Preparation and Properties of Electrospun PAN/Fe_3O_4 Magnetic Nanofibers

Biao Wang,[1] Ying Sun,[1,2] Huaping Wang[1]

[1]*State Key Laboratory for Modification of Chemical Fiber and Polymers, College of Material Science and Engineering, Donghua University, Shanghai 201620, China*
[2]*Cancer Institute, Shanghai Jiao Tong University, Shanghai 200032, China*

Received 11 May 2009; accepted 15 August 2009
DOI 10.1002/app.31288
Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyacrylonitrile (PAN)/Fe_3O_4 composite nanofibers were prepared via the electrospinning of the PAN spinning solutions with magnetite Fe_3O_4 nanoparticles. The experimental results showed that the morphology and diameter of the nanofibers strongly depended upon concentrations of PAN and salt additives in the spinning solutions. A suitable PAN concentration and LiCl additives could effectively prevent the occurrence of beads in the electrospinning process and affected the diameters of the electrospun nanofibers. The breaking strength and breaking strain decreased when the magnetite Fe_3O_4 nanoparticles were incorporated. The prepared PAN/Fe_3O_4 nanofibers were superparamagnetic at room temperature. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1781–1786, 2010

Key words: electrospinning; magnetic nanofibers; additive; polyacrylonitrile concentration

INTRODUCTION

Magnetic fibers have many applications such as magnetic paper, health-care cloth, and magnetic filters. Traditionally, magnetic fibers have been produced by coating magnetite particles on the surface of the fibers.[1–3] However, the magnetization of these products was not high enough for magnetic application because of small amounts of magnetite particles coated on the surface. Moreover, the magnetization would weaken as a result of the losses of magnetite particles after post treatments such as washing, heat setting and knitting. To obtain a magnetic fiber with higher magnetization and higher tolerance to washing, people proposed to incorporate the magnetic particles into a polymeric fiber matrix directly. In this case, the size of the magnetic particles should be very small to get a continuous spinning process. Recently, magnetic nanoparticels have been extensively used as the fillers to prepare the superfine magnetic composite fibers because of their high processability, versatility, and lower cost.[4–7]

Electrospinning is a highly versatile method to process solutions or melts into an interconnected membrane-like web of superfine fibers with a diameter ranging from a few micrometers to a few nanometers.[8–10] Because of the large surface areas and small pore sizes in comparison with commercial textiles,[11–13] the nonwoven mats composed of electrospun fibers have become excellent candidates for applications in filtration,[10,14] biomedical films,[15,16] and scaffolds for tissue engineering.[17] This novel fiber-spinning technique provides the capacity to blend a variety of types of polymers and magnetic nanoparticles to produce superfine magnetic composite fibers. In the past few years, electrospun polymer-based composite nanofibers containing magnetic nanoparticles have been described, for example, poly(F-caprolactone)/FePt,[18] poly(hydroxyethylmethacrylate)/Fe_3O_4 (or poly-L-lactide/ Fe_3O_4),[19] polymethylmethacrylate/Fe_3O_4,[20] polyaniline/Fe_3O_4,[21] and poly(ethylene oxide)/Fe_3O_4.[22] But the preparation of magnetic polymer-based nanofibers from a broad range of polymers with specific magnetic and mechanical properties is still a challenge. And the ability to electrospin the various polymer/magnetite has not been systematically studied.

Here, we describe the formation of magnetic polyacrylonitrile (PAN) nanofibers containing superparamagnetic nanoparticles (Fe_3O_4) via electrospinning. The effects of PAN concentrations of spinning

Correspondence to: B. Wang (wbiao2000@dhu.edu.cn).
Contract grant sponsor: Scientific Research Foundation for the Returned Overseas Chinese Scholars (State Education Ministry).
Contract grant sponsor: Natural Science Foundation of Shanghai; contract grant number: 09ZR1401500.
Contract grant sponsor: Shanghai Leading Academic Discipline Project; contract grant number: B603.
Contract grant sponsor: Program of Introducing Talents of Discipline to Universities; contract grant number: 111-2-04.

solutions and salt additives on the diameter and morphology of the electrospun nanofibers were studied in detail. The magnetic and mechanical properties of these nanofibers were also characterized.

EXPERIMENTAL

Materials

Poly(acrylonitrile) (PAN, M_η: 48,000) was supplied by Sinopec Shanghai Petrochemical (shanghai, China). All other materials such as *N*,*N*-Dimethylacetamide (DMAC) and sodium dodecyl benzene sulfonate were purchased from Shanghai Chemical Reagents. LiCl was purchased from Pinjiang Chemical. All chemicals were used directly without further purification.

Preparation of spinning solutions

Fe_3O_4 nanoparticles were synthesized in our lab using chemical co-precipitation method.[23,24] In a typical experiment, $FeCl_3.6H_2O$ (2.5 g) and $FeSO_4.7H_2O$ (1.7 g) were dissolved in 75 mL of deionized water. A total of 40 mL of 2*M* NaOH was added drop-wise to the mixture solution at 60°C. Then, the temperature was increased to 80°C followed by adding 10 mL of sodium oleic acid within 10 min. After that, 10 mL of polyethylene glycol was added and the reaction was kept at 40°C for 15 min. The particles were obtained by filtering, washing, and drying. The Fe_3O_4 nanoparticle-dispersed DMAC solution was prepared by dispersing the desired amount of as-synthesized Fe_3O_4 nanoparticles in DMAC solvent with 30 min sonication. The various concentrations of PAN/Fe_3O_4 nanoparticle solutions were then prepared by adding the desired amount of PAN powders directly to the Fe_3O_4 nanoparticle-dispersed DMAC solution prepared as described earlier. The solutions were stirred vigorously for at least 1 h at 80°C in order to obtain homogeneous solutions. LiCl, as a salt additive, with a weight concentration from 1 to 4 wt % was added into the spinning solutions with vigorously stirring. The weight ratio of Fe_3O_4 and PAN was set to 3 : 97 in which case the electrospinning had a relative good efficiency.

Electrospinning experiments

The electrospinning apparatus used was similar to that described by Shin et al.[25] Briefly, the solution was pumped at a constant flow rate by a syringe pump to a stainless steel capillary with inner diameter of 1mm located in the center of the upper aluminum disk. The capillary tube, also acting as an electrode, was connected to an electrical potential of 50 kV relative to a ground electrode by a high-voltage power supply (purchased from shanghai Shengfa Detection Instrument). To obtain a stable jet, the electrical voltage, solution flow rate, and the distance between the upper and lower aluminum plates were set to be 50 kV, 3.2 mL/h and 7 cm, respectively. After evaporation of the solvents from the jet stream, the composite nanofibers of PAN/Fe_3O_4 were produced and the resulting nonwoven fiber mat was collected. All electrospinning experiments were performed at room temperature.

Measurement and characterization

Viscosity was measured on an ARES-rheometer (TA Instruments) at 25°C. The conductivity was measured using a DDS-11A/C conductivity meter. The deviations from the mean of the measured viscosity and conductivity were about 5% and 9%, respectively. The images of the electrospun fibers were obtained using a JSM-5600LV scanning electron microscopy (SEM), and the diameters of the produced fibers were determined by measuring 20 randomly selected fibers for each sample. Specimens for SEM were prepared by direct deposition of the electrospun nanofibers on an aluminum foil and sputter-coating with gold using a Desk II cold sputter/etch unit (Denton Vacuum LLC, NJ). Transmission electron microscopy (TEM, Hitachi H-800) was used to study the morphology and estimate the average sizes of the nanoparticles. The magnetic properties of Fe_3O_4 nanoparticles and PAN/Fe_3O_4 nanofibers were measured using a vibrating-sample magnetometer (LakeShore, VSM7400) with an applied field between −3.5 and 3.5 kOe. The mechanical properties were measured using a Material Testing System (Instron 5565).

RESULTS AND DISCUSSION

Characterization of magnetite nanoparticles

The TEM image of as-synthesized Fe_3O_4 magnetite nanoparticles is shown in Figure 1. The Fe_3O_4 nanoparticles show a very narrow size distribution and an average diameter of about 8 nm. A typical magnetization curve of Fe_3O_4 nanoparticles is shown in Figure 2. The Fe_3O_4 nanoparticles exhibit superparamagnetic behavior at room temperature in that there is zero remnant magnetization at zero applied fields. The saturation magnetization is $\sim$ 60 emu/g that is lower than the bulk value ($\sim$ 92 emu/g). This is mainly because of the reduced particles diameter.[26]

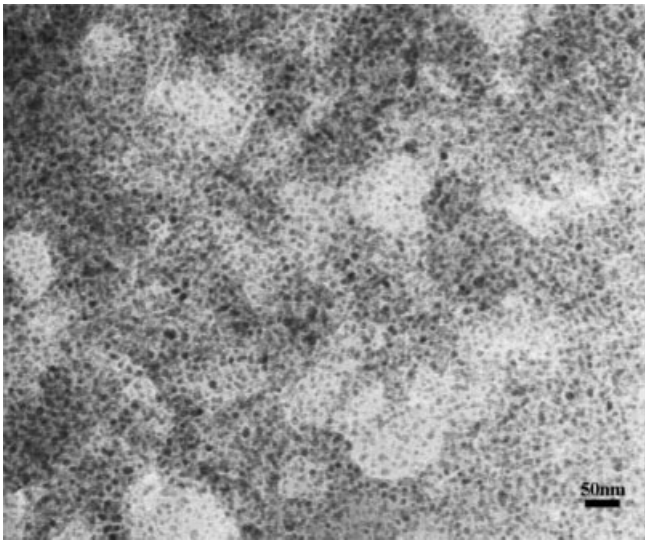

Figure 1 TEM image of Fe_3O_4 nanoparticles.

Effect of PAN concentration

Polymer concentration of the spinning solutions is one of the most important parameters in the electrospinning process because it is related to the viscosity of the solutions. To study the effects of PAN concentration on the diameters and morphologies of the PAN/Fe_3O_4 nanofibers, three PAN concentrations from 8 to 14 wt % were used in our experiments. SEM images of obtained PAN/Fe_3O_4 composite nanofibers are shown in Figure 3, and the viscosities and conductivities of different spinning solutions and the diameters of their products are listed in Table I. As can be seen from Figure 3(a), many beads appeared in the electrospun products when the PAN concentration was 8 wt %. The number of beads gradually decreased with the increase of the PAN concentration, and there were no beads in the products when the concentration exceeded 14 wt %. The diameters of produced nanofibers were also affected

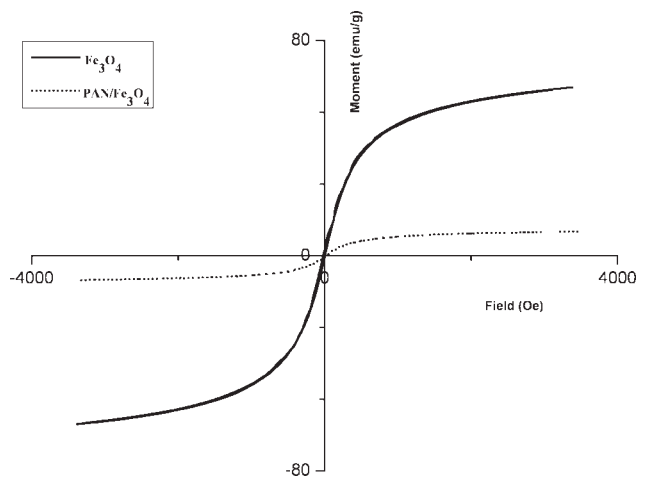

Figure 2 Magnetization curves of Fe_3O_4 nanoparticles and the nanofibers of PAN/Fe_3O_4 (97/3 w/w) prepared from the spinning solutions with 10 wt % PAN and 1 wt % LiCl additives.

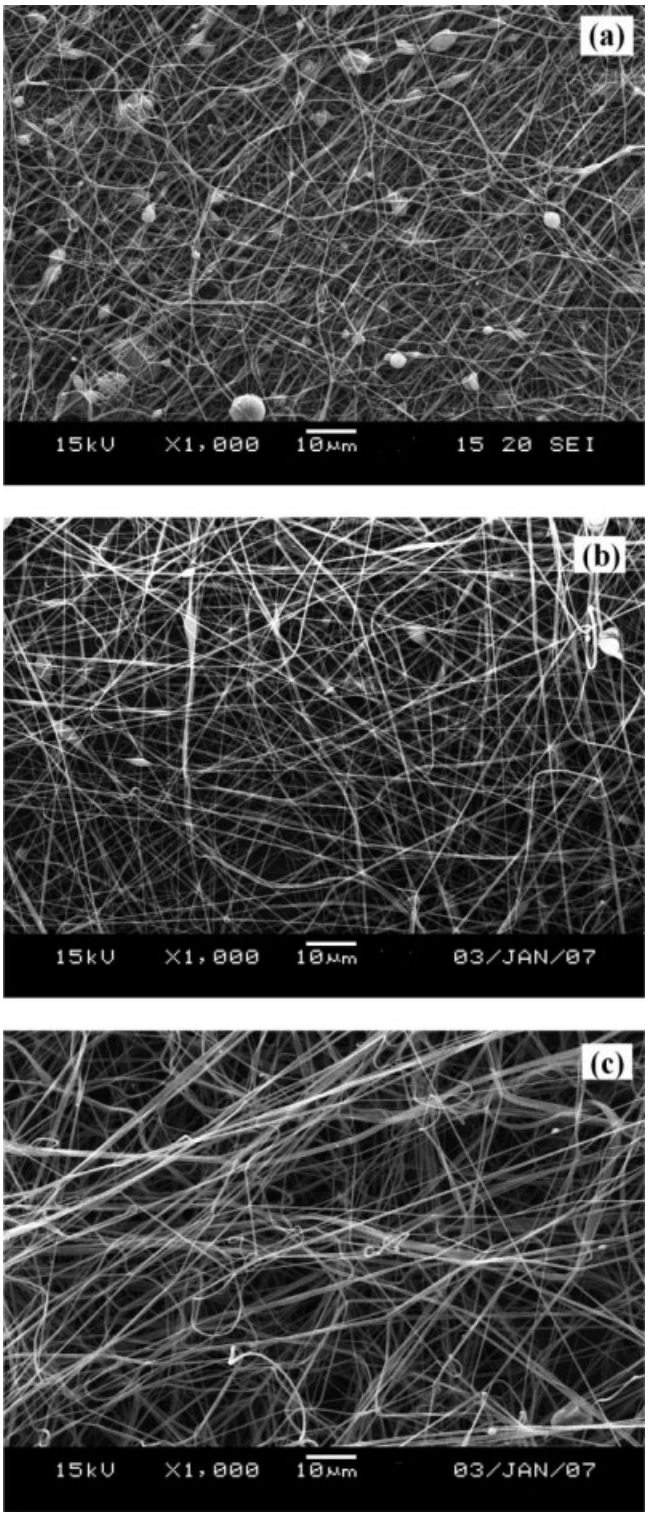

Figure 3 Some representative SEM images of PAN/Fe_3O_4 (97/3 w/w) nanofibers prepared from the solutions with (a) 8 wt % PAN, (b) 10 wt % PAN, and (c) 14 wt % PAN. The concentration of LiCl was equal to 1 wt % for all samples.

TABLE I
The Properties of Different Solutions and the Diameters of Their Products

Polymer concentration	Properties of the dopes: Conductivity (μS/cm)	Properties of the dopes: Viscosity (Pa S)	Morphology and diameters of the produced nanofibers(nm)[a]	
8 wt % PAN + 1 wt % LiCl	1654	0.13	110 ± 20	fiber + many beads
10 wt % PAN + 1 wt % LiCl	1648	0.16	155 ± 30	fiber + few beads
14 wt % PAN + 1 wt % LiCl	1249	0.25	355 ± 55	fiber (no beads)

[a] 3 wt % Fe_3O_4 in the produced PAN fibers for all samples.

by the PAN concentrations. From Table I, the average diameter of the produced fibers increased with the PAN concentrations of the solutions. Lower surface tension resulting from the lower polymer concentration may be the main factor to cause the formation of beads.[27]

Effect of salt additives

The electrical conductivity of the spinning solutions is another important factor that affects the morphologies and dimensions of the electrospun products besides the viscosity and the surface tension of the solutions.[28] Here, the solution conductivity was adjusted by changing the concentration of LiCl salt in the solutions in the range of 1 to 4 wt % and the PAN concentration was equal to 10 wt %. The conductivity of the spinning solutions increased sharply when 1 wt % of LiCl was added, but it did not increase further when the concentration of LiCl exceeded 2 wt % (Fig. 4). From the SEM images of the electrospun products, few beads appeared when the LiCl concentration was 1 wt % [Fig. 3(b)]. However, there were no beads in the products when the LiCl concentration of the solutions was from 2 to 4 wt %. No beads were found in the products when no LiCl was added, although the spinning process was not very efficient. The diameters of the electrospun fibers decreased sharply when a small amount of LiCl was added but increased with an increase of LiCl concentration from 1 wt % to 4 wt % (Fig. 5). Zong et al.[15] thought that the addition of a salt leads to better electrical conductivity of the jets, and as a result, higher electrostatic force is imposed on the jets in the electrospinning process. Therefore, the size of beads should become smaller and the diameters of the products should be thinner. Actually, the addition of LiCl also affected the viscosity of the solutions (Fig. 6). Without LiCl, the viscosity of the solution was very high and the surface tension became large that results in no beads in the products. When 1 wt % LiCl was added, the viscosity of the solutions decreased rapidly, which tended to form some beads in the products. However, the conductivity of the solutions increased sharply that should minimize the beads. When LiCl was added, both the net charge density and the viscosity of the solution changed. In this case, we think that the viscosity play a more important role than the conductivity in the formation of beads in the products. When the LiCl concentration increased from 1 to 2 wt %, both

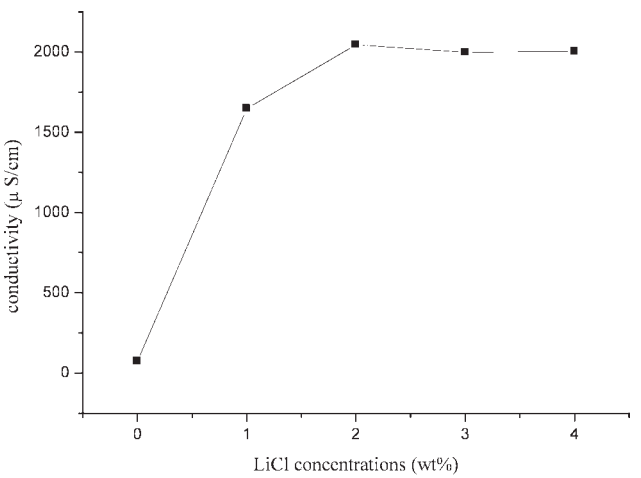

Figure 4 Relation between the solution conductivity and the LiCl concentration. The PAN concentration was 10 wt % for all samples.

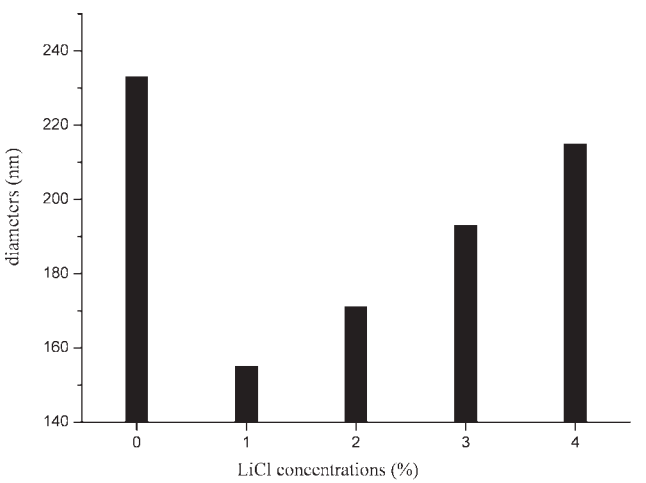

Figure 5 Relation between the LiCl concentration of the spinning solution and the diameter of their produced PAN/Fe_3O_4 (97/3 w/w) nanofibers. The PAN concentration was 10 wt % for all samples and all other conditions were equal.

of the viscosity and conductivity increased, which commonly lead to fewer beads in the products. When the LiCl increased further, the conductivity kept constant, but the viscosity kept going higher, which lead to no beads in the products.

Magnetic and mechanical properties of the nanofibers

The composite nanofibers with 3 wt % Fe_3O_4 nanoparticles were superparamagnetic at room temperature (Fig. 2), although the magnetization was much lower than that of the magnetite Fe_3O_4 nanoparticles. The mechanical properties of a nonwoven are very important if the nonwoven is used. Figure 7 shows the stress–strain curves for the mats composed of PAN nanofibers with and without Fe_3O_4 nanoparticles. The breaking strength and breaking strain decreased when the Fe_3O_4 nanoparticles were incorporated. The reason for the reduction in mechanical properties is still not clear. Further investigation on the mechanical properties of electrospun mats and the method of measurement are still in progress in our group. Better properties could be expected by adjusting the spinning conditions or by using *in-situ* polymerization to prepare the spinning solutions.

CONCLUSIONS

Superparamagnetic PAN/Fe_3O_4 composite nanofibers ranging in diameter from 110 to 355 nm were prepared via the electrospinning of the PAN spinning solutions with magnetite Fe_3O_4 nanoparticles. The effects of the concentrations of PAN and salt additives of the spinning solutions on the morphology and diameter of the produced nanofibers were studied in this work. The results showed that PAN concentration could be the key factor to affect the formation of the beads in the products and the concentrations of LiCl could address fewer effects on the bead formation. Both PAN and LiCl concentration affected the diameters of the electrospun fibers. The obtained composite nanofibers were superparamagnetic at room temperature, and the incorporation of magnetite Fe_3O_4 nanoparticles could weaken the mechanical properties of the produced mats.

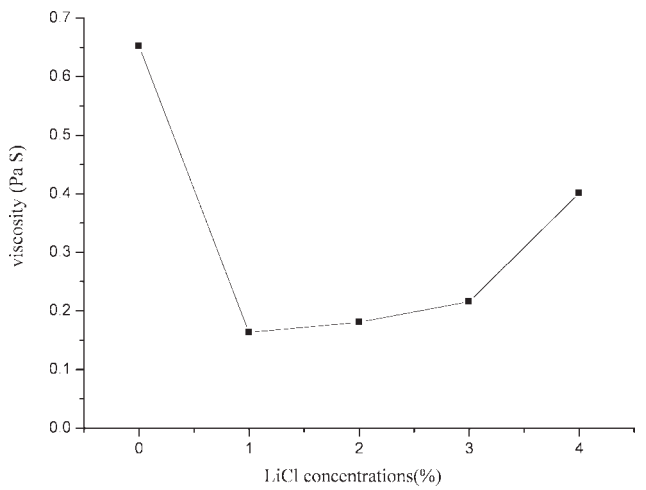

Figure 6 The relationship between the LiCl concentration and the viscosity.

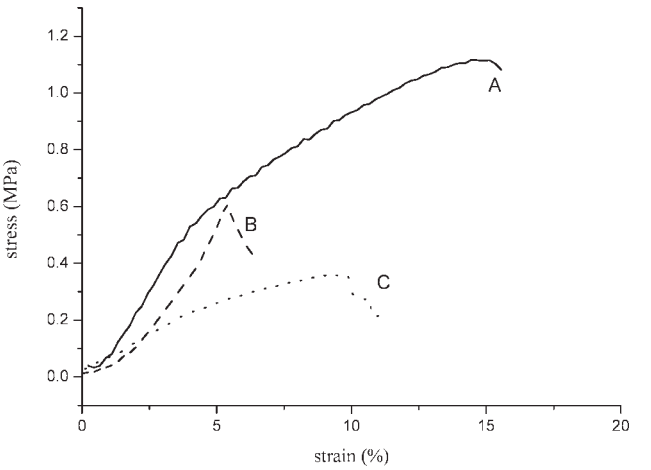

Figure 7 The mechanical properties of the PAN nanofibers (A) and PAN/Fe_3O_4 (97/3 w/w) nanofibers prepared from 14 wt % PAN + 1 wt % LiCl (B), and 10 wt % PAN + 1 wt % LiCl (C) spinning solutions. All other conditions were equal.

References

1. Rious, P.; Ricard, S.; Marchessault, R. H. J Pulp Paper Sci 1992, 18, 39.
2. Raymond, L.; Revol, J. F.; Ryan, D. H.; Marchessault, R. H. Mater Lett 1994, 6, 249.
3. Mayes, E. L.; Vollrath, F.; Mann, S. Adv Mater 1998, 10, 801.
4. Shiho, H.; Manabe, Y.; Kawahashi, N. J Mater Chem 2000, 10, 333.
5. Caruso, F.; Spasova, M.; Susha, A.; Giersig, M.; Caruso, R. A. Chem Mater 2001, 13, 109.
6. Caruso, F.; Susha, A. S.; Giersig, M.; Mohwald, H. Adv Mater 1999, 11, 950.
7. Bizdoaca, E. L.; Spasova, M.; Farle, M.; Hilgendorff, M.; Caruso, F. J Magn Magn Mater 2002, 240, 44.
8. Wan, L. S.; Wu, J.; Xu, Z. K. Macromol Rapid Comm 2006, 27, 1969.
9. Wan, Y. Q.; He, J. H.; Wu, Y.; Yu, H. Y. Mater Lett 2006, 60, 3296.
10. Gibson, P.; Schreuder-Gibson, H.; Rivin, D. Colloid Surf A 2001, 187, 469.
11. Doshi, J.; Reneker, D. H. J Electrostat 1995, 35, 151.
12. Reneker, D. H.; Chun, I. Nanotechnology 1996, 7, 216.
13. Reneker, D. H.; Yarin, A. L. Polymer 2008, 49, 2387.
14. Schreuder-Gibson, H. L.; Gibson, P. ACS Sym Ser 2006, 918, 121.
15. Zong, X. H.; Kim, K.; Fang, D. F.; Ran, S. F.; Hsiao, B. S.; Chu, B. Polymer 2002, 43, 4403.
16. Kim, K.; Yu, M.; Zong, X. H.; Chiu, J.; Fang, D. F.; Seo, Y. S.; Hsiao, B. S.; Chu, B.; Hadjiargyrou, M. Biomaterials 2003, 24, 4977.
17. Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. Polymer 1999, 40, 7397.

18. Song, T.; Zhang, Y. Z.; Zhou, T. J.; Lim, C. T.; Ramakrishna, S.; Liu, B. Chem Phys Lett 2005, 416, 317.
19. Tan, S. T.; Wendorff, J. H.; Pietzonka, C.; Jia, Z. H.; Wang, G. Q. Chemphyschem 2005, 6, 1461.
20. Pavan Kumar, V. S.; Jagadeesh Babu, V.; Raghuraman, G. K.; Dhamodharan, R.; Natarajan, T. S. J Appl Phys 2007, 101.
21. Xiao, Q.; Tan, X. K.; Ji, L. L.; Xue, J. Synth Met 2007, 157, 784.
22. Wang, A.; Singh, H.; Hatton, T. A.; Rutledge, G. C. Polymer 2004, 45, 5505.
23. Sun, Y.; Wang, B.; Hui, C.; Wang, H. P.; Jiang, J. M. J Macromol Sci B 2006, 45, 653.
24. Sun, Y.; Wang, B.; Wang, H. P.; Jiang, J. M. J Colloid Interface Sci 2007, 308, 332.
25. Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. Appl Phys Lett 2001, 78, 1149.
26. Liu, C.; Zhang, Z. J. Chem Mater 2001, 13, 2092.
27. Liu, Y.; He, J. H.; Yu, J. Y.; Zeng, H. M. Polym Int 2008, 57, 632.
28. Greiner, A.; Wendorff, J. H. Angew Chem Int Ed 2007, 46, 5670.