

Self-Assembly and Photopolymerization of Diacetylene Molecules on Surface of Magnetite Nanoparticles

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An amphiphilic diacetylene compound was deposited on the surface of nano sized magnetite particles (Fe_3O_4) using a self-assembly method. The diacetylene molecular assembly formed on the surface of nanoparticle was subjected to photopolymerization. This resulted in the formation of a polymeric assembly on the surface of the nanoparticles in which the adjacent diacetylene molecules were connected through conjugated covalent networks. The presence of immobilized polymer species on the surface of nanoparticles is expected to protect them from agglomeration and ripening, thereby stabilizing their physical properties. In this work, Fe_3O_4 nanoparticles were prepared by chemical coprecipitation method and the diacetylene molecule 10,12-pentacosadiynoic acid (PCDA) was anchored to the surface of Fe_3O_4 nanoparticles through its carboxylate head group. Irradiation of UV light on the nanoparticles containing immobilized diacetylenes resulted in the formation of a polymeric assembly. Presence of diacetylene molecules on the surface of nanoparticles was confirmed by X-ray photoelectron spectroscopy and FT-IR measurements. Photopolymerization of the diacetylene assembly was detected by UV-Visible spectroscopy. Magnetic properties of the nanoparticles coated with polymeric assembly were investigated with SQUID and magnetic hysteresis showed superparamagnetic behaviors. The results put forward a simple and effective method for achieving polymer coating on the surface of magnetic nanoparticle.

Key Words : Magnetite nanoparticles, Superparamagnetism, Diacetylenes, Self-assembly, Photopolymerization

Introduction

Magnetic nanoparticles have been the subject of intensive research for their potential applications in the fields like high-density data storage, magnetic resonance imaging, biochemistry, hyperthermia, *in vivo* drug delivery, etc.¹⁻⁷ The magnetic properties of nanoparticles decisively depend on their size, owing to the dependence of their relaxation of magnetization orientation on the particle size. Controlling the size distribution and obtaining the thermal as well as chemical stability of nanoparticles are therefore among the pivotal concerns in an application point of view of these materials. These necessities are effectively achieved by the surface modification of magnetic nanoparticles.⁸ Polymer coating is a widely used method for the surface modification of magnetic nanoparticles. Noguchi *et al.* reported the emulsion polymerization of styrene and methyl methacrylate in the presence of a ferrofluid.⁹ Sunderland *et al.* used the *in situ* polymerization for the synthesis of conducting polymer-magnetic inorganic nanomaterials.¹⁰ Recently Sun *et al.* reported the photochemical polymerization of acrylamide on the magnetite nanoparticle surface which can overcome the drawbacks of microemulsion polymerization and emulsion polymerization due to the absence of initiators.¹¹

Diacetylenes are classes of compounds which contain two triple bonds in conjugation. They have a unique property of photopolymerization upon absorption of UV light of 254 nm

(Figure 1). Diacetylenes substituted with various side chains readily undergo photopolymerization in a wide range of organized structures, such as single crystals, Langmuir-Blodgett films, self-assembled monolayers, liposomes or vesicles, and solutions. Photopolymerization in diacetylene molecular assemblies is central to a broad scope of research interests due to the unique mechanical, optical and electronic properties of polydiacetylenes resulting from it. The photopolymerization results in the formation of polydiacetylenes which contain a highly conjugated molecular structure with single, double and triple bonds in conjugation with each other. Polydiacetylene species have relevant durability and robustness along with unique optical and electronic proper-

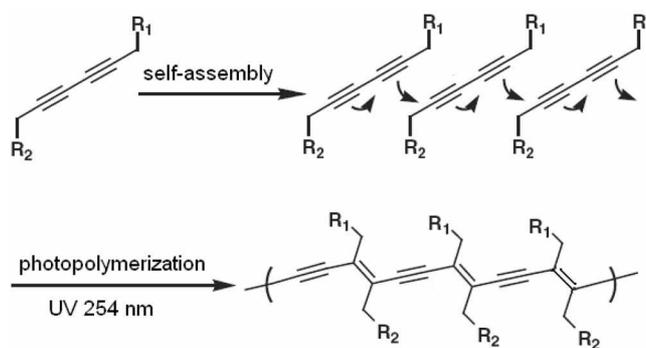


Figure 1. Schematic representation of the photopolymerization of diacetylene compounds upon irradiation with UV light.

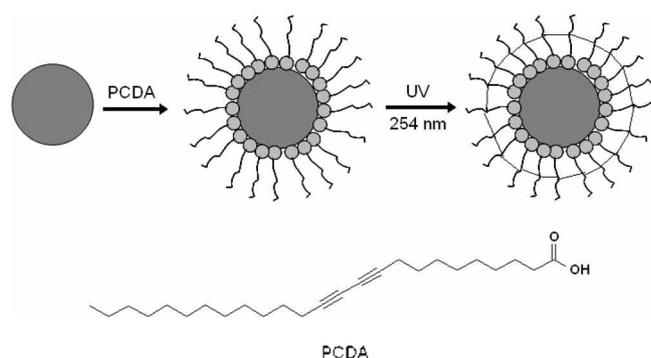


Figure 2. Schematic illustration of the self-assembly and photopolymerization of PCDA on the surface of Fe_3O_4 nanoparticles.

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This work describes a simple approach to obtain a robust and inert coating of polydiacetylene network on the surface of nanoparticles without affecting the nanocrystal structure and magnetic behavior of the nanoparticles. The surface of Fe_3O_4 nanoparticles was modified by the self-assembly of an amphiphilic diacetylene molecule and photopolymerization of the diacetylenes on the surface of nanoparticle systems (Figure 2). The presence of immobilized polymer species was expected to stabilize the morphology and physical properties including the superparamagnetic nature of the magnetite nanoparticles.

Experimental Section

Chemicals. The diacetylene compound 10,12-pentacosadiynoic acid (PCDA) and ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from Fluka. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Aldrich. Ammonium hydroxide (NH_4OH) and hydrochloric acid (HCl) were purchased from Samchun Chemical. They were used as received. Water was purified with a Millipore water treatment system (Sartorius arium 611) and all other solvents used were of HPLC grade.

Synthesis of magnetite nanoparticles. Magnetite (Fe_3O_4) nanoparticles were synthesized using a chemical coprecipitation method which was reported elsewhere.¹⁸⁻²⁰ Briefly, ferrous chloride tetrahydrate (3.16 mmol) and ferric chloride hexahydrate (6.78 mmol) were added to deionized water (20 mL) and heated to 80 °C under nitrogen in a three-necked, round-bottomed flask, while magnetically stirring the mixture. Ammonium hydroxide solution (5 mL; 28%) was injected into the mixture. It was heated for additional 1 h. After this, the entire mixture was neutralized with 1 M HCl . Magnetite nanoparticles were magnetically decanted and washed three times with deionized water and dried *in vacuo*.

Immobilization and photopolymerization of diacetylene on magnetite particles. The self-assembly of diacetylene monomers on the surface of nanoparticles was carried out according to a published procedure.²¹ A 6 mM solution of PCDA was prepared in chloroform. Fifty milligrams of

magnetic nanoparticle powder was gently mixed with 25 mL of PCDA solution in a round-bottomed flask while purging nitrogen through the solution. The flask was then sealed and shaken for 24 hours using a laboratory shaker. The resultant particles were separated by centrifugation and washed with chloroform and hexane to remove unbound surfactant. Photopolymerization of diacetylene on the surface of nanoparticles was carried out by irradiating a dispersion of nanoparticle in chloroform with a low powered UV lamp for 10 min using radiation of 254 nm.

Characterization. X-ray powder diffraction (XRD) patterns were measured with a Rigaku X-ray diffractometer, D/MAX-2500, on θ - 2θ scanning mode at Center for Scientific Instruments at Kyungpook National University. The measurements were performed under the conditions of 40 kV, 30 mA, and $\text{Cu K}\alpha$ radiation ($\lambda = 1.540 \text{ \AA}$). The size, shape and morphology of nanoparticles were investigated with JEM-2100 F, Jeol field emission transmission electron microscope (FE-TEM) at Korea Basic Science Institute. The samples were dispersed in chloroform and were dropped and dried over a copper grid for TEM measurement. X-ray photoelectron spectroscopy (XPS) analyses were performed with an ESCALAB-MK (VG Company) instrument. Photoemission was stimulated by a monochromated $\text{Al K}\alpha$ radiation (1486.6 eV) with the operating at 12 kV and a 0.10 eV/step interval. Binding energies of spectra were referenced to the C (1s) binding energy set at 284.6 eV. Magnetic hysteresis measurements of samples were carried out at room temperature on powder samples of the complex using a Quantum Design MPMS *XL* magnetometer equipped with a 50-kG magnet. UV-Visible absorption spectra of the samples were measured using a Scinco S-4100 UV-Visible spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin-Elmer Spectrum BX spectrophotometer.

Results and Discussion

Crystal structure of nanoparticles. The crystal structure of Fe_3O_4 nanoparticles coated with polydiacetylene was characterized with powder XRD analysis. XRD pattern of the Fe_3O_4 nanoparticles obtained is shown in Figure 3. This indicates the nanocrystal nature of the sample. The position and relative intensity of the peaks are in good agreement with the standard Fe_3O_4 powder diffraction data (JCPDS No. 19-0629).¹¹ Characteristic peaks corresponding to (220), (311), (400), (422), (511) and (440) planes of the nanocrystals were observed. This suggests that the magnetite nanoparticles prepared were pure with spinel structure of the particles. Furthermore, the nanocrystal nature of the particles were unaltered upon the self-assembly and photopolymerization of PCDA. Size of the nanocrystals was calculated with Scherrer's formula, using full width at half maximum of different XRD peaks. The particle size obtained in all calculations was in the range of 10 to 12 nm, which is comparable to the particle sizes observed in TEM images.

A high resolution TEM image of the nanoparticles is

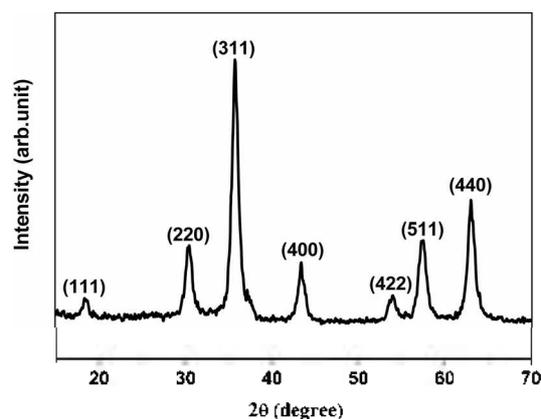


Figure 3. Powder XRD pattern of nanoparticle immobilized with polydiacetylene on the surface.

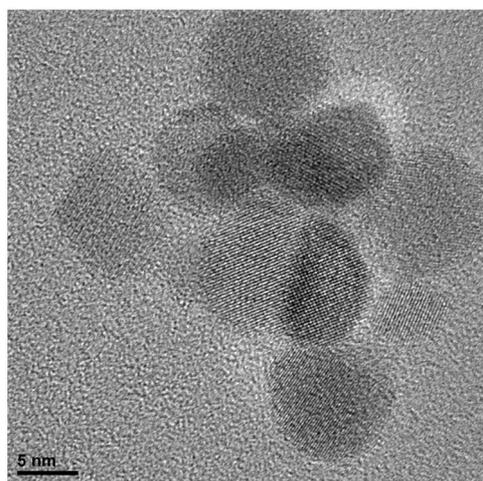


Figure 4. TEM image of magnetite nanoparticles coated with polydiacetylene.

shown in Figure 4. This indicates the morphology of the nanoparticles as spherical and size less than 10 nm. Lattice fringes of the nanoparticles are visible in the image, suggesting the crystalline character. The size distribution of the particles can be observed as nearly monodisperse. The particles are not appearing as well separated in the image. We assume that this is due to the strong magnetic attraction between the particles.

Attachment of PCDA on the surface of nanoparticles. X-ray photoelectron spectroscopy is a sensitive and effective tool for analyzing the chemical structure and bonds on the surface of nanoparticles. In order to detect the self-assembly of PCDA on the surface of magnetite nanoparticles, the XPS spectra of the samples before and after the self-assembly process were recorded. The XPS analysis of a sample containing a physical mixture of Fe_3O_4 and PCDA was also carried out. The XPS spectra obtained for different samples are shown in Figure 5, Figure 6 and Figure 7. The band positions in XPS spectra are given in Table 1. The C (1s) peak positions were obtained as shown in Figure 5. For all the three samples, a high intensity peak is present at 284.55 eV, which corresponds to the carbon atoms of hydrocarbon

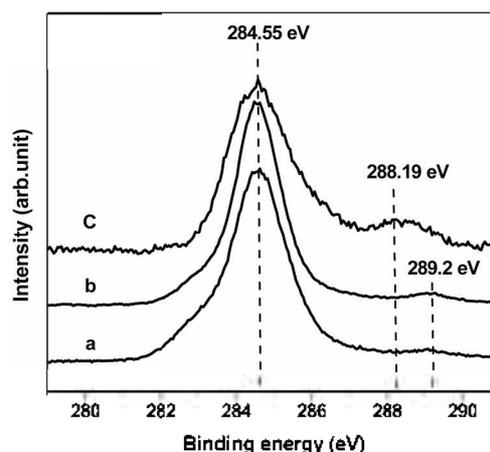


Figure 5. C (1s) region of the XPS spectra of (a) PCDA, (b) physical mixture of Fe_3O_4 nanoparticles and PCDA, and (c) Fe_3O_4 nanoparticle with PCDA attached on the surface.

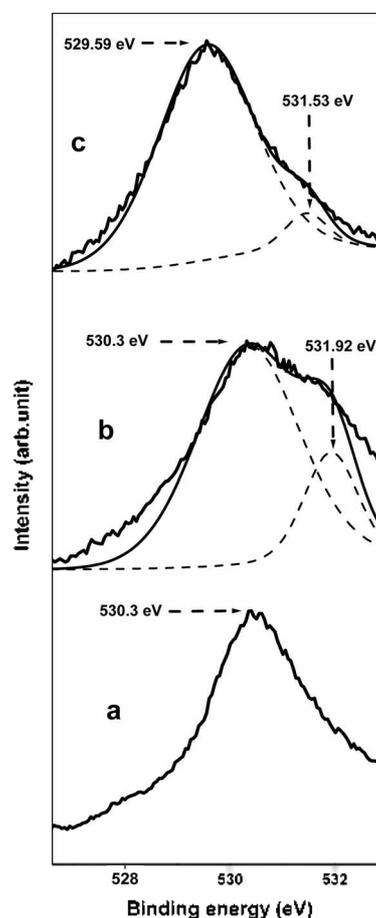


Figure 6. O (1s) region of the XPS spectra of (a) Fe_3O_4 nanoparticle with no surfactant, (b) physical mixture of Fe_3O_4 nanoparticles and PCDA, and (c) Fe_3O_4 nanoparticle with PCDA attached on the surface.

chain. Sample containing self-assembled PCDA on the surface shows two peaks at 284.55 and 288.19 eV, respectively. The peak at 284.55 eV is due to the carbon atoms of the hydrocarbon chain and peak at 288.19 eV corresponds to the carbon of carboxylate ($-\text{COO}$) group. This peak is absent

both in the pure PCDA sample and physical mixture sample. The C (1s) peak corresponding to carboxylic carbon (-COOH) usually appears around 290 eV. A low intensity hump can be seen at 289.2 eV in the pure PCDA sample and physical mixture sample corresponding to this. This was absent in the diacetylene coated nanoparticle sample, indicating that there is no free carboxylic acid on the surface of nanoparticles and PCDA gets attached to the nanoparticle surface through the carboxylate group.

XPS spectra in the O (1s) region of all samples are shown in Figure 6, along with deconvolution plots. Nanoparticles without polydiacetylene on the surface have only one peak in the O (1s) region at 530.3 eV, which is corresponding to the surface O atoms of Fe₃O₄. Nanoparticles coated with polydiacetylene gave a spectrum which can be deconvoluted into two graphs with peaks at 529.59 eV and 531.53 eV. The peak at 529.59 eV is corresponding to O of Fe₃O₄ and peak at 531.53 eV corresponds to O of carboxylate. A decrease in Binding energy for O of Fe₃O₄ was observed after the attachment of PCDA to the surface. This can be due to the contributions of conjugated oxygens from carboxylate group interacting with iron ions on the surface.²¹ The graph for physical mixture of PCDA and magnetite particles appeared to be composed of two curves which showed peaks at 530.3 eV and 531.92 eV, corresponding to the O atom of Fe₃O₄ and O atom of carboxylic (-COOH) group.

Characteristic binding energy values for Fe (2p_{3/2}) core level electrons were obtained at 711 eV. Fe (2p_{1/2}) peaks were obtained at 725.6 eV.²² Both the Fe (2p) bands of the XPS spectra showed no significant shift in the binding energy values before and after the self-assembly. The XPS data thus give evidence for the attachment of PCDA to the surface of nanoparticles through the interaction between carboxylate groups and iron ions on the surface.

In the FT-IR analysis, two weak peaks were observed at 2920 cm⁻¹ and 2853 cm⁻¹ (data not shown) which are attributed to the vibrations of symmetric and unsymmetrical C-H stretching. The comparatively low intensity of peaks is due to the relatively less concentration of the surfactant

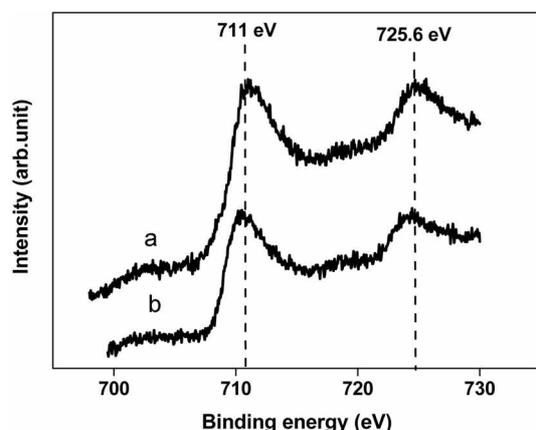


Figure 7. Fe (2p) region of the XPS spectra of (a) Fe₃O₄ nanoparticle with no surfactant, and (b) Fe₃O₄ nanoparticle with PCDA on the surface.

Table 1. XPS Data of the nanoparticles

Sample	Binding Energy, eV	Assignments	
Fe ₃ O ₄ without capping	Fe (2p)	725.60	Fe 2p _{1/2}
		711.00	Fe 2p _{3/2}
	O (1s)	530.30	O of Fe ₃ O ₄
Physical mixture of PCDA and Fe ₃ O ₄	C (1s)	284.55	Aliphatic carbon
		289.20	C of -COOH
	Fe (2p)	725.60	Fe 2p _{1/2}
		711.00	Fe 2p _{3/2}
	O (1s)	530.30	O of Fe ₃ O ₄
	531.92	O of -COOH	
Fe ₃ O ₄ capped with PCDA	C (1s)	284.55	Aliphatic carbon
		288.19	C of -COO ⁻
	Fe (2p)	725.60	Fe 2p _{1/2}
		711.00	Fe 2p _{3/2}
	O (1s)	529.59	O of Fe ₃ O ₄
	531.53	O of -COO ⁻	

compared to the Fe₃O₄ nanoparticles. A peak was observed at 1630 cm⁻¹, which is characteristic of the C=O stretching of the carboxylate group attached to the nanoparticle surface. This C=O stretching peak is different in frequency with the peak obtained at 1693 cm⁻¹ for carboxylic group of pure PCDA (Figure 8). The FT-IR spectra thus give further evidence for the attachment of PCDA to the nanoparticles through the chemisorption of carboxylate group on the surface of nanoparticles.

Formation of polydiacetylene on nanoparticles. The UV-Visible spectra of the nanoparticle systems are given in Figure 9. Optical absorption in polydiacetylene occurs *via* a π -to- π^* absorption within the linear π conjugated polymer network. Typically, the polydiacetylene assembly has two spectroscopically distinct phases in the monolayers on the flat solid substrate; called as blue and the red forms.^{23,24} These forms have absorption at 650 and 540 nm, respectively. Absorption maxima of the polymerized forms depend on extends of conjugation after the polymerization. The more the conjugation length, the higher will be the absorption wavelength. In this work, the size of the nanoparticles is

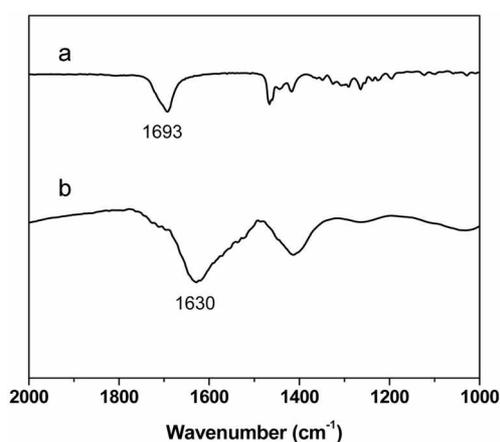


Figure 8. FT-IR spectrum of (a) PCDA, and (b) Fe₃O₄ nanoparticle with PCDA on the surface.

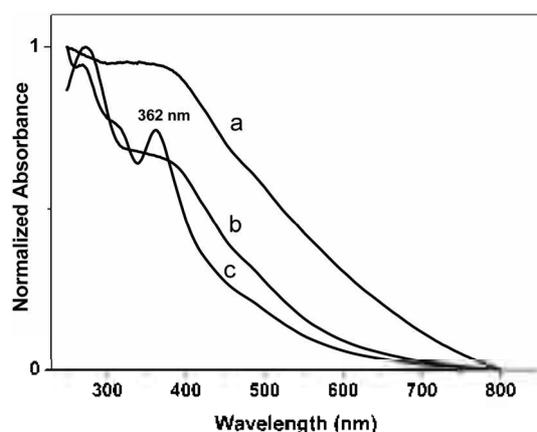


Figure 9. Absorption spectra of (a) Fe_3O_4 nanoparticle without surfactant, (b) Fe_3O_4 nanoparticle capped with PCDA, and (c) Fe_3O_4 nanoparticles containing poly diacetylene on the surface.

less than 12 nm and the conjugation length of polydiacetylene network is expected to be much shorter when compared to systems like monolayers. In the UV spectra, we could notice a new peak arising after the irradiation of a dispersion of diacetylene coated nanoparticle with UV light of 254 nm. The appearance of a new peak at 362 nm is assumed to be corresponding to the presence of polymerized diacetylene on the surface of nanoparticles. This peak is assumed to be arising from the absorption property of the conjugated polymer formed on the nanoparticles after irradiation with UV light. Furthermore, the absorption property of the magnetite nanoparticle having polydiacetylene coating on the surface remains unchanged for several weeks of storage. The stability of polydiacetylene monolayer on the nanoparticle surface is thus implied from this fact.

Superparamagnetic behavior of nanoparticles. Magnetic properties of the nanoparticle system were investigated with a Superconductor Quantum Interference Device (SQUID). It has been known that the condition for superparamagnetic behavior of a nanocrystallite is that the anisotropy energy is approximately equal to the thermal agitation energy.¹¹ When the size of an ultra fine magnetic crystallite is below a critical value, it has only one magnetic domain and shows no magnetism in zero magnetic fields. This type of behavior is called superparamagnetism. The estimated critical size for Fe_3O_4 nanoparticles is 25 nm, below which it will be superparamagnetic.²⁵ The size (~10 nm) of nanoparticles prepared in our experiment falls below this size limit and the superparamagnetic nature is expected. The M - H measurements were done at room temperature. Magnetic field swept back and forth between 50 and -50 kOe. The magnetic hysteresis loop obtained for the samples are shown in Figure 10. As shown in the figure, the characteristic features of superparamagnetic behavior are exhibited by the samples. Almost immeasurable coercivity was shown for Fe_3O_4 nanoparticles with and without polydiacetylene coating. This gives evidence for the superparamagnetic nature of the samples.

The saturation magnetization for nanoparticles without

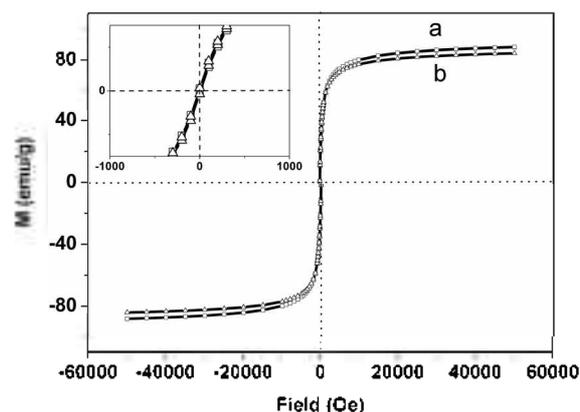


Figure 10. Magnetic hysteresis curves of (a) Fe_3O_4 , and (b) polydiacetylene coated Fe_3O_4 measured at room temperature.

coating was detected to be 88.13 emu/g and that for polydiacetylene-coated nanoparticles was found to be 84.13 emu/g. The decrease in saturation magnetization for the coated system is due to the decrease in mass of the magnetic material present in the sample. Even when the magnetic properties are measured after two weeks of preparation of the polydiacetylene capped nanoparticles, the magnetic behavior remained the same. This gives indication to the stability imparted by the polydiacetylene coating to the nanoparticles and rules out the possibility of agglomeration or ripening and the consequent change in size.

Conclusions

Crystalline Fe_3O_4 nanoparticles were prepared by chemical coprecipitation method. An amphiphilic diacetylene compound is self-assembled and photopolymerized on the surface of nanoparticles. Nanoparticles were characterized by powder XRD, XPS, FT-IR and UV-Visible spectroscopic methods as well as TEM and SQUID measurements. Polydiacetylene coated nanoparticles showed good stability, superparamagnetic behavior and exhibited high saturation magnetization and susceptibility to external magnetic field. The process of photopolymerization of diacetylenes is used to impart stability to superparamagnetic magnetite nanoparticles for the first time. Furthermore, self-assembly and photopolymerization of bolaamphiphilic diacetylene molecules on magnetic nanoparticles can give stable nanoparticle systems which will be greatly useful in many applications.

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