

# Electrospinning and Porosity Measurements of Nylon-6/Poly(ethylene oxide) Blended Nonwovens

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## ABSTRACT

A simple method was used to prepare a nonwoven fabric of intimately co-mingled Nylon-6 and Polyethylene oxide (PEO) electrospun fibers by spinning fibers onto a rotating collector. Electrospinning parameters for each polymer were independent. Fiber mixture and distribution was uniform throughout the depth of the fabric. Porosity and pore size distribution of the materials were measured before and after a washing treatment. The PEO component was removed during the washing step to create increased pore size in the remaining fabric. This study indicates a simple method to create nanofiber nonwovens of multiple dissimilar polymers and provides a strategy for controlling pore size distribution independently from fiber formation.

## INTRODUCTION

Many of the potential uses for nonwoven fabrics comprised of nanofibers are expected to take advantage of the large specific surface area, high porosity and small pore size of these fabrics<sup>1,2</sup>. Both theoretical models<sup>3</sup> and experimental studies<sup>4</sup> have indicated that fiber diameter strongly influences the pore diameter in the fabric, with smaller fiber diameters resulting in smaller pores. For some applications, however, it would be interesting to combine the increased surface area associated with fine fibers with larger pores for fluid or cell transport. To accomplish this, the pore size must be de-linked from the fiber diameter.

The strategy employed in the work reported here is to create a nonwoven fabric by intimately blending two nanofibers of dissimilar polymers during the electrospinning process. One of these fibers will then be selectively dissolved to increase the void volume and associated pore size. Electrospinning multiple polymers from multiple spinnerets into a single nonwoven fabric has been approached in several ways. Side-by-side arrays of spinnerets have been used to increase the rate of electrospun nonwoven production. Fibers produced from adjacent spinnerets are overlap somewhat, but are not

intimately mixed in the resulting fabrics.<sup>5</sup> The tendency of fibers formed in side-by-side charged jets to resist mingling is easily explained by electrostatic repulsion of similarly charged materials.<sup>6</sup> Other strategies for mingling materials in an electrospun nonwoven fabric have included side-by-side<sup>7,8</sup> or core/sheath<sup>9-11</sup> arrangements of two materials from a single spinneret. Many interesting structures have been produced by these methods, but spinning conditions for the two materials are not completely independent. Frequently, both polymers are soluble in the same solvent. The applied voltage is necessarily the same for both materials.

To spin two dissimilar polymers from different solvents at different applied voltages, a simple electrospinning set up was arranged as shown in *Figure 1*. Each material is spun from a separate spinneret with separate high voltage sources. Since the charge drops with the distance squared to the grounded collector, no electrical field interference was expected at the rotating collector and none was observed. The collector rotated rapidly enough to create an intimate mixture of the two different fibers, but not rapidly enough to impart anisotropy or alignment in the resulting fabric. Porosity of the fabrics was measured before and after one of the fibers was removed by selective dissolution. Using this method, an intimately mixed fabric of two dissimilar polymers was created and porosity and pore size distribution was de-linked from fiber diameter.

## EXPERIMENTAL

### Materials and Solution Preparation

Polyamide-6 (Nylon-6,  $M_n = 10,000$ g/mol), poly(ethylene oxide) (PEO,  $M_v = \sim 400,000$  g/mol) and two fluorescent dyes, 5wt% Eosin Y aqueous solution and 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (Solvent Green 7), were purchased from Sigma-Aldrich.

Nylon-6 was dissolved in 88% formic acid at the con-

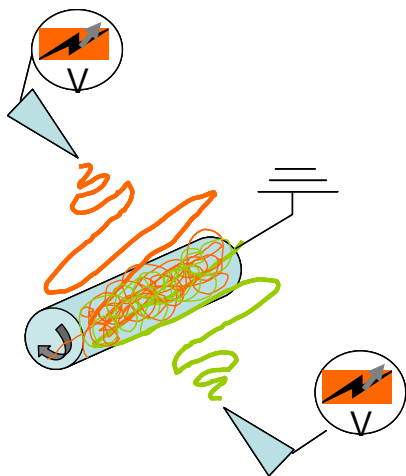


Figure 1. Two electrospinning units were positioned on opposite sides of a spinning collector. Electrospinning parameters for each apparatus could be controlled independently. The spinning grounded collector mixed the fibers in the resulting nonwoven fabric.

centration of 20% w/w and PEO was dissolved in deionized water at the concentration of 6% w/w. For fluorescence observations, solvent Green 7 and Eosin Y were added to nylon-6 and PEO solutions, respectively, at the concentration of 5% based on the weight of polymers.

### **Electrospinning Conditions**

Nylon-6 and PEO fibers were electrospun from two single syringes and collected by a stainless steel mandrel rotating at 350 rpm. The two syringes were set up at either side of the mandrel with a tip-to-collector distance of 14 cm to minimize the electrostatic repulsion between the two polymer solution jets. A 24 gauge and a 22 gauge needle were used for electrospinning of nylon-6 and PEO solution, respectively. The same solution feeding rate of 0.2 ml/hr was applied for both solutions. The electrospinning voltage was 28 kV for nylon-6 solution and 9.9 kV for PEO solution. Based on mass throughput, the resulting Nylon-6 + PEO fabrics were 77% Nylon-6 and 23% PEO by weight.

### **Measurement and Characterization**

The morphology of the electrospun fibers was observed with a scanning electron microscope (SEM, LEICA 440). The fibers were coated with gold and observed under 25 kV accelerating voltage. Width of 100 randomly selected PEO and nylon-6 fibers were measured on SEM photomicrographs and analyzed using image analysis software (Scion Image, NIH Image software) to obtain the fiber size distribution. The fluorescence measurements were conducted with

a confocal microscope (Leica TCS SP2) equipped with three lasers: a 4-line argon (452, 475, 488, 514 nm); a green HeNe (543 nm); and a red HeNe (638 nm) and each was fully adjustable by means of an Acousto-Optical Tunable Filter (AOTF). Four fluorescence detectors and one transmitted detector allowed simultaneous capture of four colors plus brightfield. Signals from the two different fluorescent dyes inside nylon-6 and PEO fibers were obtained simultaneously and the images were merged to determine the fiber distribution inside the fibrous mats.

The porosity of electrospun fibrous mats was measured using a capillary flow porometer (CFP-1100-AEHXL, PMI Inc.). During the porosity measurement, a fibrous mat was completely saturated with a liquid with very low surface tension to make all the pores of the air filter media to be covered by the liquid. When the applied air pressure exceeds the capillary attraction of the liquid in the pores, air will pass through the sample. Smaller pores have a higher capillary attraction than larger pores and thus smaller pores open up at higher pressures. Bubble point is the point when the largest pore is opened up by the air. So the bubble point pore diameter is the largest pore diameter of the sample. Porometry samples were 3cm by 3cm squares. Sample to sample mass variation was less than 10%.

## **RESULTS AND DISCUSSION**

Electrospinning conditions for PEO and Nylon-6 were optimized individually to produce uniform fibers with consistent diameters (*Figure 2*). Nylon-6 fibers spun as described above have been extensively characterized in our laboratory<sup>5,12</sup>. Spinning conditions for each material were significantly different, requiring different solvents (88% Formic Acid and water) and different applied voltages (28 kV and 9.9 kV). Since the volatility of both solvents was similar, the target distance was 14cm for each. It would not have been possible to spin fibers from both of these solutions from a side-by-side spinneret arrangement based on the different solvents and voltages required.

Fiber size distributions are presented in *Figure 3*. As previously reported<sup>5, 12</sup> the nylon-6 fibers had true nanoscale dimensions with average diameters of 90 nm. The PEO fibers were slightly larger, with all fibers measured greater than 100nm in diameter. Fiber diameters of Nylon-6 fibers range from 50 to 180 nm. Diameters of the PEO fibers are slightly larger and range from 150 to 300nm. Both nylon-6 and PEO fibers have a range of morphologies, including round fibers, some flattened oval shaped

fibers and occasional beads along the fiber surface. Fibers are not oriented or aligned in the mats and have a random distribution of orientation despite collection on a rotating collector.

A green fluorescent dye was added to the Nylon-6 spinning dope and a red fluorescent dye was added to the PEO spinning dope for ease of differentiating the fibers in the blended fabrics. *Figure 4* provides confocal microscopy images of the fibers containing fluorescent markers. Although there is no measurable change in the fiber diameters as a result of adding the fluorescent marker to the spinning dope, more

droplets are evident on the nonwoven fabrics. The droplets and bright spots may indicate imperfect distribution of the fluorescent dyes within the electrospun fibers. Individual fibers are clearly visible in the confocal microscope. This marker system allows straightforward differentiation between nylon-6 and PEO fibers in blended nonwoven fabrics.

With a fluorescent dye added to each spinning solution as a marker, Nylon-6 and PEO were spun simultaneously at a rotating mandrel. With the man-

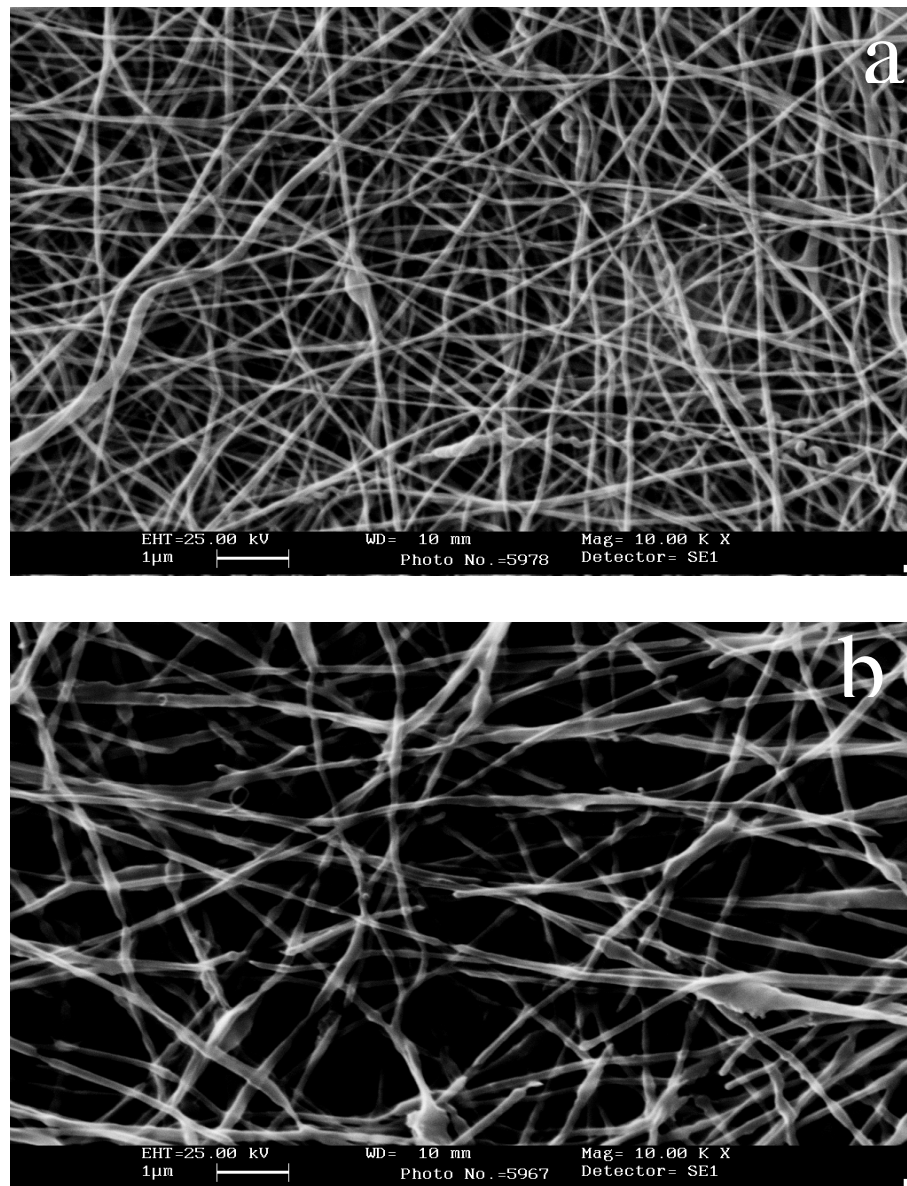


Figure 1. SEM photomicrographs of electrospun a) Nylon-6 and b) PEO fibers. The size bar is 1  $\mu\text{m}$ .

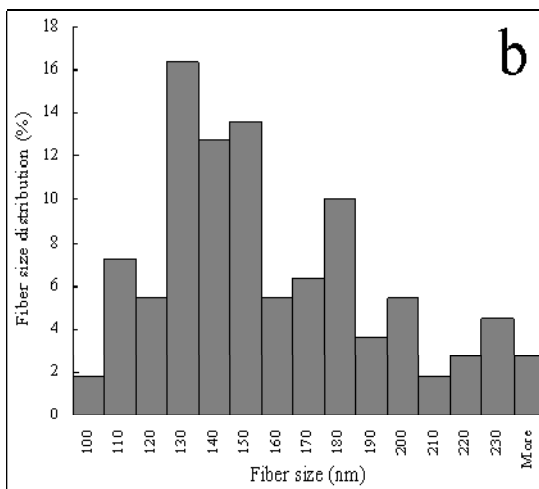
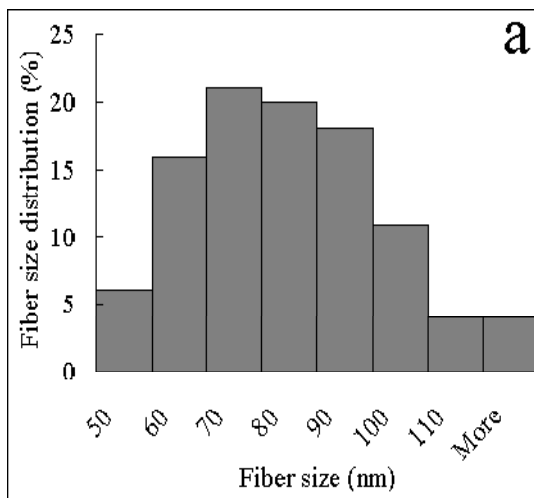


Figure 3. Fiber size distribution for (a) polyamide-6 fibers and (b) PEO fibers.

drel rotating at 350 rpm, no significant alignment or machine direction was induced in the electrospun fabrics. Previous workers using rotating mandrels have reported no significant alignment at speeds of 500 rpm and measurable anisotropy at collection speeds of 4500 rpm.<sup>13</sup> In the Nylon-6 + PEO fabrics formed here, the effect of the rotating mandrel on the structure and properties of the fabric was insignificant. Spinning both fibers at opposite sides of the rotating mandrel has, however, resulted in an intimately blended fabric containing both Nylon-6 and PEO. Confocal microscopy images (Figure 5) of the bicomponent fabrics taken at the fabric surface and 10, 20 and 30  $\mu\text{m}$  below the fabric surface confirm that the blending is uniform through out the fabric. With fiber diameters on the order of 200nm,

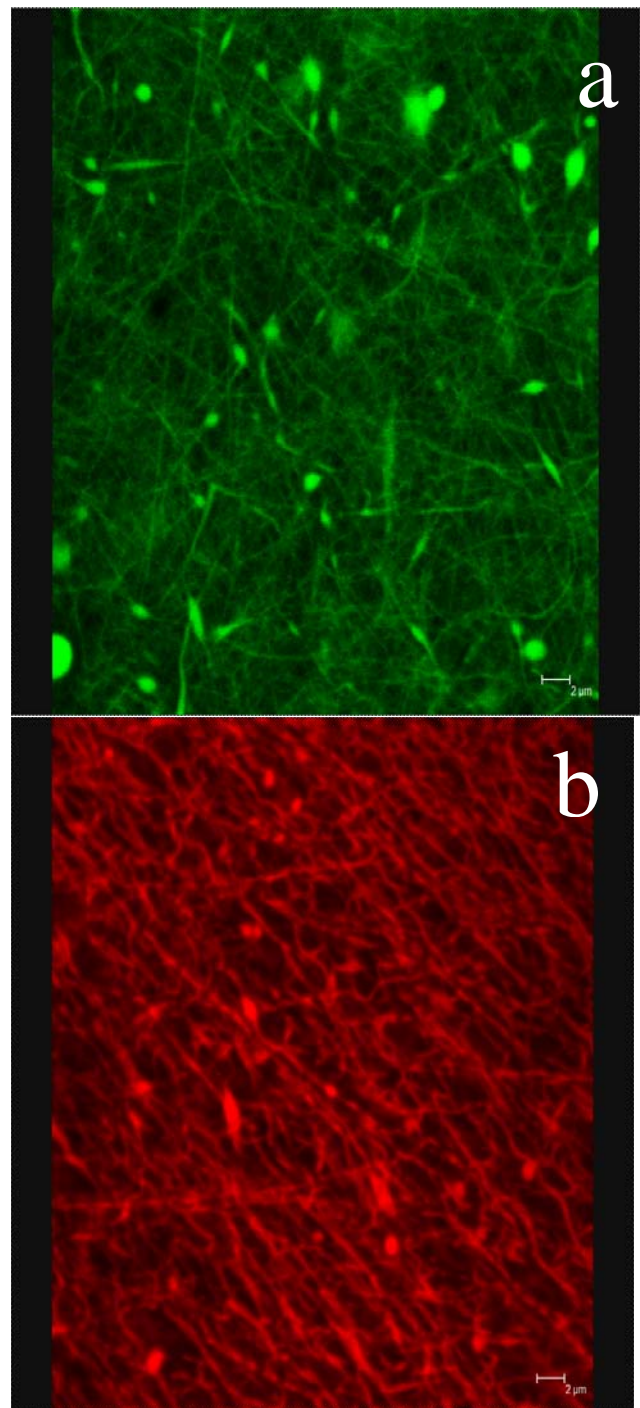


Figure 4. Confocal laser scanning microscope images of electrospun (a) nylon-6 fibers with the addition of 5% Solvent Green 7 fluorescence dyes and (b) PEO fibers with the addition of 5% Eosin Y fluorescence dyes. The magnification bars in the images are 2  $\mu\text{m}$ .

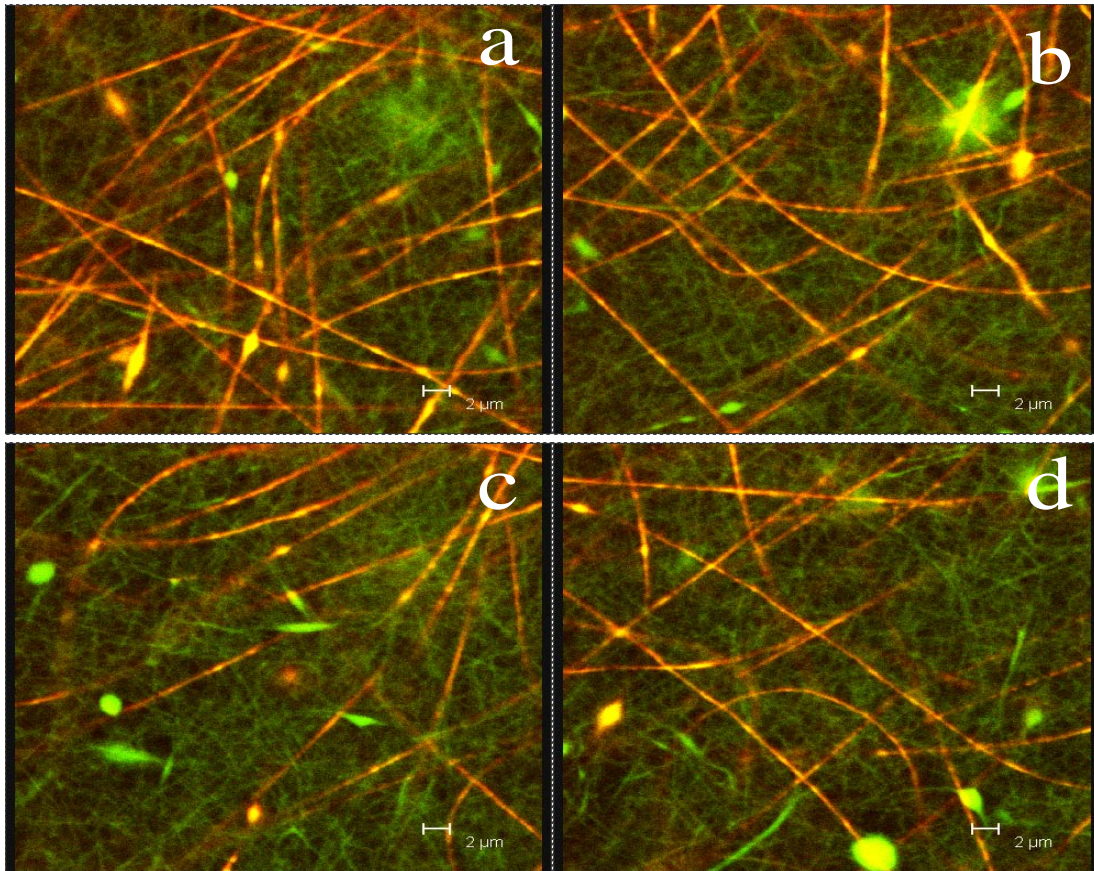


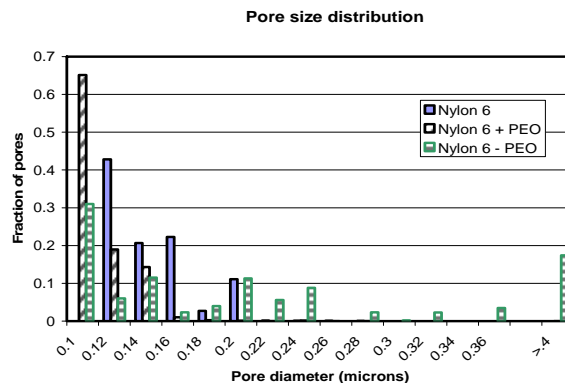
Figure 5. Confocal laser scanning microscope images of nylon-6+PEO bi-component fibrous membrane. (a), (b), (c) and (d) are the images of four sections taken at the step distance of 10  $\mu\text{m}$  starting from the surface. The magnification bars in the images are 2  $\mu\text{m}$ .

10  $\mu\text{m}$  represents a thickness of 50 fiber diameters between images in *Figure 3*.

Pore size and pore size distribution of the Nylon-6 and Nylon-6+PEO blend fabrics were measured. In order to increase the pore sizes of the bi-component

fibrous mats, nylon-6 + PEO electrospun fibrous mats were immersed in water for 24 hours to remove the PEO component, followed by drying in vacuum oven for another 24 hours. After the water treatment, the thicker PEO red fibers as shown in *Figure 4* were dissolved and the fibrous mats showed a red color,

TABLE I.  
Pore size distribution of Nylon 6, Nylon 6 +PEO and Nylon 6 - PEO (PEO removed) electrospun nonwoven fabrics



which was due to the absorption of the red fluorescent dyes during their dissolution.

Pore size distribution of nylon-6, nylon-6 + PEO and nylon-6 – PEO fabrics is presented in *Table I*. Nylon-6 – PEO indicates the fabric with PEO removed from a nylon-6 + PEO starting material. Both the nylon-6 and nylon-6+PEO fabrics have very small pore sizes and narrow pore size distributions. Few pores with diameters greater than 200 nm were measured for either the nylon-6 or nylon-6 + PEO fabrics. With PEO removed, however, the nylon-6 – PEO fabric has a significantly broad pore size distribution, with pore diameters ranging from 100 nm to nearly a micron. With PEO removed, 50% of pores are larger than 200 nm in diameter. The remaining nylon-6 fibers were not affected by the PEO removal. In flow situations, larger pores will fill first and at lower pressure. Additionally, larger pores contain a greater overall fraction of the pore volume within a material. The distribution presented in *Table I* represents the number distribution of pores. The volume distribution of pores would be shifted towards the larger pore diameters in proportion with the diameter cubed.

## CONCLUSIONS

Fibers electrospun from two different polymer solutions using two single syringes could be mixed together homogeneously. The simple technique presented allows each of two dissimilar materials to be electrospun independently, but collected into a single cohesive nonwoven fabric. Electrospinning voltage, feed rate, needle size and needle-to-collector distance were optimized for each polymer solution. Each fiber retains the dimensions and properties obtained when electrospun individually. Additionally, fibers in the resulting nonwoven fabric are intimately mixed and no effects of electrical field interference are evident.

In this study, one water soluble polymer, PEO, was incorporated. By removing the fiber component “spacer”, a significant proportion of large (400 nm to 1 micron) pores were created. PEO constituted 23% by weight of the electrospun fabrics. Removal of the PEO, however, changed the pore size distribution in the fabric from a narrow distribution of pores less than 200nm in diameter to a broad distribution with pore sizes ranging from 100 nm to 1 micron in diameter. This represents a first step in creating electrospun nonwoven fabrics with pore size distribution controlled independently of fiber diameter.

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