Study on the Effect of Inorganic Salts on the Alignment of Electrospun Fiber

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ABSTRACT: Well-aligned and highly ordered architectures are always required in many fields, such as tissue engineering, electronics, and preparation of composite materials. In this study, electrospun mats with well-aligned fibers and various fiber assemblies were successfully fabricated by electrospinning of poly(vinylbutyral) (PVB)/inorganic salt solution under the optimal salt condition. Then, the effect of inorganic salts on the degree of electrospun fiber alignment was comprehensively investigated, and the results indicated that the viscosity and conductivity of the solutions were the key factors influencing the degree of fiber alignment. It was expected that this simple and feasible method could be helpful for the fabrication of the well-aligned electrospun fibers and various fiber assemblies. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1047–1052, 2011

Key words: electrospinning; fibers; morphology; orientation; inorganic salt

INTRODUCTION

Electrospinning is a simple and versatile method for manufacturing continuous fibers from the micron diameter down to the nanometer diameter and has great potential for different applications.[1–5] In general, two kinds of fiber arrangements can be obtained via electrospinning: aligned and randomly distributed fibers. Up to now, many investigations have been done to fabricate highly aligned electrospun fibers and various fiber assemblies,[6–9] due to the needs for many applications, especially for tissue engineering, electronics, and preparation of composite materials.[6,7,10,11] For example, aligned electrospun fibers show morphological similarities to the natural extracellular matrix (ECM) of some tissues, such as tendon and ligament.[12] Moreover, many researchers have found that fiber arrangement can greatly affect the morphology and direction of cell growth.[11,13]

The morphology and arrangement of the electrospun fibers were influenced by processing parameters, such as the applied voltage, the solvent composition, and the concentration of the spinning solution.[14–19] Recent studies indicated that inorganic salt additives also affected the structure of the electrospun fibers.[18–25] For example, Liu found that bead-on-string structure could be prevented by adding LiCl into the spinning solution.[25] Zhang and Mit-uppatham both observed that the diameter of the electrospun fibers greatly changed with addition of NaCl.[19,26] In addition, Barakat found the spider-net structure formation by introducing inorganic salts (NaCl, KBr, and $CaCl_2$) into the polymeric solutions.[23] Moreover, some researchers also found that porous electrospun fibers could be generated by adding inorganic salt into the polymeric solution. Gupta fabricated porous nylon-6 fibers by electrospinning of nylon-6 with addition of gallium trichloride ($GaCl_3$), followed by subsequent removal of the $GaCl_3$ salt by soaking fibers into water to form porous structure.[24] However, a detailed study on the effect of inorganic salts on the degree of fiber alignment has not been reported yet.

In this study, electrospun fabrics with aligned and various stacked fibers had been prepared under the optimal inorganic salt condition, and to achieve a better understanding of the key parameters on the fiber alignment, the effect of inorganic salt concentration and the different kinds of inorganic salts on the degree of fiber alignment were both investigated.

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EXPERIMENTAL

Materials

Anhydrous ethanol was purchased from Shanghai Zhenxing Chemcial No.1 Factory. Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), calcium chloride anhydrous ($CaCl_2$), and poly(vinylbutyral) (PVB) were all purchased from Sinopharm Chem. Reagents. All reagents used in the experiment were of analytical grade and were used as received without further purification.

Electrospinning process

In this study, two kinds of solutions were prepared during the electrospinning process, shown as follows: Three kinds of inorganic salts ($Ca(NO_3)_2{\cdot}4H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$) with the same molar quality 0.001 mol (the corresponding mass was 0.3, 0.2, and 0.1 g, respectively) were added to study the effect of different kinds of salts on fiber alignment. In each experiment, 0.001 mol salts were added into the mixing solution consisting of 0.3 g PVB and 5 mL ethanol to make homogenous solutions for electrospinning. Typical spinning parameters were as follows: the applied voltage was controlled at 5 kV; the distance between the tip of the needle and the collector was 10 cm; the flow rate of the solution was 0.5 mL/h and the collector comprised of a rotating drum 8 cm in diameter, rotating at 750 rpm. This low rotation speed was selected to differentiate the effect of the rotation and the inorganic salts on the alignment of the electrospun fibers. In another experiment, different amount of $Ca(NO_3)_2{\cdot}4H_2O$ (0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g) were added in polymer solution to investigate the effect of the concentration of the salts under the same spinning condition.

The viscosity of spinning solution was determined by a viscometer (NDJ-8S Digital LCD Viscometer, China), and the conductivity of spinning solution was measured with a conductivity meter (Eutech Instruments CyberScan Con 1500, Japan). The average value of viscosity and conductivity was obtained through three repeated preparations.

All the experiments were carried out at room temperature, and the relative humidity was about 60%, and all the electrospun mats were vacuum dried for 3d to completely remove any residual solvent before further characterization.

Fabrication of aligned fiber assemblies

Complex aligned fiber assemblies were fabricated by electrospinning of multiple layers onto the aluminum foil with different fiber orientation (0°, 45°, 60°, and 90°). Figure 1(a1–d1) schematically illustrated the process for the preparation of electrospun mats with stacked structures. As shown in Figure 1(d1), three steps are involved in the process: (1) depositing the first layer onto the aluminum foil; (2) taking off the aluminum foil from the rotated drum and rotating it by 90° in a clockwise direction and stacking the second layer onto the first one; (3) repeating the process three times until the stacked mat was fabricated completely. Each layer was collected for a period of 15 min. Similarly, by changing the rotation angle to about 45° and 60°, the other two stacked architectures were generated.

Characterization of electrospun mats

The morphology of the electrospun mats was observed by using an optical microscope (Leica 020-520-07DM/LP, Germany) and a field-emission scanning electron microscope (FESEM, JSM-6700F, Japan) at an accelerating voltage of 10 kV. The optical photograph of electrospun mats were taken by a digital camera (Canon Digital IXUS 9015, Japan). For SEM observation, the surface of the electrospun mats was coated with gold. The degree of alignment of the electrospun fibers was determined by analysis of SEM images manually. From each image, at least 30 fibers in the specific direction (0°, 45°, 60°, 90°, and 135°) were randomly selected, and the angle ⊖ between the long axes of the fibers and the direction of the rotated drum was measured to get an average value for the statistical analysis.

RESULTS

Fabrication of electrospun mats with well-aligned and stacked fibers

The electrospun mats with well-aligned PVB fibers and complex fiber assemblies were obtained by electrospinning of PVB/ethanol/salt solution with 0.001 mol $Ca(NO_3)_2{\cdot}4H_2O$ as the optimal inorganic salt condition [shown in Fig. 1(a2–d2) and 1(a3–d3)]. The degree of fiber alignment in all directions were also quantified by introducing ⊖ [shown in Fig. 1(a4)], the angle between the long axes of the fibers and the rotation direction of the drum. From the image analysis on alignment, as shown in Fig. 1(a4–d4), it was obvious to find that almost all the fibers were deposited in the expected direction (all the fibers were within 10° of the rotation direction of the drum).

As mentioned above, highly aligned fibers and complex fiber assemblies were successfully obtained by introducing inorganic salts into the spinning solution. To achieve a better understanding of the key parameters on the fiber alignment, the effect of salt concentration and the kind of the salt were both systematically investigated.

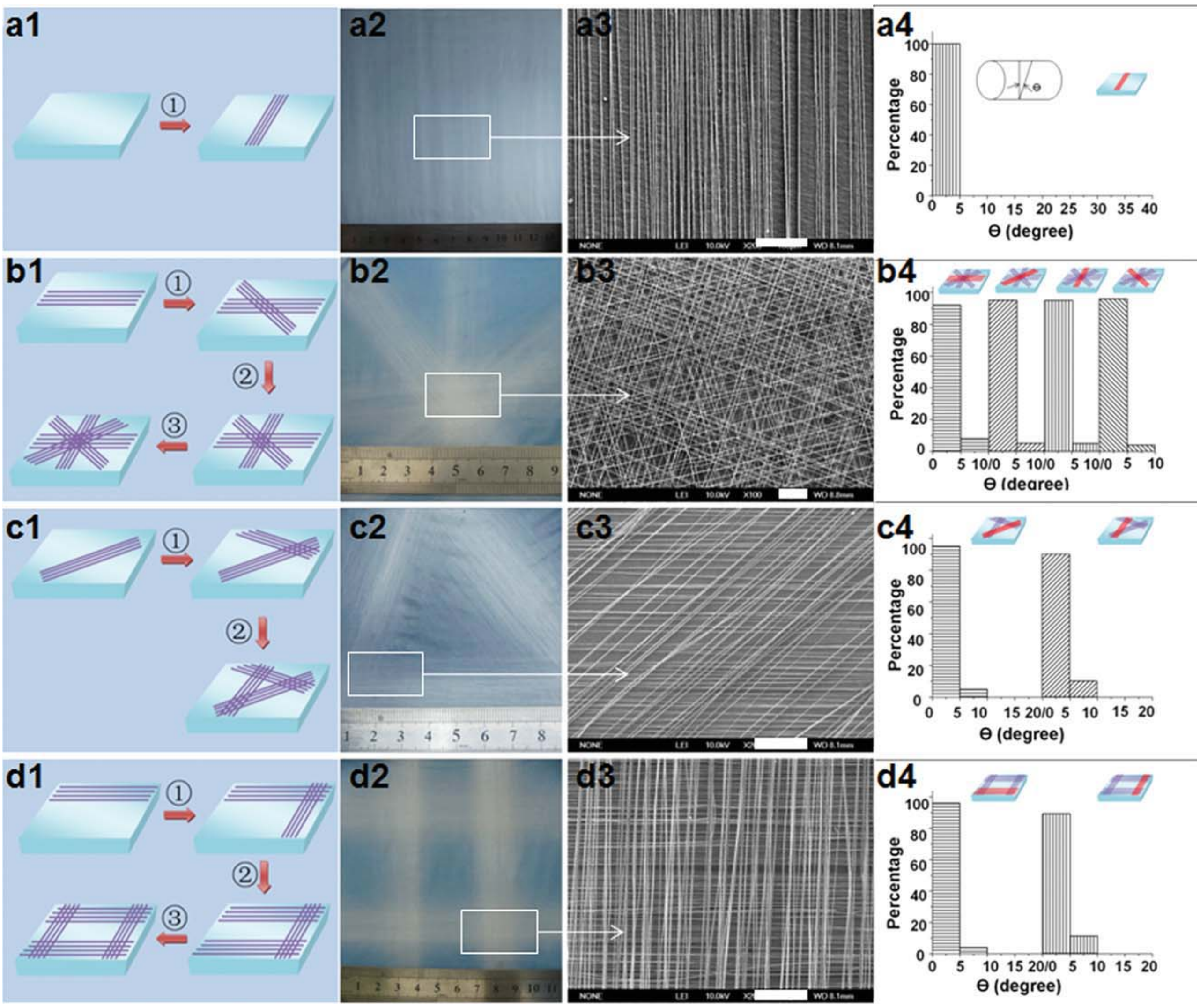

Figure 1 Schematic illustration of the process to fabricate electrospun mats with different stacked structures (a1, b1, c1, and d1). Digital and SEM images of electrospun fabrics generated by rotating the substrate at an angle of 0° (a2, a3), 45° (b2, b3), 60° (c2, c3), and 90° (d2, d3). The distribution of the electrospun fiber alignment in the special direction (Red lines showed the corresponding direction) (a4, b4, c4, and d4). Scale bar = 100 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of inorganic salt concentration on the degree of fiber alignment

PVB/ethanol/inorganic salt solutions containing different amount of $Ca(NO_3)_2 \cdot 4H_2O$ were electrospun to test the inorganic salt addition on the fiber alignment, and the results were shown in Figure 2(a–e). Obviously, better alignment was achieved with the addition of ionic salts as compared with control, and the electrospun fibers were almost parallel by adding 0.3 g $Ca(NO_3)_2 \cdot 4H_2O$ into the PVB solution [Fig. 2(d)]. Additionally, the experiments with the addition of 0.4 and 0.5 g inorganic salts were also carried out, and the results showed no significant differences on the degree of fiber alignment as compared with 0.3 g salts (data not shown). However, with further increasing the amount of the salt up to 0.6 g, the degree of fiber alignment decreased slightly [Fig. 2(e)]. In addition, both the viscosity and conductivity of spinning solutions were gradually increased as the amount of the salt increased, as seen from [Fig. 2(f)].

Effect of different inorganic salts on the degree of fiber alignment

As seen from Figure 3(a–c), all the electrospun fibers with different inorganic salts, such as $Ca(NO_3)_2 \cdot 4H_2O$, $MgCl_2 \cdot 6H_2O$, and $CaCl_2$, were deposited in a parallel fashion, and no obvious difference was found on the degree of fiber orientation. Figure 3(d) showed the viscosity and conductivity of the spinning solutions, which did not show significant difference between different kinds of salts.

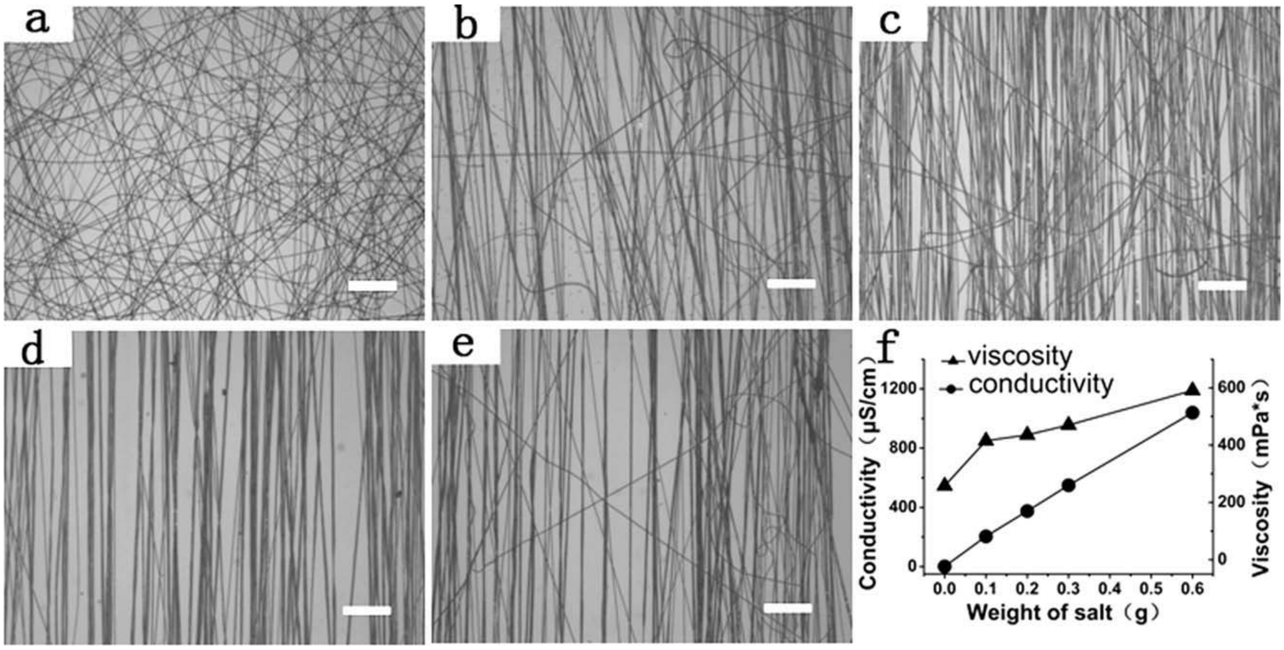

Figure 2 Optical images of PVB fibers electrospun from PVB/ethanol/inorganic salt solutions with different amount of $Ca(NO_3)_2·4H_2O$ added [(a)0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.6 g]. (f) Effect of the inorganic salt addition on the viscosity and electrical conductivity of spinning solutions. Scale bar = 100 μm.

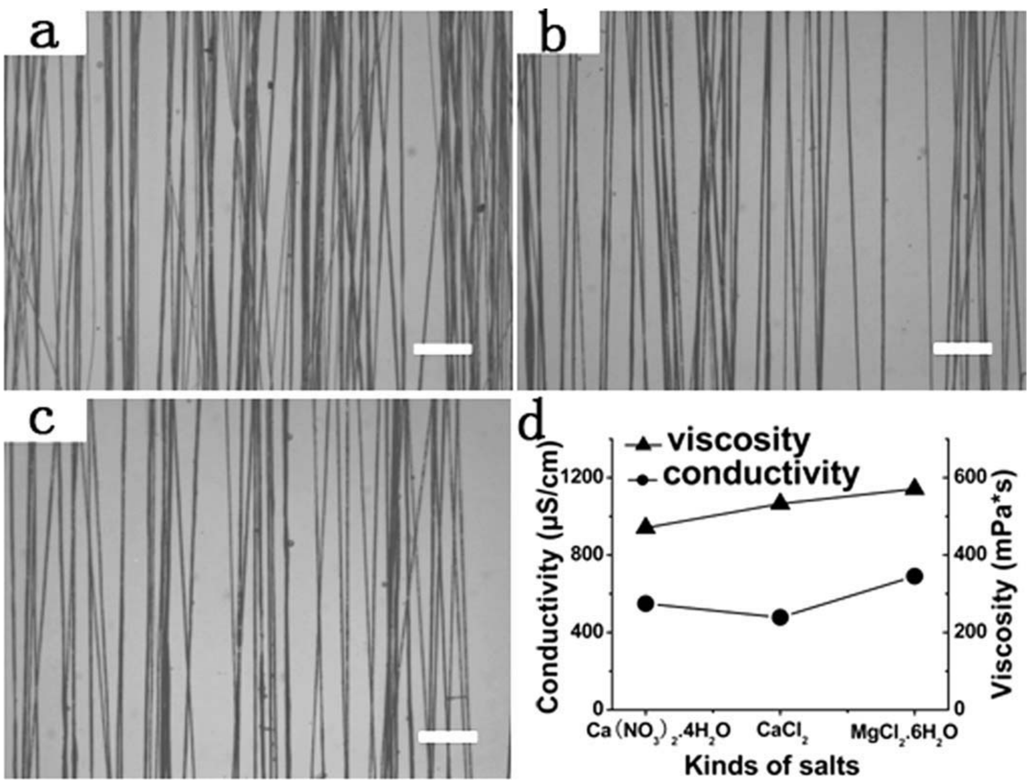

Figure 3 Optical images of PVB fibers electrospun from PVB/ethanol/inorganic salt solutions with different kind of salts added [(a) $Ca(NO_3)_2·4H_2O$; (b) $CaCl_2$; (c) $MgCl_2·6H_2O$]. (d) Effect of the different kinds of inorganic salts ($Ca(NO_3)_2·4H_2O$; $CaCl_2$; $MgCl_2·6H_2O$) with the same molar quality addition on the viscosity and electrical conductivity of spinning solutions. Scale bar = 100 μm.

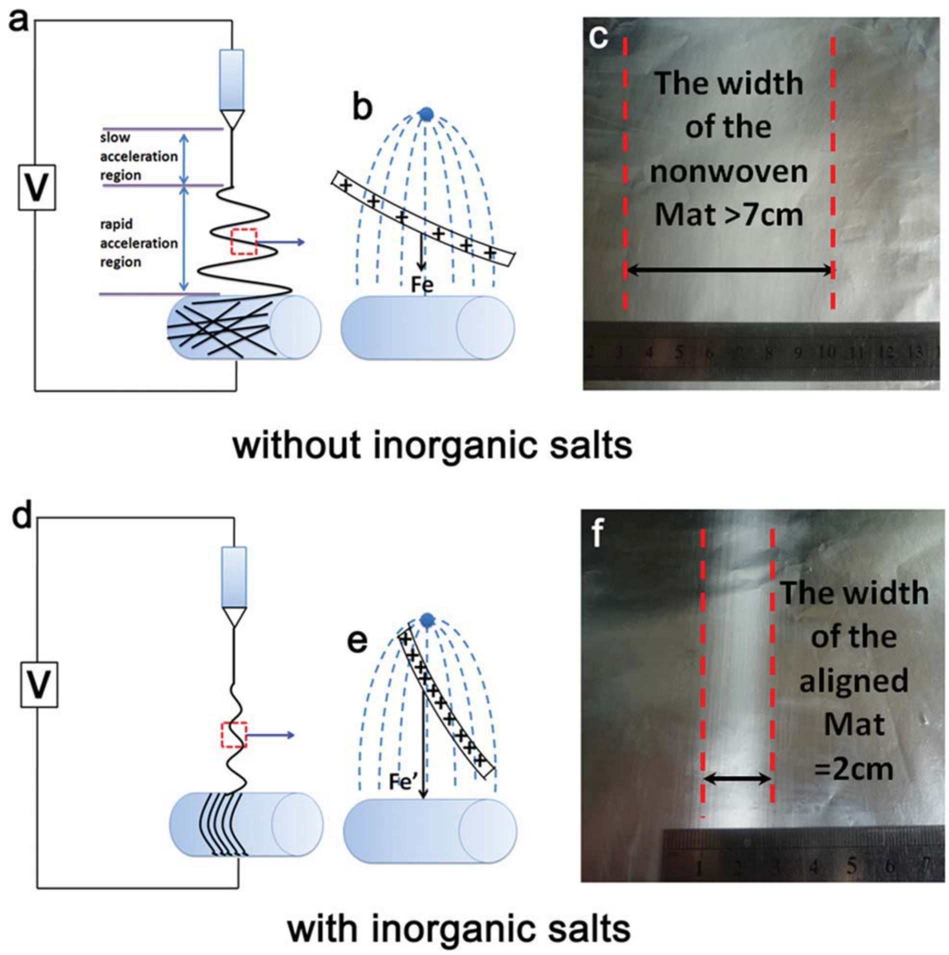

Figure 4 Schematic illustration of the travelling path of the jet and the force (Fe) exerted on the jet originated from the electrostatic interaction between the external electrical field and the surface charges on the jet, and the digital images of the corresponding electrospun mats with different width under the different salt conditions: (a, b, and c) without inorganic salts; (d, e, and f) with inorganic salts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DISCUSSION

In a typical electrospinning process, the applied voltage generated sufficient electrostatic forces to deform the polymer meniscus into a conical shape called Taylor cone. When the electrostatic charge overcame the surface tension of the Taylor cone, the polymer jet was initiated, and it was only stable near the tip of the needle and then experienced a rapid whipping and acceleration process due to the electrostatic interaction between the external electrical field and the surface charges on the jet.[3,27] Finally, the electrospun fibers were randomly distributed on the drum, as shown in Figure 4(a,b).

In our study, it was clearly observed that without the addition of the inorganic salt, the fibers deposited randomly onto the entire area of the collector due to the strong whipping of the jet, and the width of the obtained electrospun mat was more than 7 cm [shown in Fig. 4(c)]. In contrast, with the addition of inorganic salts, the whipping of the jet became much weaker, and the electrospun fibers were only deposited onto the center of the collector and the width of the obtained electrospun mat became much smaller (2 cm), and the fibers were all well-aligned on the collector [Fig. 4(f)].This phenomenon could be explained as the following. When enough inorganic salts were added into the spinning solution, the conductivity of the solution greatly increased, which led to the high net charge density on the surface of the jet,[18,26] so the electrostatic force (Fe) was remarkably increased [Fig. 4(e)].[17,26,28] The repulsion forces between the surface charges of the fibers also increased, and they might result in a stronger whipping of the jet. However, as compared with the large stretching force (Fe), which was exerted on the jet under a very high electrical field (the applied voltage was controlled at 5 kV), the repulsion forces were relatively small, so the jet was pulled and travelled almost along the direction of the stretching force (the direction of the electric field), and the whipping of the jet became weak [Fig. 4(d)]. From another point of view, the highly charged jet was unstable during the electrospinning process. To make the spinning system stable, the jet tended to travel at the shortest path to discharge immediately, thus the electrospun fibers were focused and only deposited in the center of the collector; finally, the fibers were pulled by the rotated drum in a highly aligned fashion.

It was also noticed that the alignment of the fibers was dependent on the amount of the inorganic salts. This was easy to understand that, when a small amount of inorganic salt (e.g., 0.1 g) was added into the spinning solution, the electrostatic force was not high enough to suppress the bending instability of the jet and the whipping of the jet was still strong, so the electrospun fibers deposited in a randomly distributed fashion. As the amount of the salts increased to a range between 0.3 and 0.5 g, the force was high enough to suppress almost the rapidly whipping of the jet, so the fibers deposited in an aligned fashion. The degree of the alignment decreased slightly as the amount of the salt increased up to 0.6 g. Though the bending instability of the jet became weaker after adding large amount of salt, the viscosity of the solution was greatly increased,[29] which made the tip blocked slightly, and the collection process became discontinuous, additionally, the high electrical conductivity might also have negative effect on the fiber alignment, since the addition of large amount of salt resulted in an increase of conductivity of the spinning solution and highly conductive solution was not suitable for electrospinning. Therefore, both the conductivity and viscosity of the solution, which were mainly determined by the concentration of the salts, were the dominant factors influencing the fiber alignment. In contrast, different inorganic salts at same concentration did not affect the fiber orientation. The degree of the fiber alignment was all similar, when different kinds of salts with the same molar quality were added into the polymeric solutions as shown in Fig. 3(a–c), which was attributed to the fact that viscosity and conductivity of these solutions of different kinds of salts did not show significant difference as shown in Figure 3(d), and the electrostatic force was high enough to almost suppress the bending of the jet, and the fibers deposited in a highly aligned fashion.

CONCLUSIONS

In this study, we comprehensively investigated the effect of inorganic salts on the degree of electrospun PVB fiber alignment. The results indicated that both viscosity and conductivity of the solutions were the dominant factors influencing the fiber alignment. The degree of fiber orientation gradually increased with the increase of the conductivity of the solution. However, as the amount of salt continued to increase, the degree of fiber alignment started to decrease, due to the large viscosity and high conductivity of the solution. In addition, under the optimal spinning parameters, we successfully fabricated aligned electrospun fibers, and various aligned fiber assemblies were generated by rotating the substrate at different angles (45°, 60°, and 90°). Based on the results presented, it was expected that this simple and feasible approach could be helpful for fabrication of the well-aligned electrospun fibers and various fiber assemblies.

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