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Control of the morphology of micro/nano-structures of polycarbonate via electrospinning

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Many of the applications proposed for bioassays, scaffolds for tissue engineering, filtrations, and supports for catalysts require polymeric membranes with large specific surface areas. Polycarbonate (PC) is a possible candidate for these applications because of its excellent mechanical performance and good biocompatibility. Electrospinning is a simple and effective method for large-scale fabrication of micro-/nano- fibrous membranes with large specific surface areas. How to control the morphology of electrospun PC fibers, however, has not been systematically investigated. We describe the controllable fabrication of continuous and uniform PC fibers. We electrospin PC/chloroform solutions doped with different types of surfactants including anionic, zwitterionic, nonionic and cationic surfactants. Only cationic surfactants can lead to the successful fabrication of uniform PC fibers. After the analysis of the correlation between solution properties such as viscosity, surface tension, and conductivity and the morphology of electrospun fibers, we conclude that the addition of cationic surfactants such as cetane trimethyl ammonium bromide (CTAB) that leads to a decrease in viscosity is the main factor responsible for the formation of PC fibers. The demonstration of the fabrication of uniform PC fibers will lend experience to processing other polymers into fibers via electrospinning.

electrospinning, polycarbonate, nanofibers, morphology control, surfactants

Electrospinning (ES) is a simple and effective technique for producing nanomaterials with large specific surface areas[1–8]. ES typically utilizes a high electric field to stretch a polymeric solution into fibers. Fabrication and application involving ES have been reviewed by several groups[9–11]. Up to date, various materials such as bio-macromolecules, synthetic polymers, polymers containing nanoparticles/drugs/DNA/biological cells, and even small molecules like phospholipids have been fabricated into fibers via ES[11,12].

Many of these demonstrations are based on the hypothesis that the presence of sufficient intermolecular interactions that act as chain entanglements is the most important factor for the formation of fibers[5,12,13]. Generally, a high concentration can endow the polymer solutions with sufficient chain entanglements, leading to the formation of fibers; but high concentrations usually result in high viscosity, hampering the formation of fibers. The key to successful electrospinning of fibers, therefore, is the balance between solution concentration and viscosity (although other factors such as conductivity and surface tension of polymer solutions may influence the process as well). For instance, some polymers, such as chitosan, alginate and polycarbonate (PC), were not easily electrospun into fibers. To solve this problem, researchers have introduced additives such as co-polymers, surfactants or special solvents into the polymeric solution. Chitosan is a natural polymer with poor spin-nability because at low concentrations (such as 2 wt%

in 1% acetic acid) the solution was both too viscous to electrospin and had insufficient chain entanglements on the molecule scale. Yamamoto et. al. used trifluoroacetic acid as the solvent to dissolve chitosan to obtain chitosan solutions with a relatively high concentration (8 wt%) and low viscosity, and successfully fabricated chitosan fibers[14,15]. Alginate was hard to electrospin because the gelation of alginate solution starts to occur at very low concentrations (e.g. 2 wt% in deionized water). Zhang et al. demonstrated that poly (ethylene oxide) (PEO) and Triton X-100 could aid alginate to form fibers because PEO and Triton increased the gelation concentration[16]. Similarly, cellulose was also electrospun into nanofibers recently[17,18]. Demonstration by Long et al. that phospholipid could be electrospun into fibers expanded the scope of materials that allow processing by electrospinning from polymers to low molar-weight molecules[12], which further validated the hypothesis that the overlap and entanglement of polymeric chains is the determining factor for the formation of continuous fibers.

Up to now, the electrospinning of PC is still challenging. In our efforts to control the morphology of electrospun PC mats, we attempt to modulate the solution properties, especially the concentration and the viscosity by adding surfactants, so as to achieve a balance between chain entanglements and viscosity. PC is a widely used thermoplastic due to its excellent mechanical performance and good biocompatibility. PC membranes with large specific surface areas are widely used in bioassays[19], scaffolds for tissue engineering[20], filtrations[21], and supports for catalysts[22]. Many investigators have attempted to investigate the electrospinning of PC. We have used surfactants to generate smooth PC fibers that form a membrane for microfluidic immunoassays in HIV diagnosis[2]. Sung et al. studied the influence of solvent and voltage on the morphologies of electrospun PC[23]. They obtained beaded fibers and raisin-like structures. Kim[24] and Park[25] fabricated electrospun nanofibers of carbon nanotubes/PC nanocomposites, respectively. Recently, Park et al. prepared PC fibers by adding quaternary ammonium salt into PC/chloroform solutions to generate smooth PC fibers with a mean diameter of about 1 μm[26]. Nevertheless, many applications require that the electrospun fibers should be continuous, uniform with relatively small diameters. Despite all these efforts, the fabrication of uniform and continuous PC electrospun fibers has not been systematically investigated. Our aims in this study, therefore,

are: (i) to produce continuous, uniform PC fibers; (ii) to explore the mechanism of how surfactants may influence electrospinning.

1 Materials and methods

1.1 Materials

Polycarbonate (PC) with an average molecular weight of 45000 was from ACROS OGANICS. Sodium dodecyl sulfate (SDS), betaine hydrochloride (BHC), Tween 80, cetane trimethyl ammonium bromide (CTAB), dodecyl trimethyl ammonium bromide (DTAB), and chloroform were from Beijing Chem. Co. (Beijing, China). All reagents were used directly without any purification.

1.2 Preparation and characterization of PC solutions

We dissolved a measured amount of PC granules in chloroform at room temperature and obtained transparent solutions. Viscosity was characterized by a digital viscometer (SNB-1, Shanghai Nirun Intelligent Technology Co., Ltd., China). Surface tension was measured by a surface tension meter (Dataphysics, DCAT 21, Germany). Conductivity was measured by a conductivity meter (DDS-307, Rex Shanghai, China). All measurements were conducted at room temperature corresponding to the electrospinning condition (25℃).

1.3 Electrospinning

We employed a DC high-voltage generator (Spellman SL150) to produce voltages ranging from 0 to 50 kV. The solution was contained in a 5 ml syringe with a flattened needle. A syringe pump was used to feed the polymeric solution. A sheet of aluminum foil was placed under the syringe as the collector. The anode was connected with the needle, and cathode with the aluminum foil. All operations were conducted at 25℃.

1.4 Scanning electron microscopy (SEM)

We used SEM (Hitachi, S3400 and S4800) to observe the morphology of the electrospun mats. Each sample was sputter-coated with gold (resulting in an Au coating of about 10 nm) to reduce charging effects.

2 Results and discussion

2.1 General comments on electrospinning experiment

The electrospinning setup we used was a typical appa-

ratus composed of a high voltage generator, a glass syringe with a flattened steel needle, and an aluminum foil as the collector. The anode was connected with the needle tip, and cathode with aluminum. When we applied a high voltage to the polymer solutions, the solutions were electrified with charges; the repulsion between charges and electrostatic force imposed by the electric field made the polymeric solution into a cone at the orifice of the needle tip. When the electrostatic forces surpassed the surface tension of solutions, a string of fluid jet erupted from the cone, and the initial jet would split into bunches of smaller jets. These jets rushed to the cathode, depositing on the collector randomly. At the same time, the solvent evaporated from the jets to result in solid polymeric fibers.

We defined the distance between the anode and cathode as the work distance. The work distance and the voltage were easily adjustable parameters. Generally, we fixed the work distance, and changed the voltage, so as to achieve different electric fields. These parameters allow us to control the morphologies of the resultant fibers and the assembly of fibers into mats. During electrospinning a syringe pump was sometimes needed; especially for the concentrated solutions, the pump pressure could accelerate the electrospinning rate; the pump pressure, however, almost had no influence on the morphologies of the resultant fibers. We found that electrospinning was affected by environmental factors such as temperature and humidity. In our experiments, therefore, we used an air-conditioning to maintain the temperature at 25℃; and we employed a dehumidifying machine and a humidifier to adjust the humidity to the desired ranges.

2.2 Electrospinning of PC with different types of surfactants

We initially prepared PC solutions in chloroform with a series of concentrations ranging from 8% to 14% (by weight, so are all subsequent percentage numbers). When we tried to electrospin these solutions with different voltages and work distances, we could not obtain continuous and uniform fibers. In addition, the ES rate was slow. Figure 1 shows the SEM images of two typical morphologies from PC/chloroform solutions. At relatively low concentrations (e.g., 10%, Figure 1(a)), there were no sufficient chain entanglements, thus the application of electric field resulted in formation of beads primarily due to the Rayleigh instability[7]. When the PC concentration increased to 14%, fibers formed, but the

diameters of the fibers were not uniform and the ES rate was very slow (Figure 1(b)). In this case, abundant chain entanglements were present, but the viscosity was so high that the solution could hardly squeeze out of the orifice of the needle. We measured the viscosity, surface tension, and conductivity of these solutions with different concentrations (from 8% to 14%). The conductivity of these solutions kept at zero, and the surface tension increased little (from 27.49 mN/m at 8% to 29.05 mN/m at 14%), while the viscosity increased dramatically (from 31.9 mPa·s at 8% to 248.5 mPa·s at 14%). These data indicate that in pure PC/chloroform, the increase of viscosity of PC solutions with the increase of concentrations was the key factor that determines ES processing and morphology of the electrospun mats.
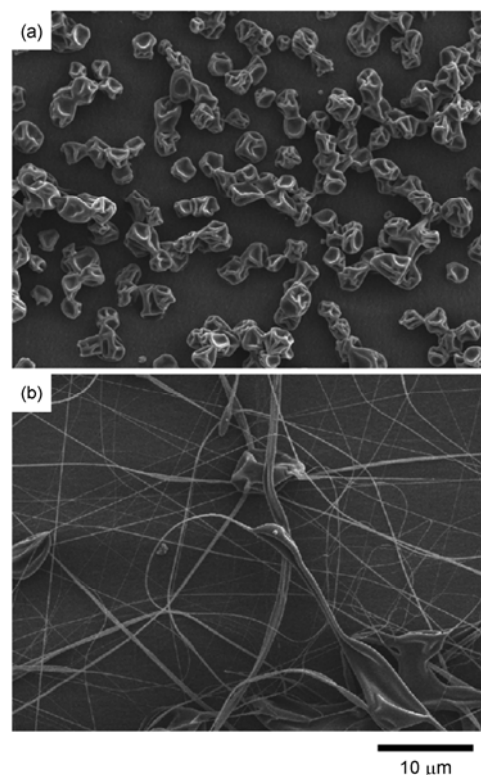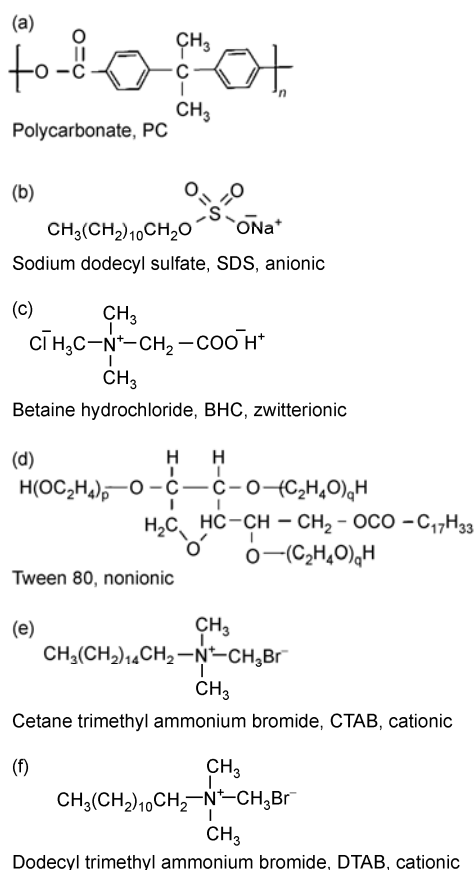

Figure 1 SEM images of electrospun PC mats at different concentrations (a) 10%, (b) 14%; Working distance 10 cm, and voltage 20 kV.

To decrease the viscosity of polymeric solutions with high-concentrations, we introduced different types of surfactants into the solutions to improve the spinnability of PC. Since we intended to fabricate PC fibers, we chose the concentration of PC solutions at 12% for the following investigations. The molecular formulas of different surfactants are outlined in Scheme 1. Anionic

Polycarbonate, PC

(a)

(b) Sodium dodecyl sulfate, SDS, anionic

(c) Betaine hydrochloride, BHC, zwitterionic

(d) Tween 80, nonionic

(e) Cetane trimethyl ammonium bromide, CTAB, cationic

(f) Dodecyl trimethyl ammonium bromide, DTAB, cationic

Scheme 1 Molecular formula of surfactants.

sodium dodecyl sulfate (SDS) and zwitterionic betaine hydrochloride (BHC) could not dissolve well in PC/chloroform solutions and did not improve the formation of smooth fibers during the electrospinning process (Figures 2(a), (b)). By contrast, nonionic Tween 80 and cationic cetyltrimethyl ammonium bromide (CTAB) completely dissolved in PC solutions; they helped to form smooth PC fibers during electrospinning (Figures 2(c), (d)). After adding Tween 80, compared with pure PC, the viscosity decreased from 124.0 to 107.5 mPa·s, the conductivity of the solutions kept at zero, and surface tension almost kept unaltered (Table 1). The improved spinnability by adding Tween (compare Figure 1(b) with Figure 2(c)), therefore, is mainly caused by the decrease of viscosity. But the PC/Tween solutions yielded beaded fibers or ribbon-like fibers (Figure 2(c)), and the ES rate was also very slow (about 0.48 mg/min, and 0.22 mg/min for pure PC). After adding CTAB into the PC/chloroform solutions, we obtained uniform and continuous fibers with a mean diameter of about 500 nm (Figure 2(d)). For PC/CTAB solutions, the surface tension did not change significantly in comparison with
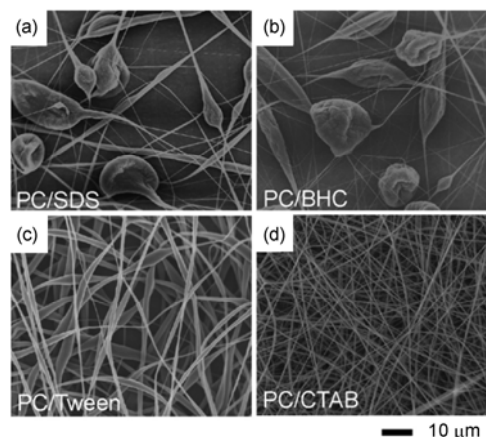

Figure 2 SEM images of electrospun mats derived from solutions by adding different surfactants into PC/chloroform (a) SDS, (b) BHC, (c) Tween, (d) CTAB. PC concentration 12%, surfactant content 0.5%, working distance 10 cm, voltage 20 kV.

pure PC and PC/Tween, but the viscosity further decreased compared with PC/Tween (see Table 1). At the same time, the conductivity increased from zero to 0.41 μS/cm compared with pure PC and PC/Tween due to the introduction of ions. The ES rate of PC/CTAB was ten times faster than pure PC. From Table 1 we can see the changes of the conductivity, viscosity, surface tension, and ES rate. The addition of Tween decreased the viscosity of PC solutions, which led to the formation of ribbon fibers with uneven diameters (Figure 2(c)). CTAB decreased the viscosity more than Tween, it allowed fibers (with almost uniform diameters, Figure 2(d)) to form. We believe that compared with data from other groups that are solely the results of increased conductivity, the decrease of the viscosity, in our case, is the main factor that leads to the successful fabrication of PC fibers. CTAB also increased the conductivity of PC solutions, which might also have aided in eliminating the ribbons and increasing ES rate[27,28].

We determined, therefore, CTAB was the optimal candidate as the additive to help electrospinning PC fibers. In the following parts we will explore the optimal experimental parameters for fabricating PC fibers.

Table 1 Solution properties of PC/chloroform after adding different types of surfactants

	Conductivity (μS/cm)	Viscosity (mPa·s)	Surface tension (mN/m)	ES rate (mg/min)
Pure PC	0.00	124.0	28.35	0.22
PC/Tween	0.00	107.5	28.69	0.48
PC/CTAB	0.41	96.7	28.55	2.20

2.3 Optimal experimental conditions for the formation of PC fibers

In order to obtain uniform and continuous fibers, we systemically investigated the relationship between the morphologies of electrospun mats and the experimental parameters (i.e., CTAB content, solution concentration, and electric field strength). First, we varied the CTAB content from 0.1%, 0.3%, and 0.5% to 1%. The corresponding SEM images displayed in Figure 3 verified that adding CTAB could greatly improve the spinnability of PC solution. When the CTAB concentration is low, the resulting fibers tend to have many beads. When the CTAB concentration is high, the resulting fibers tend to be smooth and free of beads. Table 2 illustrates the influence of CTAB content on the solution properties. A small amount of CTAB (0.1%) could decrease the viscosity of PC solution from 124.0 to 98.9 mPa·s, while further increase of CTAB content had limited influence on viscosity. Adding CTAB increased the conductivity linearly with CTAB content (due to the linear increase of ionic concentration).
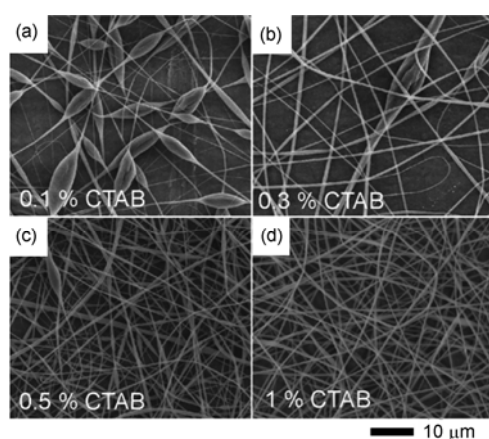

Figure 3 SEM images of electrospun mats derived from solutions with different contents of the surfactant CTAB (a) 0.1%, (b) 0.3%, (c) 0.5%, (d) 1%. PC concentration 12%, working distance 10 cm, voltage 20 kV.

Table 2 Solution properties of PC/chloroform with different CTAB content

CTAB content	Conductivity (µS/cm)	Viscosity (mPa·s)	Surface tension (mN/m)
0.1%	0.1	98.9	28.45
0.3%	0.22	96.6	28.54
0.5%	0.41	96.7	28.55
1.0%	1.01	96.5	29.32

Secondly, we used different concentrations of PC, i.e., 8%, 10%, 12% and 14% for electrospinning. All samples contain 0.5% CTAB. When we gradually increased the

PC concentrations from 8%, we obtained raisin-like beads (Figure 4(a)), beaded fibers (Figure 4(b)), and smooth and uniform fibers (Figures 4(c), (d)). When PC concentration was low, the chain entanglements were insufficient, resulting in the formation of beads; after a slight increase in PC concentration, sufficient chain entanglements could prevent electrospun jets from breaking and consequently fibers formed[11]. In order to compare the difference between pure PC and PC/CTAB, we measured the physical properties of solutions with different PC concentrations (Table 3). Compared with pure PC, the viscosity of PC/CTAB is small. At low concentrations (8% and 10%), the difference of viscosity between pure PC and PC/CTAB was small; at high concentrations (12% and 14%), the difference became large. The conductivity for all concentrations increased. The surface tension kept essentially unchanged.
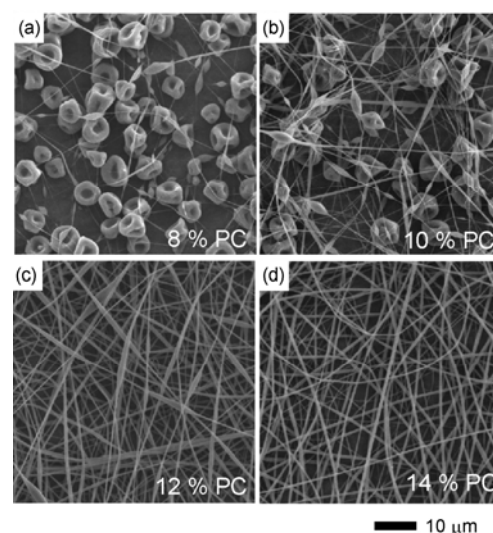

Figure 4 SEM images of electrospun mats derived from solutions with different PC concentrations (a) 8%, (b) 10%, (c) 12%, (d) 14%. CTAB content 0.5%, working distance 10 cm, voltage 20 kV.

Table 3 Solution properties of PC and PC/CTAB with different PC concentrations

	Viscosity (mPa·s)		Conductivity (µS/cm)		Surface tension (mN/m)	
	PC	PC/CTAB	PC	PC/CTAB	PC	PC/CTAB
8%	31.9	28.7	0	0.52	27.49	27.66
10%	52.2	50.8	0	0.49	28.25	28.06
12%	124.0	96.7	0	0.41	28.35	28.55
14%	248.5	208.6	0	0.34	29.05	29.80

Thirdly, we studied the effects of electric field strength on the formation of electrospun PC mats. When the voltage was smaller than 10 kV, no jets erupted from

the needle tip because electric field was insufficient to overcome surface tension; voltage larger than 10 kV could lead to fiber formation (Figure 5). We electrospun solutions for the same processing time amongst experiments with different voltage values, and found that with increasing voltage the ES rate became faster. For safety considerations, however, we usually set the voltage below 25 kV.
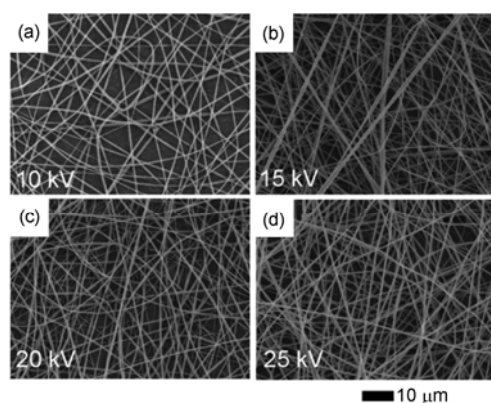

Figure 5 SEM images of electrospun mats processed at different voltages (a) 10 kV, (b) 15 kV, (c) 20 kV, (d) 25 kV. PC concentration 12%, CTAB content 0.5%, working distance 10 cm.

Having considered all experimental parameters, we determined the optimal experimental conditions as follows: PC concentration 12%－14%, CTAB content 0.5%－1%, voltage 15－20 kV, working distance 10 cm.

2.4 DTAB leading to the formation of PC fibers

To find out if other cationic surfactants might act similarly to CTAB in allowing the fabrication of PC electrospun fibers, we employed another cationic surfactant, dodecyl trimethyl ammonium bromide (DTAB) to aid the electrospinning of PC. Figure 6 shows the SEM images of PC electrospun mats after adding DTAB. After adding 0.1% DTAB, beaded fibers formed; when DTAB content reached 0.3%, we could fabricate continuous and uniform PC fibers. The solution properties of PC/DTAB (Table 4) indicated that DTAB decreased the viscosity, increased the conductivity, and had almost no effect on surface tension, a result similar to the effect of adding CTAB in PC/chloroform (c.f. Table 2).
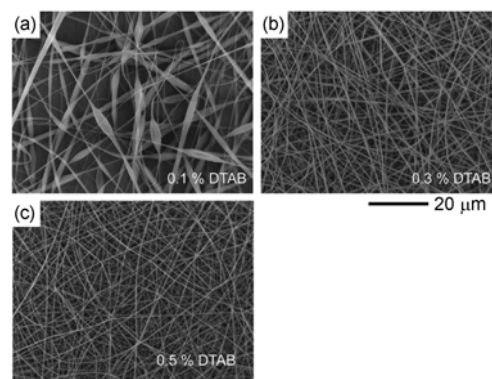

Figure 6 SEM images of electrospun mats by adding different DTAB contents (a) 0.1%, (b) 0.3%, (c) 0.5%. PC concentration 12%, working distance 10 cm, voltage 20 kV.

Table 4 Solution properties of PC and PC/DTAB with different DTAB contents

DTAB content	Conductivity (μS/cm)	Viscosity (mPa·s)	Surface tension (mN/m)
0	0	124.0	28.35
0.1%	0.12	101.5	28.83
0.3%	0.30	99.0	28.31
0.5%	0.58	99.1	28.55

3 Conclusions

We investigated how surfactants and the concentrations of polymer can control the morphology of electrospun PC fibers. The results showed that only cationic surfactants such as CTAB and DTAB could aid the formation of smooth and uniform PC nanofibers. By correlating the SEM images of electrospun mats with the physical properties of the polymeric solution, we believe that the decrease of viscosity resulting from the addition of cationic surfactants was the main reason for the improved spinnability. The balance between sufficient chain entanglements and relatively low viscosity is the fundamental determinant for the formation of electrospun fibers. We hope that the underlying principle for the successful demonstration of PC electrospun fibers will set a good example for other polymers. Along with a series of micro-/nano-technologies as tools for chemical and biological analysis developed in our group[1,2,29−31], we believe that electrospinning will be a promising technology for chemists, materials scientists, and biologists.

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