

## Short Communication

## Fabrication of one-dimensional $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$ nanochains by magnetic-field-induced precipitation polymerization

Mingliang Ma, Qiuyu Zhang\*, Jinbo Dou, Hepeng Zhang, Dezhong Yin, Wangchang Geng, Yanyang Zhou

Key Laboratory of Applied Physics and Chemistry in Space of Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710129, China

## ARTICLE INFO

## Article history:

Received 11 November 2011

Accepted 9 February 2012

Available online xxx

## Keywords:

One-dimensional nanochains

Self-assembly

Precipitation polymerization

$\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$

## ABSTRACT

One-dimensional (1D) magnetic  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains have been successfully synthesized by magnetic-field-induced precipitation polymerization using  $\text{Fe}_3\text{O}_4$  as building blocks and  $\text{P}(\text{GMA-DVB})$  as linker. The  $\text{Fe}_3\text{O}_4$  microspheres without surface modification can be arranged with the direction of the external magnetic field in a line via the dipolar interaction between  $\text{Fe}_3\text{O}_4$  microspheres and linked permanently via  $\text{P}(\text{GMA-DVB})$  coating during precipitation polymerization. The length of peapod-like nanochains can be controlled by magnetic field intensity, and the thickness of polymer shell can be tuned by the amount of monomers. Magnetic measurement revealed that these 1D peapod-like nanochains showed highly magnetic sensitivity. In the presence of magnetic field, 1D magnetic  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains can be oriented and aligned along the direction of external magnetic field.

© 2012 Elsevier Inc. All rights reserved.

## 1. Introduction

Recently, the organization of magnetic nanoparticles into 1D ordered functional structures has stimulated great interest due to their intriguing collective properties and potential applications including high-density data storage, magnetic resonance imaging, magnetic sensor, drug delivery, and other biomedical applications [1–4]. To obtain 1D magnetic nanostructures, the self-assembly of magnetic nanoparticles is projected to be an effective approach [5–8]. 1D nanochains that are difficult to achieve by other means can be prepared through this method. Until now, self-assembly method mainly included dipole-directed self-assembly [9], magnetic-field-induced (MFI) self-assembly [10–12], and templated self-assembly [13–15]. However, due to the weak or negligible anisotropic dipolar interaction between the magnetic building blocks, these ordered structures of superparamagnetic nanoparticles can hardly be maintained after the external magnetic field is removed [16].

To obtain permanent connection of one-dimensional structure, several methods have been developed through the interpenetration and bridging of polymers [17–23]. Keng et al. prepared polystyrene-coated cobalt oxide nanowires via the colloidal polymerization of polymer-coated ferromagnetic cobalt nanoparticles (PS-CoNPs) [22]. Xiong et al. prepared a unique legume-like structure of superparamagnetic Co nanoparticles through a simple magnetic-field-induced assembly approach with the assistance of

polyvinylpyrrolidone (PVP) [23]. However, the surface of these nanochains has few reactive functional groups, and they suffer from disintegration during rinsing with a good solvent [24]. Cross-linked polymeric shells are able to tackle this obstacle, but the synthesis of these organic cross-linkable surfactants was complicated. Therefore, the one-step preparation of 1D magnetic nanochains with cross-linked multifunctional polymeric shells remains a great challenge.

Herein, we presented a simple magnetic-field-induced precipitation polymerization to prepare 1D magnetic  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains with cross-linked multifunctional  $\text{P}(\text{GMA-DVB})$  shells. During the formation,  $\text{Fe}_3\text{O}_4$  microspheres without surface modification were arranged in a line by magnetic field and linked permanently with  $\text{P}(\text{GMA-DVB})$  shell after the removal of the external magnetic field. More interestingly, superparamagnetic  $\text{Fe}_3\text{O}_4$  microspheres in each peapod were regularly aligned in a line and periodically separated through the  $\text{P}(\text{GMA-DVB})$  layers with a visible interparticle spacing.

## 2. Materials and methods

## 2.1. Materials

Both glycidyl methacrylate (GMA) and divinylbenzene (DVB, 80% mixture of isomers) were purchased from Aldrich Chemical Co., USA, and purified using an inhibitor removal column (Aldrich) and stored at  $-5^\circ\text{C}$  prior to use. Analytical grade of 2,2-azobisisobutyronitrile (AIBN; Junsei) was used as an initiator without further purification. Acetonitrile (Aldrich Chemical Co., USA) in analytical grade was used as the polymerization medium. Ferric chloride

\* Corresponding author. Fax: +86 02988431675.

E-mail addresses: mamingliang@mail.nwpu.edu.cn (M. Ma), qyzhang1803@gmail.com (Q. Zhang).

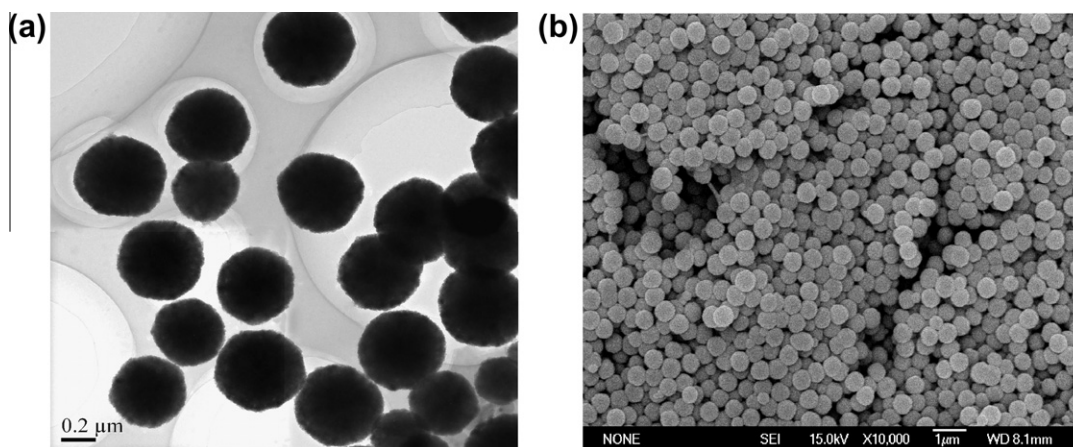


Fig. 1. TEM (a) and SEM (b) of  $\text{Fe}_3\text{O}_4$  microspheres.

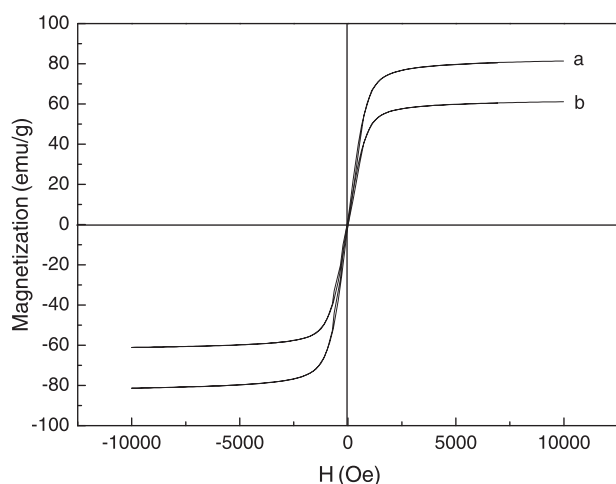


Fig. 2. The magnetization curves of  $\text{Fe}_3\text{O}_4$  prepared by solvothermal method (a) and coprecipitation method (b).

( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium acetate (NaAc), polyethylene glycol (PEG), and ethylene glycol (EG) were purchased from Shanghai Chemical Reagents Company (China) and used as received.

## 2.2. Synthesis of $\text{Fe}_3\text{O}_4$ particles

The  $\text{Fe}_3\text{O}_4$  magnetic colloidal nanoparticle clusters (CNCs) were prepared through a modified solvothermal method according to the literature with a minor modification [25]. Briefly,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (2.5 g, 5 mmol) was dissolved in EG (80 g) to form a clear solution,

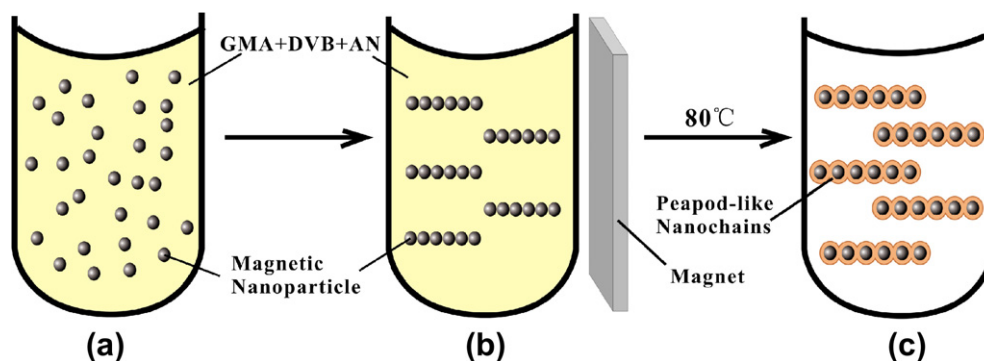
followed by the addition of NaAc (7.2 g) and PEG (2.0 g). The mixture was stirred vigorously for 1 h at 50 °C and then transferred to a teflonlined stainless-steel autoclave (100 mL capacity). The autoclave was heated to and maintained at 200 °C for 6 h and then naturally cooled to room temperature. The black magnetic CNCs were then rinsed several times with ethanol under ultrasonic conditions to effectively remove the solvent. The CNCs were separated from the supernatant by using external magnetic field during each rinsing step.

## 2.3. Synthesis and Assembly of $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA}-\text{DVB})$ peapod-like nanochains

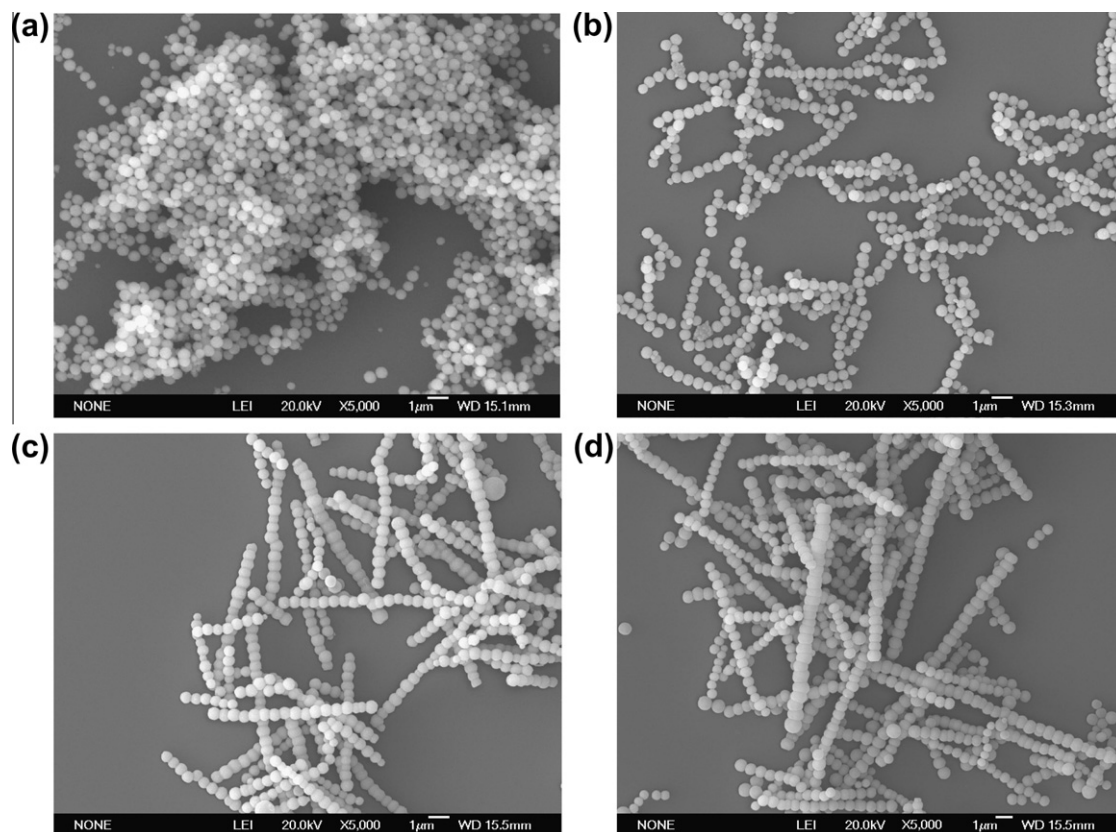
The  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA}-\text{DVB})$  peapod-like nanochains were prepared by modified precipitation polymerization without stir under magnetic field [26]. Typically, 0.050 g of  $\text{Fe}_3\text{O}_4$  microspheres was mixed with 50 g of acetonitrile solution containing 0.32 g of GMA, 0.33 g of DVB, and 0.01 g AIBN. After being degassed with nitrogen for 30 min, the solution was heated up to 80 °C. During the reaction, a plane magnet was placed to the side of the vessel with the distance of 5 cm. After 8 h of reaction, the final products were collected by magnetic separation and washed repeatedly with ethanol, and the product was dried in a vacuum oven at room temperature for 12 h.

## 2.4. Characterization

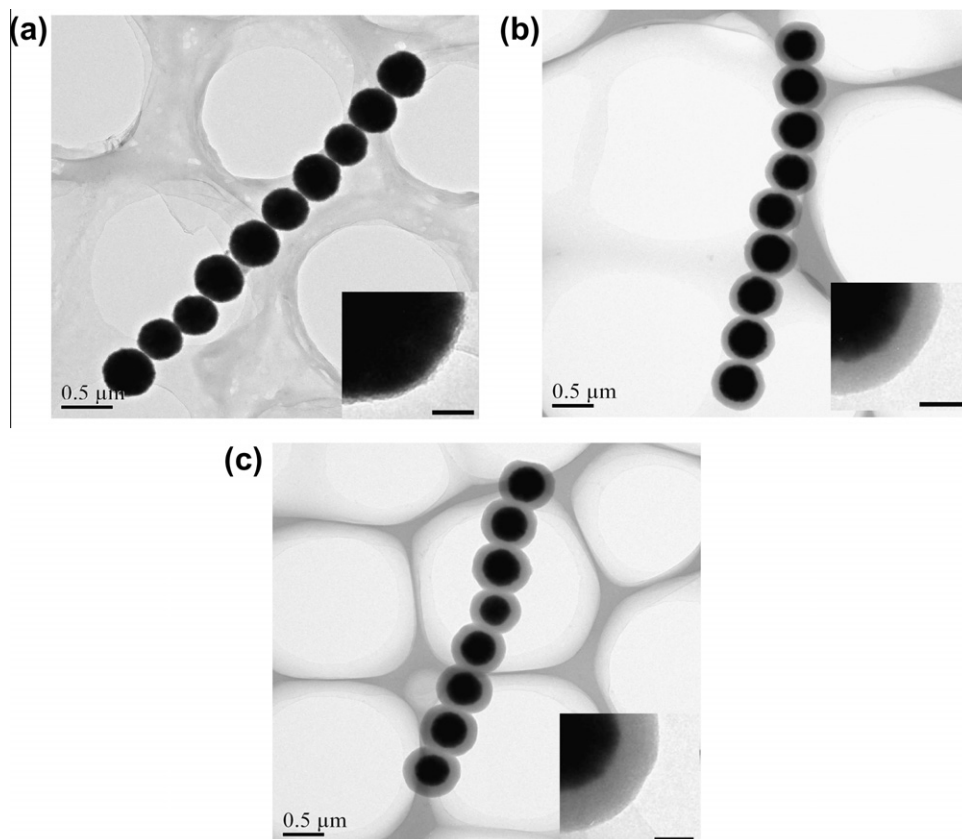
Transmission electron microscopy (TEM) images were obtained on an H-600 (Hitachi, Japan) transmission electron microscope at an accelerating voltage of 75 kV. Samples dispersed at an appropriate concentration were cast onto a carbon coated copper grid.



Scheme 1. Schematic illustration for the synthesis of 1D  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA}-\text{DVB})$  peapod-like nanochains by precipitation polymerization under external magnetic field.



**Fig. 3.** SEM images of the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains prepared with different intensity of magnetic field: (a) 0 Gs, (b) 150 Gs, (c) 400 Gs, and (d) 800 Gs.



**Fig. 4.** TEM images of the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains prepared with different amount of monomers: (a) 0.15 g, (b) 0.65 g, and (c) 1.05 g (scale of inset was 100 nm).

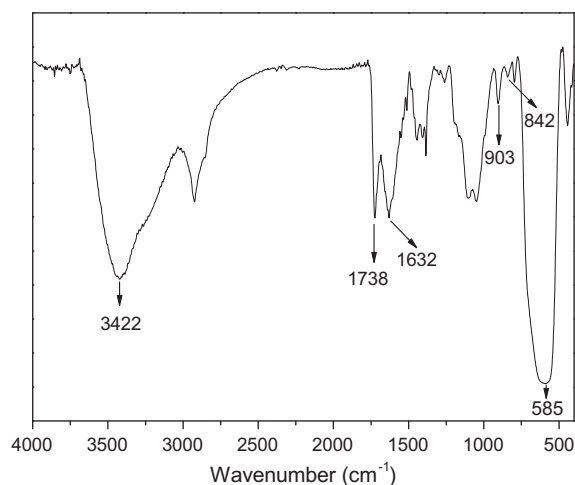


Fig. 5. FTIR spectra of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains.

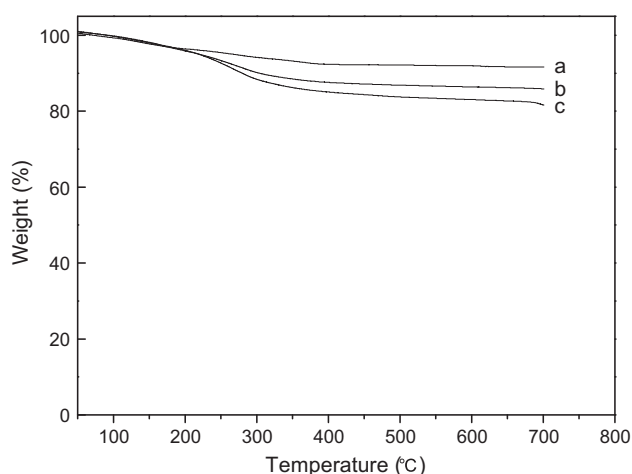


Fig. 6. The TGA curve of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains with different amounts of monomers: (a) 0.15 g, (b) 0.65 g, and (c) 1.05 g.

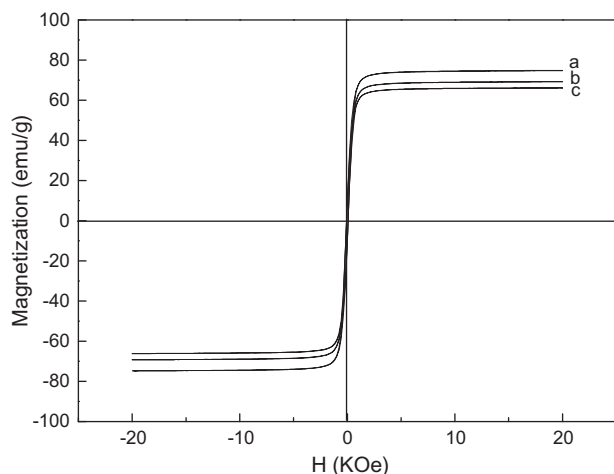


Fig. 7. Magnetization curves of  $\text{P}(\text{GMA-DVB})/\text{Fe}_3\text{O}_4$  nanochains with different amount of monomers: (a) 0.15 g, (b) 0.65 g, and (c) 1.05 g.

Scanning electron microscopy (SEM) was performed with a scanning electron microscope (SEM, JSM-6700F) at an accelerating

voltage of 20 kV. Samples dispersed at an appropriate concentration were cast onto a silicon sheet at room temperature and sputter-coated with gold.

The magnetic content of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains was determined through thermogravimetric analysis (TGA, Q50, TA instruments) in the temperature range from room temperature to 700 °C with a heating rate of 10 °C/min.

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

Fourier transform infrared spectra were determined on a TENSOR27 FTIR spectrometer (Bruker). The samples were prepared by mixing the product with KBr and pressing into a compact pellet.

Optical microscope (DMM-330C) was used to observe the orientational manipulation and assembly of peapods in an ethanol solution sandwiched between two thin cover glass slides.

### 3. Results and discussion

#### 3.1. Synthesis of $\text{Fe}_3\text{O}_4$ particles

$\text{Fe}_3\text{O}_4$  microspheres were prepared through a solvothermal method by partial reduction of  $\text{FeCl}_3$  with EG as solvent, NaAc as electrostatic stabilization, and PEG as a surfactant against particle agglomeration at 200 °C. The  $\text{Fe}_3\text{O}_4$  microspheres have a spherical shape with a rough surface and relative uniform size around 400 nm (Fig. 1). As can be seen from Fig. 2, the magnetic response of  $\text{Fe}_3\text{O}_4$  prepared by solvothermal method was higher (81 emu/g) than that by coprecipitation method (61 emu/g) [27], showing the  $\text{Fe}_3\text{O}_4$  prepared by solvothermal method was easier to be controlled by external magnetic field.

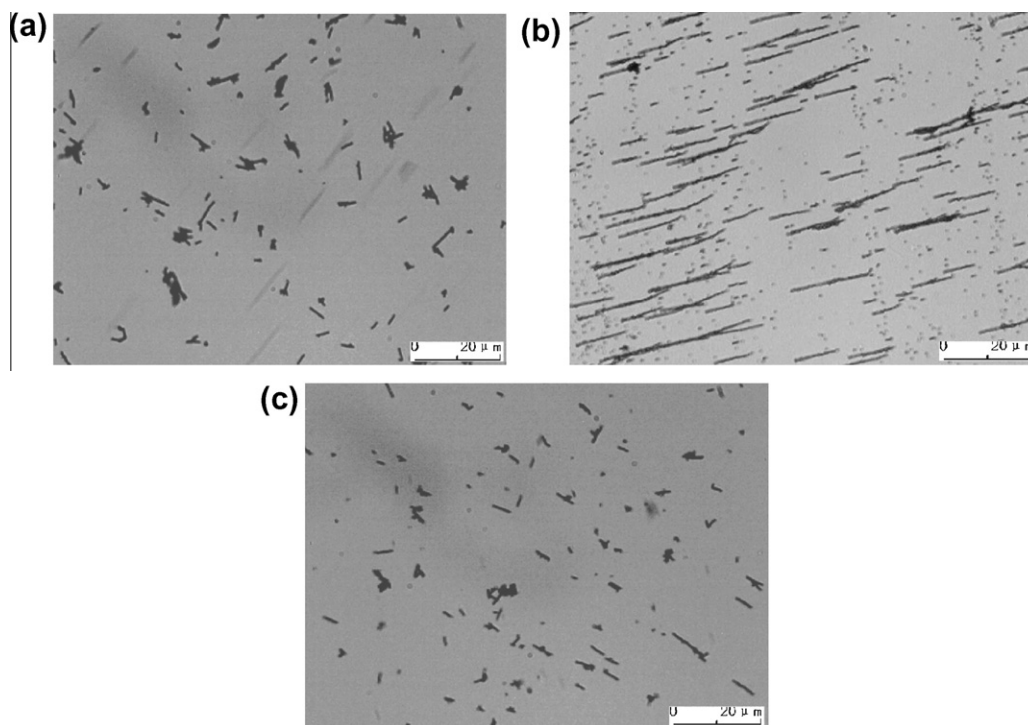
From the characterizations above, the  $\text{Fe}_3\text{O}_4$  microspheres synthesized by solvothermal method have high magnetic response and a narrow size distribution, which can meet the requirements to prepare the 1D nanochains.

#### 3.2. Synthesis and self-assembly of 1D $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$ peapod-like nanochains

The assumed formation procedure of the 1D magnetic nanochains can be schematically illustrated in Scheme 1.  $\text{Fe}_3\text{O}_4$  microspheres were dispersed in a solvent (a). After a plane magnet was employed, the  $\text{Fe}_3\text{O}_4$  microspheres slowly moved toward the side of the vessel. Because the field-induced magnetic dipolar interaction of the  $\text{Fe}_3\text{O}_4$  microspheres was stronger than Brownian motion and electrostatic repulsion, the  $\text{Fe}_3\text{O}_4$  microspheres would tend to reorient along the direction of magnetic force lines in a head-to-tail configuration (b). When the temperature increased, the precipitation polymerization of GMA and DVB would take place on the surface of the preassembled  $\text{Fe}_3\text{O}_4$  particles by hydrogen bond between hydroxyl groups of  $\text{Fe}_3\text{O}_4$  and ester groups of GMA monomer [28], and a continuous  $\text{P}(\text{GMA-DVB})$  would be formed along the surface of  $\text{Fe}_3\text{O}_4$  nanochains to get the permanently linked 1D assemblies. Thus, 1D permanently linked  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like magnetic nanochains could exist stably even after the removal of the external magnetic field (c).

SEM images of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains prepared with different intensity of magnetic fields are shown in Fig. 3. As can be seen from Fig. 3, the strength of external magnetic field has great impact on the length of magnetic nanochains in solution. As the intensity of magnetic field was 0 Gs, there was no nanochain (a). As the intensity of magnetic field was 150 Gs, the nanochains were short (b). When the strength of magnetic field increased up to 400 Gs, the length of the nanochains became longer, and many separated single nanochains were produced (c). Fur-





**Fig. 8.** Optical microscope images of 1D  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like chains dispersed in a liquid film encapsulated between two glass slides without (a and c) and with (b) external magnetic field.

ther increasing the strength of magnetic field up to 800 Gs resulted in more separated long chains being formed (d).

It can be seen from Fig. 4 that magnetic  $\text{Fe}_3\text{O}_4$  microspheres were regularly embedded in the continuous  $\text{P}(\text{GMA-DVB})$  shell along 1D nanochains. The peapod-like  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  has an almost standard chain shape with visible interparticle spacing between adjacent particles. With increasing the amount of monomers from 0.15 to 0.65 and 1.05 g, the thickness of polymer shell increased from 15 to 80 and 130 nm. In practical applications, there are several advantages for  $\text{P}(\text{GMA-DVB})$  coating by precipitation polymerization. Firstly, the as-prepared magnetic nanochains without any surface modification under external magnetic field can be directly encapsulated by a  $\text{P}(\text{GMA-DVB})$  shell. Secondly, during the precipitation polymerization, the  $\text{P}(\text{GMA-DVB})$  can fill the interparticle gap, bind the neighboring  $\text{Fe}_3\text{O}_4$  microspheres together, and eventually convert the loosely connected particle into stable 1D peapod-like nanochains. Thirdly, the coating layer of  $\text{P}(\text{GMA-DVB})$  can protect magnetic particles from corrosion in an acidic environment, and  $\text{P}(\text{GMA-DVB})$  is easily modified with various functional groups to expand its application by reactive epoxy group.

The FTIR spectra of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains are shown in Fig. 5. The strong IR absorption band at  $585\text{ cm}^{-1}$  is characteristic of the Fe-O vibrations. Strong peaks at  $1738\text{ cm}^{-1}$  and  $1632\text{ cm}^{-1}$  correspond to the C=O and C=C stretching adsorption bond, respectively. The peaks at  $842\text{ cm}^{-1}$  and  $903\text{ cm}^{-1}$  correspond to the epoxy group in GMA, and the peak at  $3422\text{ cm}^{-1}$  is attributed to hydroxyl (—OH) bond of the ring opening reaction [26]. All these results suggest that the surface of magnetic microspheres has been successfully coated with polymer shell.

The magnetic content of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains was studied by TGA, and the results are shown in Fig. 6. The weight loss was from the decomposition of the polymer component in the shell layer of the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  nanochains. The whole weight loss for these nanochains increased with the increase

in the feed of monomers to the magnetite seeds. The iron oxide content of these nanochains during the calcinations was 91, 85 and 81 wt.%, respectively. This result is consistent with the result from TEM images from Fig. 4.

The magnetic behavior of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains is of great importance for practical applications. The magnetic hysteresis loop of the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  nanochains showed the saturation magnetization ( $M_s$ ) from (a) to (c) in Fig. 7 is 74.1, 69.2 and 66.5 emu/g, respectively. The  $M_s$  of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  nanochains was lower than that of the  $\text{Fe}_3\text{O}_4$  microspheres (81.4 emu/g) due to the  $\text{P}(\text{GMA-DVB})$  shell in the peapod-like nanochains. Thus, an easy and efficient way to separate the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  nanochains from a suspension system is to use an external magnetic field [29].

The magnetic response of the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  nanochains on the external magnetic field can be clearly observed through optical microscopy (Fig. 8). A magnet was induced to control the orientation of the samples conveniently. Without an external magnetic field, the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  peapod-like nanochains were well dispersed in ethanol, showing various chain lengths due to their random orientations (a). The chains appeared significantly longer than the individual peapods, suggesting additional chaining of peapods due to the induced magnetic interparticle attraction (b). Upon removal of the magnet, all of the long chains were disassembled into individual peapods with random orientations again (c).

#### 4. Conclusions

One-dimensional peapod-like nanochains of superparamagnetic  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-DVB})$  nanochains have been prepared by magnetic-field-induced precipitation polymerization. The magnetic field was employed to arrange  $\text{Fe}_3\text{O}_4$  microspheres along the lines of magnetic force in a head-to-tail configuration, and  $\text{P}(\text{GMA-DVB})$  was employed to link the ordered 1D nanochains permanently

through the P(GMA–DVB) layers. The studies showed that this new method was suitable to get the permanently linked 1D peapod-like nanochains possessing high magnetic saturation and high magnetic content. This unique 1D peapod-like nanochains consisting of Fe<sub>3</sub>O<sub>4</sub> microspheres would provide a new model system for the study of magnetization properties of 1D ordered magnetic nanochains.

### Acknowledgments

We greatly appreciate the support of the National Natural Science Foundation of China (51173146), National Basic Research Program of China (2010CB635111), Basic Research Foundation of Northwestern Polytechnical University (G9KY1020 and JC201019), and the key programs of international technology cooperation of Shaanxi province (2011KW-12).

### References

- [1] M.R. Gao, S.R. Zhang, J. Jiang, Y.R. Zheng, D.Q. Tao, S.H. Yu, *J. Mater. Chem.* 21 (2011) 16888.
- [2] Y. Xu, J. Yuan, B. Fang, M. Drechsler, M. Müllner, S. Bolisetty, M. Ballauff, A.H.E. Müller, *Adv. Funct. Mater.* 20 (2010) 4182.
- [3] P.Y. Keng, B.Y. Kim, I. Shim, R. Sahoo, P.E. Veneman, N.R. Armstrong, H. Yoo, J.E. Pemberton, M.M. Bull, J.J. Griebel, E.L. Ratcliff, K.G. Nebesny, J. Pyun, *ACS Nano* 3 (2009) 3143.
- [4] S.V.N.T. Kuchibhatla, A.S. Karakoti, D. Bera, S. Seal, *Prog. Mater. Sci.* 52 (2007) 699.
- [5] Q. Dai, D. Berman, K. Virwani, J. Frommer, P.O. Jubert, M. Lam, T. Topuria, W. Imano, A. Nelson, *Nano Lett.* 10 (2010) 3216.
- [6] T. Harada, T.A. Hatton, *Langmuir* 25 (2009) 6407.
- [7] S. Srivastava, N.A. Kotov, *Soft Matter* 5 (2009) 1146.
- [8] S. Singamaneni, V.N. Bliznyuk, C. Binek, E.Y. Tsybal, *J. Mater. Chem.* 21 (2011) 16819.
- [9] F. Zhang, C.C. Wang, *J. Phys. Chem. C* 112 (2008) 15151.
- [10] Y. Sahoo, M. Cheon, S. Wang, H.E. Luo, P. Furlani, P.N. Prasad, *J. Phys. Chem. B* 108 (2004) 3380.
- [11] J. Gong, S. Li, D. Zhang, X. Zhang, C. Liu, Z. Tong, *Chem. Commun.* 46 (2010) 3514.
- [12] J. Jiménez, R. Sheparovych, M. Pita, A.N. García, E. Dominguez, S. Minko, E. Katz, *J. Phys. Chem. C* 112 (2008) 7337.
- [13] H.W. Liang, S. Liu, S.H. Yu, *Adv. Mater.* 22 (2010) 3925.
- [14] D. Zhang, Y. Wang, *Mater. Sci. Eng. B* 134 (2006) 9.
- [15] M. Liu, J. Lagdani, H. Imrane, C. Pettiford, J. Lou, S. Yoon, V.G. Harris, C. Vittoria, N.X. Sun, *Appl. Phys. Lett.* 90 (2007) 103105.
- [16] G. Cheng, D. Romero, G.T. Fraser, A.R.H. Walker, *Langmuir* 21 (2005) 12055.
- [17] P.Y. Keng, I. Shim, B.D. Korth, J.F. Douglas, J. Pyun, *ACS Nano* 1 (2007) 279.
- [18] J. Yuan, Y. Xu, A.H.E. Müller, *Chem. Soc. Rev.* 40 (2011) 640.
- [19] C. Goubault, F.L. Calderon, J.L. Viovy, J. Bibette, *Langmuir* 21 (2005) 3725.
- [20] B.D. Korth, P. Keng, I. Shim, S.E. Bowles, C. Tang, T. Kowalewski, K.W. Nebesny, J. Pyun, *J. Am. Chem. Soc.* 128 (2006) 6562.
- [21] Q. Yan, A. Purkayastha, D. Gandhi, H. Li, T. Kim, G. Ramanath, *Adv. Mater.* 19 (2007) 3286.
- [22] P.Y. Keng, B.Y. Kim, I.B. Shim, R. Sahoo, P.E. Veneman, N.R. Armstrong, H. Yoo, J.E. Pemberton, M.M. Bull, J.J. Griebel, E.L. Ratcliff, K.G. Nebesny, J. Pyun, *ACS Nano* 3 (2009) 3143.
- [23] Y. Xiong, Q. Chen, N. Tao, J. Ye, Y. Tang, J. Feng, X. Gu, *Nanotechnology* 18 (2007) 345301.
- [24] J.F. Zhou, L.J. Meng, X.L. Feng, X.K. Zhang, Q.H. Lu, *Angew. Chem. Int. Ed.* 49 (2010) 8476.
- [25] H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, *Angew. Chem. Int. Ed.* 44 (2005) 2782.
- [26] J.M. Jin, J.M. Lee, M.H. Ha, K. Lee, S. Choe, *Polymer* 48 (2007) 3107.
- [27] F.G. Guo, Q.Y. Zhang, B.L. Zhang, H.P. Zhang, L. Zhang, *Polymer* 50 (2009) 887.
- [28] B. Liu, W. Zhang, F. Yang, H. Feng, X. Yang, *J. Phys. Chem. C* 115 (2011) 15875.
- [29] Z. Zhang, H. Duan, S. Li, Y. Lin, *Langmuir* 26 (2010) 6676.