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# Continuous polymer nanofiber yarns prepared by self-bundling electrospinning method

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ABSTRACT

Continuous polymer nanofiber yarns were manufactured by self-bundling electrospinning method. Compared with typical electrospinning setup, the special difference in this method was that a grounded needle tip was used to induce the self-bundling of polymer nanofibers at the beginning of electrospinning process. Four kinds of polymer self-bundling yarns, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), polyacrylonitrile (PAN), poly(L-lactic acid) (PLLA) and poly(*m*-phenylene isophthalamide) (PMIA), were prepared successfully by using this self-bundling electrospinning method. Good alignment of polymer nanofibers in self-bundled yarns was confirmed by SEM observation. It was found out that the conductivity of the polymer solution was crucial to achieve stably continuous self-bundled fiber yarns. A possible mechanism for the self-bundling formation of align nanofiber yarn was proposed.

## 1. Introduction

Electrospinning is a simple and versatile process offering unique capabilities for making fibers from polymer solutions and melts with diameters ranging from the nano- to microscale [1,2]. A variety of polymer, ceramic and composite nanofibrous materials have been successfully prepared by electrospinning, which created interesting applications in fields of filtration, protective clothing, self-cleaning, drug delivery, tissue engineering, electronic and photonic devices, etc. [3–9]. However, the application is somewhat limited so for, as most of the electrospun fibers are in the form of isotropic non-woven mats [10–12]. Current interests in nanostructured materials have stimulated renewed efforts in electrospinning. Aligned nanofibers in particular can be tailored for use in microelectronics, photonics and in a variety of electrical, optical, mechanical, and biomedical applications [13]. Recently, a number of approaches have been developed to obtain aligned electrospun nanofibrous structures, including the use of a rotating mandrel collector [14–19], dual grounded collection plate [20–22], a copper wire drum [23], a scanning tip [24], a water reservoir collector [25], dynamic liquid support system [26], two oppositely metallic spinneret [27], multiple field [28], and parallel auxiliary electrodes [29].

As we know, a typical electrospinning involves the application of electrostatic force between polymer solution kept in a syringe and a counter metal electrode such as a plate or a rotating drum kept at a suitable distance. With the application of sufficiently high electrical field, the electrostatic forces overcome the surface tension of the polymer solution, resulting in the ejection of a thin jet from the pendent drop of polymer solution formed at the tip of the spinneret, known as "Taylor cone" [1]. Although the charged jet then undergoes a stable stretching firstly, it starts bending and whipping randomly soon in order for further stretching of the jet and evaporation of solvent [30,31]. Electrospun fibers can be collected in the form of textile where the fibers are more or less oriented parallel to the direction of rotation [14] if the target is a drum rotating at high surface velocity. The alignment of the electrospun fibers was enhanced with the increase of the surface velocity of the rotating drum but some extent of randomly distributed fibers existed. This is because the velocity of jet whipping is so fast that the electrospun fibers could not be taken-up at a matching velocity by the drum.

In this paper, the electrospinning jet motion will be investigated under different conditions such as the polymer solutions with different conductivity or inducing the electric field shape change with a grounded needle tip. A novel self-bundling electrospinning method was developed to provide a simple method for generating continuous aligned electrospun fiber yarn. Compared with typical electrospinning setup, the special thing in this method is that a grounded needle tip is used to induce the self-bundling of polymer nanofibers at the beginning of electrospinning process. The effect of the conductivity of the solution on self-bundling electrospinning was also studied. It is believed that the conductivity of polymer solution is a very important factor in the process of self-

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bundling electrospinning. In previous reports [32–34], researchers only paid attention to the effect of conductivity of polymer solution on the morphology and size of single fiber deposited on a collector but ignored its influence on the motion of the polymer solution jet.

## 2. Experimental

### 2.1. Materials

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) ($M_n =$ 460,000, HV content 3%) was kindly supplied by Ningbo Tianan Co. as an injection-molding grade and was purified before use. Polyacrylonitrile (PAN) was purchased from Aldrich with a glass transition temperature ($T_g$) of 85 °C and a melting temperature ($T_m$) of 317 °C. Poly(L-lactic acid) (PLLA) was a commercial poly-L-lactide granulate (identified as L9000) with a glass transition temperature ($T_g$) of 60 °C and a melting temperature ($T_m$) of 170 °C from Biomer of Krailling, Germany. Poly(*m*-phenylene isophthalamide) (PMIA) was purchased from XH company, China. $CH_2Cl_2$, dimethyl formamide (DMF), and benzyl triethylammonium chloride (BTEAC, a kind of organic salt) were purchased from Shanghai Chemical Reagent Plant.

### 2.2. Electrospinning

PHBV was dissolved in $CH_2Cl_2$ to make 2 wt% solution. Typical electrospinning parameters were as follows: the applied electric voltage was 10 kV, the distance between the spinneret and the grounded drum was 15 cm, and the solution feed rate was 20 μL/min.

PAN was dissolved in DMF to make 10 wt% solution. Typical electrospinning parameters were as follows: the applied electric voltage was 9 kV, the distance between the spinneret and the grounded drum was 15 cm, and the solution feed rate was 20 μL/min.

PLLA was dissolved in a mixture of $CH_2Cl_2$ and DMF (75/25 wt/wt) to make a 12 wt% solution. Typical electrospinning parameters were as follows: the applied electric voltage was 18 kV, the distance between the spinneret and the grounded drum was 15 cm, and the solution feed rate was 80 μL/min.

PMIA was dissolved in [bmim][$BF_4$] (a kind of ionic liquid (IL) which is soluble in water and non-volatile at room temperature, synthesized in lab [35]) at a concentration of 4 wt%. Typical electrospinning parameters were as follows: the applied electric voltage was 20 kV, the distance between the spinneret and the grounded drum was 20 cm, and the solution feed rate was 20 μL/min.

All experiments were conducted at room temperature in air.

### 2.3. Yarn manufacture

To manufacture the nanofibrous yarn, a grounded needle tip is used to induce the self-bundling of polymer nanofibers at the beginning of electrospinning process, then a self-bundled polymer nanofiber yarn will be produced, pull the yarn back and wind on a grounded rotating collector, as shown schematically in Fig. 1. In some cases, small amount of organic salt is introduced in polymer solutions to increase the conductivity, making the self-bundling process more stable and easier.

### 2.4. Measurements

The conductivity of the polymer solution was measured with a conductivity tester (DDSI-308A, Shanghai Precision Instrument Co.). The morphology of the electrospun sample was examined by scanning electron microscopy (SEM) (JSM-5600LV, Japan).

The photograph of the electrospinning jet motion in the instability region was taken by a common digital camera (Olympus E380D, Japan).

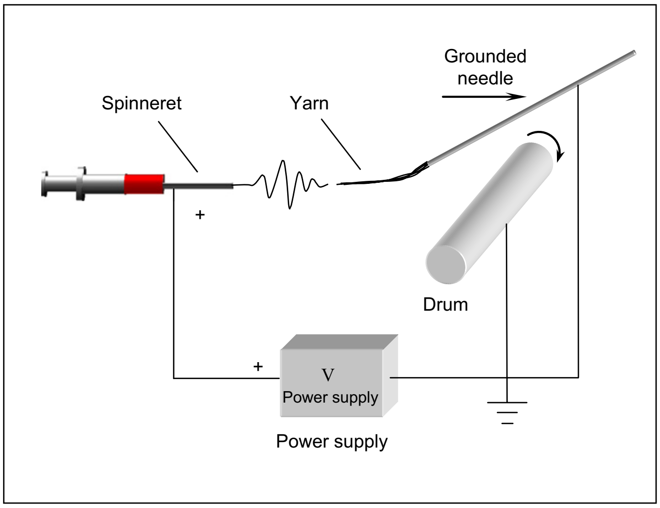

**Fig. 1.** Schematic diagram of the self-bundling electrospinning set up for polymer fiber yarn manufacture.

## 3. Results and discussion

The typical electrospinning apparatus consists of three major components: a high-voltage power supply, a spinneret (a metallic needle), and a grounded collector. The spinneret is connected to a syringe in which the polymer solution is hosted. The applied voltage is usually in the range of 1–30 kV over a distance of 5–30 cm between the spinneret and the collector. When the electric field is applied, the polymer droplet at the nozzle of the spinneret deforms from a hemispherical to conical shape commonly known as the Taylor cone. A jet of polymer emerges from the deformed droplet when the accumulated charge on the droplet surface overcomes the surface tension. The electrified jet begins to stretch and whip around forming a long and thin thread. The liquid jet is continuously elongated and the solvent is evaporated during the whipping stage leaving an almost dry polymer fiber behind. Attracted by the grounded collector placed under the spinneret, the charged fiber is often deposited as a randomly oriented non-woven membrane. In the following context, four kinds of polymer solutions with different conductivity are used for electrospinning to investigate the self-bundling phenomenon during the electrospinning process.

The typical photograph of the instability region of a jet electrospun from a 2 wt% PHBV/$CH_2Cl_2$ solution was shown in Fig. 2A. The image clearly depicts a typical motion of a spinning jet as it traveled toward the target. It was obvious that the jet was initially a straight line, then whipped around and spread, and the resulting fibers formed a random membrane or network on the collector surface as shown in Fig. 2B. However, if a grounded metallic needle was used to approach the spinneret, the splaying fibers would be focused to converge on the tip of metallic needle. This phenomenon was called “self-bundling”. Unfortunately, the splaying fibers were only focused and deposited on the surface of the needle at the very beginning, it was very difficult to induce the self-bundled fiber yarn growth. Occasionally, the length of not more than 1 cm yarn was obtained on the tip of the needle during this process. Fig. 2C shows the SEM image of the PHBV self-bundled nanofiber yarn. The fibers in the yarn seem to be aligned along the axial direction of the yarn with slightly twisting. But as shown in the SEM image of the yarn with higher magnification (Fig. 2D), it was found clearly that large portion of fibers deposited randomly in the yarn.

When small amount of organic salt was added in PHBV/$CH_2Cl_2$ solution, a remarkable change of the instability region of the jet was

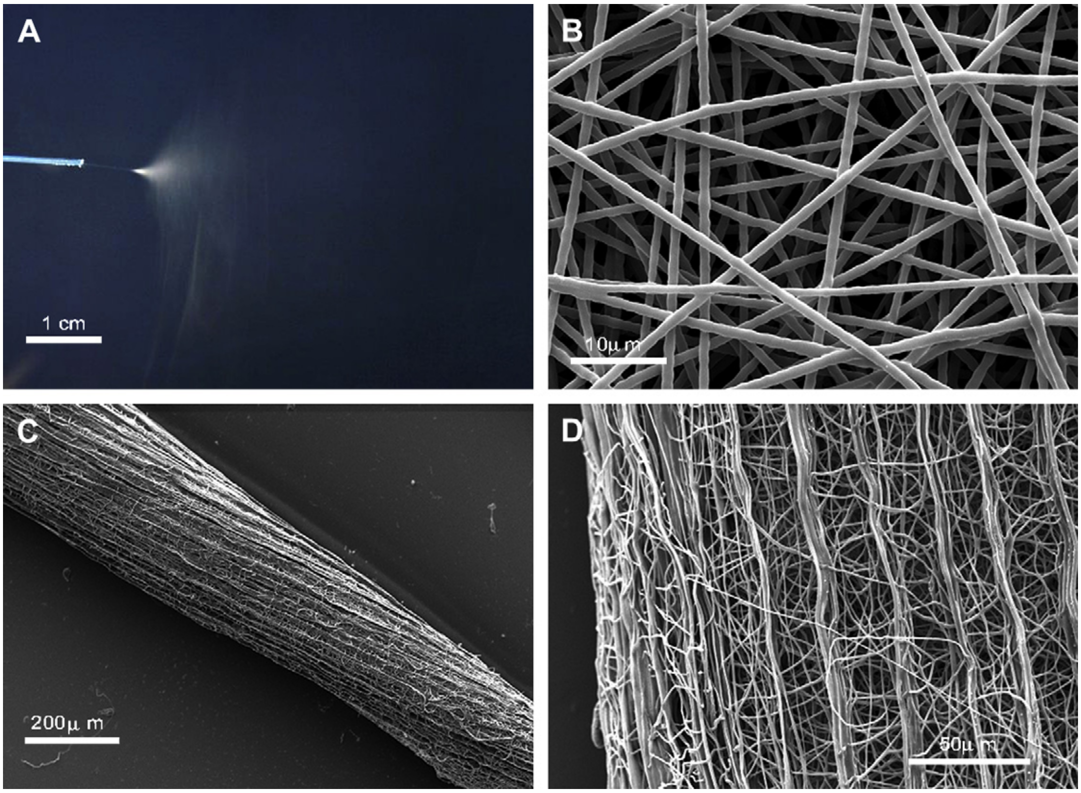

**Fig. 2.** (A) Photograph of the instability region of a jet electrospun from a 2 wt% PHBV/$CH_2Cl_2$ solution; (B) SEM image of PHBV non-woven mat; (C) SEM image of the PHBV fiber yarn without organic salt; (D) SEM image of the PHBV fiber yarn with higher magnification.

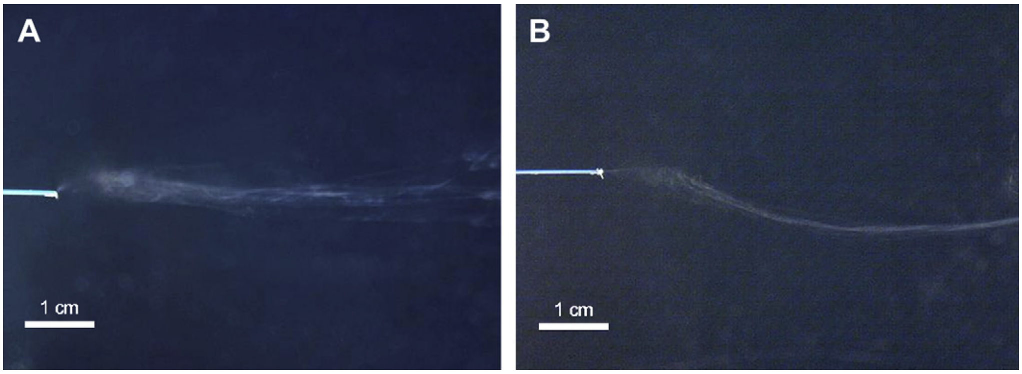

**Fig. 3.** Photographs of the instability region of a jet electrospun from a 2 wt% PHBV/$CH_2Cl_2$ solution with different amount of BTEAC. (A) 1 wt%; (B) 2 wt%.

observed (without the inducement of needle tip). Fig. 3A showed the photograph of a spinning jet electrospun from 2 wt% PHBV/$CH_2Cl_2$ solution with 1 wt% organic salt BTEAC (based on the solution weight). The straight line disappeared and the whipping region was restricted to a loose bundle. When the concentration of BTEAC increased to 2 wt%, the electrospinning jet was focused and self-bundled into a fine yarn as it traveled to the collector (Fig. 3B). The addition of small amount of BTEAC to PHBV solutions resulted in a significant increase in conductivity of PHBV solutions, as shown in Table 1. Therefore, it was believed that the conductivity of the PHBV solution was a very important factor affecting the motion of the jet. However, in previous literatures [32–34], they mainly

**Table 1**
Experimental data of self-bundling electrospinning from four kinds of polymer solutions with different conductivity

| Samples | PHBV/$CH_2Cl_2$ solution 2 wt% | | | PAN/DMF solution 10 wt% | | | PLLA/DMF/$CH_2Cl_2$ solution 12 wt% | | | PMIA/IL solution 4 wt% |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration of BTEAC (wt%) | 0 | 1 | 2 | 0 | 0.5 | 1 | 0 | 0.5 | 1 | 0 |
| Conductivity (μS/cm) | 0.60 | 218 | 463 | 52.8 | 759 | 909 | 2.85 | 487 | 722 | 1060 |
| Continuous self-bundling using grounded needle | − | + | + | + | + | + | − | + | + | + |
| Continuous self-bundling without grounded needle | − | − | + | − | + | + | − | + | + | + |

"+": Yes, "−": No.

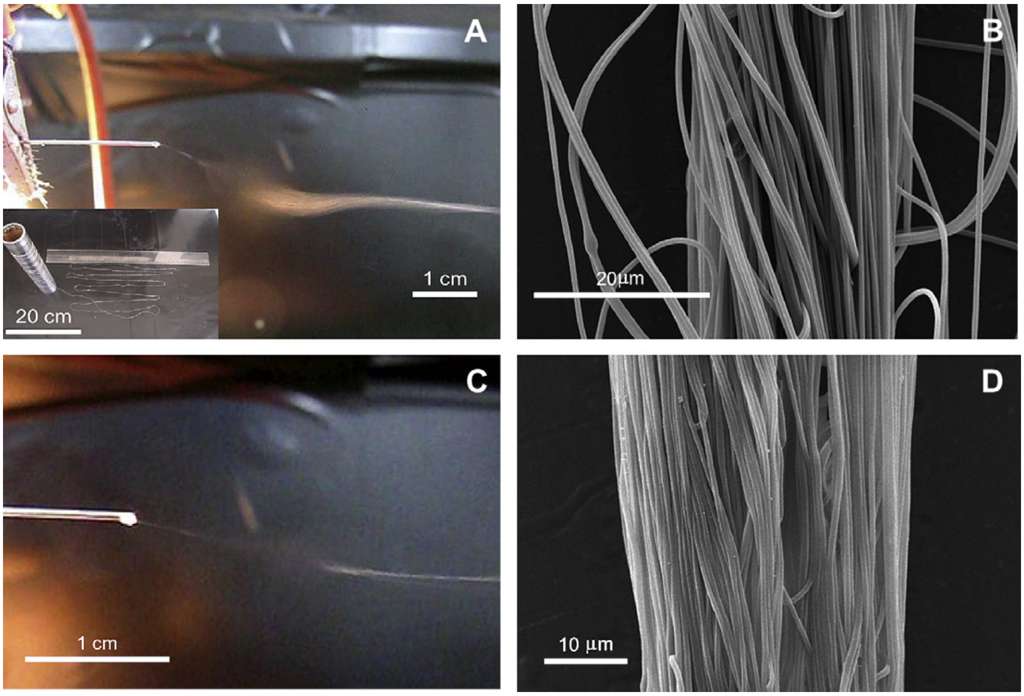

**Fig. 4.** (A) Photograph of the jet electrospun from 10 wt% PAN/DMF solution (without organic salt) induced by a grounded needle tip, with a photograph of the yielded PAN fiber yarn in the insert; (B) SEM image of PAN fiber yarn from PAN/DMF solution without organic salt; (C) photograph of the jet electrospun from 10 wt% PAN/DMF solution (with 0.5 wt% organic salt) without the use of grounded needle tip inducement; (D) SEM image of PAN fiber yarn from PAN/DMF solution with organic salt.

focused on the effect of conductivity of polymer solution on the morphology and the size of single fiber deposited on a collector.

In the following experiment, 10 wt% PAN in DMF solution was used for self-bundling electrospinning study, as shown in Fig. 4. When a grounded metallic needle was used to approach the spinneret, the random motion fibers were converged into a yarn and grown on the needle, as shown in Fig. 4A. Then pull the yarn backward and wind it around the rotating grounded drum. The suitable surface velocity of the drum was about 0.2 m/s. If the surface velocity of the drum increases continuously, the self-bundling process will be broken down and the jet starts random whipping again. The reason for this phenomenon is that the formation of the self-bundling of jet is induced by the tip of grounded needle firstly and then by the tip of the yarn. When the surface velocity of the drum was higher than the velocity of the yarn's growing, there was no tip available to induce the self-bundling of jet. A representative photograph of yielded PAN yarn electrospun from 10 wt% PAN solution was shown in the insert in Fig. 4A, the yarn could be very long depending on the volume of feeding polymer solution. The SEM image of the PAN fiber yarn (Fig. 4B) revealed that most of the single fibers in the yarn were aligned along one direction. Nevertheless, the surface of yarn is a little fluffy. Bent fiber loops were also observed which indicated that the fibers were folded in the yarn. The average diameter of PAN fiber in the yarn is about 1.5 μm. By using a grounded metallic needle induction, it was quite easy to obtain winded PAN yarn just like that in traditional spinning. However, this method can't be applied for PHBV fiber yarn collection from 2 wt% PHBV/$CH_2Cl_2$ solution without organic salt. This is because the conductivity of PAN/DMF solution is 52.8 μS/cm, which is much higher than that of PHBV/$CH_2Cl_2$ solution (0.6 μS/cm). But the conductivity of PAN/DMF solution is still not high enough to induce the self-bundling of the electrospun jet automatically without the use of needle tip induction. The inducement of grounded needle must be used for the self-bundling electrospinning experiment of PAN/DMF solution. When small amount of organic salt BTEAC (0.5 wt%) was added into PAN/DMF solution, the conductivity of PAN solution increased remarkably to 759 μS/cm, the self-bundling of PAN jet spontaneously occurred without the use of grounded needle tip inducement, the electrospinning jet was self-bundled in a fine yarn as it traveled to the collector (as shown in Fig. 4C). The winding process became more stable and the suitable surface velocity for the drum was about 0.9 m/s. The alignment of the electrospun fibers in the yarn was enhanced as shown in Fig. 4D. In addition, the average diameter of PAN fiber in the yarn was found to decrease to about 700 nm. The above results demonstrated that the stability of self-bundling and the alignment of fibers in the yarn could be improved through the addition of organic salt. Meanwhile, the average diameter of the single fibers in the yarn decreased since the addition of organic salt increased the charge density in jet and thus, stronger elongation force is imposed to the jets.

During the self-bundling electrospinning process, we found that the self-bundling yarn was easy to swing with an adjacent grounded needle moving. This is because surface velocity of the drum is not so fast, and the tensile force of winding was lower than the attracted force of the adjacent grounded needle. As can be seen from Fig. 5, one could also easily stack the aligned self-bundling yarn into film with controllable reciprocating motion of a grounded metallic needle. By controlling the motion of the grounded metallic needle, it was quite easy to stack aligned self-bundling yarn of PLLA into membrane, as shown in Fig. 6A. The SEM image of the self-bundling yarn of PLLA electrospun from 12 wt% PLLA solution with 0.5 wt% BTEAC was shown in Fig. 6B. As can be seen, PLLA electrospun fibers in the yarn were well-aligned.

Next case is a solution system (PMIA/[bmim][$BF_4$]) using ionic liquid (IL) as solvent for the self-bundling electrospinning experiment. As we know, ionic liquids are defined as a liquid material containing only ionic species without any neutral molecules. In consequence, ionic liquids possess some peculiar properties such as negligible vapor pressure, high thermal stability, ability to dissolve organic, inorganic and polymeric materials, and especially high conductivity. Definitely, PMIA/IL solution was a kind of solution with a high conductivity even without any addition of organic salt. The conductivity of 4 wt% PMIA/[bmim][$BF_4$] solution was 1060 μS/cm.

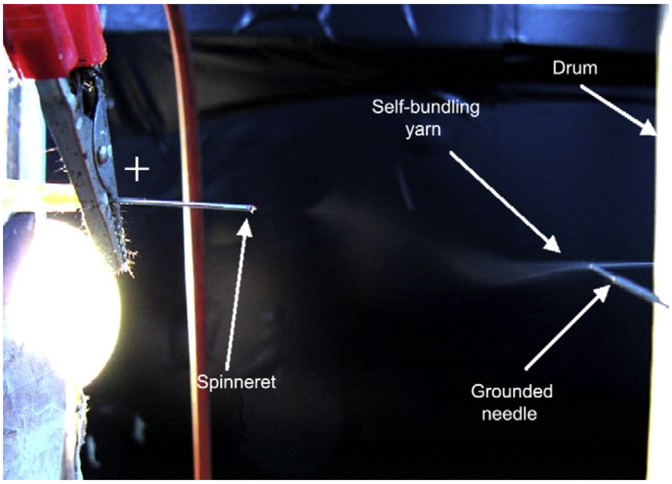

**Fig. 5.** Photograph of self-bundling electrospinning process for yarn membrane preparation with controllable reciprocating motion of a grounded metallic needle.

As the ionic liquid was non-volatile and miscible with water, a grounded water bath was used as the collector to remove the solvent. During the electrospinning, it was very easy to self-bundle without the use of needle tip induction, and the electrospinning jet motion was similar to that from PHBV solution with high conductivity as shown in Fig. 3B. Fig. 7 showed the self-bundled yarn electrospun from 4 wt% PMIA/IL solution. The average diameter of single fiber is only about 500 nm. The surface of the yarn is very rough, due to the fact that water only washed out the ionic liquid, while a small quantity of PMIA dissolved in the ionic liquid was separated out and adhered to the surface of the yarn.

In the above experiments, the addition of organic salt and a grounded metallic needle were used to achieve the continuous self-bundling yarn. The experimental data listed in Table 1 demonstrated that the increase of conductivity of the polymer solution was in favor of the self-bundling in electrospinning process, and the grounded metallic needle was used to induce the self-bundling when the conductivity of the polymer solution was not high enough. In case the conductivity of polymer solution is lower than 10 μS/cm, the self-bundling of jet can just occur simultaneously with the grounded needle approaching but just for a moment and the splaying jet will appear again. If the conductivity of polymer solution is between 10 and 400 μS/cm, the self-bundling electrospinning occurred continuously for yarn collection with the inducement by an adjacent grounded metallic needle. When the conductivity increases further, the jet can self-bundle easily without the inducement of needle tip. It should be noted that, for polymer solution with high conductivity, the grounded needle inducing is unnecessary, and there is no significant difference for continuous self-bundling whether needle tip inducing is used or not.

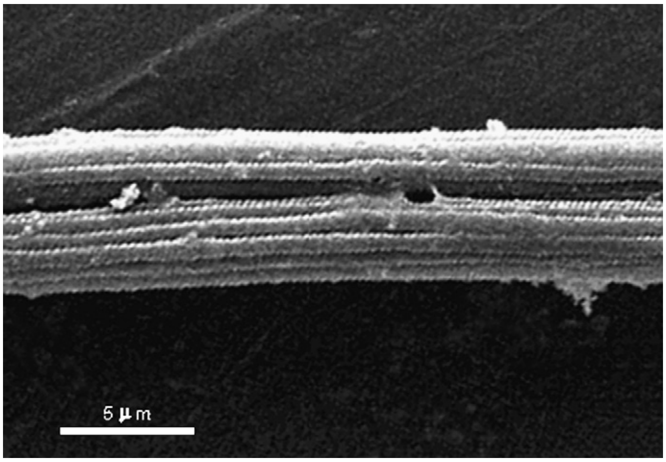

**Fig. 7.** SEM image of PMIA fibers electrospun from 4 wt% PMIA/IL solution.

In the electrospinning process, the exclusive driving force for the formation of ultrafine fiber is the electrostatic interaction. Therefore, it is believed that the electrostatic interaction should be the primary driving force for the self-bundling of electrospun jet. To understand the procedure and the mechanism of electrospun self-bundling more easily, the schematics of the whole procedure for the self-bundling electrospinning are illustrated in Fig. 8. As can be seen from Fig. 8A, the positively charged jet emerges from the spinneret and begins to stretch and whip splaying toward the collector at the beginning. Once a grounded metallic needle is approaching the spinneret, negative charges are inducted at the tip of grounded needle which change the shape of electrostatic field. The principle for the shape of the electrostatic field is that any positive and negative electrodes will create an electric field between them, the electric field lines start from positive charge and terminate at negative charge. The direction of the electrostatic field at each location is the tangent direction of the field lines, and the electrostatic field strength increases with the increase of the density of the field lines. As we know, the charged jet motion is mainly controlled by the electrostatic forces imposed by the electrostatic field as it is ejected. Thus, when a grounded needle is close to the splaying jet, the splaying jet will be focused to converge on the tip of needle, and then deposits on the needle tip and discharges through needle, which prefers the following deposition on the tail of the fibers so as to decrease the gap between the spinneret and needle tip, as shown in Fig. 8B. The residual solvent in the fiber yarn makes the yarn conductive if the polymer solution for

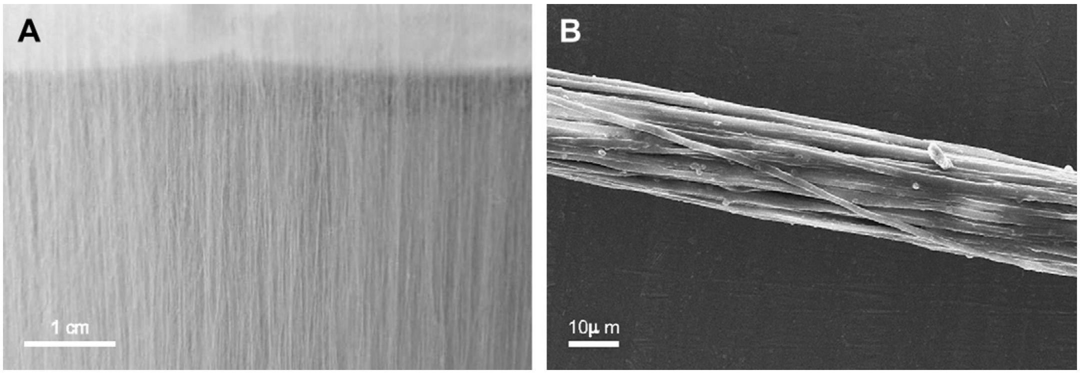

**Fig. 6.** (A) Photograph of the stacked PLLA yarn membrane; (B) SEM image of the self-bundling yarn of PLLA electrospun from 12 wt% PLLA/DMF/$CH_2Cl_2$ solution with 0.5 wt% organic salt.

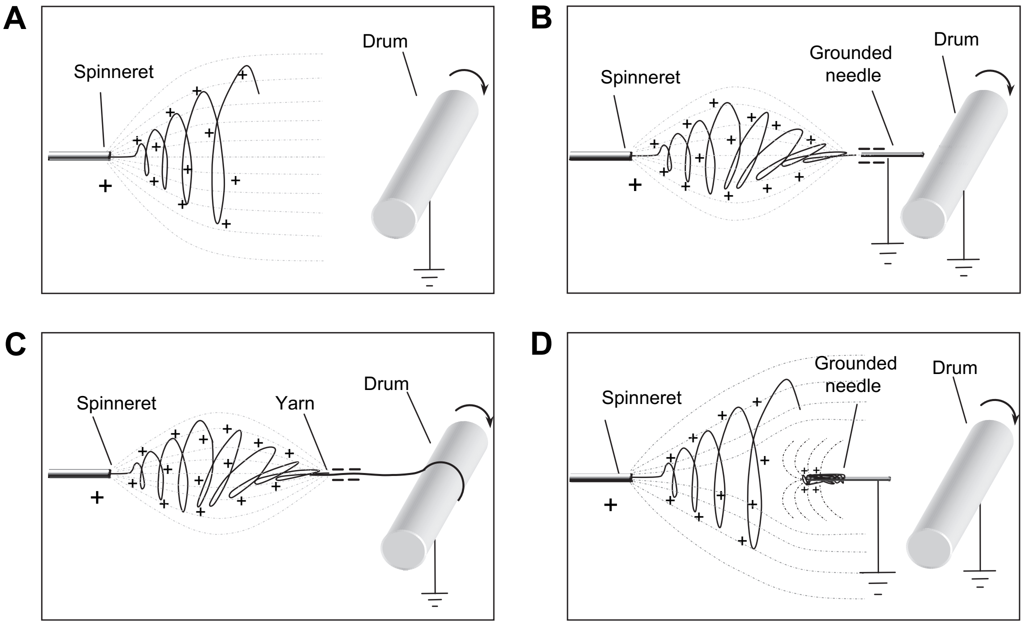

**Fig. 8.** Schematic illustration of the mechanism of the self-bundling electrospinning using grounded metallic needle. For self-bundling electrospinning experiments from polymer solution with conductivity in the range of 10 and 400 μS/cm: (A) typical splaying jet; (B) self-bundling induced by grounded needle tip; (C) yarn growth and yarn collect. For self-bundling electrospinning experiments from polymer solution with conductivity lower than 10 μS/cm (D).

electrospinning has appropriate conductivity and the positive charges can be discharged through the fibers, the yarn starts growing on the needle tip, then pull the yarn backward manually and wind it around the rotating grounded drum (Fig. 8C). In this way, the jet will be folded and parallel aligned to form a continuous self-bundling yarn.

If the conductivity of the polymer solution is very low, the fibers deposited on the needle tip will become insulated. When the non-conductive fibers cover the surface of the needle and form an insulated layer with enough thickness, the charged jet deposited on the needle will discharge difficultly. A small quantity of positive charges will be cumulated on the surface of the needle. Subsequently, the shape of electrostatic field will be transformed into the shape created between two positive electrodes with different electric quantity and the grounded drum, then the charged jet will be no longer converged on the needle and will not prefer to deposit further on the needle, which means the electrospinning jet will spray and deposit randomly on the drum (behind the needle as shown in Fig. 1) again, as shown in Fig. 8D. This is the reason why the PHBV self-bundling of electrospinning jet can keep just for very short time and the bundled fiber yarn can't grow longer on the needle tip from PHBV/$CH_2Cl_2$ solution with very low conductivity. Actually, similar phenomenon was observed in Katta's work [23], in which electrospun fibers with good alignment were obtained on the surface of copper wire drum collector at the very beginning, but after period of time the fibers spun in random patterns and alignment was gradually lost as the thickness of the fiber mat increased.

When conductivity of the polymer solution is high enough such as the 2 wt% PHBV/$CH_2Cl_2$ solution with the addition of 2 wt% BTEAC, 10 wt% PAN/DMF solution with 0.5 wt% BTEAC, 12 wt% PLLA/DMF/$CH_2Cl_2$ solution with 0.5 wt% BTEAC and 4 wt% PMIA/IL solution, the inducement of the grounded needle tip is unnecessary. The higher conductivity of the polymer solution resulted in the faster discharge as soon as any parts of charged fiber touches the drum, which leads the other part of the fiber to release positive charges before depositing on the drum (Fig. 9A). Negative charges will be inducted on this part of fiber by the electrostatic field, which makes this part of fiber be attracted by the spinneret and suspended, as shown in Fig. 9B. This part of fiber acts as grounded needle tip to induce the self-bundling. Meanwhile, increase of the conductivity of polymer solution increases the charge density in ejected jets and thus, stronger focus forces are imposed to the jets, the jets will deposit on the needle tip or the tail of the yarn more compactly and quickly. The growing speed of the yarn is so fast that the velocity of the drum must be increased. It is believed that the stronger focus forces and the higher velocity of the drum contributed to the better alignment of the fibers in the self-bundling yarn.

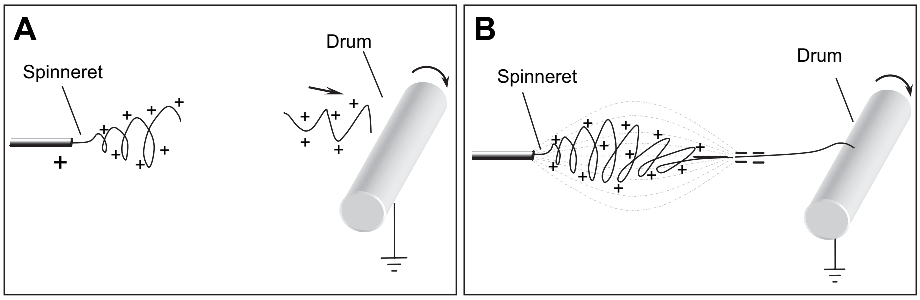

**Fig. 9.** Schematic illustration of the mechanism of the self-bundling electrospinning experiment from polymer solution with conductivity higher than 400 μS/cm: (A) self-bundled automatically; (B) yarn growth and collect.

## 4. Conclusion

In this work, self-bundling electrospinning has been used to provide a simple method for generating continuous electrospun yarns with good alignment and yarn membranes. Four kinds of different polymer solutions with different conductivity were used for self-bundling electrospinning. The experimental results revealed that the conductivity of polymer solution was the most important parameter to achieve continuous self-bundled nanofiber yarns by self-bundling electrospinning method. When the conductivity of polymer solution is lower than 10 μS/cm, the jet self-bundling can occur only for moment even an adjacent grounded metallic needle tip is used to induce. When the conductivity of polymer solution is between 10 and 400 μS/cm, the self-bundling of electrospinning jet is achieved for continuous yarn collection through the induction by an adjacent grounded metallic needle. When the conductivity increases further, the jet self-bundling occurs automatically without the induction of needle tip. Meanwhile, the alignment of the separate fibers in the self-bundling yarn is enhanced with the increase of the conductivity of polymer solution. A possible mechanism for the self-bundling formation of the yarn is proposed. It is believed that high conductivity of the polymer solution results in the change of the shape of the electrostatic field, which is the fundamental factor for the self-bundling. Besides the conductivity, some other parameters such as velocity of the drum, applied voltage and humidity of air also affect the stability of self-bundling, and further studies are being carried out. This method can be extended easily to generate well-aligned nanofiber yarns and yarn membranes from a rich variety of polymers by adjusting the conductivity of polymer solution and using of a grounded metallic needle.

## Acknowledgment

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