Effect of Ionic Salts on the Processing of Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) Nanofibers

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ABSTRACT: We studied the effect of nanofiber uniformity on electrospinning due to the charging of added ionic salts, as compared to the droplet current nonadded ionic salts and the charge-to-mass ratio of a highly conducting liquid. Various ionic salt concentrations were investigated. For an ionic salt concentration of 0.01 mol %, an applied electric field of 15 kV, and a spinning distance of 15 cm, the experimental results show that uniform nanofibers that did not contain any beads were synthesized with an optimal ionic salt concentration, when the convective current was two orders of magnitude higher than the nonadded ionic salt droplet current. The obtained fibers were uniform, with diameters of around 70 nm. We were able to produce these uniform nanofibers by controlling the balance between two opposing factors during electrospinning, by increasing the number of charge carriers and decreasing the viscosity of the solution. The effect of the ionic salts on the morphology of the electrospun nanofibers was investigated with field-emission scanning electron microscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1388–1393, 2005

Key words: electrospinning; current; ionic salt; nanofiber

INTRODUCTION

Electrospinning can be used to fabricate nanofibers. Recently, electrospun nanofibers have attracted a great deal of attention in actuator[1] and sensor[2] applications. The electrospinning process involves a polymer solution that is charged under a high voltage, which is then ejected from a needle or capillary tip. The ejected polymer solution forms a so-called Taylor cone at the tip and is drawn toward a grounded collector, for example, a flat screen or drum. During the ejection, the jet travels toward the collector, and the solvent evaporates, depositing a nonwoven fiber mat on the collector. These mats are typically composed of very small fibers, with diameters ranging from tens of nanometers to a few micrometers.[3–5]

Electrospinning can trace its roots back to electrostatic spraying. When a jet of a conducting liquid, such as water, is subjected to a high direct-current (dc) electric field, the jet experiences a lateral mode of instability due the liquid's fast charge relaxation time. This lateral mode of instability has been investigated and reported by several researchers.[6–8] However, there has been no systematic study to relate the level of discharge current to the main droplet current produced by such a breakup mechanism. This lack of theoretical and experimental analysis of the whipping mode of instability is probably due to the complexity and chaotic nature of the process. In the case of low-viscosity liquids, the jet decomposes into droplets as a result of the low surface tension. For high-viscosity liquids, the final products are formed as fibers or beads and are determined by a combination of the electrospinning parameters. The formation of electrospun fibers containing beads is related to the instability of the polymer solution jet,[9] and the breakup of the jet depends on the critical electric current. The higher the electric current the jet carries, then the less likely it is to form droplets. A higher net charge density of the polymer solution, therefore, can yield thinner fibers with no beads. Reneker et al.[5] characterized the bending instability of a charged jet during electrospinning, and Shin et al.[10] studied the instability of an electrically forced fluid jet. Both groups argued that the essential mechanism of electrospinning was that of a rapidly whipped fluid jet.

Usually, the electric current arising from the ionic conduction of the charges in a polymer solution is assumed to be negligible in the electrospinning process.[11] The only mechanism of charge transport is assumed to be the flow arising from the polymer solution jet from the capillary tip to the collector. Thus, when all the other electrospinning parameters are held constant (especially the feed rate of the polymer solution to the capillary tip and the applied voltage), an increase in the electrospinning current generally results in an increase in the mass flow rate of the polymer solution jet from the capillary tip to the grounded collector. If the net charge density carried by the jet in

the electrospinning process is primarily affected by the mass flow rate of the polymer solution, the conductivity of the polymer solution is the most important experimental variable when all the other process parameters are fixed. For example, Zong et al.[12] showed the effect of various types of salt on the morphology of electrospun membranes. The added salts resulted in a higher charge density on the surface of the ejected jet during electrospinning, and thus, a higher electrical charge could be carried by the electrospun jet. In addition, the charge density was uniformly distributed because the charge density on the surface of the jet was enhanced by the ionic salts.

Generally, beaded fibers disappear when the net charge density carried by the spinning polymer solution jet increases above a certain value, and the addition of ionic salts increases the net polymer solution or jet surface charge density. It is important therefore, to study the effect of the addition of ionic salts on the processing of electrospun nanofibers and on the resulting morphologies of the resulting electrospun nanofibers.

The goal of our research was to investigate the effect of different concentrations of ionic salts on polymer solutions in the electrospinning process, with the aim to produce nanofibers that contained no beads. The influence of the salt concentration on the morphology of the electrospun nanofibers was investigated with field-emission scanning electron microscopy (FESEM).

EXPERIMENTAL

Materials

Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS), with an average molecular weight of 2×10^6 g/mol, sodium chloride (NaCl), and calcium chloride (CaCl$_2$) were purchased from the Aldrich Chemical Co. (Milwaukee, WI). All of the other chemicals were used without any further purification.

Preparation of electrospun nanofibers

The electrospinning apparatus consisted of a syringe pump (KD Scientific Co.), a metal needle, a grounded target (consisting of aluminum foil fixed to a drum), and a high-voltage supply (Nano Technics Co., Korea). A voltage of 20 kV was applied to the polymer solution, and the distance between the needle tip and the target surface was 15 cm. Electrospinning was then carried out for 30 min at room temperature. The polymer solution was delivered with a syringe pump to control the feed flow rate (10 μL/min). The resulting fibers were collected on a metal drum rotating at 500 rpm to produce a sheet of nonwoven fabric. We prepared the polymer solutions (5 wt %) at room temperature over a 12-h period by gently stirring solutions
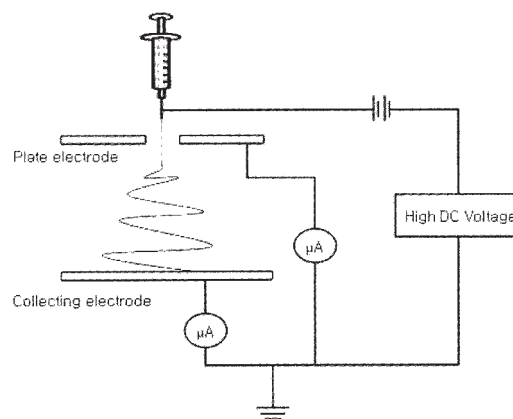

Figure 1 Schematic drawing of the experimental setup used for measurement of the electrospinning current.

containing different concentrations (0.0001, 0.001, 0.01, and 0.1 mol %) of NaCl and CaCl$_2$ salts in distilled water. The polymer solution was placed in a 5-mL syringe attached to a syringe pump (KD Scientific Co.) placed in a horizontal mount. All the electrospinning parameters were fixed to determine the effect of the concentration of NaCl and CaCl$_2$ on the electrospinning process and fiber morphology.

Characterization

The viscosity of the polymer solutions was determined with a Brookfield digital viscometer (model DV-II, Middleboro, MA) at 25°C. The conductivity of the salt solutions was determined with a conductivity meter (Hana Instruments, model HI 9385, Seoul, Korea) at 25°C. A schematic drawing of the experimental apparatus used to determine the discharge and droplet currents is shown in Figure 1. The key feature of this setup was its capability to discriminate between the discharge and main droplet currents. The main droplets passed through the opening of the electrode into the collector, where the current was measured with an electrometer. On the other hand, the discharge currents were monitored on a plate electrode. When satellites formed, the droplets exhibited different trajectories. The deflection of the discharge currents was due to both the applied and space charge fields.

To measure the deposition rate, the electrospun polymer was cut into 3 cm $\times$ 3 cm squares, and each electrospun slice was then weighed. This was repeated five times on at least two separate samples. The diameters and the morphologies of the electrospun nanofibers were determined with FESEM (Jeol JSM-6700F, Japan) after the samples had been coated with a gold film. Analysis of the fiber diameters and determination of the number of beads were based on the assessment of a minimum of 10 image fields obtained from two separate samples.
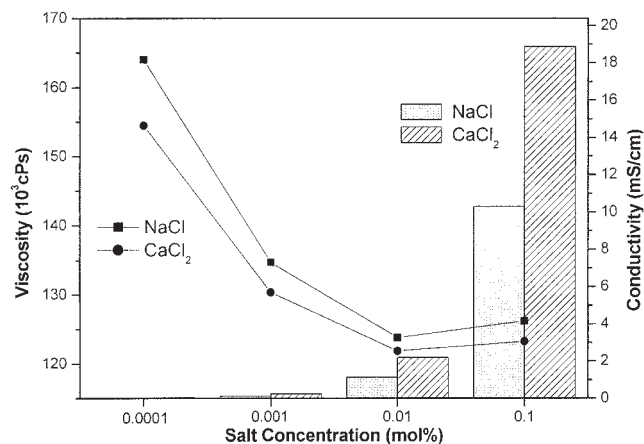
Figure 2 Effect of ionic salt concentration on the polymer viscosity and conductivity of the salt solution.

RESULTS AND DISCUSSION

The usual processing parameters for electrospinning include concentration, distance from the tip to the collector, applied voltage, and feed rate. Moreover, conductivity and viscosity are also very important parameters for the electrospinning process. Figure 2 shows the effect of the ionic salt concentration on the polymer viscosity and the conductivity of the salt solution. The conductivity of the salt solution increased with increasing concentration of ionic salt, as was expected. On the other hand, the polymer viscosity decreased with increasing concentration of ionic salt. The ionic salts used were soluble in water, as was the PAMPS, and these could form charged ions. The ionic conductivity of a polymer electrolyte depends on both the concentration of the conducting species and on its mobility. At higher added salt concentrations, the number of charge-carrier ions correspondingly increases, and the polymer solution viscosity decreases, which also reflects the increased ionic mobility. The buildup of charge carriers is offset by the retarding effect of ion aggregates, such as the formation of ion pairs and triplets, which constrain the ionic and polymer segmental mobility.

Taylor[13] observed that in a monomeric fluid, lower viscosities resulted in the breakup of the electrically driven jet into individual droplets; that is, as the viscosity increases, higher electrical forces are required to overcome both the surface tension and the viscoelastic forces that stretch the fibers. A higher electrical force confers a higher charge density on the surface of the ejected jet. Demir et al.[14] showed that the flow rate of an ejected jet and the charge density (or current) are directly related. As a result, the flow rate of a jet increases as the charge density increases. The presence of an ionic salt makes it easier for more electric charge to exist on an ejected jet's surface for a given electrical force. As a result of the addition of an ionic salt, the mass flow of an ejected jet increases from the capillary tip to the collecting screen.

Under an applied dc potential, the conducting liquid jet becomes an equipotential surface. As a consequence, the radial component of the field dominates the tangential (or axial) component. The nonuniformity of the applied electric field produces interfacial deformations in the jet, and the amplitude of these electrically induced deformations is proportional to the strength of the applied field. The shape and position of the deformations propagate along the surface of the traveling jet when it is some distance away from the capillary tip, and the peaks and valleys of these deformations run perpendicular to the axis of the jet. This electrically driven motion of the jet is known as *whipping*, or *lateral instability*.

Due to the high sensitivity of the previously discussed process, the whipping and segmentation of the jet do not follow a predetermined pattern and appear to be chaotic in nature. However, the degree of whipping depends on the strength of the applied dc field and the type of source liquid. From consideration of the minimum surface energy, the molecular and surface tension forces tend to decrease the surface area and the distance between the molecules (i.e., the intermolecular distance) and, hence, maintain the liquid in a state of equilibrium. On the other hand, the electrical force increases the surface area so that the energy component due to the surface charge is minimized. These competing effects attempt to minimize the surface energy and result in a sudden increase in the surface area.[6] The increase in area is manifested as a rapid sidewise displacement of parts of the liquid jet. Hence, large looping filaments are formed on alternate sides of the jet axis. Generally, this extremely unstable lateral instability mode produces an elongation of the liquid jet, which leads to the breakup of the jet, resulting in the production of beaded nonuniform nanofibers. The available experimental evidence suggests that these droplets are not only different in size, but the patterns that lead to their formation are significantly different.

A plot of the observed discharge current versus applied voltage is shown in Figure 3(a). The discharge current exhibited by the polymer solution with added ionic salt was much higher than that of the polymer solution in distilled water. This may have been due to the dissociation of impurities. The polymer solution with added ionic salt contained the salt elements and other impurities, which as a result of the high electric field, dissociated into ions, which increased the ionic current. The experiment revealed that the discharge current increased more rapidly with increasing conductivity than the viscosity decreased. The data for the polymer solution with added ionic salt suggest that most of the discharge current was due to the ionic
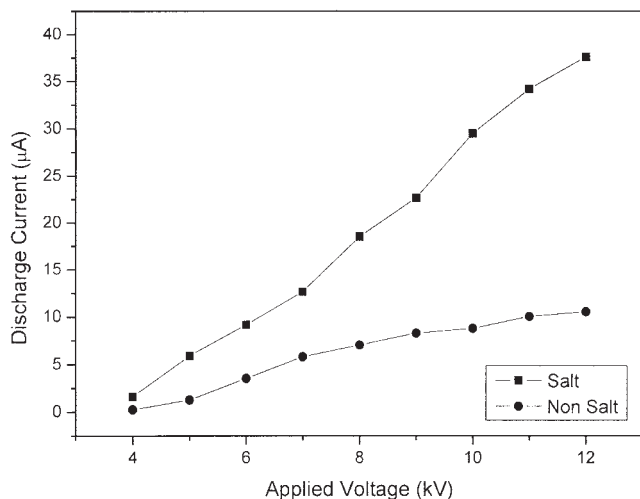
(a)
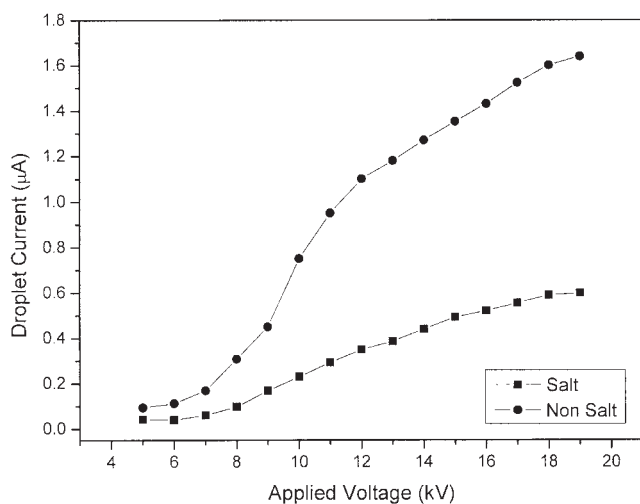
(b)

Figure 3 Relationship between the (a) discharge current and (b) droplet current for the comparison of an added salt polymer solution (0.01 mol %) and a pure-water polymer solution.

current resulting from the ionization of the impurities within the liquid.

Figure 3(b) shows the droplet current as a function of the applied dc voltage. For the polymer solution with added ionic salt, the droplet current was lower than the polymer solution with distilled water because most of the system current was associated with the discharge current. As shown by the experimental results, the discharge current was two orders of magnitude higher than the main droplet current. This indicates that most of the current drawn from the power supply was associated with the undesirable discharge current.

Figure 4 shows the dependence of the deposition rate on the ionic salt concentration. Due to the high conductivity of the polymer solution with added ionic salt, it exhibited the highest droplet current. The

charge-to-deposition ratio increased with increasing ionic salt concentration. This was because as the ionic salt concentration increased, more charge carriers were produced, which resulted in a more highly charged jet. In the case of the polymer solution with added ionic salt, a current of a few microamperes was recorded on the plate electrode, even though the plate was observed to be dry. In such a case, the plate current could only be attributed to the surface ionization of the jet, which was due to the conductivity of the working fluid.

The lowest ionic salt concentration showed the lowest deposition rate. At this concentration, the polymer solution on the surface of the ejected jet was less affected by the increased charge from the presence of the ionic salt. At higher ionic salt concentrations of 0.01 mol % or greater, there was evidently a sufficient surface charge on the ejected jet to cause the deposition of droplets. The addition of an ionic salt formed a more highly charged jet when it was driven by an electric field.

Figure 5 shows a representative scanning electron microscopy (SEM) image of the nanofibers formed by electrospinning solutions with different NaCl concentrations. All of the other electrospinning parameters were kept constant: polymer concentration = 5 wt %, applied voltage = 20 kV, deposition distance = 15 cm, and polymer solution feed rate = 10 μL/min. Figure 3 shows that different ionic salt concentrations had effects on the final fiber morphology. The changes in morphology of the nanofibers were a result of a combination of factors related to the increase in ionic salt concentration. The lowest ionic salt concentration PAMPS solutions were deposited as nonuniform fibers that contained beads. At higher salt concentrations of 0.01 mol %, no beads were formed (see Fig. 6). There was evidently sufficient electric charge on the surface of the ejected jet to break down the electrically driven jet and allow the electrostatic stress to elongate the jet. There was a balance between these two oppos-
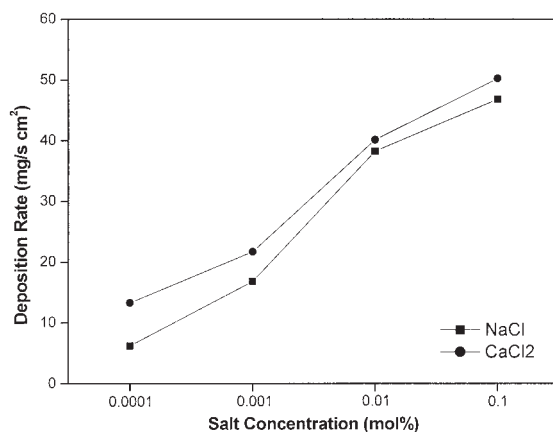

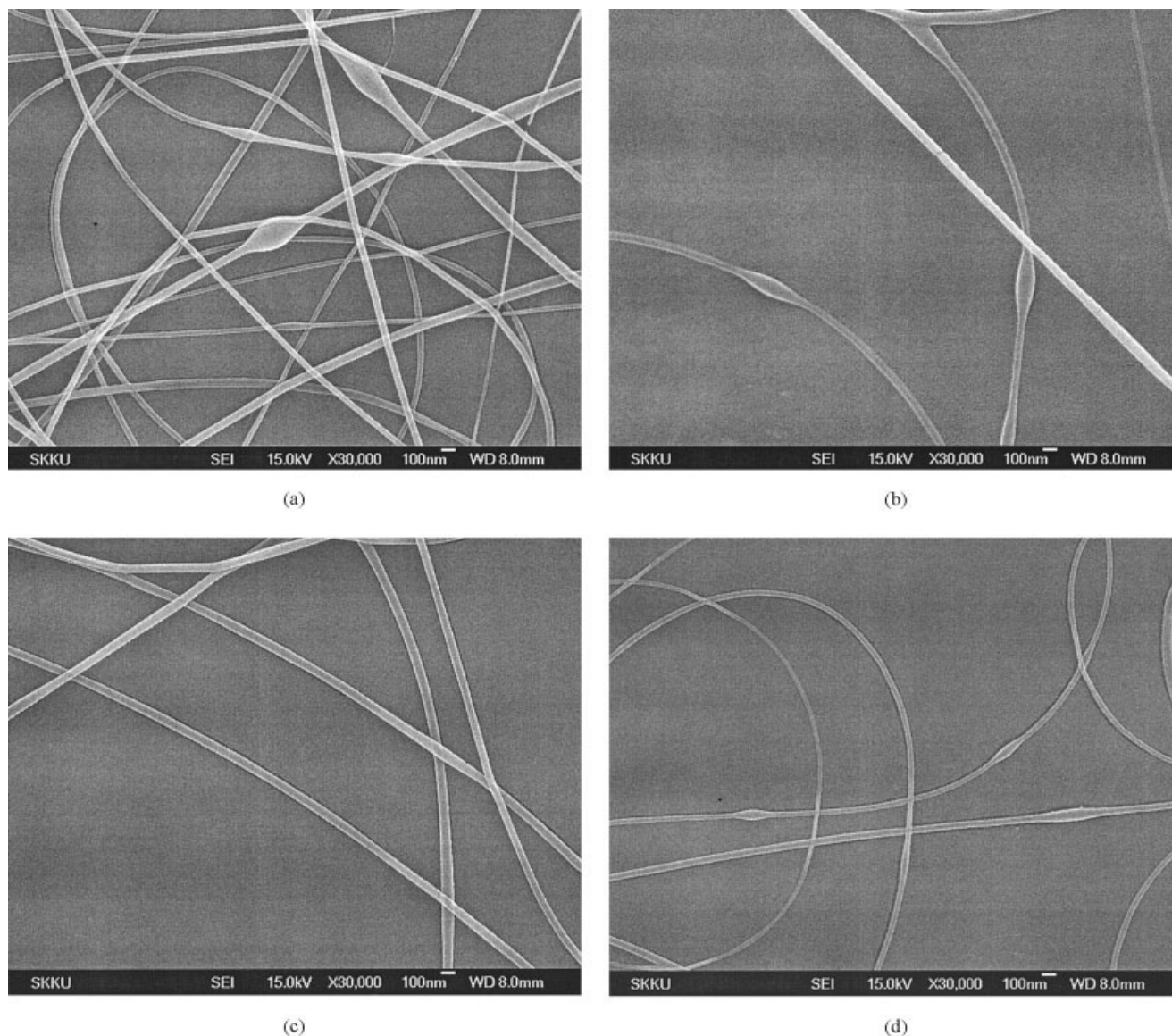**Figure 4** Dependence of the deposition rate on the concentration of ionic salt.

Figure 5 SEM images of PAMPS nanofibers formed by the electrospinning of a 5 wt % solution with an applied voltage of 15 kV, a feed rate of 10 μL/min, and NaCl concentrations of (a) 0.0001, (b) 0.001, (c) 0.01, and (d) 0.1 mol %.

ing forces in the electrospinning process created by increasing the number of charge-carrier ions and decreasing the viscosity. At an added salt concentration of 0.1 mol %, we observed the smallest fiber diameter. However, beads reappeared at this concentration. This phenomenon shows that the PAMPS solutions were too conductive to be drawn into uniform fibers before the breakdown of the molecular chain entanglement could occur. Deitzel et al.[9] claimed that the instability of an ejected jet with an excess charge density contributed to an increase in the number of beads. It is important that the excess electrical charge perturbed the ejected jet to obtain uniform fibers under an applied electric field. This behavior can be explained by the higher charge density on the surface of the ejected jet during electrospinning after the addition of an ionic

salt, and thus, more electric charge was carried by the electrospun polymer solution. As the charge carried by the jet increased, higher elongation forces were imposed on the jet under the applied electrical field. According to previous reports,[4,5,9,10] the overall tension in the fibers is dependent on self-repulsion from the excess charges on the jet. Therefore, as the charge density increases, the diameter of the resulting fibers and the number of beads decrease.

Figure 7 shows the average diameter of the nanofibers and contains a bar chart showing the average number of beads at any given salt concentration. The diameter of the fibers and the number of beads were related to the ionic salt concentration through the balancing of the two opposing factors during electrospinning. The fibers from the 0.0001 mol % salt solu-

tion exhibited the largest average fiber diameter of around 75 nm, whereas the fibers from the 0.01 mol % salt solution exhibited the smallest average fiber diameter of around 43 nm. However, the observed increase in the number of beads at an ionic salt concentration of 0.1 mol % was due to the excess net charge that flowed into the jet as it passed through the capillary tip. The morphology of the final fibers was changed from the uniform fibers that were electrospun without containing any beads.

CONCLUSIONS

The electrospinning process was shown to produce nanofibers that did not contain any beads, and the effect of the addition of ionic salt on the processing of nanofibers was established. The experimental evidence indicates that the optimum current approach pertaining to the disintegration of a charged liquid jet is valid. The data provide considerable insight into the relative magnitude of the discharge current and the droplet current, especially for the electrospinning of a polymer solution containing an added ionic salt. The results obtained confirm that ionic salts increased the electric charge density during electrospinning. Morphological control of beads and fiber morphology were achieved by balancing two opposing factors: the number of charge carriers in the polymer solution and the viscosity of the solu-
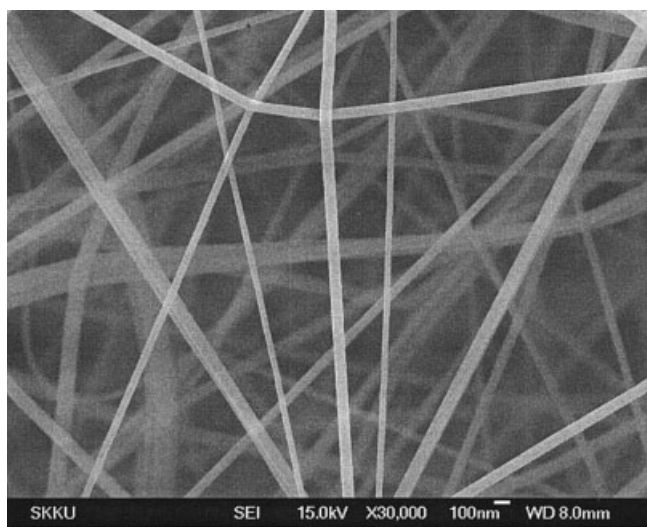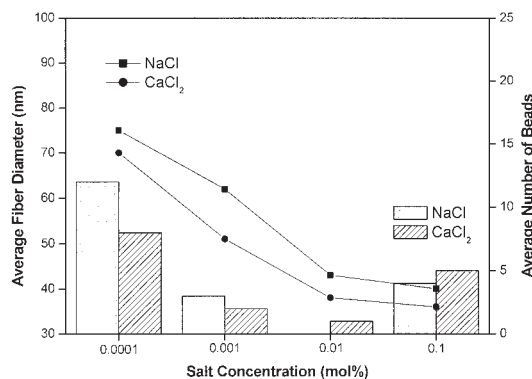
Figure 7 Effect of ionic salt concentration on the average fiber diameter and number of beads in the electrospun nanofibers.

tion. Through the addition of an ionic salt, the combination of these parameters could be tailored to generate uniform-diameter nanofibers that contain no beads. The electrospun nanofibers with a uniform diameter prepared in this study have potential use in electric-field-driven actuators.

References

1. Pawlowski, K. J.; Belvin, H. L.; Raney, D. L.; Su, J.; Harrison, J. S.; Siochi, E. J. Polymer 2003, 44, 1309.
2. Kwoun, S. J.; Lee, R. M.; Han, B.; Ko, F. K. Model Simul Microsyst 2001, 2, 338.
3. Reneker, D. H.; Chun, I. Nanotechnology 1996, 7, 216.
4. Fong, H.; Chun, I.; Reneker, D. H. Polymer 1999, 40, 4585.
5. Reneker, D. H.; Yariu, A. L.; Fong, H.; Koombhongse, S. J Appl Phys 2000, 87, 4531.
6. Magarvey, H.; Outhouse, E. J Fluid Mech 1962, 13, 151.
7. Huebner, A. J. Fluid Mech 1969, 38, 679.
8. Asano, K.; Yatsuzuka, K. Proceedings of ESA-IEJ Joint Symp Electrostatics 1998, 108.
9. Deitzel, J. M.; Kleinmer, J.; Harris, D.; Beck Tan, N. C. Polymer 2001, 42, 261.
10. Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. Polymer 2001, 42, 9955.
11. Jaeger, R.; Bergschoof, M.; Martini, I.; Batlle, C.; Schonhem, H.; Varcso, G. J. Macromol Symp 1998, 127, 141.
12. Zong, X.; Kim, K.; Fang, D.; Ran, S.; Hsiao, B. S.; Chu, B. Polymer 2002, 43, 4403.
13. Taylor, G. T. Proc R Soc London Ser A 1964, 280, 383.
14. Demir, M. M.; Yilger, I.; Yilgor, E.; Erman, B. Polymer 2002, 43, 3303.

Figure 6 Uniform nanofibers containing no beads formed by electrospinning with 0.01 mol % NaCl.