern Instruments).

The hydrophilicity of magnetic composite microsphere was evaluated on a contact angle determination apparatus (JY-82, Chengde equipment company, Chengde, China). The sample was prepared through pressing magnetic composite microspheres into a compact pellet on the glass substrate, and then the contact angle between sample and water was measured.

Thermogravimetric analysis (TGA, Q50, TA instruments) was used to determine the average magnetic content of magnetic composite microspheres samples. The magnetic content of $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ was given according to the weight percentage of the residue after thermal analysis from room temperature to 600°C with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

The magnetic properties of magnetic particles were assessed using a vibrating sample magnetometer (VSM, LakeShore 7307).

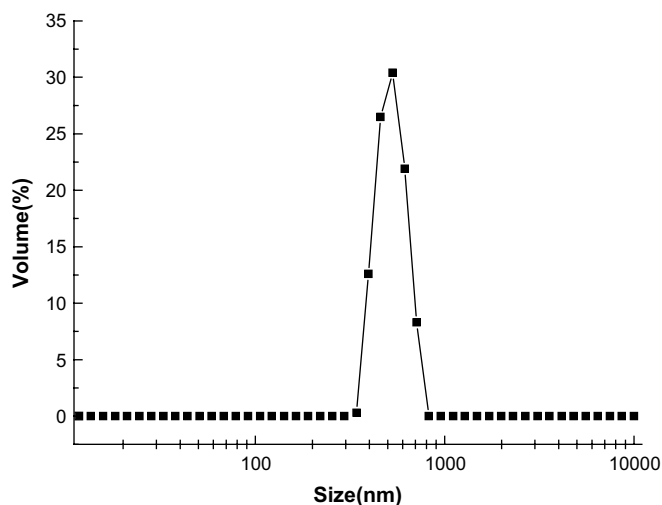


Fig. 3. The particle size distribution of $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ microspheres.

3. Results and discussion

3.1. Characterizations of magnetic nanoparticles and magnetic composite microspheres

Fig. 1 shows the FTIR spectra of Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ microspheres. In Fig. 1a, the characteristic absorption band of Fe_3O_4 appears at 585 cm^{-1} [19]. The broad band centered around 3380 cm^{-1} is assigned to the hydroxyl group, which is attributed to residual water on the surface of Fe_3O_4 nanoparticles. While in Fig. 1b, the two absorption bands mentioned above almost disappeared, and many characteristic absorption bands of $\text{P}(\text{AA-MMA-St})$ occur. For example, the peaks at 1149 and 1244 cm^{-1} ascribe to methoxy stretch vibrations. The peaks at 2996 , 2950 , and 1446 cm^{-1} are the absorption bands of methyl and methylene. The peaks at 750 and 700 cm^{-1} belong to the absorption bands of St units. The peak at 1735 cm^{-1} corresponds to carbonyl stretch vibration. All these results suggest that the surface of magnetic nanoparticles has been successfully coated with polymer shell.

Fig. 2 shows the TEM images of Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ microspheres. As shown in Fig. 2a, the Fe_3O_4 nanoparticles are aggregated due to their very small average particle size of around 10 nm . Fig. 2b clearly displays that Fe_3O_4 nanoparticles were successfully encapsulated into the polymer shell, and the dispersion of particles was improved greatly, which can be explained by the steric hindrance between the polymer chains on the surface of Fe_3O_4 nanoparticles [4]. The dispersed $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ microspheres with perfect sphere-shaped morphologies consist of a dark core and a light shell. The dark inner corresponds to magnetic nanoparticles, while the light outer attributes to $\text{P}(\text{AA-MMA-St})$. Particle size measurement indicated that they had an average diameter of 591 nm with a polydispersity index of 0.14 (Fig. 3). The PDI is a measure of dispersion homogeneity and ranges from 0 to 1 . Values close to 0 indicate a homogeneous dispersion while those greater than 0.3 indicate high heterogeneity [20]. Thus, the PDI data shows that the $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ composite microspheres have a relatively homogeneous particle size distribution.

Fig. 4 shows the TGA curves of Fe_3O_4 nanoparticles and magnetic $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ microspheres. As can be seen from Fig. 4, the mass loss of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ are 7% and

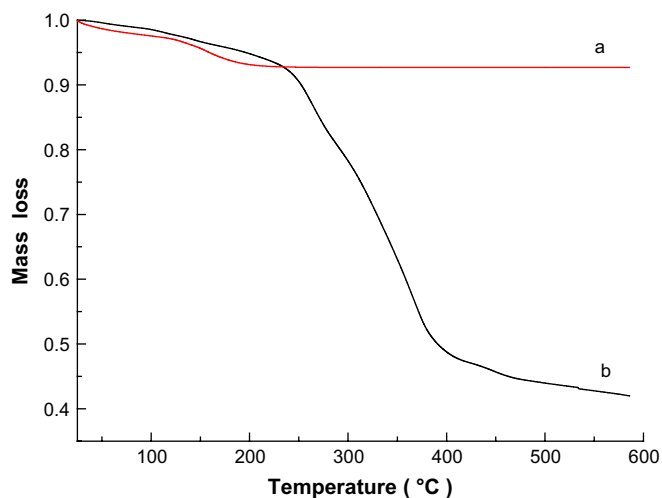


Fig. 4. The TGA curve of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ (b).

60%, respectively for the whole temperature range. The former is due to the evaporation of absorbed or crystalline water, while the later is attributed to the decomposition of grafted $\text{P}(\text{AA-MMA-St})$. Calculation results show that the magnetic content of composite microspheres can be up to 40 wt%.

Magnetic response is a fundamental property of magnetic materials. The magnetic hysteresis loop characterizes the response ability (magnetization, M) of magnetic materials to an external magnetic field (denoted by the magnetic field strength, H). It can provide the major magnetic parameters of magnetic materials, that is, saturation magnetization (M_s , it reflects the magnetizability of magnetic materials), coercive force (H_c , it characterizes the ability of magnetic materials to retain magnetization when the external magnetic field is removed) and magnetic remanence (M_r , it reflects the remaining magnetization of magnetic materials when an external magnetic field is removed). Fig. 5 gives the magnetic hysteresis loop of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$.

The magnetic parameters of two samples are collected in Table 1. As shown in Table 1, in the case of Fe_3O_4 nanoparticles, a value of saturation magnetization of 55.046 emu/g was determined, and the small coercivity and remanence values indicate a superparamagnetic

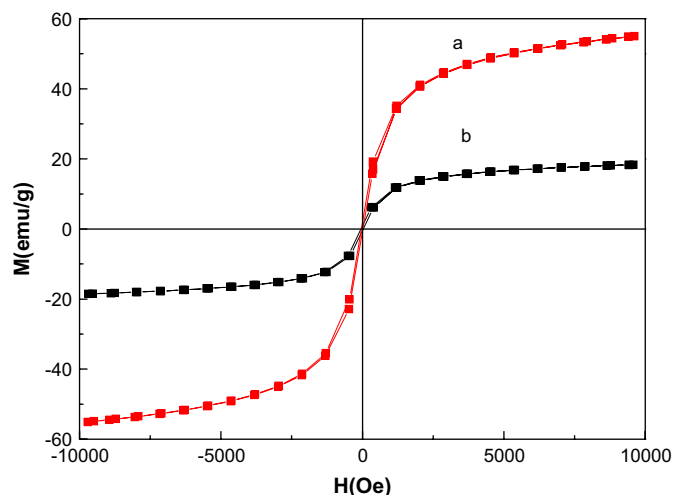


Fig. 5. The magnetization curves measured at room temperature for Fe_3O_4 nanoparticles (a) and $\text{Fe}_3\text{O}_4/\text{P}(\text{AA-MMA-St})$ composite microspheres (b).

Table 1

The magnetic parameters of Fe_3O_4 nanoparticles and magnetic composite microspheres.

| Sample | M_s (emu/g) | M_r (emu/g) | H_c (Oe) |
|---------------------------------------|---------------|---------------|------------|
| Fe_3O_4 nanoparticles | 55.046 | 1.144 | 24.4 |
| Magnetic composite microspheres | 18.430 | 0.638 | 38.3 |

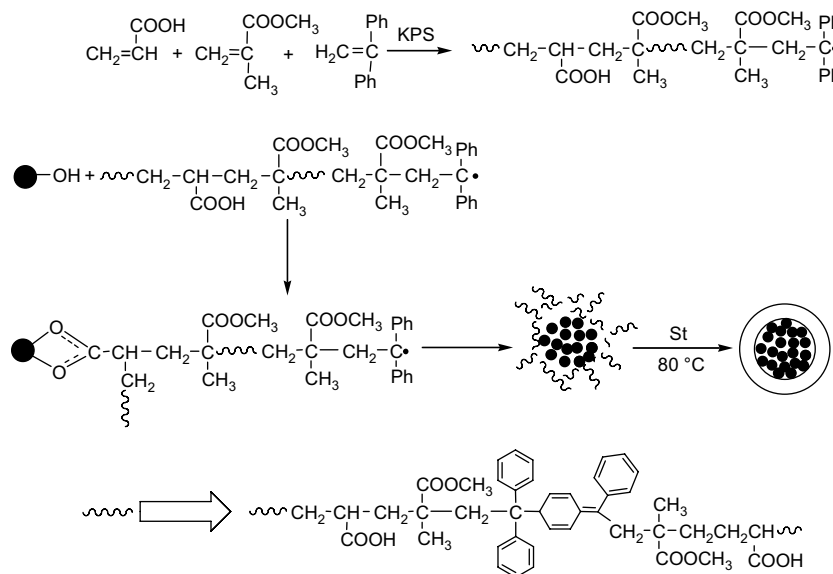
behavior. The particle size of the magnetic nanoparticles was about 10 nm, and each particle corresponds to a single crystal domain, exhibiting only one orientation of the magnetic moment [7], thus the magnetic nanoparticles exhibit superparamagnetic properties. The data of coercivity and remanence demonstrate that the magnetic composite microspheres also exhibit superparamagnetism. The saturation magnetization of the magnetic composite microspheres was found to be 18.430 emu/g, which is lower than that of the magnetic nanoparticles. This can be explained by containing the nonmagnetic polymer shell on the magnetic composite microspheres. In addition, according to the saturation magnetization, the magnetic content of composite microspheres can be calculated to be 33%. Differences between the magnetic content determined by TGA and that obtained by saturation magnetization can be attributed to the following fact. During the preparation of magnetic composite microspheres, part of Fe_3O_4 encapsulated inside the composite microspheres can be transformed into Fe_2O_3 induced by high temperatures, oxidizing effect of persulfate initiator, and some oxygen present in aqueous medium [21,22]. Because the saturation magnetization of Fe_2O_3 nanoparticles is lower than that of Fe_3O_4 nanoparticles [23], the magnetic content from VSM results is lower than the TGA result.

3.2. Preparation mechanism for magnetic composite microspheres

As illustrated in Scheme 1, the preparation of magnetic composite microspheres consists of two steps. One is the synthesis of amphiphilic precursor polymer by a surfactant-free terpolymerization of MMA, AA, and DPE, and the immobilization of precursor polymer on the surface of Fe_3O_4 nanoparticles through chemisorptions, namely, the interaction between the carboxyl of precursor polymer and the hydroxyl group from the Fe_3O_4 nanoparticle's surface. The other is the polymerization of St and residual methacrylate initiated by the DPE-containing precursor polymer absorbed on the magnetic nanoparticle's surface to form magnetic polymer microspheres.

In the first step, MMA reacts with AA in the presence of DPE to form an amphiphilic precursor oligomer. DPE exerted a significant control effect on the polymerization kinetic. As depicted in Fig. 6, the copolymerization of AA and MMA in the absence of DPE is much too fast, especially during the initial stage of polymerization. But the polymerization rate clearly decreases in the presence of DPE.

As expected, the presence of DPE also influences the molecular weight. SEC-MALLS analysis shows a strong decrease in the molecular weight, for example, $M_n = 8013$, and $M_n = 27010$ in presence and absence of DPE, respectively. Both the kinetic analysis and the molecular weight data show that DPE takes part in radical copolymerization of MMA and AA in a way that is comparable to that of degradative chain transfer agents as it causes a drastic decrease in both the rate of polymerization and the average degree of polymerization. It is worthy of note that the decreasing polymerization rate offers enough time for amphiphilic precursor polymer to modify the surface of Fe_3O_4 nanoparticles and then to capulize them. In addition, according to the description in Ref. [24], the DPE is probably present in the copolymer chains in the form of a quinoid recombinant dimer structure as shown in Scheme 2.



Scheme 1. Illustration of formation process of the magnetic composite microspheres.

This chemical structure of DPE-containing precursor polymer was confirmed by ^1H NMR and UV-vis analysis. As shown in Fig. 7, besides the peaks between 1 and 4 ppm due to P(AA-MMA), the spectra show the characteristic signals of aromatic protons of the DPE units at 6.8–7.5 ppm and the protons of semi-quinoid ring at 5.0–6.0 ppm [25]. Further support for the semi-quinoid structure was obtained from UV-vis absorption spectrum (Fig. 8). The UV-spectrum of P(AA-MMA) copolymer shows a broad absorption band between 250 and 270 nm corresponding to the semi-quinoid structure [24]. Because many carboxylic groups in the polymer chain, P(AA-MMA) can be grafted on the surface of Fe_3O_4 nanoparticles through carboxylates linkage between the Fe_3O_4 and the polymer chain (Scheme 1). This process led to the surface modification of the magnetic nanoparticle. As a result, the hydrophobicity of magnetic nanoparticles increased, and the contact angle changed

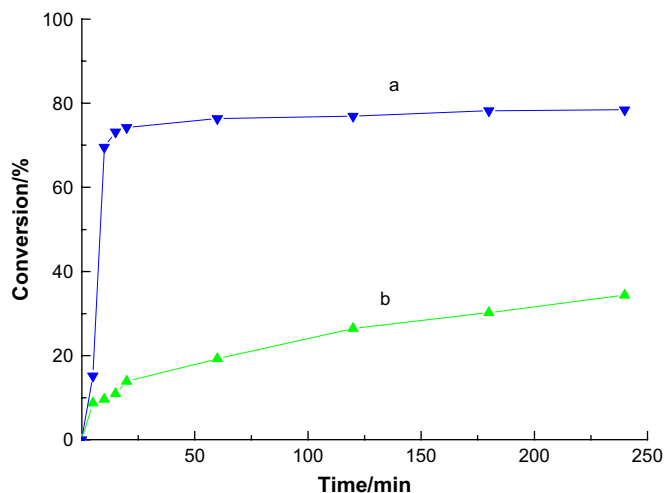
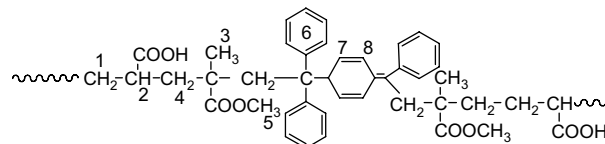


Fig. 6. Conversion-time plot of emulsifier-free emulsion copolymerization of MMA and AA in absence (a) and presence (b) of DPE, recipe: 0.15 g of AA, 3 g of MMA and 30 g of water, 10 g of KPS solution (1% w/w in water), 25.2 g of magnetic fluid (0.2 g magnetic nanoparticles in 25 g of water), 0 g of DPE (case “a”) or 0.05 g of DPE (case “b”), 80 °C.

from 17° (pure magnetic nanoparticles) to 50° (encapsulation for 4 h). Furthermore, this interaction also immobilized a lot of semi-quinoid structures on the surface of magnetic nanoparticles.

In the second step, according to the structural control mechanism of DPE in radical polymerization as discussed in Ref. [26], the semi-quinoid is able to form macromolecular radicals by attack of foreign radicals. And then the macromolecular radicals initiated St and residual methacrylate polymerization on the surface of magnetic nanoparticles to form magnetic composite microspheres. Here we paid particular attention to copolymerization site of St and residual methacrylate. In order to verify the existence of copolymerization on the magnetic nanoparticles, we calculated the monomers conversion after the first step polymerization, and compared the characterization results of polymer shell P(AA-MMA-St) with those of DPE-containing precursor P(AA-MMA).

Fig. 9 shows the ^1H NMR spectrum of polymer shell P(AA-MMA-St). In this spectrum, the signals from 0.8 to 1.2 are attributed to the *alpha*-methyl protons (*dH*) from MMA unit with different tacticities. The peaks at 0.84, 1.02 and 1.21 ppm arise from syndiotactic (*rr*), atactic (*mr*), and isotactic (*mm*) methyls respectively [27–29]. The peak at 3.6 ppm is ascribed to the proton (*eH*) of methyl ester from MMA unit [30]. The peaks at about 7.3 and 2.88 ppm are assigned to aromatic protons (*hH*) and methine protons (*gH*) from St unit, respectively [30,31]. The absorption from 1.4 to 2.4 ppm is due to the methylene protons (*aH*, *cH*, *fH*) from AA, MMA and St, and the absorption of methine proton (*bH*) from AA unit is also overlapped in this region [32–35]. Fig. 10 shows the ^{13}C NMR spectrum of polymer shell of magnetic composite microspheres. As shown in Fig. 10, the signals at 177(4C), 53(6C), 51(2C) and 21(5C) are due to the carbons of AA and MMA units, the peaks at 128(9C) and 39(8C) are attributed to the carbons from St.



Scheme 2. The chemical structure of precursor polymer.

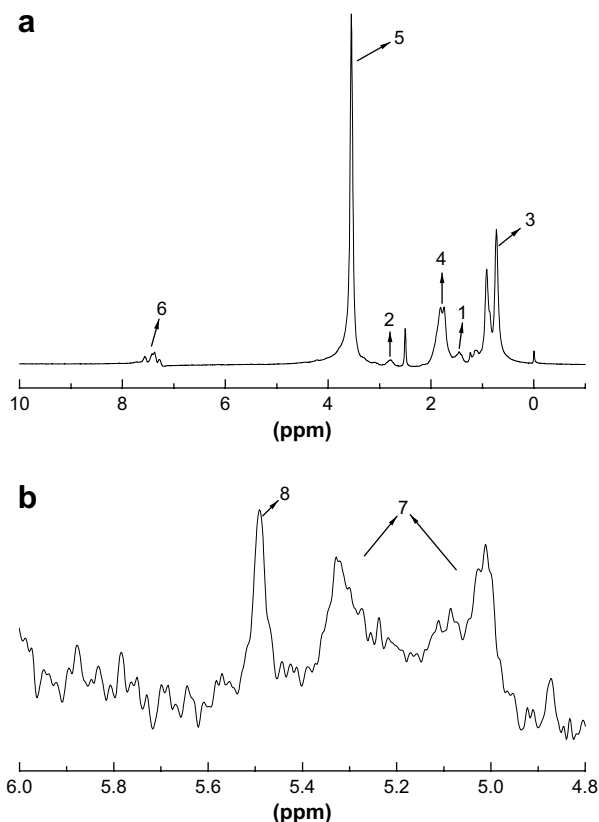


Fig. 7. The ^1H NMR spectrum (a) and its magnified spectrum (b) of precursor polymer ($\text{DMSO}-d_6$ as solvent).

Comparing the NMR spectra of polymer shell P(AA–MMA–St) with that of DPE-containing precursor P(AA–MMA), it was found that the characteristic peaks of semi-quinoid structure of DPE disappeared and characteristic peaks of St units occurred in Figs. 9,10. In addition, the molecular weight of P(AA–MMA–St) increases (see Table 2) compared with DPE-containing precursor P(AA–MMA). The monomers conversion was calculated to be 35% after the first step polymerization. All results showed that copolymerization of some St, residual methacrylate, and precursor polymer P(AA–MMA) occurred on the surface of magnetic nanoparticles.

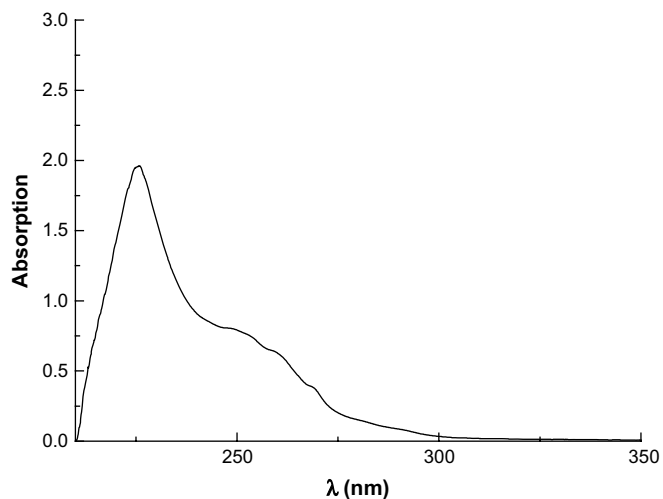


Fig. 8. UV-spectrum of DPE-containing P(AA–MMA) precursor polymer (THF as solvent).

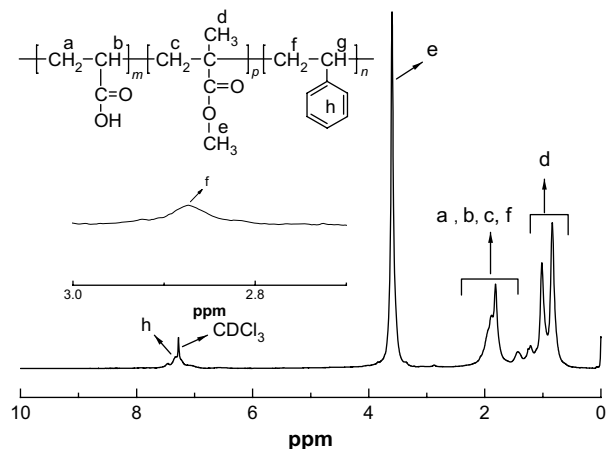


Fig. 9. ^1H NMR spectrum of polymer shell of $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ (CDCl_3 as solvent).

The formation process of magnetic composite microspheres was also recorded using TEM images. Fig. 11 shows the TEM images of magnetic composite microspheres at different polymerization time. As can be seen from these pictures, after addition of Fe_3O_4 nanoparticles for 5 min, the precursor polymer obtained began to capsulize magnetic nanoparticles, and dispersed the aggregated Fe_3O_4 nanoparticles. After 10 min, some preliminary magnetic composite microspheres formed. The composite microsphere's surface was rather rough and some interparticle bridging was in existence. As the polymerization proceeded, the composite microspheres grew in size and their shapes became more and more spherical and smooth. At last, the core-shell composite microspheres with perfect sphere-shaped morphologies were obtained. In addition, some empty particles (particles without Fe_3O_4) were also present in the TEM images. At the early stage of polymerization, the copolymer of AA and MMA participated in two processes in water, one is its interaction with magnetic nanoparticles, the

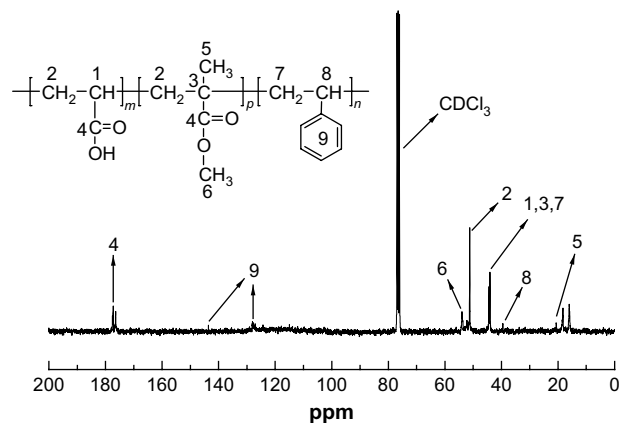


Fig. 10. ^{13}C NMR spectrum of polymer shell of $\text{Fe}_3\text{O}_4/\text{P}(\text{AA}-\text{MMA}-\text{St})$ (CDCl_3 as solvent).

Table 2

The molecular weights of polymer shell at different stages of polymerization.

| Sample | M_n (g/mol) | M_w/M_n |
|--------------|---------------|-----------|
| P(AA–MMA) | 8013 | 1.365 |
| P(AA–MMA–St) | 24430 | 1.869 |

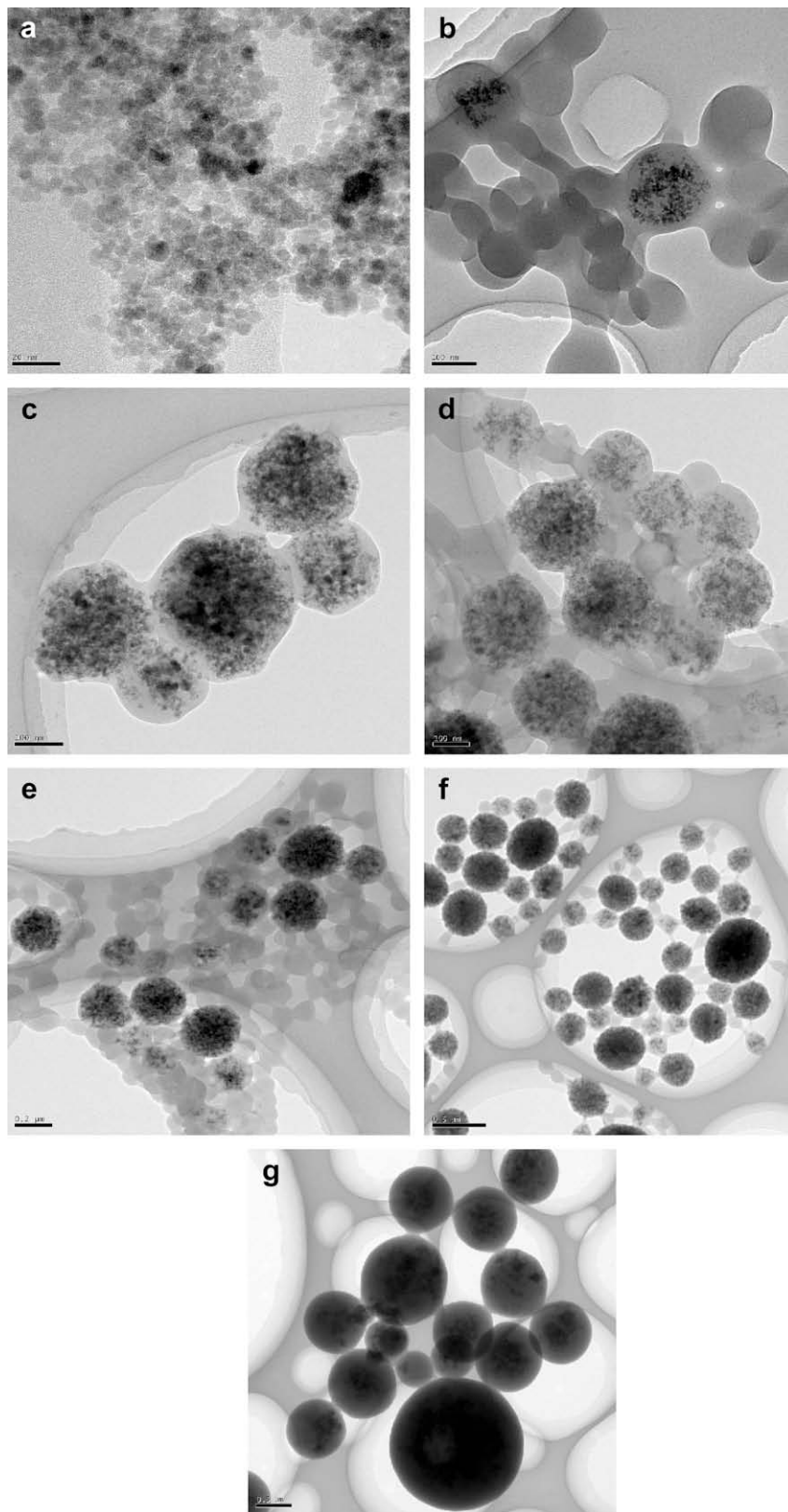


Fig. 11. TEM images of magnetic nanoparticles (a) and magnetic composite microspheres after addition of Fe_3O_4 nanoparticles for (b) 5 min, (c) 10 min, (d) 15 min, (e) 30 min, (f) 180 min, (g) 480 min.

other is its self-assembly due to amphiphilicity. Because of steric hindrance, gravitation and interface effects, it is impossible for each copolymer chain to act with magnetic nanoparticles for composite microspheres formation. Some copolymer chains were self-assembled first and then polymerized further to form empty particles.

4. Conclusions

In this paper, DPE radical polymerization was used to prepare magnetic composite microspheres. The studies show that this new method is suitable to prepare magnetic composite microspheres possessing small particle size with relatively homogeneous particle size distribution, perfect sphere-shaped morphologies, and high magnetic content. During the polymerization, the formation of DPE-containing precursor polymer P(AA-MMA) is crucial. On the one hand, it contributes to the stabilization of Fe₃O₄ nanoparticles in oil monomer St through chemical absorption. On the other hand, as a dormant chain, DPE-containing precursor polymer can be activated and then actively participate in the second polymerization of St and residual methacrylate on the surface of Fe₃O₄ nanoparticles to form magnetic composite microspheres.

Acknowledgement

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