

Electrospun poly(methyl methacrylate) nanofibers and microparticles

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Abstract Electrospinning at relatively low polymer concentrations results in particles rather than fibers. This particle-formation process can be termed as electrospray. So electrospinning/electrospray is a highly versatile method to process fibers and particles with different morphologies. In this work, poly(methyl methacrylate) (PMMA) micro- and nanostructures with different morphologies (fibers, spheres, cup-like, and ring-like) have been produced by a facile electrospinning/electrospray method. PMMA was electrospun into various morphologies from only DMF without any other solvents. Field emission scanning electron microscope (FESEM) images demonstrate the different morphologies and prove this technique to be an effective method for obtaining morphology-controllable polymer materials by changing the processing parameters. These micro- and nanostructured polymer materials may find applications in drug delivery and filtration media.

Introduction

Control of the morphology and size of micro- and nanostructured polymer materials has received increased attention due to their potential applications in pharmaceuticals, printing, perfumery, cosmetics, and agrochemicals [1–3]. Moreover, recent studies have proved the superhydrophobic peculiarities of surfaces made up of micro- and nanoparticles [4]. A large number of synthesis and fabrication

methods have already been demonstrated for generating polymer materials with different morphologies. Among these methods, electrospinning is a simple, versatile, and effective technique to fabricate 1D nanostructures, such as nanowires, nanofibers, and nanotubes [5–17]. Efforts have been devoted to electrospun polymer materials into two dimensional (2D) and three-dimensional (3D) well-ordered structures [18–20]. It is a process which uses a strong electrostatic force by a high static voltage applied to a polymer solution placed into a small nozzle. Under applied electrical force, the polymer solution is ejected from the nozzle. After the solvents are evaporated during the course of jet spraying, the electrospun polymer materials are collected on a grounded collector. The structure and the morphology of the electrospun polymer materials, be it fibers or particles, are determined by a synergetic effect of solution parameters and electrostatic forces. It has been understood for most of this century that it is possible to use electrostatic fields to form and accelerate liquid jets from the tip of a capillary [21–23]. When the polymer solution flows through the capillary, the pendent drop is highly electrified and distorted into a conical object commonly known as Taylor cone. Once the strength of the electric field exceeds the critical voltage, the electrostatic forces overcome the surface tension and force the ejection of a liquid jet. In the case of low viscosity solutions, the jet breaks up into droplets. For high viscosity liquids, the jet does not break up, but travels as a jet to the grounded target [22]. The first case is known as electrospraying [20, 24] and is used to fabricate particles. The second case is known as electrospinning and it generates polymer fibers. In other words, note that they depend strongly on the polymer concentration. Electrospinning at relatively low polymer concentrations results in particles rather than fibers. Kim et al. [25] fabricated poly(methyl methacrylate) (PMMA) particles of decreasing

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size with increasing voltage. Rietveld et al. [26] prepared poly(vinylidene fluoride) (PVDF) particles and found that the droplet size is controlled by the conductivity and flow rate of the solution. Fantini et al. [18] investigated the effect of polystyrene (PS) molecular weight on beads morphology and the fundamental role of concentration. Liu et al. [19] electrospun PMMA particles with different morphologies and discussed a qualitative relationship between the different solvent properties and the particle morphologies. Herein, we report a facile electrospun fabrication of PMMA different morphologies, such as micro- and nanofibers, spheres, cup-like, and ring-like. By changing the processing parameters, morphology-controllable polymer materials have been obtained. And the morphology evolution and the formation mechanism are studied carefully. It is noteworthy that PMMA was firstly electrospun into micro- and nanostructures with various morphologies from only single DMF without any other solvents.

Experimental procedure

Materials

Poly(methyl methacrylate) (PMMA, $M_w = 110,000 \text{ g mol}^{-1}$) were synthesized in our laboratory using cyclohexane as a solvent and benzoyl peroxide as an initiator; the molecular weights were all determined by means of gel permeation chromatography (GPC). *N,N*-dimethylformamide (DMF) was of analytical purity and was used as received from Beijing Chemicals Co., China.

Sample preparation and characterization

In the preparation of precursor solutions, DMF was used as the solvent for the PMMA. In a typical process, a controlled amount of PMMA was dissolved in DMF with vigorous stirring for 24 h. The solutions with different weight ratios of PMMA were obtained. The viscosity of various concentrations used for making the electrospun samples are listed in Table 1. Then, each composite solution was placed in a 5 mL glass syringe with a plastic

Table 1 Viscosity of various PMMA/DMF solution concentrations

Concentration (wt%)	Viscosity (Pa s)
30	3200
26	1000
22	370
14	40
10	10
8	7

Table 2 The effect of various parameters on the resulting different morphologies

Morphology	Polymer concentration (wt%)	Voltage (kV)	Collection distance (cm)	Feed rate (mL h^{-1})
Nanofiber	22	15	18	4
Microsphere	10	20	20	1
Microcup	10	20	20	2
Microring	8	20	20	2

needle being used as the nozzle. The needle was connected to a high-voltage generator, an aluminum foil served as the counter electrode. The feed rate of the solution was controlled through a syringe pump. The electrospinning was conducted at 22 °C and 32% RH. (*Note*: the choice of the temperature and relative humidity are important [27].) The polymer concentration, the voltage, the collection distance, and the feed rate were adjusted to obtain morphology-controllable polymer materials. And the effect of these processing parameters on the resulting different morphologies can be seen in Table 2.

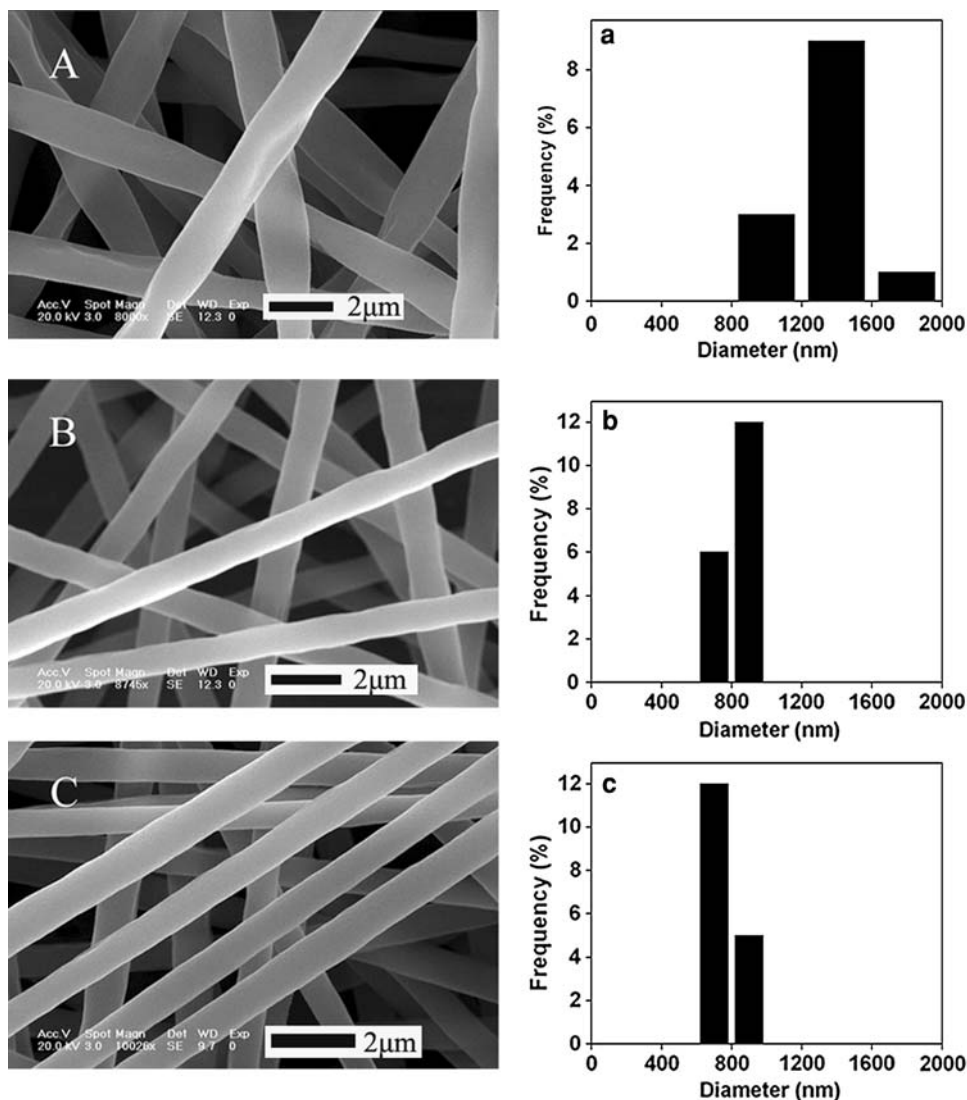
The morphology of nanofibers, spheres, cup-like, and ring-like which collected onto aluminum plates were determined by a FEI XL30 scanning electron microscopy (FESEM).

Results and discussion

Figure 1 shows the FESEM images and the diameter distribution of electrospinning products from 30, 26, and 22 wt% concentration of PMMA/DMF solution. These solutions were electrospun under an applied voltage of 15 kV, a collection distance of 18 cm and a feed rate of 4 mL/h. The electrospun product of a polymer solution showed a great dependence on the solution concentration. When the concentration of PMMA was too high, the higher viscosity solutions proved extremely difficult to force through the syringe needle of the apparatus used in these experiments, making the control of the solution flow rate to the tip unstable, thus electrospinning products were rarely obtained. Table 1 shows the viscosity of 30, 26, and 22 wt% solution. Using these solutions, the electrospinning process is predominant and only micro- and nanofibers are formed. The average diameters of fibers are ~1260, 857, and 764 nm, respectively. It is obvious that the diameter of the fibers decreases with decreasing concentration.

Electrospinning at relatively low polymer concentrations results in particles rather than fibers. This particle-formation process can be termed as electrospray. When decreasing the polymer concentration (14 wt%), all other variables are held constant, a mixture of fibers and big

Fig. 1 FESEM images and the diameter distribution of electrospinning products from PMMA/DMF solution at different concentrations: (**A** and **a**) 30 wt%, (**B** and **b**) 26 wt% and (**C** and **c**) 22 wt%



beads appears (Fig. 2a). It is obvious that the jet of polymer solution from the tip of a capillary begins to break up into droplets at concentration below 14 wt%. At a concentration of 10 wt% (Fig. 2b), the fibers disappear and the complete spheres take place. However, uniform spheres are not obtained. In order to obtain uniform diameter and regular morphology of the spheres, we further investigated the effect of other processing variables. In the course of our preparation of uniform spheres, we found that fast feed rate of the solution resulted in the appearance of the wet part on the surface of the electrospinning films. The phenomena is attributed that the more polymer solution is ejected from the nozzle and collected on a grounded collector with no time to evaporate during the course of jet spraying. So we first decreased the rate of the solution from 4 to 1 mL/h (Figs. 2b and 3b). The result confirmed that the slow feed rate is beneficial to generate uniform spheres.

To investigate the effect of applied voltage on the resulting morphologies, the polymer solution (10 wt%) was electrospun under different voltage 10, 15, and 20 kV with a fixed collection distance of 18 cm and a feed rate of 1 mL/h. The FESEM images of electrospinning from different voltage are shown in Fig. 3. When the applied voltage is low, the nonuniform and irregular spheres are observed as shown in Fig. 3a. With the increase of applied voltage, the resulting spheres show more uniform and regular morphology (Fig. 3b, c). The applied voltage 20 kV was chosen for the following study.

Another parameter that affects the resulting morphologies is the collection distance. So we investigated the effect of the collection distance on the morphologies (Fig. 4). The collection distance was 12, 14, 16, 18, and 20 cm, when the solution concentration, the applied voltage, and the feed rate were 10 wt%, 20 kV, and 1 mL/h, respectively.

Fig. 2 FESEM images of electrospinning from different concentrations: **a** 14 wt% and **b** 10 wt%. Electrospinning conditions: the voltage was 15 kV, the collection distance was 18 cm, and the feed rate was 4 mL/h

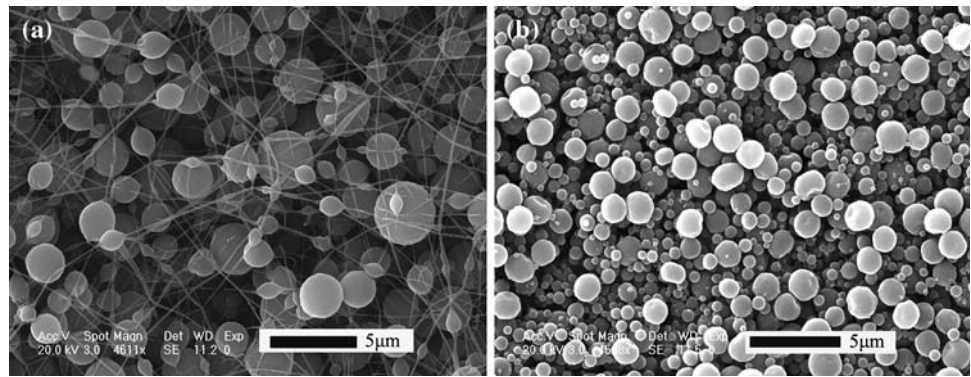
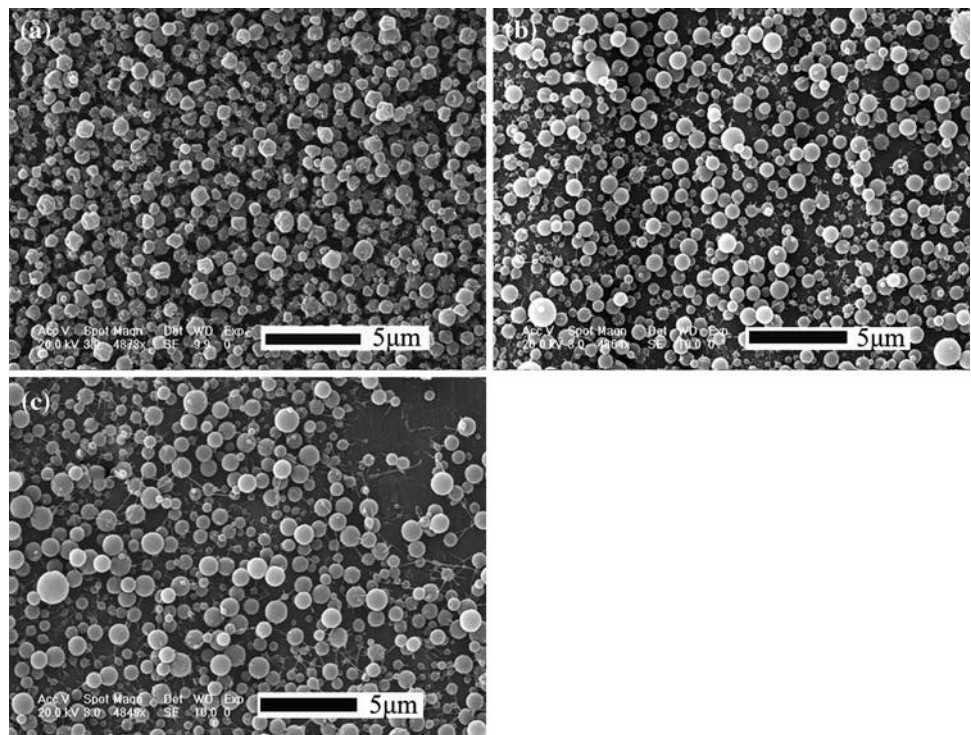


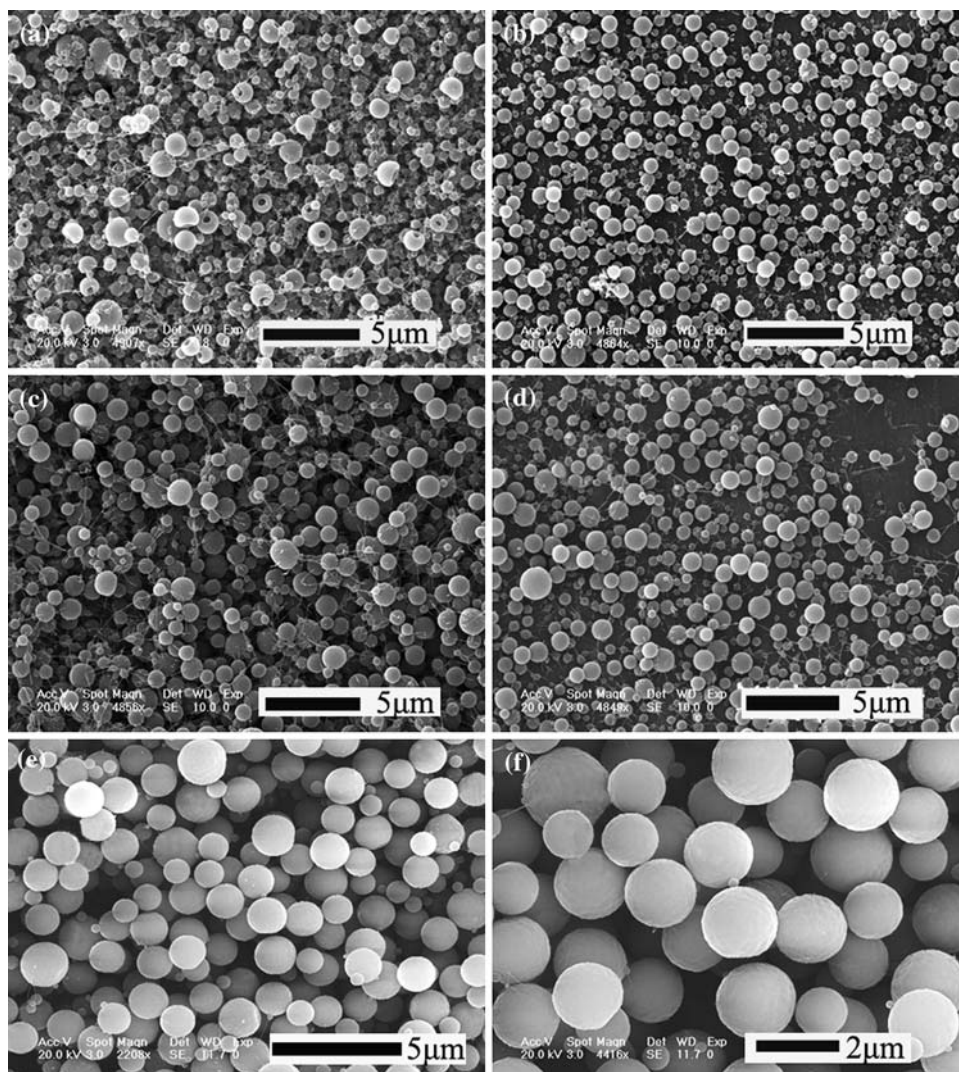
Fig. 3 FESEM images of electrospinning from different voltages: **a** 10 kV, **b** 15 kV, and **c** 20 kV



A wide range of collection distance (12–20 cm) can be applied to generate satisfactory morphologies. With the increase of collection distance, the resulting spheres show more uniform and regular morphology (Fig. 4e, f). The general overview FESEM image in Fig. 4e shows that the uniform diameter and regular morphology of the spheres are indeed formed. Figure 4f shows the enlarged image of electrospay-spheres. The diameters of the electrospay-spheres are $\sim 1.6 \mu\text{m}$. So the appropriate processing variables of the electrospay-particle (microsphere) formation were the solution concentration of 10 wt%, the voltage of 20 kV, the collection distance of 20 cm, and the feed rate of 1 mL/h. These results confirmed that high applied voltage, distant collection distance, and slow feed rate of the solution are beneficial to generate uniform spheres.

Figure 5 shows two different morphologies of electrospay-particles: cup-like (a and b) and ring-like (c and d). When all other variables of electrospay-spheres are held constant, we found that the morphology of electrospay-particles can be changed from spheres to cup-like by increasing the feed rate of the solution. At the feed rate of the solution 2 mL/h, the morphology of cup-like was produced. It is more interesting to observe that the morphology of electrospay-particles can also be changed from cup-like to ring-like by only decreasing the concentration of the solution from 10 to 8 wt%. As reported above, the electrospay of the PMMA/DMF solutions could produce different morphologies (spheres, cup-like, and ring-like). By changing the feed rate and the concentration of the solution, particles with uniform dimensions and smooth

Fig. 4 FESEM images of electrospinning from different collection distances: **a** 12 cm, **b** 14 cm, **c** 16 cm, **d** 18 cm, **e** 20 cm, and **f** magnified FESEM images of 20 cm



surfaces have been obtained. In fact, in the electro-spray-particles formation process, solvent evaporation has a great influence on the morphology of the formed particles [18]. The charged-polymer-solution jet initiating from the Taylor cone breaks up into droplets in milliseconds rather than several hours. Because of the suddenness of the process, the solution droplets are formed, the solvent has to be evaporated and the polymer has to aggregate and solidify. Then, the residual solvents diffused from the interior to the surface of the droplets and, finally, complete evaporation of solvents resulted in spheres formation. The solvent evaporation rate depends not only on the solvent's own characteristics, but also on the solution concentration. With decreasing concentration and increasing feed rate of the solution, the polymer molecules are surrounded by more and more solvent, which changed the viscosity of the solution and the surface tension of droplets. When the electrostatic forces overcome the surface tension and force

the ejection of a liquid jet, the phase separation into a solvent-rich region and a polymer-rich region appears to start at this stage, which leads to the formation of a hole and, finally, complete evaporation of solvent results in cup and ring formation [19].

Based on electrospun PMMA fibers/particles, the formation conditions and the different morphologies are shown in Fig. 6. By changing the solution concentration and electrospinning/electrospray conditions, we can produce polymer materials with different morphologies. It is noteworthy that single molecular weight PMMA ($M_w = 110,000$) was electrospun from only DMF without any other solvent. It is well-known that *N,N*-dimethylformamide (DMF) has many fascinating properties, such as high dielectric constant value, low evaporation rate, and low R_{ij}^2 value (the smaller the R_{ij}^2 value, the better the solvent for the polymer) [19], which make DMF a good solvent for PMMA.

Fig. 5 FESEM and magnified FESEM images of electrospinning from different concentrations: **a, b** 10 and **c, d** 8 wt%

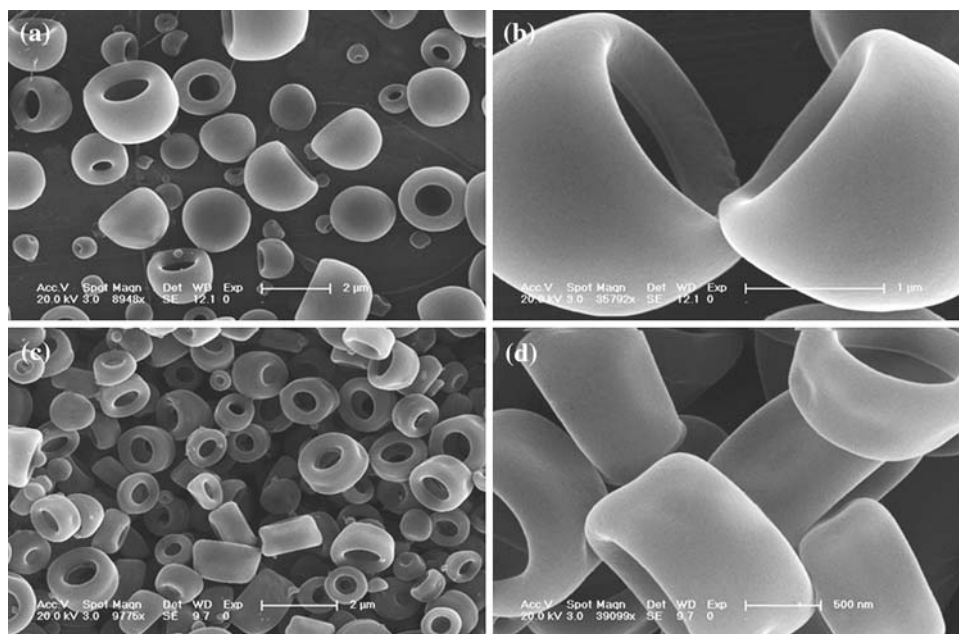
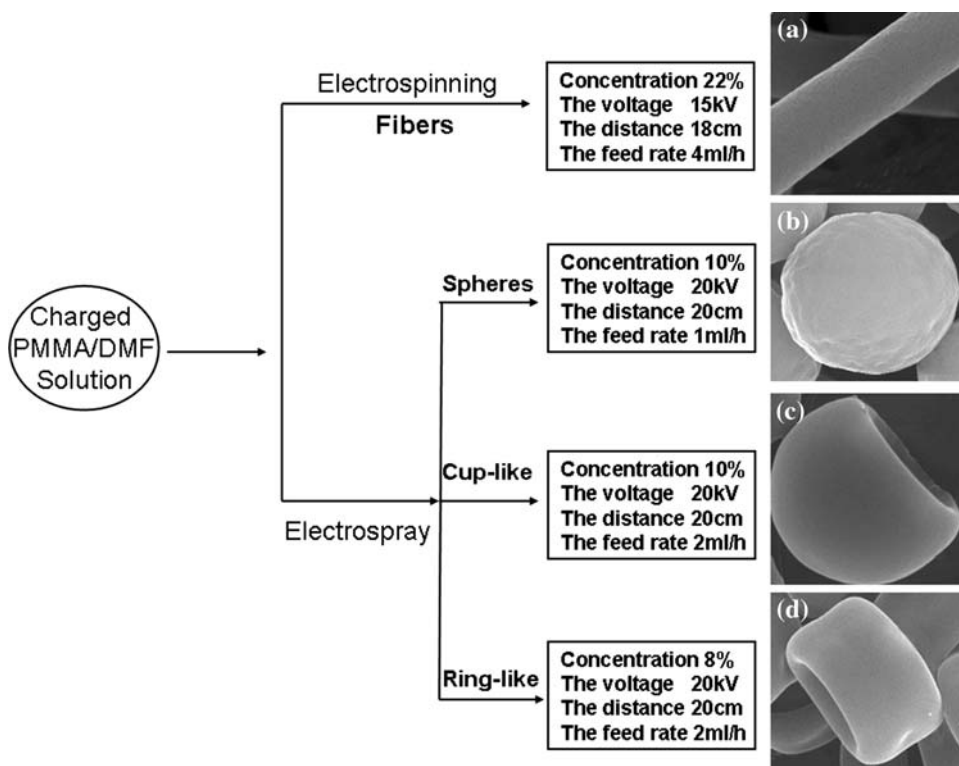


Fig. 6 Electrospinning-fibers and electro spray-particles formation conditions



Conclusion

In summary, morphology-controllable polymer materials are successfully fabricated by changing the processing parameters of electrospinning technique. FESEM images show that PMMA is electrospun into various morphologies (fibers, spheres, cup-like, and ring-like) from only DMF without any other solvents. The most important is that the

particles with ring-like are firstly prepared by electrospinning. These results demonstrated that the electrospinning/ electro spray process is an efficient approach for the preparation of polymer micro- and nanostructures with different morphologies. The electrospinning parameters determine the particle morphology. By tailoring the electrospinning process parameters, the particle morphology can be controlled based on the desired application.

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