

This article was downloaded by:

On: 15 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

Polymer-grafted magnetite nanoparticles via a facile *in situ* solution radical polymerisation

Peng Liu^a; Wu Zhong^a; Huigang Shi^b; Desheng Xue^b

^a State Key Laboratory of Applied Organic Chemistry and Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Gansu 730000, China ^b Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Gansu 73000, China

To cite this Article Liu, Peng , Zhong, Wu , Shi, Huigang and Xue, Desheng(2009) 'Polymer-grafted magnetite nanoparticles via a facile *in situ* solution radical polymerisation', Journal of Experimental Nanoscience, 4: 4, 323 – 329

To link to this Article: DOI: 10.1080/17458080903108150

URL: <http://dx.doi.org/10.1080/17458080903108150>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polymer-grafted magnetite nanoparticles via a facile *in situ* solution radical polymerisation

Peng Liu^{a*}, Wu Zhong^a, Huigang Shi^b and Desheng Xue^b

^aState Key Laboratory of Applied Organic Chemistry and Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Tianshui South Road 222, Gansu 730000, China; ^bKey Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Gansu 73000, China

(Received 16 May 2009; final version received 10 June 2009)

Polymer-grafted magnetic nanoparticles were prepared via *in situ* solution radical polymerisation. The oleic acid modified magnetic nanoparticles were prepared by the coprecipitation of magnetic nanoparticles in the presence of oleic acid. Then they were used as comonomers in the polymerisation of styrene. The products were characterised with Fourier transform infrared spectroscopy, thermogravimetric analysis and transmission electron microscope. The effect of the OA-MNPs added on the conversion of styrene (C%), the percentage of grafting (PG%) and the magnetic properties of the polystyrene/magnetic nanoparticles composites (PS/MNPs) were also investigated.

Keywords: polystyrene; magnetite nanoparticles; oleic acid; *in situ*; radical polymerisation

1. Introduction

In the last decades, magnetic nanoparticles have been widely investigated because of their unique properties compared with bulk material and their potential applications [1,2], such as cancer therapy [3], biomedicines [4], drug delivery [5], biosensors [6], molecule detection [7], immobilisation of enzymes [8], catalysts [9], adsorbents [10], nanodielectrics [11] and so on. For many applications, the control of surface functionality is a key for controlling the nanoparticles' interaction with biological species, self-assembly dispersion and compatibility with polymeric materials [12]. The surface modification of the magnetic nanoparticles is essential for inhibiting the aggregation of nanoparticles and for controlling the inter-particle interactions and dispersibility in a solvent. Furthermore, it is known that the surface chemistry of the magnetic nanoparticles is responsible for their magnetic properties because of the exceedingly high ratio of atoms at the surface to those within the particles.

*Corresponding author. Email: pliu@lzu.edu.cn

Several strategies have been developed for the surface covalent modification of the magnetic nanoparticles with polymers via the 'grafting to' methods [13] or 'grafting from' methods. For the latter approaches, a much higher percentage of grafting could be achieved because of the smaller steric hindrance [14]. However, the polymerable groups [15] or initiating groups [16,17] should be immobilised onto the surfaces of the magnetic nanoparticles before the polymerisation. The ligand-exchange step was needed for the particle size-controlled magnetic nanoparticles with surfactants [17].

In the present work, the magnetite nanoparticles (Fe_3O_4 , MNPs) were prepared with oleic acid (OA) as surfactant and then the oleic acid modified magnetite nanoparticles (OA-MNPs) were used directly as comonomers in the solution radical polymerisation of styrene. The effect of the OA-MNPs added on the conversion of styrene (C%), the percentage of grafting (PG%), and the magnetic properties of the resulting nanocomposites (PS/MNPs) and the polystyrene-grafted magnetite nanoparticles (PS-MNPs) were investigated.

2. Experimental details

2.1. Materials and reagents

Ferric chloride hexa-hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetra-hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonium hydroxide (NH_4OH , 25% of ammonia) and oleic acid (OA) were analytical grade reagents received from Tianjin Chemical Co. (Tianjin, China) and were used without further purification (i.e. were used as received). The monomer, styrene (St, analytical reagent, Tianjin Chemicals Co. Ltd, China) was dried over CaH_2 and distilled under reduced pressure. The initiator, 2,2'-azobis (isobutyronitrile) (AIBN) (Tianjin Chemicals Ltd. Co. Tianjin, China) was recrystallised in ethanol. Toluene, tetrahydrofuran (THF) and ethanol (Tianjin Chemicals Co. Ltd, China) were all analytical grade reagents. Distilled water was used throughout.

2.2. Preparation of OA-MNPs

The OA-MNPs were prepared as following: 2.07 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.81 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 100 mL water with stirring and bubbling with N_2 . Then the mixture containing 10.0 mL ammonium hydroxide, 1.0 mL OA and 15 mL water was added dropwise into the solution after it was heated to 90°C . The reacting mixture was stirred for another 30 min after the addition. Finally, the products were collected by a magnet and were rinsed with water for three times and with ethanol for one time and dried in vacuum.

2.3. Graft polymerisation

Ten millilitres styrene, 0.15 g AIBN and certain amounts of OA-MNPs (Table 1) were combined into 10.0 mL toluene. Then the mixtures were heated to 90°C and kept for 8 h with electromagnetic stirring. The magnetic nanocomposites were separated by precipitation in ethanol. The PS-MNPs were separated from the non-grafted polystyrene (PS) by the following procedure reported previously [18]: the PS/MNPs nanocomposites were extracted with toluene using a Soxhlet apparatus until PS was not eluted in the

Table 1. The effect of the amounts of the OA-MNPs added on the polymerisation.

Samples	MNPs added (g)	C% of St	PG%	MNPs content in PS/MNPs (%)
PS/MNPs 1	0.3	49.67	29.40	5.98
PS/MNPs 2	0.6	48.15	32.40	11.54
PS/MNPs 3	0.9	46.20	14.67	16.98
PS/MNPs 4	1.2	30.22	14.38	28.92

refluxing solvent (no precipitation was observed when the toluene solution was poured into ethanol).

2.4. Characterisation

Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-7 system at a scan rate of $10^{\circ}\text{C min}^{-1}$ to 800°C in N_2 . The morphologies of the magnetic nanoparticles were characterised with a JEM-1200 EX/S transmission electron microscope (TEM). The powers were dispersed in toluene in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film. The magnetic properties were detected by vibrating sample magnetometer (VSM) (Lakeshore 7304).

The conversion of styrene (C) and the percentage of grafting (PG) were calculated according to the work reported previously [19].

3. Results and discussion

3.1. Oleic acid modified magnetite nanoparticles

The TEM image of the OA-MNPs was shown in Figure 1. It could be dispersed perfectly in toluene with the particle diameters of about 10 nm. The FT-IR spectrum reveals the nature of the bond that is formed between OA and the surface atoms. The antisymmetric and symmetric vibrations at 2920 and 2850 cm^{-1} , respectively, are clearly observed due to the aliphatic alkyl chains (Figure 2). The presence of two peaks at 1520 and 1425 cm^{-1} , attributed to the carboxylate unit vibration modes, shows that oleic acid is bound through the carboxylate anions, i.e. chemisorptions of the surfactant on the iron oxide surface. Except the chemisorbed amount, a physisorbed part was also present as evidenced by a less intense peak at 1721 cm^{-1} ($-\text{COOH}$) because the miscibility of oleic acid with ethanol is low [20,21].

The TGA curve of the OA-MNPs was shown in Figure 3. The total OA content chemisorbed and physisorbed was found to be more than 30% of the OA-MNPs. The saturation magnetisation value of the OA-MNPs is 32 emu g^{-1} at 25°C and neither remanence nor coercivity is observed (Figure 4), which indicates that the OA-MNPs are superparamagnetic.

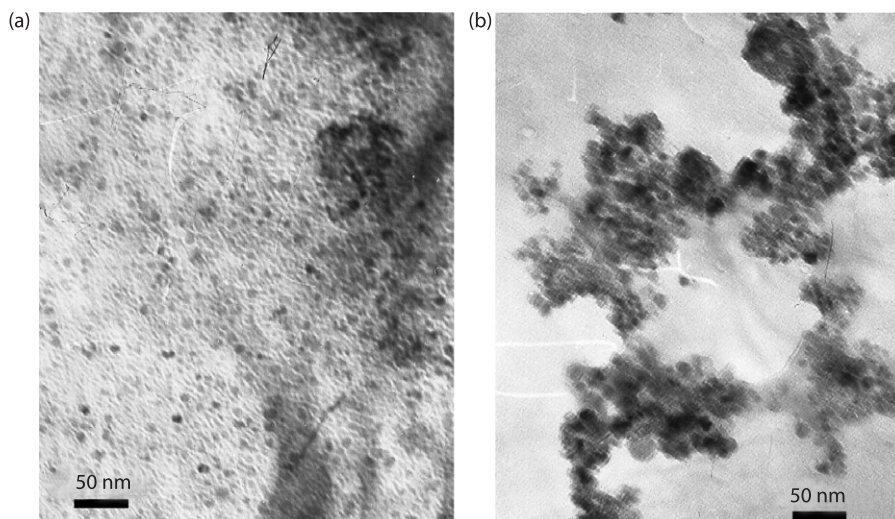


Figure 1. TEM images of OA-MNPs (left) and PS-MNPs (right).

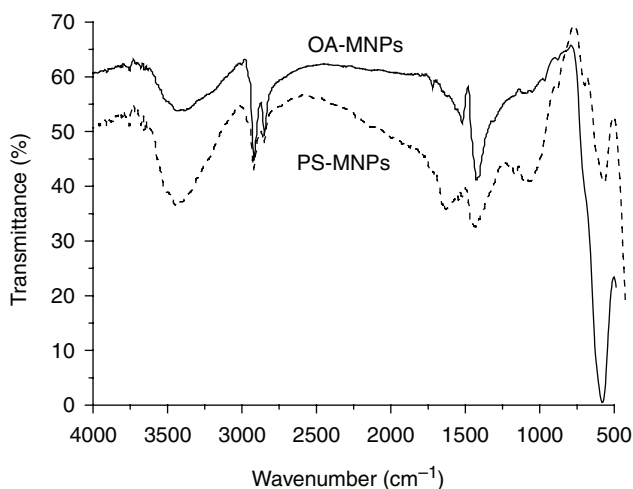


Figure 2. FT-IT spectra of OA-MNPs and PS-MNPs.

3.2. PS/MNPs

The *in situ* solution radical polymerisation of styrene was carried out with different OA-MNPs added as shown in Table 1. The conversion of styrene (C%) was found to be less than 50% and decreased with the increase in the OA-MNPs added. This is due to the effect of more oleic acid introduced [22]. The room temperature saturation magnetisation value of the PS/MNPs nanocomposites increased from 0.9 emu g⁻¹ with 0.30 g OA-MNPs added in the *in situ* polymerisation to 12 emu g⁻¹ with 1.20 g OA-MNPs added because of the increasing of the MNPs content in the PS/MNPs nanocomposites (Figure 4(a)). The four PS/MNPs nanocomposites, with different OA-MNPs added, also showed no coercivity.

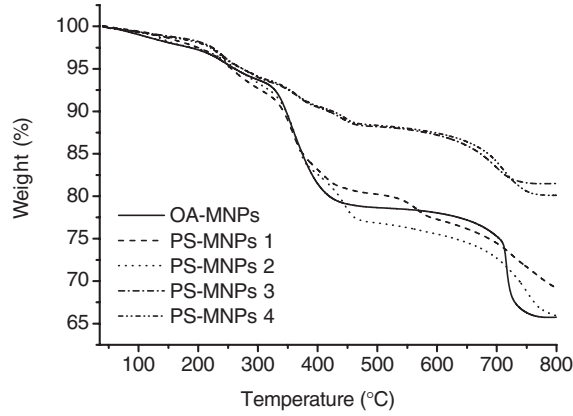


Figure 3. TGA curves of PS-MNPs samples.

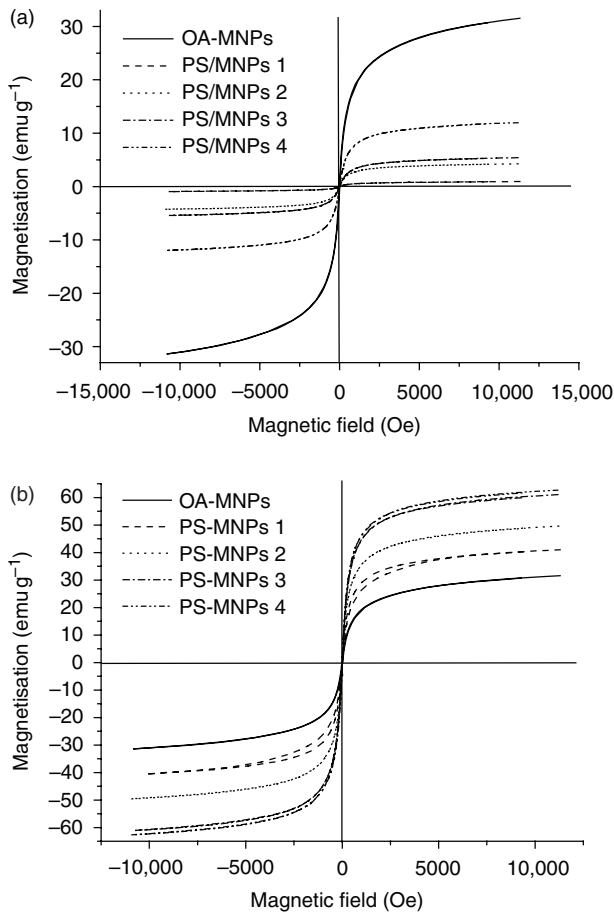


Figure 4. Room temperature magnetisation curves of: (a) PS/MNPs samples and (b) PS-MNPs samples.

3.3. Polystyrene-grafted magnetite nanoparticles

The PS-MNPs were characterised with FT-IR, TGA, TEM and magnetisation after being separated by extraction. The characteristic absorption peaks at 580 cm^{-1} attributed to the Fe–O structure were found to be weak, compared with the FT-IR spectrum of the PS-MNPs shown in Figure 2. The absorbance band at 699 cm^{-1} attributed to the phenyl structure appeared. It indicated that the polystyrene chains had been successfully grafted onto the surfaces of the MNPs via the *in situ* radical polymerisation.

The percentage of the grafting (PG%) of the PS-MNPs is given in Table 1, calculated from the TGA curves (Figure 3). The maximum PG% was achieved with 0.60 g OA-MNPs added in the *in situ* polymerisation. For the other three samples, the weight losses until 500°C were less than that of the OA-MNPs. This is due to the superfluous oleic acid molecules physisorbed on the surfaces of the MNPs, which could be washed off during the *in situ* polymerisation.

Some aggregations of the MNPs were found in the PS-MNPs (Figure 1). It might be due to the washing off of the oleic acid molecules physisorbed on the surfaces of the MNPs in the toluene solution.

The room temperature saturation magnetisation value of the PS-MNPs nanocomposites increased from 41 emu g^{-1} with 0.30 g OA-MNPs added in the *in situ* polymerisation to 63 emu g^{-1} with 1.20 g OA-MNPs added (Figure 4(b)). The saturation magnetisation values of the four PS-MNPs samples were higher than that of the OA-MNPs and increased with the increasing of the MNPs content in the PS-MNPs. All of the samples exhibit apparent superparamagnetism at room temperature due to their small particle size, that is, they do not retain any magnetism in the absence of an external magnetic field. The coercivity was zero, indicating that the domain size of the Fe_3O_4 particles in each nanosphere was smaller than the critical diameter. As a result of higher magnetisation, a clear magnetic response was evident and could readily be used to move and collect the PS-MNPs with an external magnetic field.

4. Conclusions

In this work, PS-MNPs were successfully prepared by the *in situ* solution radical polymerisation of styrene and the OA-MNPs were prepared by the coprecipitation in the presence of oleic acid. The general method could be extended to other vinyl monomers and used to produce magnetic nanocomposites.

References

- [1] A.H. Lu, E.L. Salabas, and F. Schuth, *Magnetic nanoparticles: Synthesis, protection, functionalization, and application*, Angew. Chem. Int. Ed. 46 (2007), pp. 1222–1244.
- [2] S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst, and R.N. Muller, *Magnetic iron oxide nanoparticles: Synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications*, Chem. Rev. 108 (2008), pp. 2064–2110.
- [3] G.F. Goya, V. Grazu, and M.R. Ibarra, *Magnetic nanoparticles for cancer therapy*, Curr. Nanosci. 4 (2008), pp. 1–16.
- [4] S.A. Corr, Y.P. Rakovich, and Y.K. Gun'Ko, *Multifunctional magnetic-fluorescent nanocomposites for biomedical applications*, Nanoscale Res. Lett. 3 (2008), pp. 87–104.

- [5] M. Namdeo, S. Saxena, R. Tankhiwale, M. Bajpai, Y.M. Mohan, and S.K. Bajpai, *Magnetic nanoparticles for drug delivery applications*, J. Nanosci Nanotechnol. 8 (2008), pp. 3247–3271.
- [6] S.H. Gee, Y.K. Hong, D.W. Erickson, M.H. Park, and J.C. Sur, *Synthesis and aging effect of spherical magnetite (Fe_3O_4) nanoparticles for biosensor applications*, J. Appl. Phys. 93 (2003), pp. 7560–7562.
- [7] M. Magnani, L. Galluzzi, and I.J. Bruce, *The use of magnetic nanoparticles in the development of new molecular detection systems*, J. Nanosci Nanotechnol. 6 (2006), pp. 2302–2311.
- [8] A.K. Johnson, A.M. Zawadzka, L.A. Deobald, R.L. Crawford, and A.J. Paszczynski, *Novel method for immobilization of enzymes to magnetic nanoparticles*, J. Nanopart. Res. 10 (2008), pp. 1009–1025.
- [9] A. Schatz, R.N. Grass, W.J. Stark, and O. Reiser, *TEMPO supported on magnetic C/Co-nanoparticles: A highly active and recyclable organocatalyst*, Chem. Eur. J. 14 (2008), pp. 8262–8266.
- [10] Y.-T. Zhou, H.-L. Nie, C. Branford-White, Z.-Y. He, and L.-M. Zhu, *Removal of Cu^{2+} from aqueous solution by chitosan-coated magnetic nanoparticles modified with α -ketoglutaric acid*, J. Colloid Interface Sci. 330 (2009), pp. 29–37.
- [11] E. Tuncer, A.J. Rondinone, J. Woodward, I. Sauers, D.R. James, and A.R. Ellis, *Cobalt iron-oxide nanoparticle modified poly(methyl methacrylate) nanodielectrics: Dielectric and electrical insulation properties*, Appl. Phys. A 94 (2009), pp. 843–852.
- [12] W. Wu, Q. He, and C. Jiang, *Magnetic iron oxide nanoparticles: Synthesis and surface functionalization strategies*, Nanoscale Res. Lett. 3 (2008), pp. 397–415.
- [13] M. Takafuji, S. Ide, H. Ihara, and Z. Xu, *Preparation of poly(1-vinylimidazole)-grafted magnetic nanoparticles and their application for removal of metal ions*, Chem. Mater. 16 (2004), pp. 1977–1983.
- [14] P. Liu, *Nanosurface-initiated living radical polymerization*, in *Polymeric Nanostructures and Their Application*, Vol. 2, H.S. Nalwa, ed., American Scientific Publishers, California, 2007, Chap. 13, pp. 513–835.
- [15] C. Flesch, Y. Unterfinger, E. Bourgeat-Lami, E. Duguet, C. Delaite, and P. Dumas, *Poly(ethylene glycol) surface coated magnetic particles*, Macromol. Rapid Commun. 26 (2005), pp. 1494–1498.
- [16] P.C. Hartmann and R.D. Sanderson, *Preparation of magnetite-polystyrene core-shell hybrid nanoparticles initiated by a covalently bonded azo compound*, Macromol. Symp. 255 (2007), pp. 24–35.
- [17] Q.-L. Fan, K.-G. Noeh, E.-T. Kang, B. Shuter, and S.-C. Wang, *Solvent-free atom transfer radical polymerization for the preparation of poly(poly(ethyleneglycol) monomethacrylate)-grafted Fe_3O_4 nanoparticles: Synthesis, characterization and cellular uptake*, Biomaterials 28 (2007), pp. 5426–5436.
- [18] P. Liu, *Facile preparation of monodispersed core/shell zinc oxide@polystyrene ($ZnO@PS$) nanoparticles via soapless seeded microemulsion polymerization*, Colloid Surf. A Physicochem. Eng. Aspects 291 (2006), pp. 155–161.
- [19] P. Liu, W.M. Liu, and Q.J. Xue, *In situ radical transfer addition polymerization of styrene from silica nanoparticles*, Eur. Polym. J. 40 (2004), pp. 267–271.
- [20] P. Dallas, A.B. Bourlinos, D. Niarchos, and D. Petridis, *Synthesis of tunable sized capped magnetic iron oxide nanoparticles highly soluble in organic solvents*, J. Mater. Sci. 42 (2007), pp. 4996–5002.
- [21] S.-Y. Lee and M.T. Harris, *Surface modification of magnetic nanoparticles capped by oleic acids: Characterization and colloidal stability in polar solvents*, J. Colloid Interface Sci. 293 (2006), pp. 401–408.
- [22] G.F. Liu and P. Liu, *Synthesis of monodispersed crosslinked nanoparticles decorated with surface carboxyl groups via soapless emulsion polymerization*, Colloid Surf. A Physicochem. Eng. Aspects (2009), in press.