

Electrospun Nonwovens of Shape-Memory Polyurethane Block Copolymers

Dong Il Cha,¹ Hak Yong Kim,¹ Keun Hyung Lee,² Yong Chae Jung,³ Jae Whan Cho,³ Byung Chul Chun⁴

¹Department of Textile Engineering, Chonbuk National University, Chonju 561-756, Republic of Korea

²Department of Advanced Organic Materials Engineering, Chonbuk National University, Chonju 561-756, Republic of Korea

³Department of Textile Engineering, Konkuk University, Seoul, 143-701, Republic of Korea,

⁴Department of Polymer Engineering, University of Suwon, Kyonggi-do, 445-743, Republic of Korea

Received 17 December 2003; accepted 3 August 2004

DOI 10.1002/app.21467

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

ABSTRACT: Synthesized shape-memory polyurethane (PU) block copolymers were used to prepare electrospun nonwovens via electrospinning. PU solutions were prepared with a mixed solvent of *N,N*-dimethylformamide and tetrahydrofuran. The electrospun PU nonwovens were prepared with hard-segment concentrations of 40 and 50 wt %. The morphology of the electrospun fibers was investigated with scanning electron microscopy. The average diameter of low-viscosity (ca. 130–180 cPs) electrospun fibers was about 800 nm, and the morphology of the electrospun nonwovens was beaded-on fibers. In contrast, the average diameter of high-viscosity (ca. 530–570 cPs) electrospun fibers was about 1300 nm. In an investigation of the mechanical properties of the

electrospun PU nonwovens, it was found that the tensile strength increased as the hard-segment concentration increased within a similar range of viscosities. Also, the tensile strength of the electrospun PU nonwovens in the machine direction was higher than that in the transverse direction because of a difference in the velocities of the drum collectors. The electrospun PU nonwovens with hard-segment concentrations of 40 and 50 wt % were found to have a shape recovery of more than 80%. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 460–465, 2005

Key words: block copolymers; polyurethanes; nanotechnology

INTRODUCTION

Shape-memory polyurethane (PU), consisting of soft and hard segments, has been extensively researched since its discovery by Mitsubishi in 1988.^{1,2} Hard segments can be formed via hydrogen bonding and crystallization, acting as physical crosslinks below the melting temperature. The reversible phase transformation of the soft segment is responsible for the shape-memory effect. These shape-memory effect can be controlled via the molecular weight of the soft segment, the molar ratio of the hard and soft segments, and the polymerization process. Its application is closely related to the glass-transition temperature (T_g).^{3,4}

Recently, interest in electrospinning has been increasing rapidly because the polymer fibers produced by this method have submicrometer diameters,^{5–10} which cause them to be of considerable value in a wide variety of applications, such as filtration,¹¹ reinforcements in composites,¹² and biomedical devices.^{13,14} Electrospinning

has been broadly researched^{15–23} since it was first patented by Formhals in 1934.²⁴

In this method, an electric field is induced by a high-voltage power supply, which is then applied to a polymer solution or melt placed in a container that has a millimeter-size nozzle. This causes it to be ejected from the capillary tip of the nozzle in the form of a liquid jet. When the electric field is increased, the hemispherical shape of the pendant droplet at the end of the capillary tip is distorted into a conical shape (a Taylor cone).²⁵ When the electric field strength overcomes the stable liquid jet, electrospinning begins at the cone tip, and the liquid moves toward the metallic collector. The solvent evaporates in the electric field formed between the capillary tip and the metallic collector.

The objective of this study was to prepare shape-memory PU nonwovens with various hard-segment ratios with the electrospinning technique and to characterize their physical and mechanical properties.

EXPERIMENTAL

Materials

Shape-memory PU block copolymers with various hard-segment ratios were synthesized according to

Correspondence to: H. Y. Kim (khy@moak.chonbuk.ac.kr).

Contract grant sponsor: Korea Research Foundation; contract grant number: D00574.

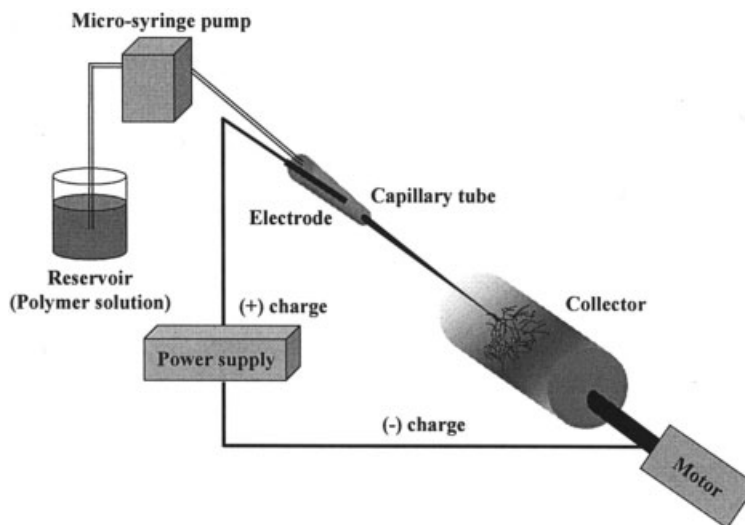


Figure 1 Schematic diagram of the electrospinning device.

previous established procedures.²⁶ The PU block copolymers were dissolved in a mixture of tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF; 60/40 v/v) at room temperature. After the electrospinning, the nonwovens were dried in a vacuum oven at 25°C for 1 week to remove the residual solvent.

Solution properties

The solution viscosity was measured at room temperature with a rheometer (DV III, Brookfield Co., Middleboro, MA) with spindle no. 3 at 100 rpm. The electric conductivity was measured with an electric conductivity meter (G series, CM-40G, TOA Electronics, Ltd., Tokyo, Japan).

Electrospinning

Each PU block copolymer solution (30, 40, or 50 wt %), prepared in a mixed solvent of THF and DMF, was kept in a 5-mL syringe attached to a capillary tip with an inner diameter of 0.6 mm. A copper wire connected to the anode was inserted into the polymer solution. The cathode was attached to a grounded rotating collector wrapped with aluminum foil. The linear velocities of the machine direction (the rotation direction of the collector) and transverse direction (the forward and backward movement of the collector) were 20 and 5 m/min, respectively.

The electric field was supplied by a high-voltage power supply (CPS-60 K02v1, Chungpa EMT, Co., Seoul, Korea) capable of generating voltages up to 50 kV

A schematic diagram of the electrospinning setup is shown in Figure 1.

Morphology

The morphology of the electrospun PU nonwovens was observed with scanning electron microscopy (SEM; GSM-5900, JEOL Co., Tokyo, Japan), and the fiber diameter and distribution were analyzed with an image analyzer (Image Proplus, Media Cybernetics Co., Santa Clara, CA).

Mechanical properties

The mechanical properties of the PU nonwovens were tested at room temperature with a universal testing machine (UTM; AG-5000G, Shimadzu, Ltd., Kyoto, Japan) at a crosshead speed of 10 mm/min. The samples were prepared in a standard dumbbell shape according to ASTM D 638, and five specimens were tested.

Thermomechanical properties

To determine the shape-memory effect of the electrospun PU nonwovens, we analyzed the relationship between the stress and strain at various temperatures with a UTM equipped with a controlled thermal chamber. The thermomechanical test was carried out with the following procedure: (1) applying deformation [i.e., the strain at 50% elongation (ϵ_m)] to the sample at a constant crosshead speed of 10 mm/min at T_k (i.e., $T_g + 20^\circ\text{C}$), (2) cooling the sample to T_1 (i.e., $T_g - 20^\circ\text{C}$) with the same value of ϵ_m , (3) keeping the sample at T_1 for 5 min upon the removal of the load, and (4) raising the temperature from T_1 to T_k and keeping it at T_k for 5 min. Under these conditions, the shape retention and shape recovery are defined as follows:

TABLE I
Solution Properties

Hard-segment concentration (wt %)	Solution concentration (wt %)	Viscosity (cPs)	Electric conductivity (mS/m)
30	36	580	0.039
	40	—	—
40	26	137	0.079
	30	570	0.040
50	30	175	0.080
	38	530	0.052

$$\text{Shape retention (\%)} = \varepsilon_u \times 100 / \varepsilon_m \quad (1)$$

$$\text{Shape recovery (\%)} = (\varepsilon_m - \varepsilon_p) \times 100 / \varepsilon_m \quad (2)$$

where ε_u is the retention strain at $T_g - 20^\circ\text{C}$ and ε_p is the recovery strain at $T_g + 20^\circ\text{C}$.

RESULTS AND DISCUSSION

Electrospinning has many parameters, which can be classified into three major categories: solution properties, control variables, and ambient conditions.^{5–10} Of these, the solution properties, which include the polymer concentration, viscosity, surface tension, and electric conductivity, depend on both the polymer and solvent. The results of these preliminary experiments allowed us to determine the optimum electrospinning condition for each PU block copolymer with various hard-segment ratios. The concentrations, viscosities, and electric conductivities of the solutions for various PUs are shown in Table I.

Typically, the morphology and diameter of electrospun fibers depend on the solution properties. Generally, the intermolecular interaction in a polymer solution of a binary system (polymer/solvent) can be either repulsive or attractive. This also depends on the solvent. In this work, a mixed solvent was used (60/40 v/v THF/DMF) to prepare the nonwovens of the electrospun PU block copolymers. Although this mixture was a good solvent for PU, neither of the two solvents was ideally suited for electrospinning. The properties of each solvent were considered in terms of their intermolecular interactions, boiling points, and viscosities in a polymer solution.⁹

The SEM images of electrospun PU nonwovens prepared with various hard-segment ratios are shown in Figure 2. For a PU with a 30 wt % hard-segment concentration, the jet was broken up into droplets because of the higher viscosity of the solution [Fig. 2(a)]. As the viscosity increased, the jet was tightly focused, and this caused it to break up into droplets; therefore, the agglomeration of the fibers occurred [Fig. 2(b)]. For a PU with a hard-segment concentration of 40 wt %, the elec-

trospinning between the droplets was stabilized. At a low viscosity, the results included many bead-on-fiber structures [Fig. 2(c)]. In contrast, the formation of beads was suppressed as the viscosity was increased [Fig. 2(d)]. A broad distribution of electrospun fiber diameters was obtained, ranging from 800 to 2000 nm, and the average diameter was about 1200 nm (data not shown). A PU with a hard-segment concentration of 50 wt % produced electrospun fibers, regardless of the viscosity [Fig. 2(e,f)]. These results could be attributed to the strong interactions between the different moieties of the hard segments, such as the hydrogen bonding between the carbonyl groups and the carbonyl groups, the dipole-dipole interactions between the carbonyl groups, and the induced dipole-dipole interactions between the aromatic rings. The average diameter of the fibers electrospun from a solution with a low viscosity (175 cPs) was about 800 nm, whereas that obtained from a solution with a high viscosity (530 cPs) was about 1300 nm (data not shown).

The stress-strain curves of the PU block copolymer nonwovens electrospun from low- and high-viscosity solutions, with different hard-segment concentrations and electrospun directions, are shown in Figures 3 and 4, respectively. Generally, an analogous range of viscosities resulted in nonwovens with equivalent mechanical behaviors. However, in this study, different results were obtained, and this was probably due to the variation in the hard-segment concentration. Figure 3 shows that the tensile strength improved as the hard-segment concentration increased because of the effects of the rigid diphenyl methylene moiety coupled with hydrogen bonding and the dipole-dipole interaction, which made the PU very difficult to stretch when a higher percentage of hard segments was incorporated. Also, the tensile strength improved at a higher viscosity, as shown in Figure 4. The electrospun PU nonwovens prepared at a low viscosity [Fig. 2(e,f)] assumed the form of beads on fibers, and so the tensile strength decreased with decreasing viscosity because these beads acted as defects, exerting a powerful influence on the mechanical properties. In addition, Figures 3(b) and 4(b) show that the electrospun PU nonwovens that were spun in the machine direction produced higher stress than those that were spun in the transverse direction because the machine direction was associated with a faster velocity.

The maximum tensile stress and shape recovery of the electrospun PU block copolymer nonwovens with hard-segment concentrations of 40 and 50 wt % are shown in Figure 5. No shape recovery was observed at a hard-segment concentration of 30 wt %, however, because it was not possible to prepare a significant amount of nonwovens under these spinning conditions. The shape recovery of the PU nonwovens was measured after they were 50% deformed and kept for 5 min at 20°C below T_g and the load was removed.

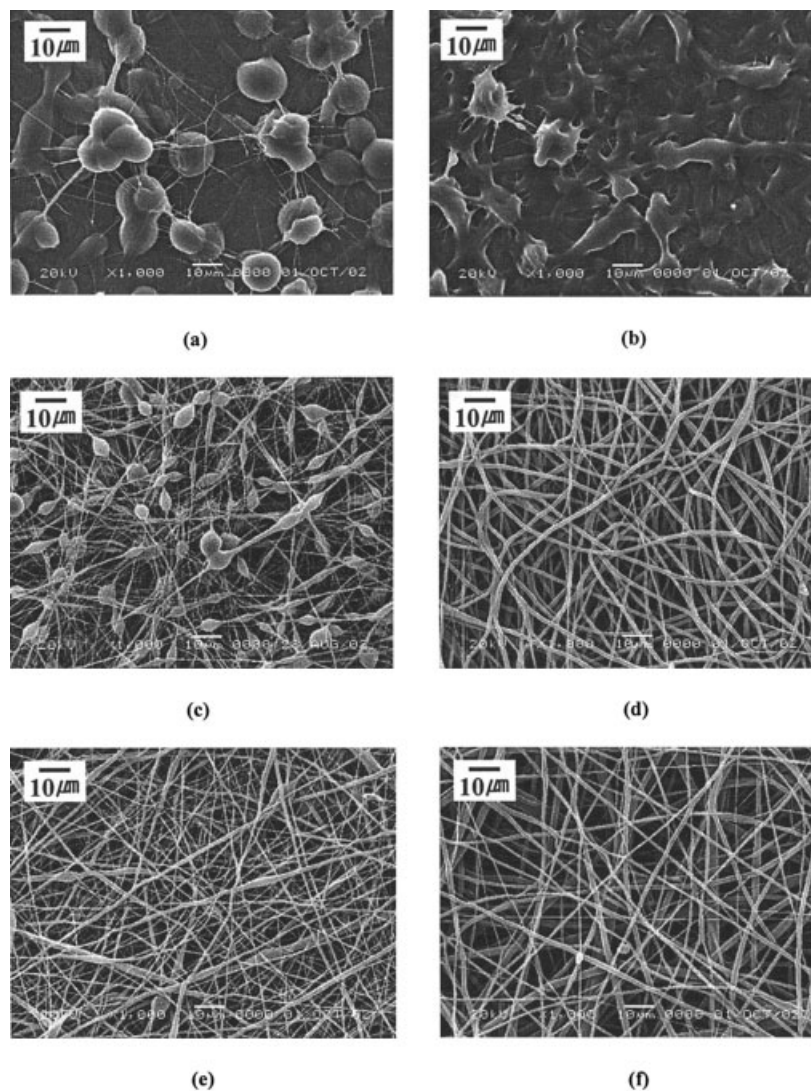


Figure 2 SEM images of electrospun PU fibers: (a) hard-segment concentration = 30 wt % and solution concentration = 36 wt %, (b) hard-segment concentration = 30 wt % and solution concentration = 40 wt %, (c) hard-segment concentration = 40 wt % and solution concentration = 26 wt %, (d) hard-segment concentration = 40 wt % and solution concentration = 30 wt %, (e) hard-segment concentration = 50 wt % and solution concentration = 30 wt %, and (f) hard-segment concentration = 50 wt % and solution concentration = 38 wt %.

Both of the tested PU nonwovens showed more than 80% shape recovery at each hard-segment concentration. When tensile stress was applied to the electrospun PU nonwovens, the soft segments, rather than the hard segments, were preferentially extended along the stress direction because the soft segments were rubbery at temperatures greater than T_g , whereas the hard segments were in a nearly glassy state. The stabilization of PU through dipole–dipole interactions, hydrogen bonding, and induced dipole–dipole interactions of the hard segments was responsible for the higher shape recovery at temperatures greater than T_g . The maximum stress at a hard-segment concentration of 40 wt % was 2 times greater than that observed at a hard-segment concentration of 50 wt %. For the film, a sample with a hard-segment concentration of 50 wt %

was not able to be elongated sufficiently for the shape recovery to be measured. In the electrospun PU nonwovens, however, the usual porous structure was observed. Nevertheless, the high pore area in the fiber-on-fiber nonwovens seemed to act as a kind of defect, marring the shape recovery. Thus, the electrospun shape-memory nonwovens in this study were likely to have relatively low shape recovery in comparison with that of the corresponding films. However, the shape memory may well be sufficient for use in practical applications in various fields.

CONCLUSIONS

Electrospun nonwovens of shape-memory PU block copolymers with hard-segment concentrations of 40

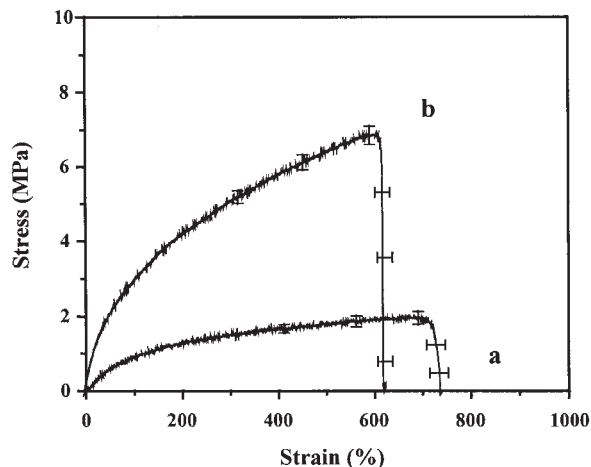


Figure 3 Stress-strain curves of PU block copolymer nonwovens prepared in the transverse direction via electrospinning as a function of the weight percentage of hard segments: (a) hard-segment concentration = 40 wt % and viscosity = 570 cPs and (b) hard-segment concentration = 50 wt % and viscosity = 530 cPs.

and 50 wt % were successfully prepared by electrospinning processing. The PU nonwovens spun at a lower solution viscosity (ca. 130–180 cPs) had an average fiber diameter of 800 nm and a beaded-on-fiber structure. In contrast, the samples spun at a high solution viscosity (ca. 530–570 cPs) showed a smooth fiber surface with an average diameter of 1300 nm. Using SEM, we observed that the electrospun PU nonwovens were composed of a broad distribution of fiber diameters. With a UTM, we observed that for a similar degree of viscosity, the electrospun PU nonwovens with a hard-segment concentration of 50 wt % had higher stress than those with a hard-segment

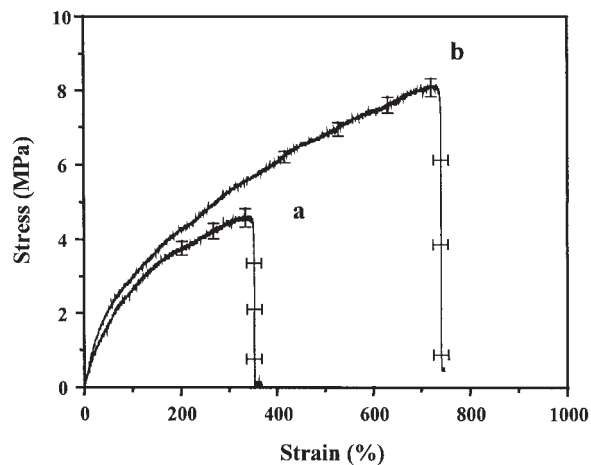
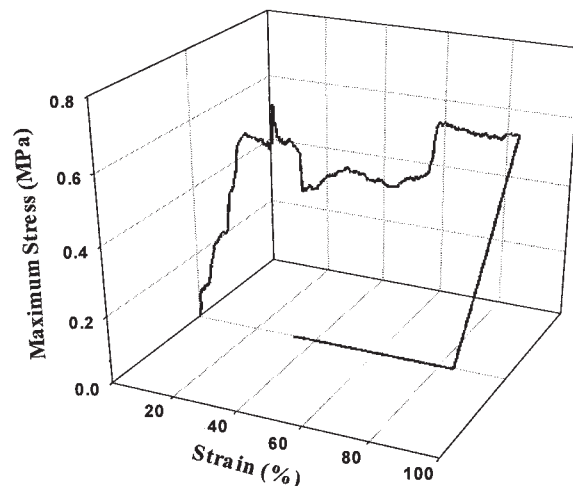
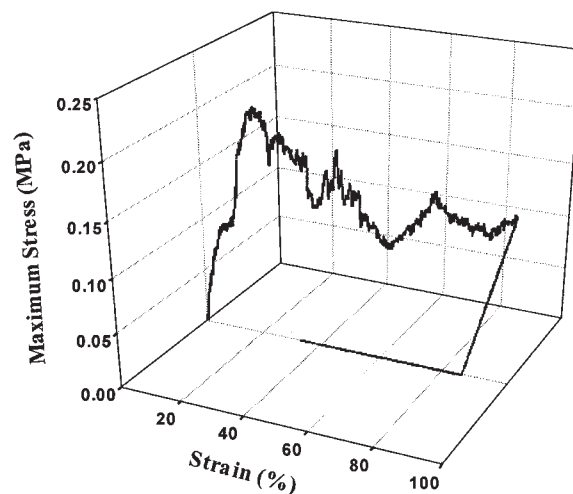


Figure 4 Stress-strain curves of PU block copolymer nonwovens prepared in the machine direction via electrospinning as a function of the viscosity at a hard-segment concentration of 50 wt %: (a) 175 and (b) 530 cPs.



(a)



(b)

Figure 5 Maximum stress and shape recovery of electrospun PU block copolymer nonwovens with hard-segment concentrations of (a) 40 and (b) 50 wt %.

concentration of 40 wt %. The mechanical properties of the electrospun PU nonwovens were also affected by the hard-segment concentration. More than 80% shape recovery was obtained in the electrospun PU nonwovens with hard-segment concentrations of 40 and 50 wt %. Consequently, we clearly established that controlling the hard-segment concentration in PU constitutes a significant parameter in the preparation of electrospun shape-memory nonwovens.

References

1. Richard, F.; Gordon, P. E. *Mater Technol* 1993, 8, 254.
2. Liang, C.; Rogers, C. A.; Malafeev, E. J. *J Intell Mater Struct* 1997, 8, 380.

3. Takahashi, T.; Hayashi, N.; Hayashi, S. *J Appl Polym Sci* 1996, 60, 1061.
4. Lai, Y. C.; Quinn, E. T.; Valint, P. L. *J Polym Sci Part A: Polym Chem* 1995, 33, 1767.
5. Deitzel, J. M.; Kleinmeyer, D.; Harris, D.; Tan, N. C. B. *Polymer* 2001, 42, 261.
6. Ohgo, K.; Zhao, C.; Kobayashi, M.; Asakura, T. *Polymer* 2003, 44, 841.
7. Lee, K. H.; Kim, H. Y.; Khil, M. S.; Ra, Y. M.; Lee, D. R. *Polymer* 2003, 44, 1287.
8. Ding, B.; Kim, H. Y.; Lee, S. C.; Shao, C. L.; Lee, D. R.; Park, S. J.; Kwag, G. B.; Choi, K. J. *J Polym Sci Part B: Polym Phys* 2002, 40, 1261.
9. Lee, K. H.; Kim, H. Y.; La, Y. M.; Lee, D. R.; Sung, N. H. *J Polym Sci Part B: Polym Phys* 2002, 40, 2259.
10. Deitzel, J. M.; Kleinmeyer, J. D.; Hirvonen, J. K.; Tan, N. C. B. *Polymer* 2001, 42, 8163.
11. Gibson, P.; Schreuder-Gibson, H.; Rivin, D. *Colloids Surf A* 2001, 187, 469.
12. Bergshoef, M. M.; Vancso, G. J. *Adv Mater* 1999, 11, 1362.
13. Li, W. L.; Laurencin, C. T.; Caterson, E. J.; Tuan, R. S.; Ko, F. K. *J Biomed Mater Res* 2002, 60, 613.
14. Kenawy, E. R.; Bowlin, G. L.; Mansfield, K.; Layman, J.; Simpson, D. G.; Sanders, E. H.; Wnek, G. E. *J Controlled Release* 2002, 81, 57.
15. Megelski, S.; Stephens, J. S.; Chase, B.; Rabolt, J. F. *Macromolecules* 2002, 35, 8456.
16. Fong, H.; Reneker, D. H. *J Polym Sci Part B: Polym Phys* 1999, 37, 3488.
17. Liu, H.; Hsieh, Y. L. *J Polym Sci Part B: Polym Phys* 2002, 40, 2119.
18. Doshi, J.; Reneker, D. H. *J Electrostat* 1995, 35, 151.
19. Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. *Polymer* 2001, 42, 9955.
20. Yarin, A. L.; Koombhongse, S.; Reneker, D. H. *J Appl Phys* 2001, 90, 4836.
21. Feng, J. *J Phys Fluids* 2002, 14, 3912.
22. Shao, C.; Kim, H. Y.; Gong, J.; Lee, D. R. *Nanotechnology* 2002, 13, 635.
23. Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. *Adv Mater* 2001, 13, 70.
24. Formhals, A. U.S. Pat. 1,975,504 (1934).
25. Tayler, G. I. *Proc R Soc London Ser A* 1969, 313, 453.
26. Lee, B. S.; Chun, B. C.; Chung, Y. C.; Sul, K. I.; Cho, J. W. *Macromolecules* 2001, 34, 6431.