

Dipolar Chains and 2D Aligned Stripes of Polymer-Coated Magnetic Iron Colloid

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ABSTRACT: Studies on the self-assembly of core-shell magnetic nanospheres under or without an external magnetic field are the subject of intense research. It is believed that after being coated by organic molecules, the magnetic nanoparticles can still have chance to form chain-like structure driven by the dipole-dipole interactions while the coated shell minimizes the effect of Van der Waals attractions. However, still there are no direct experimental observations for polymer-modified magnetic colloids sized hundreds of nanometers. In this article, PEG- and PSt-coated Fe_2O_3 nanospheres were synthesized and their self-assembly behaviors were studied. MFM and TEM measurements

reveal that the prepared spheres owning a core-shell structure. Under zero magnetic field, a direct observation of chain-like structure was achieved for the PEG-coated magnetic colloids. For the PSt-modified magnetic spheres, there formed a 2D aligned stripes pattern at the surface of mica when the suspending of sample was dried under an external magnetic field. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4211–4215, 2006

Key words: magnetic; polymer; core-shell; nanoparticle; self-assembly; AFM; TEM

INTRODUCTION

The self-assembly of soft materials, especially magnetic colloids, is a key issue not only for practical applications, but also for the fundamental insight in dipolar fluids.¹ In 1970, de Gennes and Pincus predicted that colloidal particles with an electric or magnetic dipole moment would self-assemble into flexible chains.² Though some simulation predict the presence of chain-like structures, no direct evidence of the existence of linear chains of dipoles in experimental has been reported in the absence of magnetic field before 2003.^{3–5} Philipse and coworkers and Safran reported the first direct experimental observation, using cryogenic electron microscopy, of chain-like structures in dispersions of magnetic particles in organic solvent.^{6,7} They found that the coated thick surfactant layer could efficiently minimize the effect of Van der Waals attraction, which made the dipole-dipole interactions prominent. The dipole-dipole interactions can be tuned by the particle size variation,⁸ and the chain-like structures only formed when the particle's size is

bigger enough. In their studies, the size of particles is only several nanometers. Generally, the weak dipole-dipole interactions between the magnetite particles are not sufficient to result in the chain formation. Additionally, due to the Van der Waals interactions, when the contact distance of nanoparticles is short enough, clusters form during the evaporation process. These clusters usually exhibit larger dipole-dipole moments that can result in the formation of chain-structures.⁹ Is it possible to directly form chain-like structure for polymer-coated magnetic colloids with much bigger size? Theoretically, the much bigger magnetic colloids may also have chance to form chain-like structure in zero field. However, until now, still there are no experimental results to support this.

Fabrication of core-shell magnetic colloid sized tens to hundreds of nanometers is also currently of immense interest for various applications in materials science and medicine, for it combines the properties of the individual magnetic particles and the nonmagnetic sphere dispersions.^{10–12} Several studies reported that those kinds of magnetic colloid could form 1D chain-like structures under an external magnetic field.^{13–16} The long-range self-assembly of magnetic colloids is a complex process that involves numerous competing effects, including the coupling of each particle's dipole moment to the applied field, magnetic dipole-dipole interactions, electronic polarization interactions, thermal kinetic, etc.¹⁷ Monte Carlo simulations show that the core-shell magnetic particles also have a chance to

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form 2D stripe structures under an appropriate density and temperature.¹⁸ However, still there are no direct observations experimentally. For this study, we synthesized PEG-coated and polystyrene-coated magnetic iron colloids in size about 100–200 nm, respectively. A dipole–dipole induced chain-like structure was found for PEG-coated magnetic colloid in zero magnetic field, and a 2D aligned stripes structure was found for PS-coated magnetic colloid under an external field.

EXPERIMENTAL

Fe₂O₃-PEG magnetic colloid

The colloid was synthesized by chemical precipitation of iron(III) in sodium hydroxide with oxidation by hydrogen peroxide. Briefly, 2.085 g FeSO₄·7H₂O was dissolved in 25.0 mL ultrapurity water (Millipore-Q) with two drops of 2.0 mol/L H₂SO₄. Then, 0.66 mL of 30% H₂O₂ was added to oxidize Fe(II) into Fe(III). PEG was mixed with the ionic solution and 4.0 mol/L NaOH solution was added to adjust the pH to 10. Then, the mixture solution was heated at 60°C for 6 h.

Fe₂O₃-PEG-PSt magnetic colloid

The PEG-protected magnetic fluid was centrifuged and cleaned by ultrapurity water several times to remove the uncoated PEG polymer and other chemicals. Then, the solid was suspended by water and ethanol, and then 0.1 g distilled styrene was added. The emulsion polymerization of styrene was carried out under the assistant of ultrasound at power of 300 W.¹⁹ After the reaction, the product was separated from the system by an external magnetic field, and the homopolymers of styrene was separated by decantation. Then, it was suspended in methanol by ultrasound and cleaned several times. Finally, the product was deposited by centrifugation and was dried at 50°C in vacuum.

Sample characteristics

Two kinds of samples were prepared. For the first one, suspension of Fe₂O₃-PEG was moved by a micropipette, and deposited on new cleaved mica in free of an external magnetic field for self-assembly. For the second one, suspension of Fe₂O₃-PEG-PSt was deposited on new cleaved mica and let the solvent dried under an external magnetic field with 0.165 T.

A Nanoscope IIIa (Digital instruments, Santa Barbara, CA) was used for AFM and MFM measurements. With the magnetic clamps, the samples were stuck with the double-sided tape to the stage. Soft tapping conditions were used to avoid particle displacements or height artifacts. Lift mode in tapping

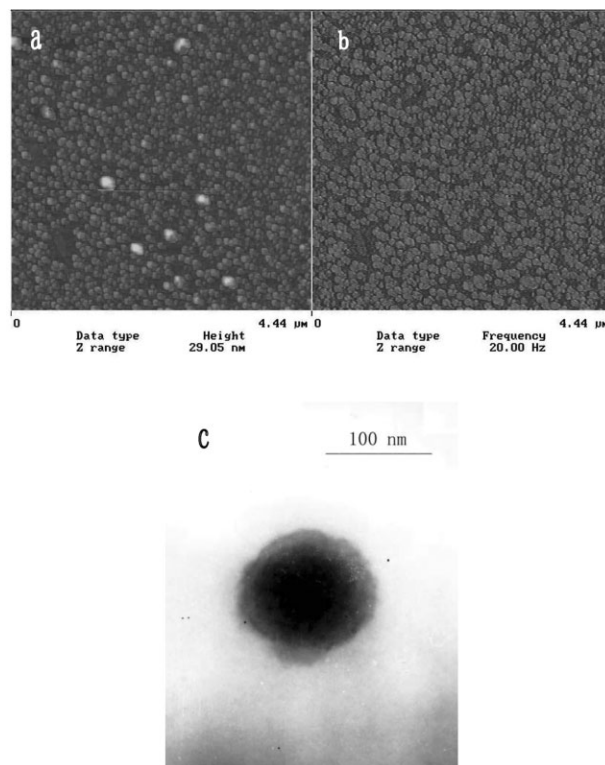


Figure 1 AFM topography (a) and MFM frequency (b) images of Fe₂O₃-PEG spheres. (c) TEM image of one Fe₂O₃-PEG sphere with a core–shell structure.

was used to record the magnetic signal by means of the phase-detection or frequency-detection mode. A high magnetic moment MFM tip was used. Images were recorded at slow scan rates of 0.5–1.0 Hz. The hysteresis loop of the sample was measured by a VSM (BHV-55, Riken denshi). The samples were also analyzed by FTIR (VECTOR-2, Bruker) and XRD (M18X, MAC Sci.) to identify its chemical information. XRD data were collected using Co K α radiation ($\lambda = 1.78892 \text{ \AA}$). For TEM measurement, the suspension of magnetic particles was directly deposited on a TEM grid and dried under vacuum. TEM image was taken with a Hitachi H-800 TEM.

RESULTS AND DISCUSSION

First, we synthesized the PEG protected magnetic iron colloids. After preparation, the colloids were immediately deposited onto new cleaved mica and dried in air at room temperature for AFM/MFM measurements. Figures 1(a) and 1(b) show the AFM height and MFM frequency images of Fe₂O₃-PEG colloid, respectively. Some spheres appear, and the size of the spheres is about 60–140 nm (most of them are about 60 nm). MFM image indicates the spheres owing magnetic properties. Figure 1(c) shows the TEM image of one sphere, a clear core–shell structure can be found.

The dark core with radius about 40 nm is the magnetic iron segments while the PEG shell with thickness of about 10 nm. It is believed that the shell would reduce the effect of Van der Waals attraction between magnetic colloids. Theoretically, the magnetic dipole moment of a hard core of radius r and bulk saturation magnetization M_s is $\mu = 4\pi r^3 M_s / 3$. The dipole-dipole interaction between two magnetic spheres at contact can be described as μ^2 / σ^3 , where σ is the effective hard-sphere diameter, consisting of the core diameter r and the thickness of the polymer shell.^{6,20} So a bigger core with a thinner shell should exhibit a stronger dipole-dipole interaction. Experimentally, the magnetic colloid solution was stored at room temperature for 72 h, and then it was deposited onto mica. AFM/MFM studies show that the PEG-coated magnetic iron spheres formed a chain-like structure under zero magnetic field, as shown in Figure 2. It can be said that the big polymer-coated magnetic iron colloids could also form chain-like structure by the dipole-dipole self-assembly.

To obtain more stable core-shell magnetic colloids, polymerization of monomer in the presence of magnetite had been explored recently.²¹ In this study, polystyrene (PSt) coated iron was synthesized by aqueous emulsion polymerization of styrene in the presence of Fe₂O₃-PEG fluid under the assistant of ultrasound. Figures 3(a) and 3(b) show the AFM and MFM images of the as-prepared colloids, and Figure 3(c) shows the TEM image. It can be clearly seen that the as-formed particles are in the size from 150 to 200 nm, while a fine core-shell structure was observed by TEM. The shell is obviously thicker than that of PEG-coated spheres, indicating some styrene polymerized

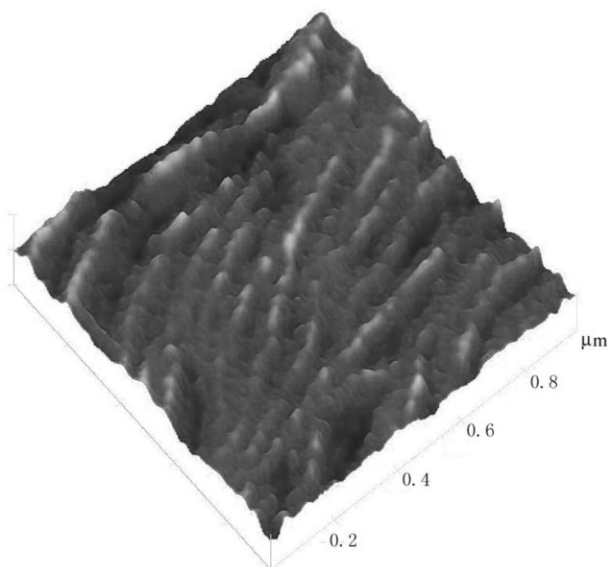


Figure 2 AFM images of the chain-like structures formed by PEG-coated magnetic spheres through self-assembly in zero field.

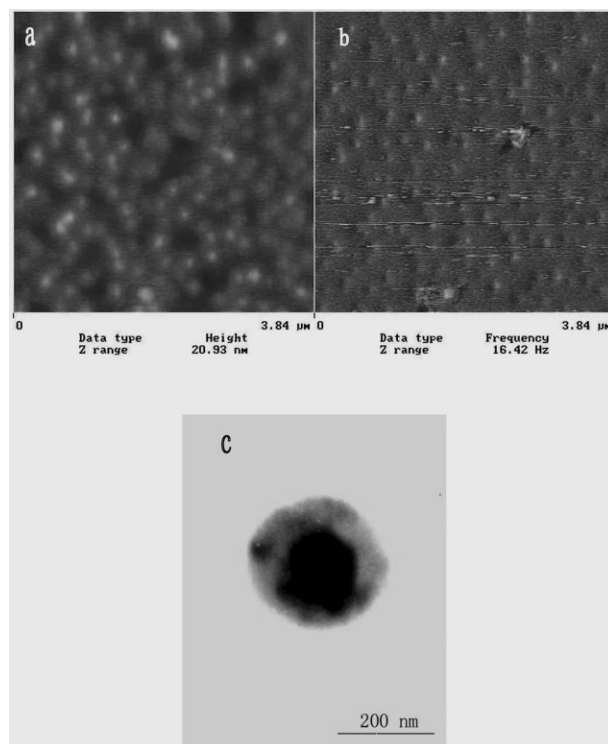


Figure 3 AFM topography (a) and MFM frequency (b) images of Fe₂O₃-PEG-PSt spheres. (c) TEM image of one sphere with a core-shell structure.

outside the sphere. For the thickness of the shell, the dipole-dipole interaction of this kind of spheres should be smaller because of the larger distance, and no chain-like self-assembly structure be found in zero magnetic field. However, if the solution was put into a parallel external magnetic field during the solvent evaporation, there formed some regular 2D stripes, as shown in Figure 4. The pattern can be formed in large scale as shown in Figures 4(a) and 4(b), both AFM height (a) and phase (b) images in lift-mode were recorded. Figures 4(c) and 4(d) are the zoom-in scanning AFM/MFM images of the same sample. It can be found that the width of the stripe is about 150 nm, a little smaller than they exist in single sphere, indicating an overlap of the shells between adjacent spheres. For further insight the magnetic property of the pattern structure, the MFM frequency image was also recorded. Figure 5(b) shows the frequency image, while Figure 5(a) shows the height image. In MFM frequency image, the stripes pattern can also be found. However, some chains show bright while some show dark, indicating the up or down of the magnetization.

The chemical composition of the samples was measured by FTIR spectra. Figure 6 shows the FTIR of coating polymers and as-prepared core-shell magnetic spheres. (PEG (a), PSt (b), Fe₂O₃-PEG (c), and Fe₂O₃-PEG-PSt (d)). The absorbency at 3440.4, 1467.6, 1110.8, and 842.7 cm⁻¹ are the characteristic peaks of

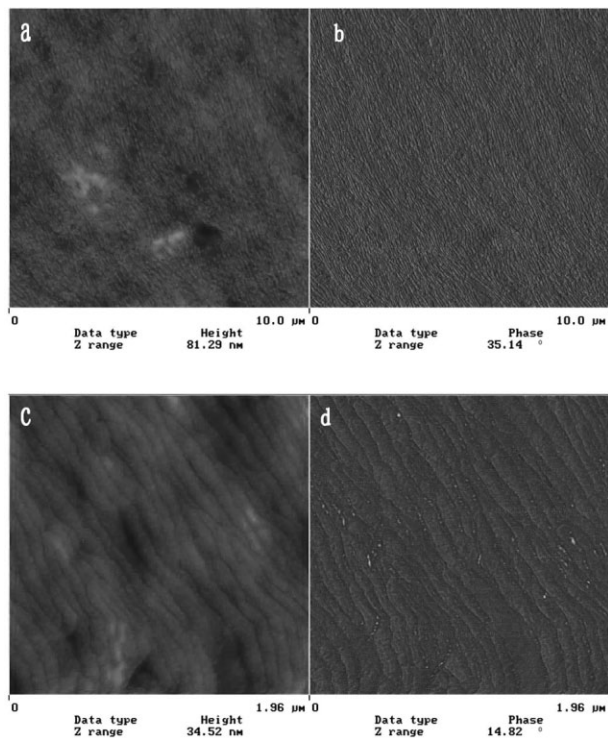


Figure 4 AFM topography (a) and MFM phase (b) images of the 2D stripes pattern formed by assembly of Fe_2O_3 -PEG-PSt spheres under an external magnetic field of 0.165 T. (c) and (d) are zoom-in scanning image of the same sample.

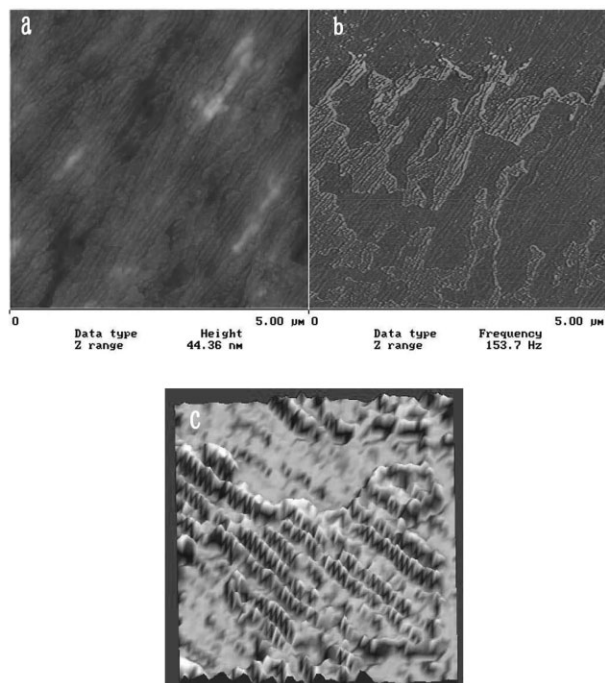


Figure 5 AFM topography (a) and MFM frequency (b) images of the 2D stripes pattern formed by assembly of Fe_2O_3 -PEG-PSt spheres under an external magnetic field of 0.165 T. (c) is an enlarged image of (b), the chain consists of single spheres.

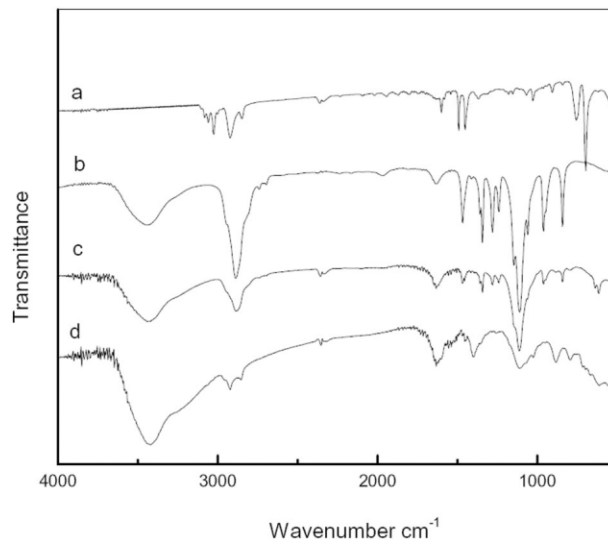


Figure 6 FTIR spectra of PSt (a), PEG (b), Fe_2O_3 -PEG (c), and Fe_2O_3 -PEG-PSt (d).

—OH group of PEG, and 2888.8, 1358.6–1241.9, and 962.3 cm^{-1} corresponds to —CH group of PEG. The absorbency at 622, 697, and 766 cm^{-1} are the characteristic peaks of phenyl of polystyrene. So from Figures 6(c) and 6(d), the prepared magnetic spheres are Fe_2O_3 -PEG and Fe_2O_3 -PEG-PSt, respectively.

Figure 7 shows the XRD pattern of the Fe_2O_3 -PEG-PSt spheres. Both the characteristic diffractive peaks of polymer and Fe_2O_3 appear. The peaks correspond to the (220), (311), (400), (422), (511), and (440) of Fe_2O_3 (standard ICDD PDF Card No. 39-1346).^{22,23} Peak at about 20° corresponds to the characteristic of PS crystalline, and at about 27° corresponds to the characteristic of PEG.²⁴ XRD pattern also reveal that the formed magnetic colloid consist of both polymer and iron magnetite.

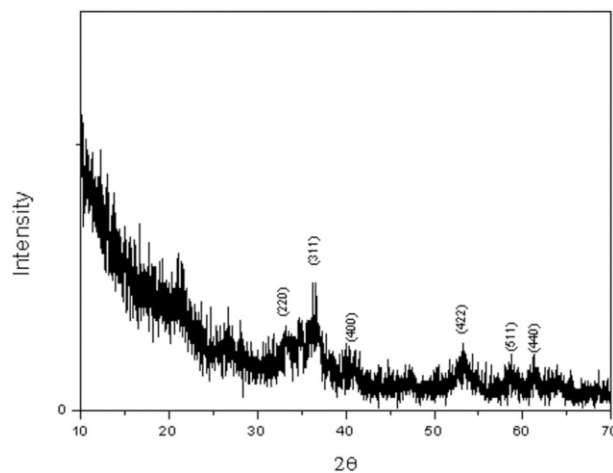


Figure 7 XRD pattern of Fe_2O_3 -PEG-PSt spheres.

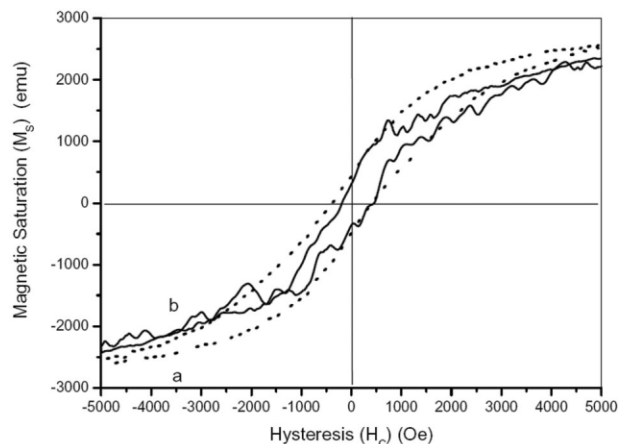


Figure 8 Hysteresis loops of Fe_2O_3 -PEG (a) and Fe_2O_3 -PEG-PSt (b) spheres at room temperature.

Figure 8 shows the hysteresis loops of both Fe_2O_3 -PEG (a) and Fe_2O_3 -PEG-PSt (b) spheres measured at room temperature, and it indicates that the saturation magnetization of Fe_2O_3 -PEG-PSt spheres is a little bigger than that of Fe_2O_3 -PEG spheres. The coercivity of Fe_2O_3 -PEG is of 470 Oe with a symmetrical hysteresis loop, and of Fe_2O_3 -PEG-PSt the hysteresis loop is asymmetry. The results show that both polymer-coated spheres are ferromagnetic.

CONCLUSIONS

In conclusion, polymer-coated magnetic iron colloids in size of 100–200 nm were synthesized by precipitation or ultrasonic emulsion polymerization methods. AFM and TEM studies reveal the core-shell structure of the prepared spheres, while MFM and hysteresis measurements reveal their magnetic properties. It was found experimentally for the first time that the PEG-coated magnetic colloid can form chain-like self-assembly structure by only the dipole-dipole interactions in free of an external magnetic field. Under an

external magnetic field, the polystyrene-coated magnetic colloid forms a 2D aligned stripes pattern.

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