

# Aligned Electrospun Nanofibers Induced by Magnetic Field

Dongzhi Yang, Jianfeng Zhang, Jing Zhang, Jun Nie

State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Received 21 February 2008; accepted 27 June 2008

DOI 10.1002/app.28896

Published online 10 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Electrospinning has been extensively explored as a simple and versatile method for drawing fibers. The nanofibers are usually collected as nonwoven mats. The results presented in this article show that the electrospun nanofibers can be uniaxially aligned by introducing two nonconductive ferrite magnets collector, and polymer chains parallel to the fiber axis for the aligned nanofibers. The alignment of the nanofibers was characterized by use of digital cameras and field emission scanning electron microscopy. Alignment on the molecular

level was investigated by polarized Fourier transform infrared spectroscopy, polarized Raman spectroscopy, and wide-angle X-ray diffraction. Such uniaxially oriented nanofibers exhibit a variety of potential applications in the areas of biomaterials, microelectronics, and photonics. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3368–3372, 2008

**Key words:** electrospinning; fibers; magnetic field; orientation

## INTRODUCTION

Electrospinning (ES) has several advantages over conventional melt spinning including a simpler setup and the use of a smaller amount of material. ES can make fibers with diameters ranging from the nano to micrometers with large specific surface area, large void volumes, and an interconnected porous network. Electrospun nanofibers have potential applications in composite materials, reinforcements, electrochemical sensing, tissue engineering, microelectronics, photonics, which often require well-aligned and highly ordered architectures.<sup>1–5</sup> In the process of ES, collected fibers are typically randomly oriented in the form of nonwoven. In the area of electronic, photonic devices, tissue engineering, and composite materials, it is very meaningful to prepare systematic structures to broaden the applications of ES nanofibers. Macroscopic alignment of nanofibers has been improved in the past by using different methods including the use of a scanning tip,<sup>6</sup> a rotating mandrel collector,<sup>7–9</sup> a copper wire drum,<sup>10</sup> and conducting plates.<sup>11</sup> For example, Matthews et al. used a rotating and grounded mandrel to collect fibers. By controlling the rotation speed of the mandrel, collagen fibers aligned along the axis of

rotation were obtained. Katta et al. employed a macroscopic copper wire-framed rotating drum as the collector, and the electrospun fibers collected on the drum as it rotated were parallel to each other. Li et al. prepared parallel nanofibers using a collector consisting of two pieces of electrically conductive substrate separated by a gap. Yang et al. also demonstrated a method that generates parallel fibers via ES magnetic-particle doped polymers in a magnetic field.<sup>12</sup> While less attention was paid to polymer solution ES without magnetic-particle.

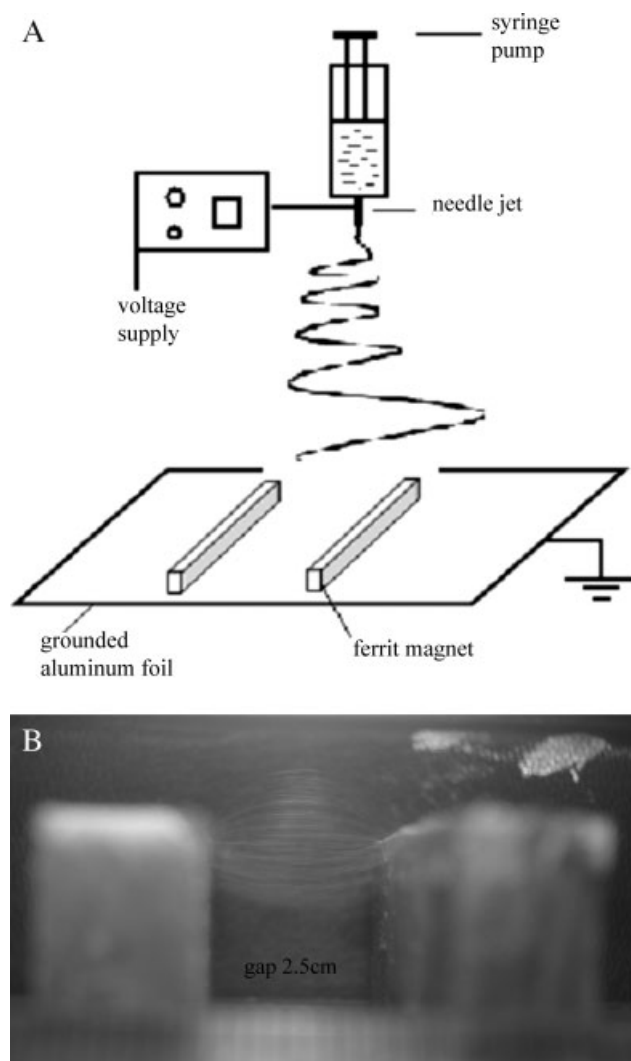
In this article, a novel ES setup by magnetic approach using two strips of nonconductive ferrite magnets, which was separated as collector of aligned nanofibers, was reported. And this method involves a polymeric solution without magnetic nanoparticles. The fiber alignment was confirmed by using digital cameras and field emission scanning electron microscopy. Alignment on the molecular level was investigated by polarized Fourier transform infrared spectroscopy, polarized Raman spectroscopy, and wide-angle X-ray diffraction.

## EXPERIMENT

Figure 1(A) illustrated the schematic setup of ES. It is essentially the same as the conventional configuration except for the use of two strips of ferrite magnets collector separated by a gap. The width of the gap could be varied from several of millimeters to several centimeters.

Correspondence to: J. Nie (niejun@mail.buct.edu.cn).

Contract grant sponsor: Natural Science Foundation of Beijing University of Chemical Technology.



**Figure 1** (A) Schematic setup of collection aligned fibers. The collector based on a pair of split ferrite magnets. (B) Digital photo of parallel magnets collector with aligned fibers.

In a typical procedure for ES, poly(ethylene oxide) (PEO,  $M_w$   $5 \times 10^6$  g mol $^{-1}$ , Aldrich, Milwaukee, WI) was used to prepare a 4 wt % solution (ethanol/water = 2/3). The PEO solution was held in a plastic syringe with tip inner diameter of 0.57 mm, and using a syringe pump at a constant rate of 1 mL/h. The ferrite magnet with a surface magnetic field strength 12T was placed at a distance of 20 cm below the droplet. An electric potential of 7.5 kV was used between the syringe needle and the grounded aluminum foil. As a control experiment, nanofibers were also electrospun without the magnetic field to obtain a nonwoven mat. All the experiments were performed at ambient temperature (25°C).

A sample of aligned fibers was analyzed by a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Ltd., Tokyo, Japan) to characterize alignment. Diameter measurement of the fibers was taken on more than 50 fibers from three different

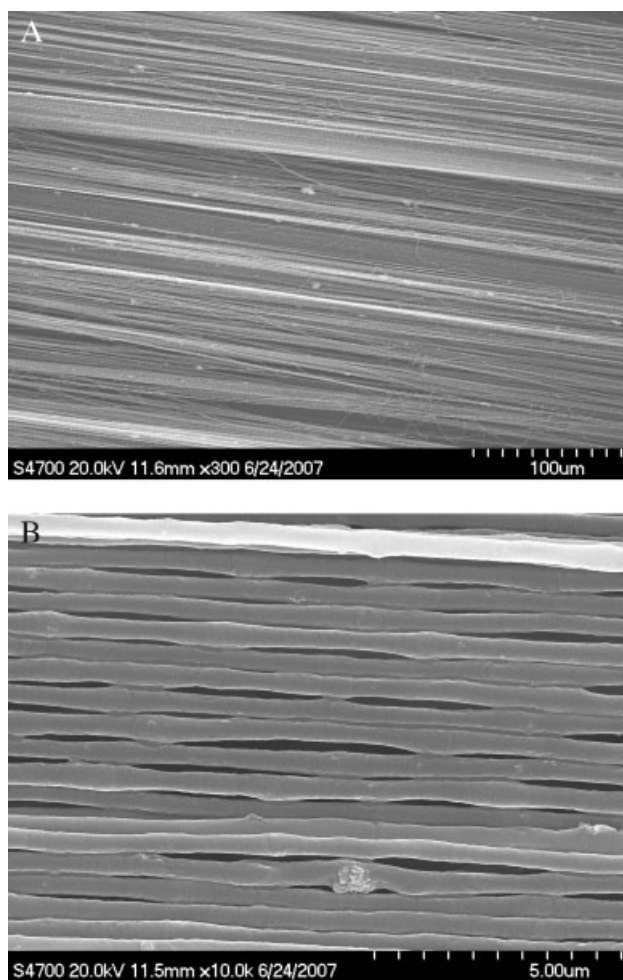
SEM images. Polarized FTIR spectroscopy (Nicolet FTIR-560, Madison, WI) and polarized Raman spectroscopy (Nicolet FTIR-560, USB) was used to investigate molecular orientation in the aligned fibers. WAXD (D/max-RB, Rigaku, Tokyo, Japan) patterns were taken by using Ni-filtered Cu  $K\alpha$  radiation. The diffraction scans were collected at  $2\theta = 5^\circ$ – $60^\circ$ .

## RESULTS AND DISCUSSION

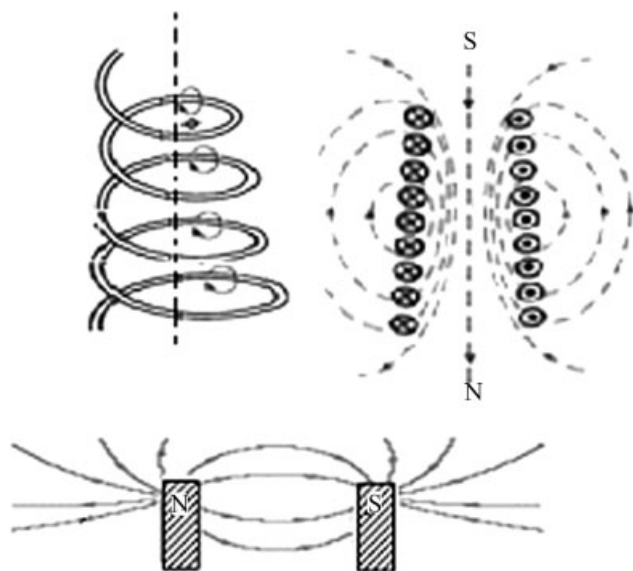
### Uniaxial alignment of nanofibers

The fibers were first recorded by a digital camera [Fig. 1(B)]. The image clearly showed that the PEO nanofibers were uniaxially aligned across the gap with their longitudinal axes oriented perpendicular to the edge of the gap. Further SEM observation of nanofibers collected in the magnetic field revealed highly ordered fibers with diameter around 500 nm [Fig. 2(A,B)].

The alignment of the nanofibers could be explained by the magnetic field generated by the



**Figure 2** SEM images of aligned PEO nanofibers collected across the void gap between two ferrite magnets with different magnification. A: 300 $\times$  magnification; B: 10000 $\times$  magnification.



**Figure 3** The mechanism analysis of a charged nanofiber aligned along magnetic field.

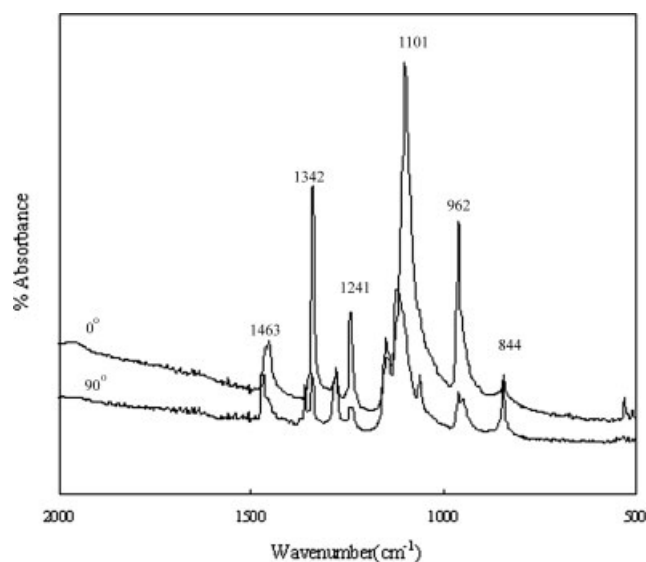
separated nonconductive ferrite magnets and by the motion of the charged nanofiber. The mechanism of this electrospinning process could be described as follows: electrospun jet could be seen as an electrifying solenoid during the ES process, its every turns would generate a magnetic field, and its direction was shown by the arrow in Figure 3. When the electrospun fiber approached to the collector based on a pair of split ferrite magnets, interaction between generated magnetic field by the fiber and collection magnetic field would force the fibers to align along the collection magnetic field.

To prove our explanation that the magnetic field was indeed responsible for the alignment of the polymeric fibers, we carried out an additional experiment. In one experiment, the magnets were replaced by two plastic plates, so that the ES was carried out without a collected magnetic field. The fibers were collected in nonwoven mats. The method using two nonconductive ferrite magnets as collectors is fundamentally different from previously reported methods in preparing aligned ES fibers. For example, two pieces of conductive substrates as collectors, the driving force was the electrostatic interaction. The magnets we used were insulators, being made of two nonconductive ferrite magnets. These experiments confirmed our explanation that the magnetic field is the real reason to produce aligned ES fibers.

### Alignment on the molecular level

#### Polarized FTIR and Raman spectroscopy

The presence of molecular orientation in the fibers could be proved by polarized IR measurement as



**Figure 4** Polarized FTIR spectra of aligned PEO nanofibers 0° (and 90°) means that polarized radiation parallel (perpendicular) to the fiber direction. For aligned PEO nanofibers, the peaks intensities of 0° are greater than those for 90°.

shown in Figure 4, peak assignments and the dichroic ratio were listed in Table I.

For the isotropic fibrous mat, polarized FTIR spectra in parallel and perpendicular direction were the same. However, for aligned PEO fibers, the bands attributed to the  $\nu(\text{C-H})$  at  $2890\text{ cm}^{-1}$ ,  $\omega(\text{C-H})$  at  $1342\text{ cm}^{-1}$ ,  $\nu(\text{C-O-C})$  at  $1101\text{ cm}^{-1}$ , and  $r(\text{C-H})$  at  $962\text{ cm}^{-1}$  had higher intensities when the electric vector was parallel to the fiber axis than when it is perpendicular to the fiber axis. The reason could be attributed to molecular orientation of the polymer backbones along the fibers' axes. When most of the PEO chains were oriented in a fibers' axes direction, the electric vector along this direction encountered a large number of C—O—C bonds and C—H bonds, coupling with the change in dipole moment of their

**TABLE I**  
Absorbance Bands, Assignments, and Dichroic Ratio of Oriented Electrospun PEO Fibers for FTIR and Raman Spectra<sup>13,15–17</sup>

Infrared (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	Assignment <sup>a</sup>	Dichroic ratio
2,890	2,885	$\nu(\text{CH}_2)$	
1,342	Inactive	$\omega(\text{CH}_2)$	2.56
1,101		$\nu(\text{COC})$	2.54
962		$r(\text{CH}_2) + \nu(\text{CH}_2)$	2.68
844	842	$r(\text{CH}_2)$	
1,241	1,126	$\nu(\text{CC})$	
1,282	1,280	$t(\text{CH}_2)$	
Inactive	1,074	$\nu(\text{COC})$	
1,463	1,443	$\delta(\text{CH}_2)$	

<sup>a</sup>  $\nu$  = stretch,  $\omega$  = wag,  $r$  = rock,  $t$  = twist,  $\delta$  = scissors.

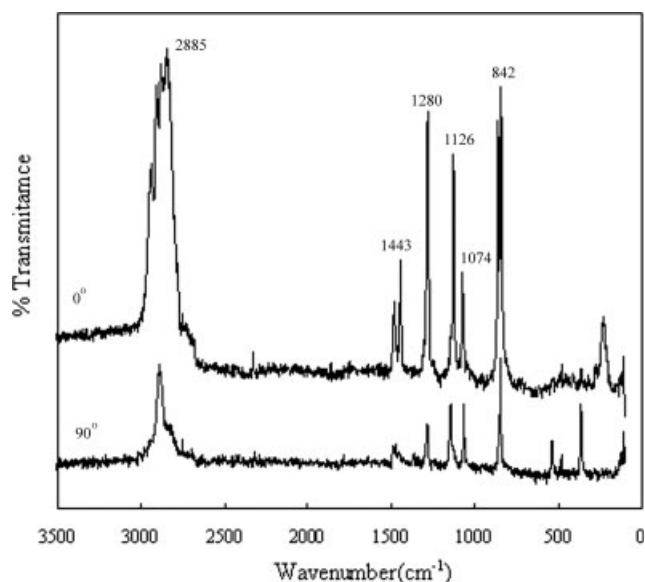
respective vibrations, resulting in higher absorbance intensities in fibers' axes direction.<sup>13</sup>

The aligned extent of polymer molecules could be evaluated by a dichroic ratio ( $R$ ), which can be calculated using the formula,  $R = P_{\parallel}/P_{\perp}$ , where  $P_{\parallel}$  = parallel-polarized infrared absorbance intensity ( $\psi = 0^{\circ}$ ), and  $P_{\perp}$  = perpendicularly polarized infrared absorbance intensity ( $\psi = 90^{\circ}$ ) for a particular vibration. For a randomly oriented sample,  $R = 1$ , and for a complete uniaxially oriented sample,  $R = \text{infinity}$ . For the prepared samples in this work,  $R$  at  $1342 \text{ cm}^{-1}$  attributed  $\omega(\text{C-H})$  of PEO, whose transition moment was parallel to the main chain direction,<sup>14,15</sup> was 2.56. Similarly,  $R$  for the other stronger "parallel" IR bands at  $1101$  and  $962 \text{ cm}^{-1}$  were 2.54 and 2.68, respectively. These results indicate that polymer chains of PEO along the fiber direction collected in the magnetic field.

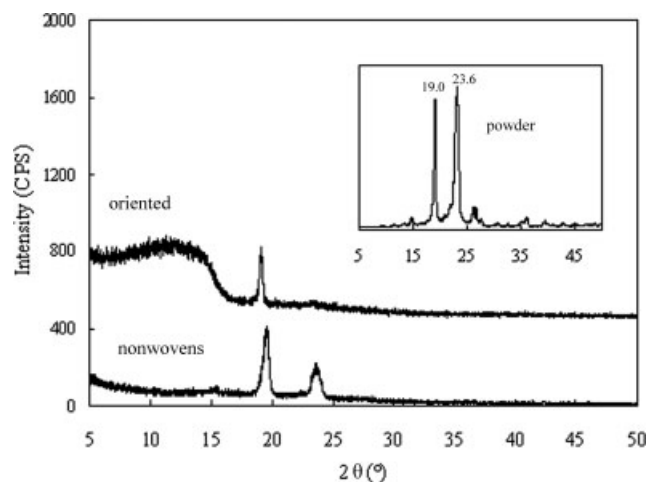
Polarized Raman spectra of aligned PEO nanofibers (Fig. 5) confirmed the molecular orientation observed in FTIR experiments. The bands attributed to  $t(\text{CH}_2)$  at  $1280 \text{ cm}^{-1}$ ,  $\nu(\text{CC})$  at  $1126 \text{ cm}^{-1}$ ,  $\nu(\text{COC})$  at  $1074 \text{ cm}^{-1}$ , and  $r(\text{CH}_2)$  at  $842 \text{ cm}^{-1}$  had higher scattering intensities in the  $\psi = 0^{\circ}$  than that of the  $\psi = 90^{\circ}$ . This result indicated the anisotropic scattering properties of oriented polymer chains.

#### XRD characterizations—Crystal orientation within the fibers

Respective XRD patterns obtained for a pure PEO powder, nonwoven mat, and bundles of oriented nanofiber were shown in Figure 6, respectively.



**Figure 5** Polarized Raman spectra of aligned PEO fiber. For the uniaxially oriented PEO fibers, the peak intensities were greater in  $\psi = 0^{\circ}$  than  $\psi = 90^{\circ}$ .



**Figure 6** WAXD pattern of PEO powder, nonwovens, and oriented nanofiber.

For PEO powder, a peak at  $2\theta = 19.0^{\circ}$  from the 120 reflection and another stronger peak at  $2\theta = 23.6^{\circ}$  were observed. The pattern of PEO nonwoven mat was similar to that of PEO powder. Whereas in the case of a high orientation fibers, the main crystalline peak at  $2\theta = 19.0^{\circ}$  was sharp and the crystalline peak at  $2\theta = 23.6^{\circ}$  was absent. The sharp 120 reflections indicated that the PEO crystals were oriented with the chain axis preferentially aligned along the nanofiber axis.<sup>18</sup> And the absence of crystalline peak at  $2\theta = 23.6^{\circ}$  was precisely because of the fiber orientation.

#### CONCLUSIONS

In this work a novel technique based on ES for generating uniaxially aligned nanofibers was demonstrated. PEO nanofibers were successfully well aligned along the nanofibers axes between two strips of nonconductive ferrite magnets. The aligned nanofiber has the potential applications such as fiber-reinforcement, fiber-oriented liquid crystal, and tissue engineering. It is necessary to explore new and efficient way which could generate well-aligned nanofiber mats.

The authors appreciate the support from Program for Changjiang Scholars and Innovative Research Team in University.

#### References

- Bhattacharai, S. R.; Bhattacharai, N.; Yi, H. K.; Hwang, P. H.; Cha, D. I.; Kim, H.Y. *Biomaterials* 2004, 25, 2595.
- Xu, C. Y.; Inai, R.; Kotaki, M.; Ramakrishna, S. *Biomaterials* 2004, 25, 877.
- Soundarrajan, P.; Patil, A.; Dai, L. *J Vac Sci Technol A* 2003, 21, 1198.
- Doshi, J.; Reneker, D. H. *J Electrostat* 1995, 35, 151.
- Bergshoef, M. M.; Vancso, G. *J Adv Mater* 1999, 11, 1362.



6. Rouhollah, J.; Mohammad, M.; Seyed, A. H. R. *J Appl Polym Sci* 2006, 101, 4350.
7. Shields, K. J.; Beckman, M. J.; Bowlin, G. L.; Wayne, J. S. *Tissue Eng* 2004, 10, 1510.
8. Matthews, J. A.; Wnek, G. E.; Simpson, D. G.; Bowlin, G. L. *Biomacromolecules* 2002, 3, 232.
9. Teo, W. E.; Kotaki, M.; Mo, X. M.; Ramakrishna, S. *Nanotechnology* 2005, 16, 918.
10. Katta, P.; Alessandro, M.; Ramsier, R. D.; Chase, G. G. *Nano Lett* 2004, 4, 2215.
11. Li, D.; Wang, Y.; Xia, Y. *Nano Lett* 2003, 3, 1167.
12. Yang, D. Y.; Lu, B.; Zhao, Y.; Jiang, X. Y. *Adv Mater* 2007, 19, 3702.
13. Kakade, M. V.; Givens, S.; Gardner, K.; Lee, K. H.; Chase, D. B.; Rabolt, J. F. *J Am Chem Soc* 2007, 129, 2777.
14. Enriquez, E. P.; Granick, S. *Colloids Surf A* 1996, 113, 11.
15. Hoffmann, C. L.; Rabolt, J. F. *Macromolecules* 1996, 29, 2543.
16. Tadokoro, H.; Chatani, Y.; Yoshihara, T.; Tahara, S.; Murahashi, S. *Macromol Chem* 1964, 73, 109.
17. Yoshihara, T.; Tadokoro, H.; Murahashi, S. *J Chem Phys* 1964, 41, 2902.
18. Salalha, W.; Dror, Y.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. *Langmuir* 2004, 20, 9852.