Electrospinning of Polyacrylonitrile Nanofibers

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ABSTRACT: Polyacrylonitrile (PAN) was electrospun in dimethylformamide as a function of electric field, solution flow rate, and polymer concentration (C). The fiber diameter increased with C and ranged from 30 nm to 3.0 μm. The fiber diameter increased with the flow rate and decreased when the electric field was increased by a change in the working distance; however, it did not change significantly when the electric field was varied by a change in the voltage at a given working distance. The fibers below about 350 nm diameter contained beads, whereas above this diameter, bead-free fibers were obtained. For PAN with a molecular weight of 100,000 g/mol, the fiber diameter scaled as $C^{1.2}$ and $C^{7.5}$ at low (5.1–16.1 wt %) and high (17.5–22.1 wt %) C values, respectively. Both concentrations were in the semidilute entangled regime, where the specific viscosity scaled as $C^{4.4}$, consistent with De Gennes's scaling concepts. In the semidilute unentangled regime (0.5–3.1 wt %), where the viscosity scaled as $C^{1.3}$, microscopic or nanoscopic particles rather than fibers were obtained. Concentration-dependent electrospinning studies were also carried out for higher molecular weight PAN (250,000 and 700,00 g/mol). The results of these studies are also presented and discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1023–1029, 2006

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INTRODUCTION

Electrospinning is used to process nanometer- to micrometer-diameter fibers[1] and microscopic particles of various geometries[2] and has been demonstrated on more than 50 polymers.[3–8] During electrospinning, when an applied voltage is balanced with the surface tension (γ), the Taylor cone is initiated,[9] and with a further increase in voltage, a jet of charged solution, melt, or sol–gel is ejected. After traveling in a straight line for a certain distance, the jet undergoes whipping instability, resulting in bending and stretching and finally gets to the grounded target to form a fiber mat.[10] The fiber mat features a high porosity and high specific surface area and has applications in biomaterials (e.g., tissue engineering,[11] drug delivery,[12] biosenssor[13]), protective clothing,[14] filtration media,[15] and charge storage devices (supercapacitor and battery).[16–18]

Although electrospinning was first demonstrated in 1930s,[19] current interest in electrospinning dates back to the early 1990s, and the number of publications on the subject is rapidly increasing. Electrospinning is being practiced on natural polymers,[20] synthetic polymers,[21] biopolymers,[22] polymer solutions,[23] polymer melts,[24] liquid-crystalline polymers,[25] polymer blends,[26] and sol–gel ceramic precursors.[27] It can be used to process nanometer- to micrometer-diameter solid, porous,[28] hollow, or bicomponent continuous fibers,[29] microscopic cups, and nanowires.[30] Electrospinning can be used to make randomly oriented fiber mats and highly oriented fibers.[31,32] For many applications, precise diameter control during electrospinning is essential. The fiber diameter (d) and morphology are mainly controlled by the processing parameters, including flow rate (Q) and electric field [voltage electric field (E_V)/distance electric field (E_d)], and solution properties, including viscosity (η), γ, and conductivity.[33] High-η solutions result in bead-free, relatively large diameter fibers.[34–36] It has been shown that the polymer entanglement concentration is the minimum concentration for the formation of continuous fibers rather than droplets.[37] d of nylon decreased with increasing electric field.[38] The voltage also affects the shape and distribution of the defects. In electrospun polycarbonate, the defects changed from a global mushroom to a spindle shape due to the stronger stretching force with increasing voltage.[39] A number of excellent reviews on the subject have been published.

Polyacrylonitrile (PAN) is a carbon fiber precursor and is also used for activated carbon. Carbonized and activated electrospun PAN fibers are attractive for supercapacitor electrodes,[40] catalysis,[41] and other applications.[42] The diameter of the precursor PAN fiber affects the carbonization and activation conditions, the structure and properties of the ultimate carbon fiber, and the pore size and the pore size dis-

TABLE I
d **Values of Electrospun PAN Copolymer (MW = 100,000 g/mol) Fibers at Various Cs and Voltages**

C (wt %)	d (nm)				
	13 kV	16 kV	22 kV	25 kV	27 kV
5.1	50 ± 10	50 ± 10	50 ± 10	60 ± 10	80 ± 20
9.6	100 ± 10	80 ± 20	70 ± 10	100 ± 20	100 ± 20
13.8	160 ± 10	120 ± 20	150 ± 20	130 ± 30	130 ± 40
16.1	190 ± 20	230 ± 30	170 ± 40	240 ± 40	240 ± 40
17.5	**350 ± 20**	**400 ± 90**	**370 ± 40**	**380 ± 20**	**450 ± 80**
19.0	**450 ± 80**	**500 ± 120**	**590 ± 100**	**400 ± 60**	**600 ± 90**
19.7	**770 ± 60**	**800 ± 150**	**660 ± 40**	**760 ± 80**	**800 ± 130**
20.3	**900 ± 130**	**1200 ± 60**	**1100 ± 150**	**1000 ± 120**	**1200 ± 110**

The distance from needle to the target was 10 cm, and Q was 1 mL/h. Bead-free fibers are in bold.

tribution of the activated carbon product. Therefore, the control of *d* becomes an important factor. To achieve the effective *d* control, we report a systematic electrospinning study of PAN/*N,N*-dimethylformamide (DMF) solution as a function of the solution concentration, electric field, and solution *Q*.

EXPERIMENTAL

Poly(acrylonitrile-*co*-methyl acrylate) copolymer [molecular weight (MW) = 100,000 g/mol, containing about 4 wt % methacrylate copolymer] and PAN homopolymer (MW = 250,000 and 700,000 g/mol) obtained from Exlan Corp. of Osaka, Japan, was dried at 95°C *in vacuo* for 48 h and dissolved in DMF obtained from Aldrich (Milwaukee, WI), Rheology of the PAN/DMF solutions was carried out on a Hakke RS150 rheometer with a bob and cup arrangement at room temperature (the inner diameter of the cup was 5.5 cm; the gap between the bob and cup was 0.5 cm). γ was measured by a surface tensiomat (Fisher Scientific, Pittsburgh, PA) at room temperature. In a horizontal electrospinning set up, the PAN/DMF solution was loaded into a syringe and delivered to the tip of an 18-gauge (0.84 mm diameter) stainless steel needle with a syringe pump (Fisher Scientific). A Gamma high-voltage research power supply (model GPR-3060D, Ormond Beach, FL) was applied to the solution via the needle. The electrospun mats were collected on the aluminum foil wrapped on a grounded steel sheet. Scanning electron microscopy

was done on gold-sputter-coated mats with LEO 1530 thermally assisted field emission gun (FEG) scanning electron microscope (Oberkochen, Germany). The scanning electron microscopy images were used for *d* determination. An average value of 40 *d* measurements for each spinning condition for PAN with a MW of 100, 000 g/mol are reported in Tables I–III.

RESULTS AND DISCUSSION

The η values of the PAN solutions (MW = 100, 000 g/mol) as a function of shear rate are plotted in Figure 1. Zero shear viscosity was determined at each concentration, and the specific viscosity (η_{sp}) was calculated with the following equation:

$$\eta_{sp} = (\eta_s - \eta_0)/\eta_0$$

where η_s and η_0 are the zero shear viscosities of the solution and solvent, respectively. η_{sp} for various MW PANs are plotted as a function of concentration in Figure 2. η_{sp} scaled as $C^{1.3}$ and $C^{4.4}$ (where C is the polymer concentration) for PAN with a MW of 100,000 g/mol, as $C^{0.45}$, $C^{1.7}$, and $C^{3.6}$ for PAN with a MW of 250,000 g/mol, and as $C^{0.68}$, $C^{2.1}$, and $C^{3.9}$ for PAN with a MW of 700,000 g/mol. According to De Gennes's scaling concept, a polymer in a good solvent can be classified into four regimes with the following exponents: dilute ($\eta \approx C^1$), semidilute unentangled ($\eta \approx C^{1.25}$), semidilute entangled ($\eta \approx C^{4.8}$), and concentrated regime ($\eta \approx C^{3.6}$).[43] The entanglement concentration is the critical

TABLE II
d **Values of Electrospun PAN Copolymer (MW = 100,000 g/mol) Fibers at Various Qs and Solution Concentrations**

Q (mL/h)	d (nm)							
	5.1 wt %	9.6 wt %	13.8 wt %	16.1 wt %	17.5 wt %	19.0 wt %	19.7 wt %	20.3 wt %
0.5	30 ± 20	50 ± 20	80 ± 20	150 ± 30	200 ± 40	**350 ± 70**	**400 ± 60**	**600 ± 90**
1	50 ± 10	70 ± 10	150 ± 20	170 ± 40	**370 ± 40**	**590 ± 100**	**660 ± 40**	**1100 ± 150**
4	150 ± 40	**400 ± 49**	**460 ± 60**	**500 ± 80**	**700 ± 60**	**800 ± 90**	**900 ± 70**	**1350 ± 110**
6	300 ± 60	**900 ± 70**	**1000 ± 80**	**1200 ± 150**	**1500 ± 100**	**1650 ± 110**	**1800 ± 110**	**2000 ± 110**

The voltage was 22 kV, and the distance from the needle to the target was 10 cm. Bead-free fibers are in bold.

TABLE III
d **Values of Electrospun PAN Copolymer (MW = 100,000 g/mol) Fibers at Various E_d Values and Solution Concentrations**

E_d (V/cm)	*d* (nm)							
	5.1 wt %	9.6 wt %	13.8 wt %	16.1 wt %	17.5 wt %	19.0 wt %	19.7 wt %	20.3 wt %
4400	30 ± 10	60 ± 20	90 ± 20	120 ± 20	300 ± 60	**400 ± 90**	**490 ± 80**	**700 ± 100**
2200	50 ± 10	70 ± 10	150 ± 20	170 ± 40	**370 ± 40**	**590 ± 100**	**660 ± 40**	**1100 ± 150**
1467	60 ± 20	80 ± 20	120 ± 30	280 ± 50	**570 ± 70**	**650 ± 80**	**800 ± 90**	**1100 ± 100**
1100	70 ± 20	100 ± 20	200 ± 20	**380 ± 60**	**700 ± 100**	**800 ± 100**	**940 ± 80**	**1200 ± 130**

Q = 1 mL/h. Bead-free fibers are in bold.

concentration between the semidilute unentangled and semidilute entangled regimes. The scaling relationship was also experimentally studied. It has been reported that $\eta \approx C^{1.1-1.4}$ for the semidilute unentangled regime and $\eta \approx C^{4.25-4.5}$ for the semidiluted entangled regime. In general, the scaling exponents vary depending on the polymer, polymer conformation, and interaction between the polymer and the solvent. Factors such as branching and solubility[44,45] result in different exponents. In this study, PAN copolymer solutions with a MW of 100, 000 g/mol with $\eta_{sp} \approx C^{1.3}$ and $\eta_{sp} \approx C^{4.4}$ were in the semidilute unentangled and semidilute entangled regimes, respectively, and the PAN homopolymer solutions with a MW of 250,000 g/mol with $\eta_{sp} \approx C^{0.45}$, $C^{1.7}$, and $C^{3.6}$ and with a MW of 700, 000 g/mol with $\eta_{sp} \approx C^{0.68}$, $C^{2.1}$, and $C^{3.9}$ were in the dilute, semidilute unentangled, and semidilute entangled regimes, respectively. The entanglement concentrations for PANs with MWs of

100,000, 250,000, and 700,000 g/mol were determined to be 5.1, 3.1, and 1.5 wt %, respectively.

The scanning electron micrographs of electrospun PAN (100, 000 g/mol) copolymer solutions in a concentration range of 0.5 to 21 wt % are given in Figure 3. At low concentrations (0.5–3.1 wt %), nanoscopic to microscopic particles were obtained (typical size = 400–800 nm). Above the entanglement concentration (5.1 wt %), beaded (30 to ~ 300 nm diameter) and bead-free fibers (~ 350–2.0 μm) were obtained (Tables I–III and Fig. 3). For all the three PANs, the continuous fibers were obtained above their entanglement concentrations. This was consistent with Long et al.'s[37] work on the electrospun poly (ethylene terephthalate-*co*-ethylene isophthalate) copolymer (PET-*co*-PEI).

At low *C* values, bead formation is a common problem in electrospinning.[46,47] The drawability of the polymer solutions and melts is governed by the η/γ ratio.[48] The values of η, γ, and η/γ for several PAN (MW = 100,000 g/mol) concentrations in DMF
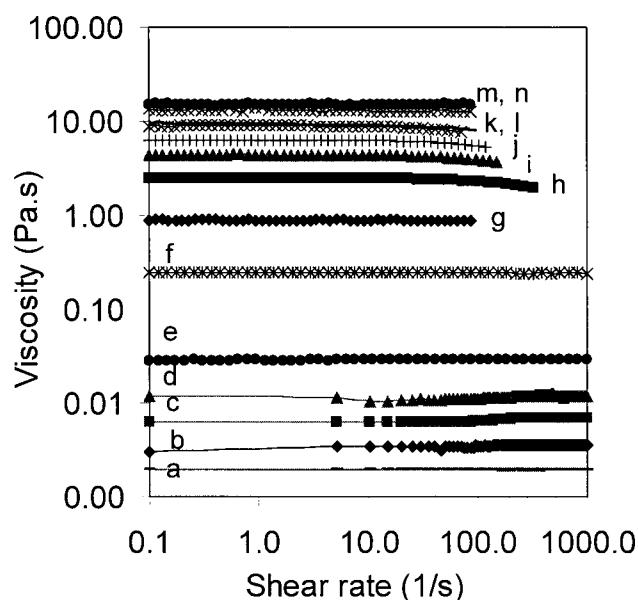

Figure 1 η of the PAN copolymer solutions (MW = 100,000 g/mol) as a function of the shear rate at various concentrations (from bottom to top): (a) 0.5, (b) 1.1, (c) 2.1, (d) 3.1, (e) 5.1, (f) 9.6, (g) 13.8, (h) 16.1, (i) 17.5, (j) 19.0, (k) 19.7, (l) 20.3, (m) 21.2, and (n) 22.1 wt %.
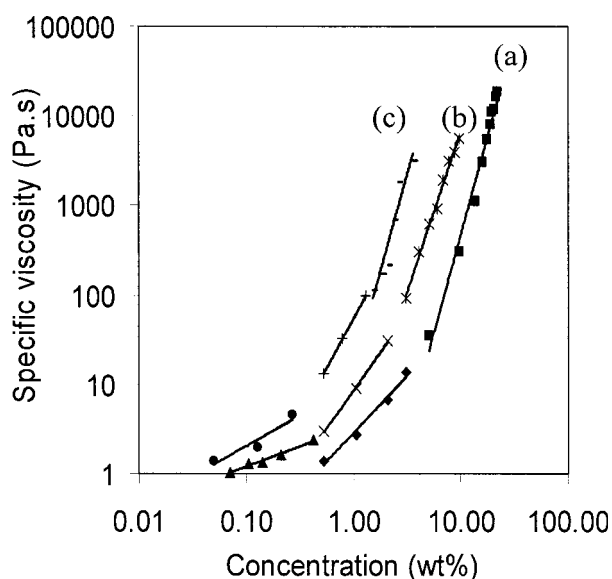

Figure 2 η_{sp} as a function of the concentration of the PAN solutions: (a) PAN copolymer with a MW of 100,000 g/mol, (b) PAN homopolymer with a MW of 250,000 g/mol, and (c) PAN homopolymer with a MW of 700,000 g/mol.
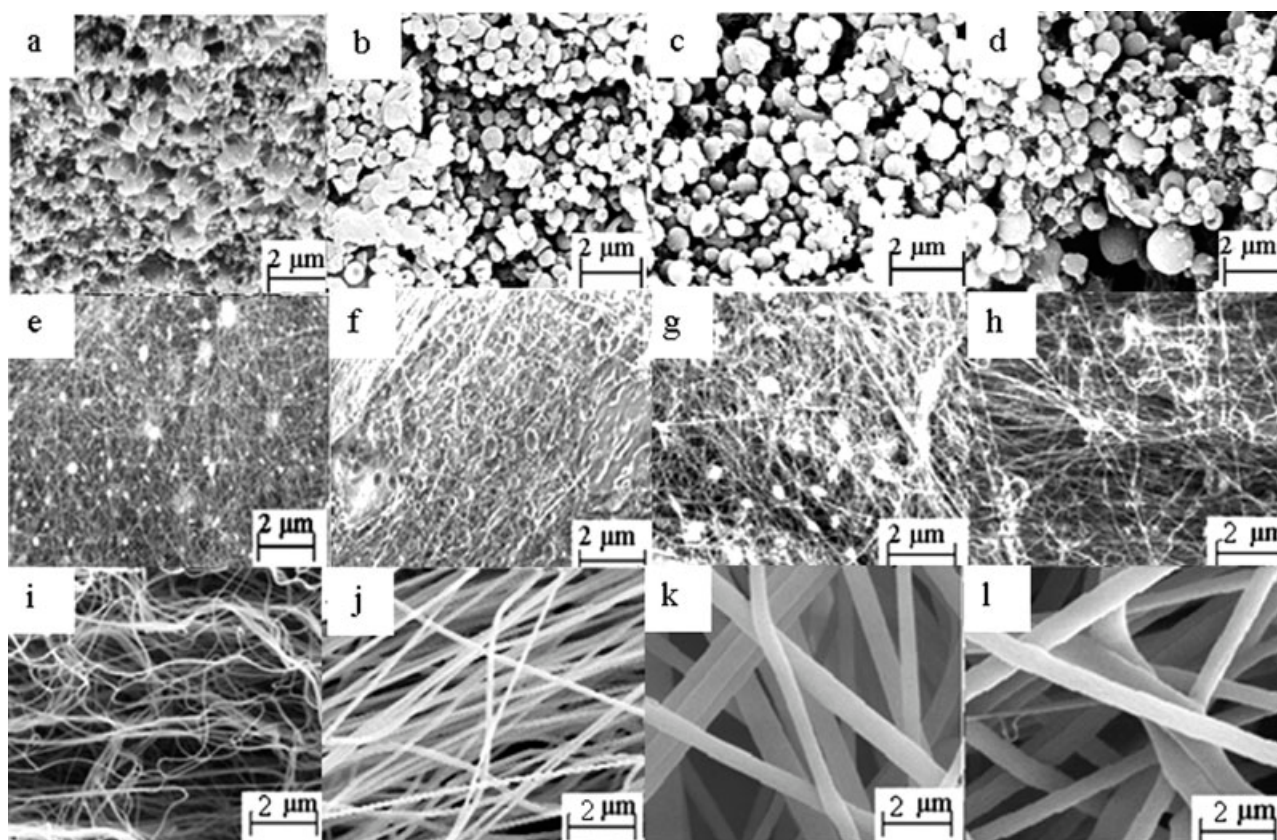
Figure 3 Scanning electron micrographs of electrospun PAN copolymer fibers (MW = 100,000 g/mol) at various concentrations [voltage = 22 kV; Q = 1 mL/h; the distance between the tip and the target (10 cm) was kept constant]: (a) 0.5, (b) 1.1, (c) 2.1, (d) 3.1, (e) 5.1, (f) 9.6, (g) 13.8, (h) 16.1, (i) 17.5, (j) 19.0, (k) 19.7, and (l) 20.3 wt %.

are listed in Table IV. In the unentangled regime, as expected, the drawability represented by η/γ was extremely low, whereas above the entanglement concentration, significantly higher drawability values were obtained. The use of lower γ solvents, resulting in comparable η, provides better drawability, and hence, bead-free, smaller diameter fibers at lower concentration can be expected. By increasing the electrical field or η or by decreasing γ, bead formation can be suppressed. High C values result in high η and explain the formation of the bead-free fibers at such concentrations.

We varied E_d by changing the distance (5–20 cm) between the needle and the target while keeping the

voltage constant at 22 kV. d (PAN MW = 100,000 g/mol) as a function of E_d is given in Figure 4. For low concentrations and at a high electric field, the diameter was as low as 30 nm, whereas at high concentrations and at a low electric field, diameters above 1 μm were observed. For all the concentrations at a given Q, the diameter decreased with increasing electric field. We also varied E_V by increasing the voltage from 13 to 27 kV while keeping the distance constant at 10 cm. d is plotted as a function of E_V in Figure 5. Contrary to Figure 4, d did not exhibit a significant dependence on E_V. This observation was consistent with the electrospinning of polysulfone[49] and nylon. The d of polysulfone showed a slight decrease from 344 ± 51 nm to 323 ± 22 nm when the voltage was changed from 10 to 20 kV at a distance of 10 cm. However, this change in diameter was within experimental error and, therefore, could be ignored. d of electrospun nylon also did not show a monotonic decrease with increasing voltage. An increase in voltage did not have a significant effect on the diameter, whereas a change in the distance at a constant voltage affected d, even though the electric field values (E_d and E_V) were the same. The current was also observed to be different in the electro-

TABLE IV
Drawability of the PAN Copolymer
(MW = 100,000 g/mol) at Various Cs

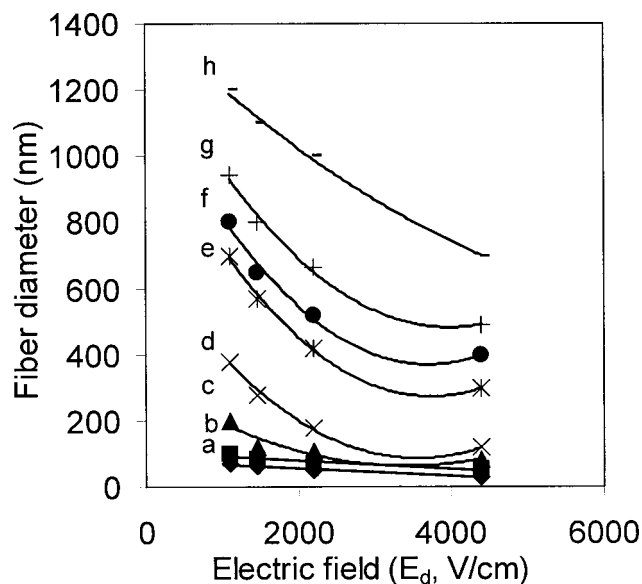| C (wt %)	η_0 (Pa s)	γ (N/m)	Drawability (η_0/γ; s/m)
0.5	0.002	0.037	0.05
3.1	0.012	0.037	0.32
13.8	0.88	0.039	23
19	6.34	0.039	163

Figure 4 d as a function of E_d for the PAN copolymer solutions at various concentrations (polymer MW = 100,000 g/mol; voltage = 22 kV; Q = 1 mL/h): (a) 5.1, (b) 9.6, (c) 13.8, (d) 16.1, (e) 17.5, (f) 19.0, (g) 19.7, and (h) 20.3 wt %.

Figure 6 d as a function of Q for the PAN copolymer solutions with various concentrations (MW = 100,000 g/mol; voltage = 22 kV; the distance from the needle to the target was 10 cm).

spinning of poly(ethylene oxide) (PEO), even though the electric fields, E_d and E_V, were equal.[50] The difference in electric field distribution and current may be responsible for the different diameter dependence on E_d and E_V.

d as a function of Q for various concentrations is plotted in Figure 6. d increased with Q. At low concentrations, diameter scaled with $Q^{1.2}$. Diameter de-
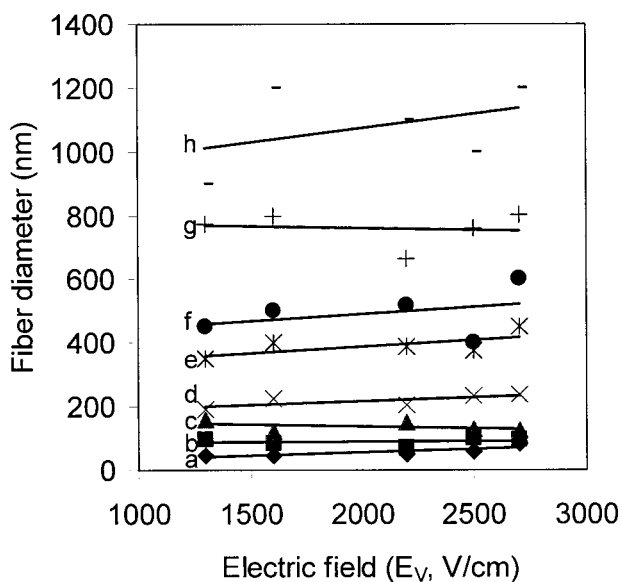
pendence on concentration decreased with increasing concentration, and at the highest concentration, diameter scaled as $Q^{0.4}$ (Fig. 7).

In this study, d exhibited two distinct power law dependences on C in the semidilute entangled regime. d scaled with the concentrations as $C^{1.2}$ and

Figure 5 d as a function of E_V for the PAN copolymer solutions at various concentrations (polymer MW = 100,000 g/mol; Q = 1 mL/h; the distance from the needle to the target was 10 cm): (a) 5.1, (b) 9.6, (c) 13.8, (d) 16.1, (e) 17.5, (f) 19.0, (g) 19.7, and (h) 20.3 wt %.
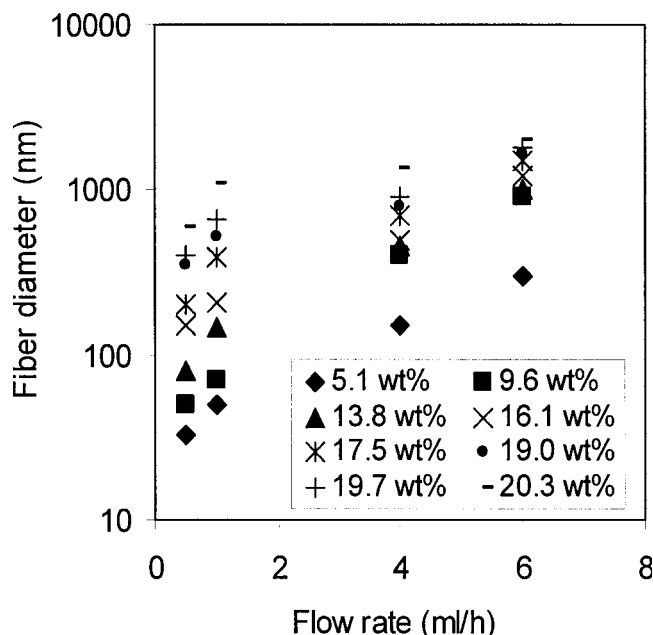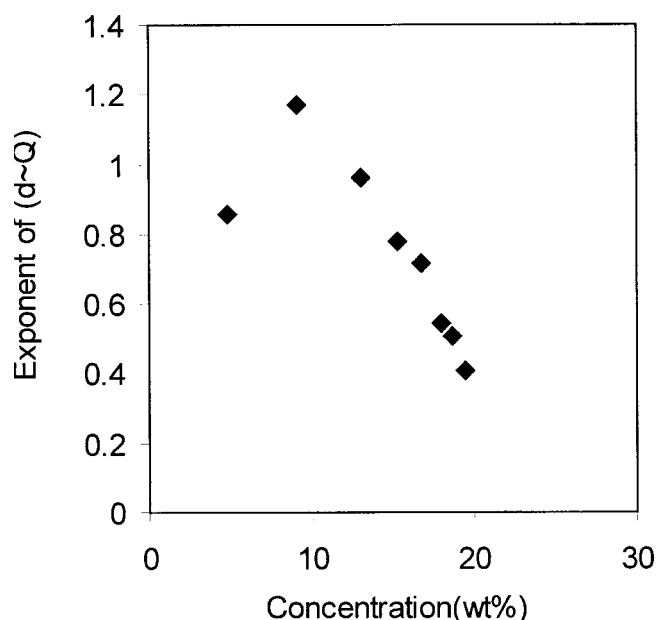

Figure 7 Exponent of d versus Q as a function of the concentration (PAN copolymer MW = 100,000 g/mol; voltage = 22 kV; the distance from the needle to the target was 10 cm).
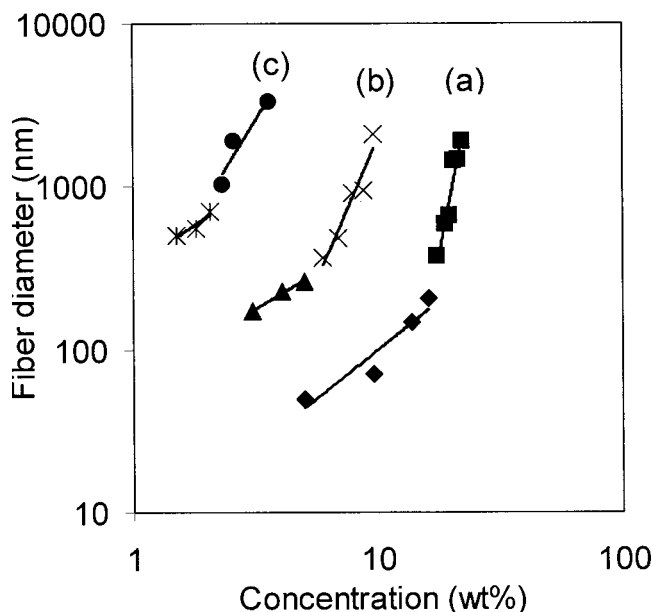
Figure 8 *d* as a function of the concentration (*Q* = 1 mL/h; voltage = 22 kV; the distance between the tip and the target was 10 cm): (a) PAN copolymer with a MW of 100,000 g/mol, (b) PAN homopolymer with a MW of 250,000 g/mol, and (c) PAN homopolymer with a MW of 700,000 g/mol.

$C^{7.5}$ for PAN with a MW of 100, 000 g/mol, scaled with concentration as $C^{0.88}$ and $C^{3.5}$ for PAN with a MW of 250,000 g/mol, and scaled with concentration as $C^{0.99}$ and $C^{2.5}$ for PAN with a MW of 700, 000 g/mol (Fig. 8). However, for a given polymer system, only one power law has been reported in the literature. The diameter scaled as $C^{0.5}$ for PEO,[51] $C^{3.0}$ for PET-*co*-PEI and polyurethane (PU),[52] $C^{3.3}$ for fibrinogen,[10] $C^{2.6}$ for polyamide 6 (PA-6),[53] and $C^{3.1}$ for poly(methyl methacrylate)[54] (PMMA; Table V). However, for poly(vinyl pyrrolidone) (PVP) diameter scaled as $C^{1.8}$ and with further increase in the concentration an upturn in the diameter was observed,[55] suggesting a second power law with the significantly higher exponent of $C^{7.0}$.

The beads on the fibers were caused either by high γ or the poor polymer chain entanglement in the solution. In the PAN solutions, γ did not change significantly with the concentration (Table IV), which suggests that the poor polymer chain entanglement was perhaps the main reason for the bead formation.

During electrospinning process, a single jet ejecting from the Taylor cone can possibly split or break up into subjets or droplets if the polymer chain entanglement is not strong enough. The sub-jets most likely result in beaded fibers. During the electrospinning of higher concentration solutions, the jet does not split due to the sufficient chain entanglement, and this single jet gets to target to form larger diameter fibers. Therefore, the different chain entanglement densities ultimately determine whether the

fiber forms from a sub-jet or a single jet, which results in different *d* dependence on the solution concentration.

The two PAN homopolymers (MW = 250,000 and 700,000 g/mol) had very comparable *d* dependences on the concentration, whereas the PAN copolymer (MW = 100,000 g/mol) exhibited a much stronger diameter dependence on concentration in the high concentration range. This study did not answer the question of whether the differences in the diameter dependence were a result of the use of copolymer in the low-MW PAN or whether these differences were simply a result of differences in MW. However, for PMMA of different MWs, only one diameter dependence on MW was reported.

CONCLUSIONS

PAN copolymers and homopolymers with different MWs were electrospun in dimethyl formamide. The voltage was varied from 13 to 27 kV, the needle to the target distance was varied from 5 to 20 cm, and *Q* was varied from 0.5 to 6 mL/h. *d* decreased when the electric field was increased by a change in the distance between the needle and the target, whereas it was relatively insensitive to an increase in voltage at a given distance. *d* exhibited a strong dependence on *Q* at relatively low concentrations, and this dependence continuously decreased with increasing concentration. Electrospinning in the semidilute unentangled regime resulted in microscopic and nanoscopic particles, whereas continuous fibers were obtained when the spinning was done from the semidilute entangled regime. *d* exhibited two distinct power law dependences on the concentration in the semidilute entangled regimes ($d \approx C^{1.2}$ and $C^{7.5}$ for PAN with a MW of 100, 000 g/mol; $d \approx C^{0.88}$ and $C^{3.5}$ for PAN with a MW of 250,000 g/mol; $d \approx C^{0.99}$ and $C^{2.5}$ for PAN with a MW of 700,000 g/mol). Literature reports show that diameter scaled as C^3 or $C^{3.3}$ in PET-*co*-PEI and fibri-

TABLE V
Summary of the Power Law Relationship between *d* and the *C* Reported in the Literature and in this Study

Polymer	Exponent a ($d \approx C^a$)
PEO[51]	0.5
PET-*co*-PEI[37]	3.0
PU[52]	3.0
Fibrinogen[10]	3.3
PA-6[53]	2.6
PMMA[54]	3.1
PVP[55]	1.8, 7.0
PAN (100,000)	1.2, 7.5
PAN (250,000)	0.88, 3.5
PAN (700,000)	0.99, 2.5

nogen, whereas a significantly lower concentration dependence was obtained in PEO ($C^{0.5}$).

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