Surface modification of magnetite nanoparticles with poly(*tert*-butyl acrylate) *via* atom transfer radical polymerization

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ABSTRACT

Magnetic nanoparticles (MNPs) grafted with poly(*tert*-butyl acrylate) (poly(*t*-BA)) *via* surface-initiated atom transfer radical polymerization (ATRP) is herein presented. MNPs were synthesized *via* a thermal decomposition reaction of iron (III) acetylacetonate in benzyl alcohol to obtain narrow-size distribution particles. Magnetite nanoparticles were characterized by X-ray diffraction (XRD) technique. BTPAm was synthesized from reaction between 3-aminopropyl triethoxysilane (APS) and 2-bromoisobutyryl bromide (BIBB) that used for ATRP. Firstly, The initiator was covalently bonded onto the MNP surfaces to create active initiating sites, followed by ATRP of *t*-BA monomers to obtain poly(*t*-BA)-grafted MNPs. Nuclear magnetic resonance (NMR) was used to confirm chemical structure of BTPAm. Fourier transform infrared spectroscopy (FTIR) was used to monitor the reaction progress in each step of the syntheses. Transmission electron micrographs (TEM) revealed that the particle size was about 8 nm in diameter without significant aggregation during the preparation process. The particle size was not affected owing to the surface modification procedure.

Keywords: magnetite nanoparticle, *tert*-butyl acrylate, atom transfer radical polymerization

INTRODUCTION

Iron oxide, especially magnetite nanoparticle (MNP), has been markedly developed to such an extent that it has become possible to fabricate, characterize and specially tailor its functional properties for biomedical applications and diagnostics (Kohler *et al*., 2004; Zhang and Zhang, 2005) because its biocompatibility has already been proven (Gupta and Gupta, 2005). However, MNPs tend to agglomerate due to high surface energy of nanosize particles. Therefore, to overcome such limitations and to be able to accommodate biomedical applications, MNPs must be coated with substances enabling them more stable in physiological condition. Surface modification of MNPs with polymeric surfactant has been prevalently adopted for steric stabilization of such particles. Atom transfer radical polymerization (ATRP) from surfaces of MNPs has also been reported as a potential "grafting-from" method for surface modification. ATRP is a recently developed living/controlled radical polymerization method, which does not require stringent experimental conditions. ATRP enables for the polymerization and block copolymerization of a wide range of functional

monomers in a controlled condition, yielding polymers with narrowly dispersed molecular weights (Hu *et al*., 2006).

The aim of the current work is to adopt "grafting from" method to modify MNP surfaces with poly(*tert*-butyl acrylate) (poly(*t*-BA)) *via* ATRP. It is thought that ATRP can offer well-defined polymeric stabilizers with low molecular weight distribution on the particle surfaces. FTIR was used to monitor the reaction in each step and TEM technique was used to monitor the particle size and its distribution.

METHODOLOGY

Materials

Unless otherwise stated, all reagents were used without further purification: iron (III) acetylacetonate (Fe(acac)$_3$), 99% (Acros), benzyl alcohol (Laboratory reagent), 3-aminopropyl triethoxysilane (APS), 99% (Acros), Triethylamine (TEA) (Carto Erba), 2-bromoisobutyryl bromide (BIBB), 98% (Acros), Copper (I) bromide (CuBr), 98% (Acros), N,N,N´,N´´,N´´-pentamethyldiethylenetriamine (PMDETA), 99% (Acros). *tert*-Butyl acrylate (*t*-BA) was distilled under vacuum prior to use.

Synthesis

Synthesis of oleic acid-coated magnetite nanoparticles (MNPs) (Figure 1). MNPs were prepared *via* thermal decomposition following the method previously described (Pinna *et al*., 2005). In a typical synthesis, Fe(acac)$_3$ (1.0 g, 2.81 mmol) and benzyl alcohol (20 ml) were thoroughly mixed by magnetic stirring in a three-neck flask under a flow of nitrogen. The mixture was heated to 200 °C for 48 h. The resultant mixture was cooled down to room temperature. The precipitants were removed from the dispersion using an external magnet and they were washed with ethanol and CH$_2$Cl$_2$ repeatedly to remove benzyl alcohol. The particles were then dried at room temperature under reduced pressure. To prepare oleic acid-coated MNPs, the dried MNPs were introduced into an oleic acid solution in toluene, and ultrasonicated for 3 h.

Immobilization of 2-bromo-2-methyl-N-(3-(triethoxysilyl) propanamide (BTPAm) onto MNP surfaces (BTPAm-modified MNPs) (Figure 1). MNPs were effectively surface-modified with BTPAm to form a self-assembled monolayer *via* a silanization reaction. BTPAm was prepared from the coupling reaction between APS and BIBB. The detailed synthesis of BTPAm has been previously reported (Sun *et al*., 2007). Briefly, an MNP-toluene dispersion, BTPAm and TEA in toluene were mixed in a round bottom flask. The mixture was stirred for 24 h at room temperature under nitrogen. The particles were subsequently precipitated in methanol, followed by a magnet separation to obtain BTPAm-modified MNPs. Then, the MNPs were re-

dispersed in toluene and re-precipitated in methanol. This procedure was repeated several times. The particles were finally dried *in vacuo*.
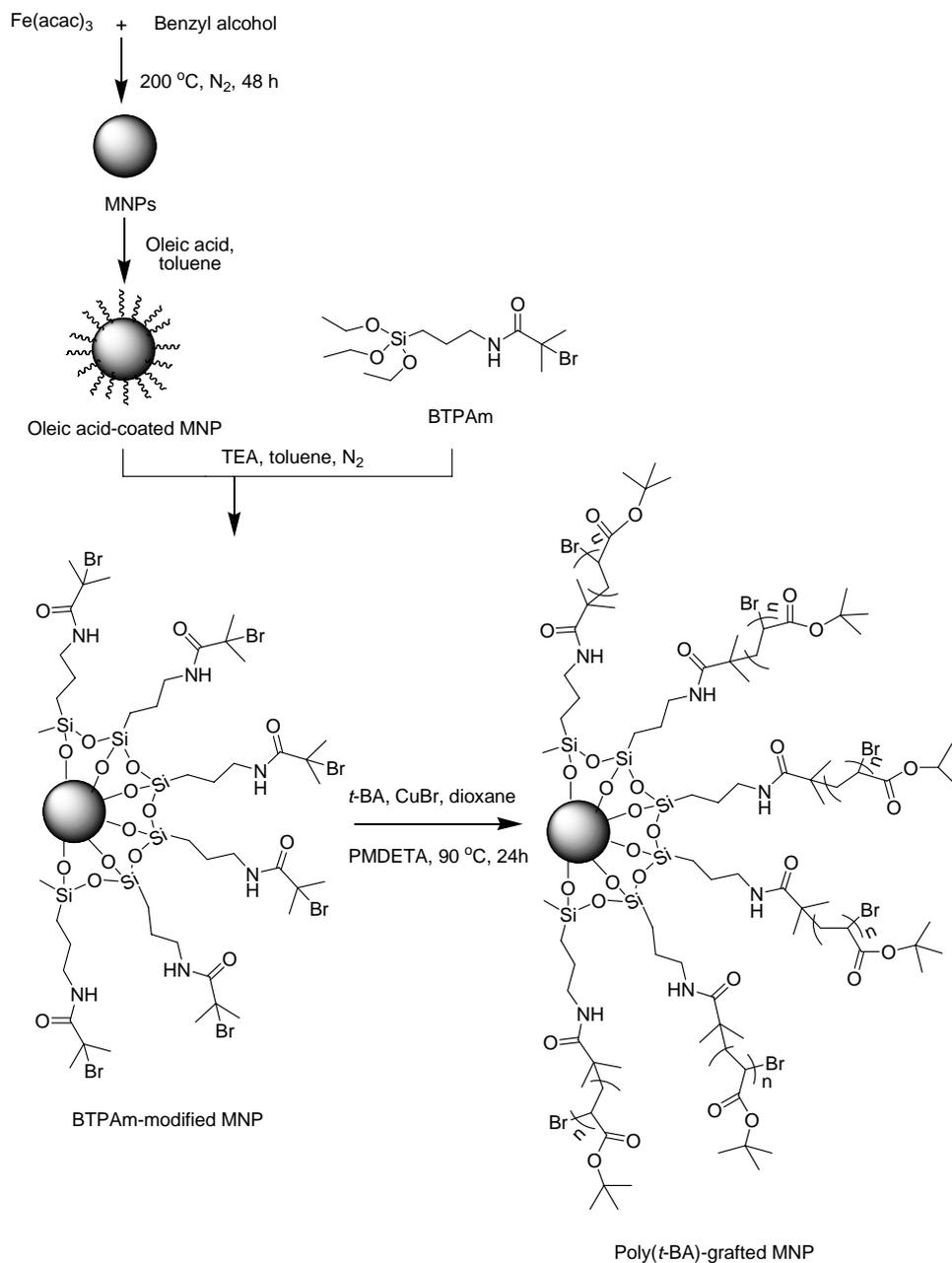
Figure 1 Synthesis of poly(*t*-BA)-grafted magnetite nanoparticles *via* ATRP reaction

Synthesis of poly(tert-butyl acrylate)-grafted magnetite nanoparticles (poly(t-BA)-grafted MNPs) via ATRP reaction. CuBr and PMDETA were first dissolved in dioxane in a schlenk flask under nitrogen blanket. The mixture was stirred until homogenous solution was observed. BTPAm-modified MNPs and *t*-BA monomer were then added into the solution *via* a syringe. The solution was stirred at 90°C for 24 h to commence ATRP reaction. The MNPs were separated from the dispersion by an external magnet and washed thoroughly with methanol and dried *in vacuo* (Figure 1).

Characterization

FTIR was performed on a Perkin-Elmer Model 1600 Series FTIR Spectrophotometer. Neat samples were directly cast onto potassium chloride plates. Proton NMR was performed on a 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. TEM images were taken using a Philips Tecnai 12 operated at 120 kV equipped with Gatan model 782 CCD camera. The sample solutions in water were cast onto carbon-coated copper grids and let to slowly evaporate at room temperature. XRD patterns of the particles were collected on a Philips X'pert X-ray diffractometer under CuK_{α} radiation ($\lambda = 1.540598$ Å) operated at 30 kV and 2θ ranging from 0 to 90°.

RESULTS AND DISCUSSION

After the decomposition reaction of the iron precursor, the as-prepared nanoparticles were characterized by XRD technique. According to an XRD pattern shown in Figure 2, it revealed diffraction peaks at (220), (311), (400), (422), (511) and (440), which are the characteristic signals of magnetite crystal with a cubic spinal structure. The position and relative intensities of all diffraction signals of the sample matched well with the characteristic peaks of magnetite crystal obtained from the magnetite standard pattern (ICSD No. 01-075-0449).
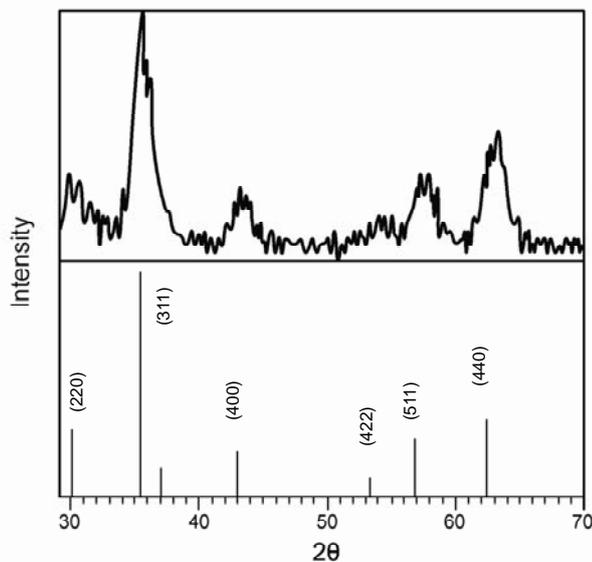
Figure 2 An XRD pattern of the as-prepared MNPs (top) compared with a
magnetite standard pattern (ICSD No. 01-075-0449) (bottom)

To prepare BTPAm-modified MNPs, APS was first coupled with
BIBB through amidization reaction to obtain BTPAm, followed by a
silanization reaction onto the MNP surfaces. In the first step, BTPAm was a
resultant product from amidization reaction between APS and BIBB.
Chemical structure and functional groups of BTPAm were characterized
using ^{1}H NMR and FTIR, respectively. Comparing with FTIR spectra of APS
(Figure 3A) and BIBB (Figure 3B), Figure 3C exhibited FTIR characteristic
absorption peaks of BTPAm (1658 cm^{-1} of -NH-<u>CO</u>- carbonyl stretching,
1112-1026 cm^{-1} of Si-O stretching, 1532 cm^{-1} of N-H bending and 3345 cm^{-1}
of N-H- stretching). The signal at 1738 cm^{-1} belonging to -(<u>CO</u>)-Br carbonyl
stretching indicated the slight remaining of unreacted BIBB after the
reaction. It is important to mention that the molar ratio of APS to BIBB used
in this step was 1:1; it is possible to have some unreacted BIBB or APS
remaining after the reaction. The mixture was used in the next step without
further purification.
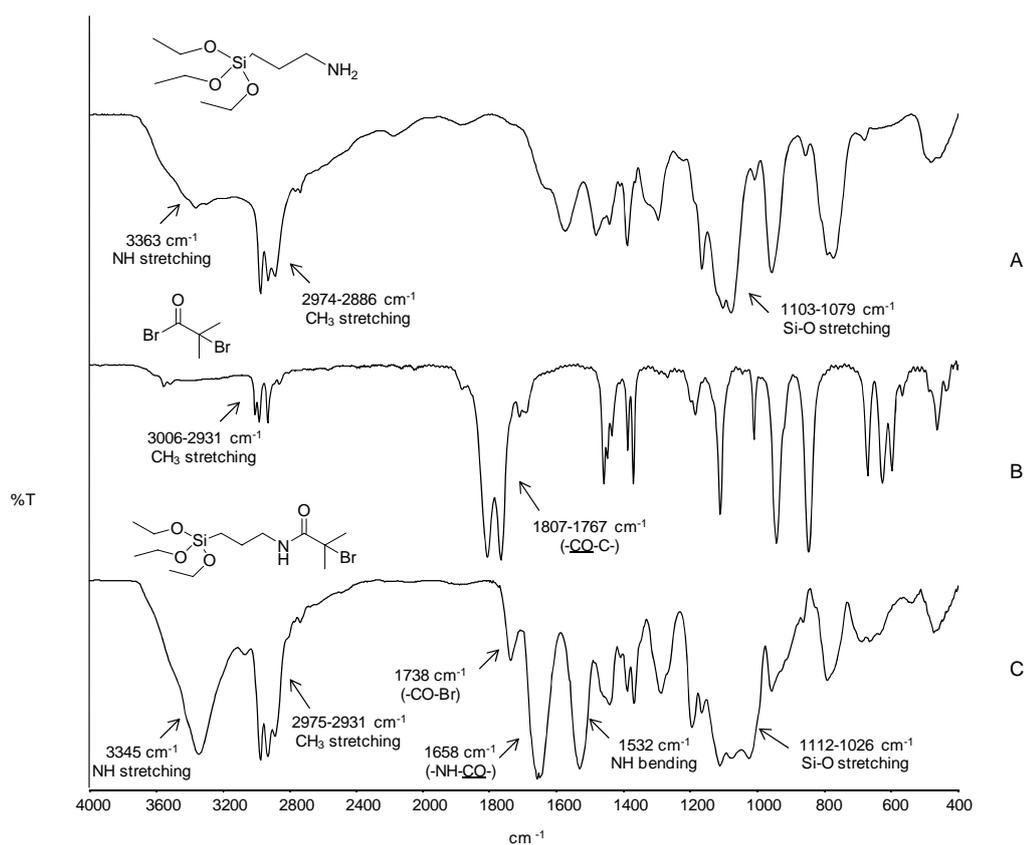
Figure 3 FTIR spectra of A) APS, B) BIBB and C) BTPAm

Figure 4C showed a ^{1}H NMR spectrum of BTPAm in comparison with APS (Figure 4A) and BIBB (Figure 4B) starting reagents. In good agreement with FTIR results, a distinctive shift of the ^{1}H NMR signal corresponding to methylene protons adjacent to NH group (from 2.50 ppm, signal *a*, to 3.22 ppm, signal *a'*) indicated the formation of BTPAm. In addition, slight shifts of other signals such as methylene protons of signal *b* (1.45 ppm) to signal *b'* (1.62 ppm), and methyl protons of signal *f* (2.50 ppm) to signal *f'* (2.40 ppm) also confirmed the formation of BTPAm.
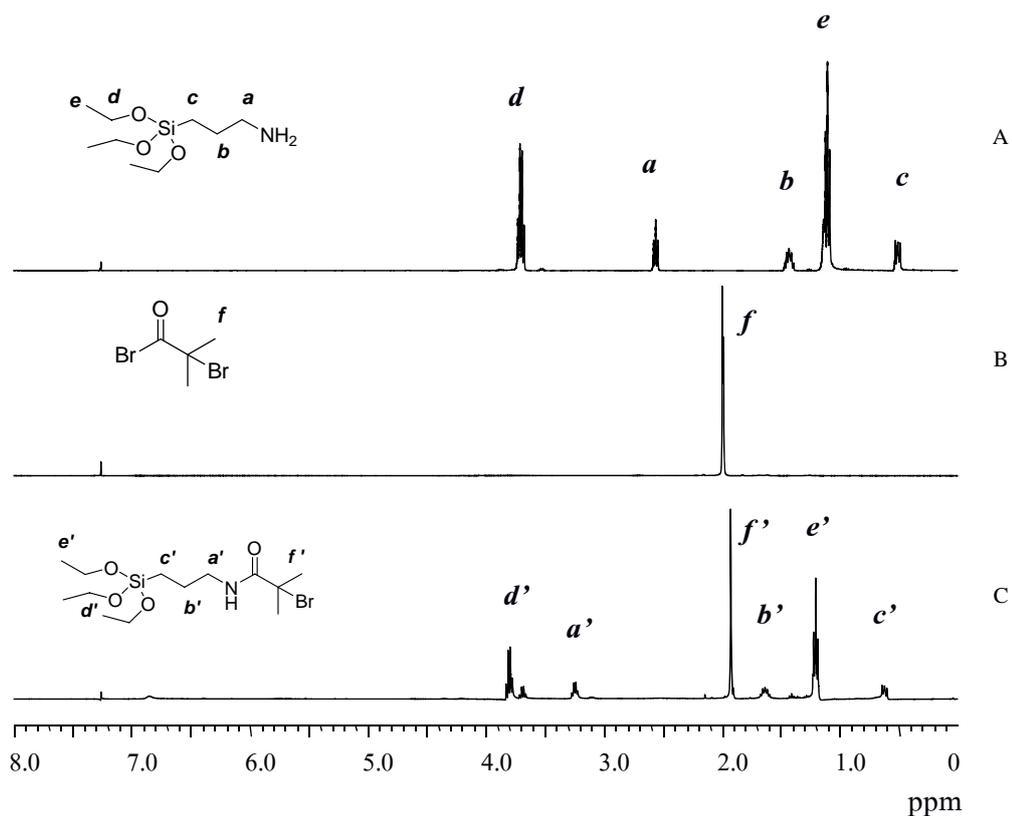
Figure 4 ^{1}H NMR spectra of A) APS, B) BIBB and C) BTPAm (solvent: CDCl$_3$)

To immobilize BTPAm on MNP surfaces, bare MNPs were first coated with oleic acid to form well dispersed MNPs in toluene. BTPAm-toluene solution was subsequently introduced into the oleic acid-coated MNP dispersion. The advantage of this procedure was that MNPs were well dispersible in the media before reacting with BTPAm. This approach allowed BTPAm to effectively silanize to their surfaces due to its greater surface approaching ability in the dispersed MNPs.
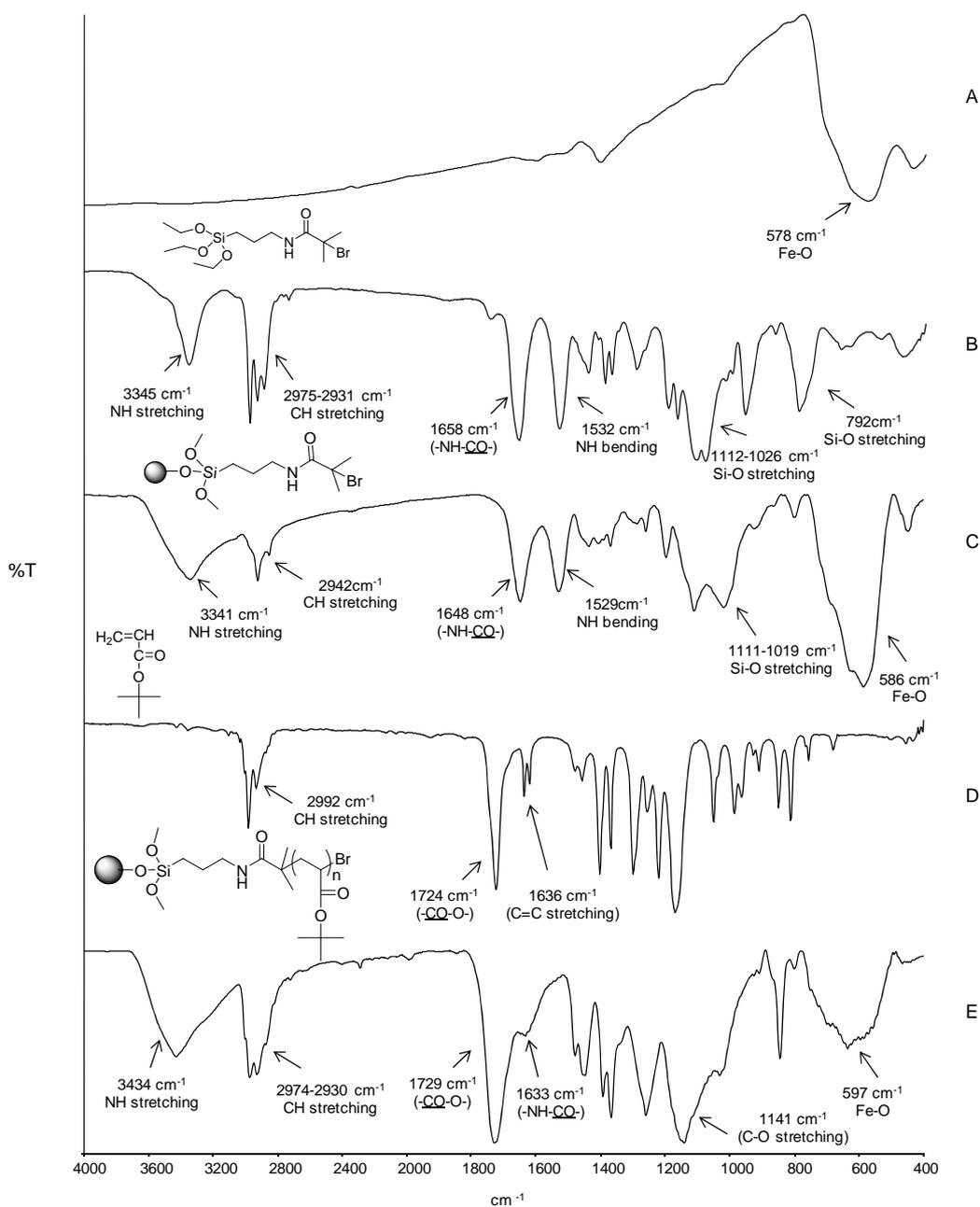
Figure 5 FTIR spectra of (A) bare MNPs, (B) BTPAm, (C) BTPAm-coated MNPs, (D) *t*-BA monomer and (E) poly(*t*-BA)-grafted MNPs
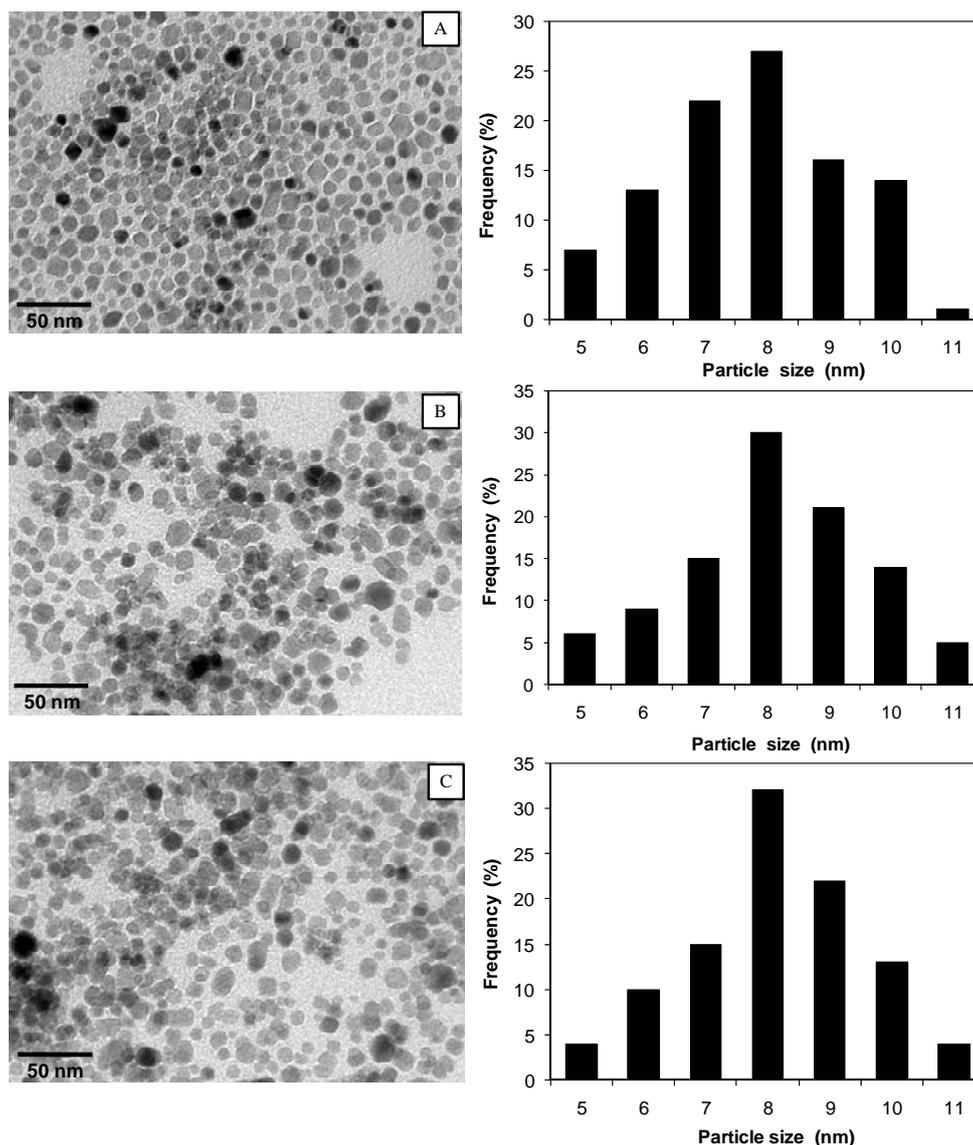
Figure 6 TEM images (left) and size distributions (right) of (A) bare MNPs
(B) BTPAm-coated MNPs and (C) poly(*t*-BA)-grafted MNPs

Figure 5C showed an FTIR spectrum of BTPAm-coated MNPs in comparison with those of bare magnetite (Figure 5A) and BTPAm (Figure 5B). BTPAm-coated MNPs exhibited characteristic absorption signals of BTPAm; 1658 cm^{-1} (-NH-<u>CO</u>- carbonyl stretching), 1111-1019 cm^{-1} (Si-O stretching), 1529 cm^{-1} (N-H bending) and 3341 cm^{-1}(N-H- stretching) (Figure 5C). In combination with a strong and broad signal of Fe-O bonds (586 cm^{-1}),

this evidenced that BTPAm was covalently bound to MNP surfaces. Figure 5E showed an FTIR spectrum of poly(*t*-BA)-coated MNPs comparing with those of *t*-BA monomer (Figure 5D). Poly(*t*-BA)-coated MNPs exhibited characteristic absorption signals of poly(*t*-BA); 1729 cm^{-1} (-(CO)-O-stretching) and 1141 cm^{-1} (C-O stretching) (Figure 5E). A sharp and strong signal of carbonyl functional group indicated the presence of poly(*t*-BA) on the particle surfaces as a result of ATRP reaction. Also, other signals corresponding to BTPAm linkers such as 1633 cm^{-1} (-NH-CO- carbonyl stretching), and 3434 cm^{-1} (N-H- stretching), were observed. A broad and strong characteristic signal of Fe-O bonds from MNP cores was obviously apparent (597 cm^{-1}).

TEM images and particle size distribution of MNPs in each step of the surface modification were illustrated in Figure 6. The particle size was in the range of 5-11 nm with the average of 8 nm in diameter without significant change in their size upon modification process.

CONCLUSIONS

This work presented a "grafting-from" method to modify MNP surfaces with poly(*t*-BA) *via* ATRP reaction. MNPs were effectively surface-modified with BTPAm to form a self-assembled monolayer by a silanization reaction. ATRP has been successfully applied to surface-initiated graft polymerization of poly(*t*-BA) in order to prepare a well-packed polymer layer on the surface of MNPs. TEM images revealed that the particle size distribution was narrow without significant change in their size after surface modification process. This "grafting from" method *via* ATRP reaction should be effectively used in the synthesis of other polymers with increasing complexity and functionality in the polymeric shell of the particles.

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