

# Recent Progress in the Preparation, Characterization, and Applications of Nanofibers and Nanofiber Membranes via Electrospinning/Interfacial Polymerization

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**ABSTRACT:** Significant progress has been made recently in the fabrication of polymeric nanofibers, their characterization and applications, new polymeric materials, theoretical analysis, and so forth. Hence, in this brief review, we report the progress made in these subjects during the last 5 years. Most of the work concerns nanofibers related to the field of medi-

cine. On the other hand, negligibly few reports have been found on nanofibers related to membrane separation processes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 756–776, 2010

**Key words:** fibers; membranes; modification; separation techniques; thin films

## INTRODUCTION

Nanofibers are defined as fibers with diameters on the order of 100 nm. In general, they can be produced by interfacial polymerization and electrospinning. However, other methods are also applicable. For example, carbon nanofibers can also be produced by catalytic synthesis. Since 1990, dramatic developments have been made in the field of nanotechnology and thus in the field of electrospinning technology. During the last 5 years, more than 10 reviews related to nanofibers have appeared in the literature.<sup>1–10</sup> These reviews are mostly concerned with the use of nanofibers in the field of medical applications. In this article, we also discuss their uses in the fields of membrane separation and water treatment.

Kumbar et al.<sup>11</sup> presented a brief review in 2006 on polymeric nanofibers as novel carriers for the delivery of therapeutic molecules. Lutolf and Hubbell<sup>4</sup> wrote a review entitled “Synthetic Biomaterials as Instructive Extra Cellular Microenvironment for Morphogenesis in Tissue Engineering.” Hawker and Wooley<sup>5</sup> wrote a review entitled “The Convergence of Synthetic Organic and Polymer Chemistries.” Recently, Liao et al.<sup>3</sup> wrote a review entitled “Biomi-

metic Electrospun Nanofibers for Tissue Generation,” in which they briefly described several typical electrospun nanofiber materials and composites that have great potential for tissue generation; they also described their fabrication, advantages, drawbacks, and future prospects. Saw et al.<sup>9</sup> wrote a review article entitled “Polymeric Nanofibers in Tissue Engineering,” in which they discussed the history, classification, and fabrication of nanofibers, their applications in medicines, and their advantages and disadvantages. Burger et al.<sup>1</sup> wrote a review in which they provided a selective description of the fabrication of nanofibrous membranes and their applications with specific examples in anti-adhesion in surgery and ultrafiltration in water treatment. Kaur et al.<sup>6</sup> wrote an article about next-generation fibrous media for water treatment. Frenot and Chronakis<sup>7</sup> and Chronakis<sup>12</sup> wrote brief reviews on nanofibers assembled by electrospinning. They discussed the recent control of nanofiber morphology, structure, and surface functionality and strategies for assembling nanofibers; they also wrote about determining appropriate conditions for the electrospinning of various polymers and biopolymers. Venugopal and Ramakrishna<sup>8</sup> wrote a brief review on the application of polymer nanofibers in biomedicine and biotechnology. Huang et al.<sup>13</sup> in 2003 wrote a review on polymer nanofibers produced by electrospinning and their applications in nanocomposites. Greiner et al.<sup>2</sup> wrote a minireview entitled “Biohybrid Nanosystems with Polymer Nanofibers and

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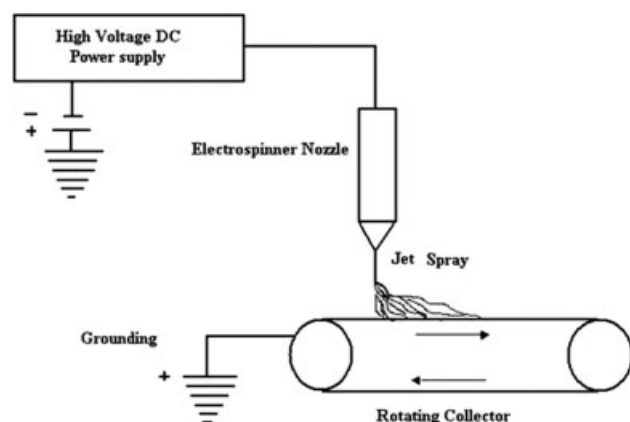


Figure 1 Schematic diagram of electrospinning.

Nanotubes," in which advanced techniques for the preparation of nanofibers of various shapes, such as core-shell fibers, hollow fibers, and rods and tubes from natural and synthetic polymers, were mentioned. These techniques, including electrospinning, co-electrospinning, and specific template methods, allow the direct incorporation not only of semiconductor or catalytic nanoparticles or chromophores but also of enzymes, proteins, microorganisms, and so forth during the preparation process into the nanostructure in a very gentle way. The range of applications of such biohybrid systems is extremely broad, including the fields of biosensors, catalysis, drug delivery, and optoelectronics.

The concept of using static electricity to move fluids is not new.<sup>14</sup> Formhals<sup>15</sup> in 1935 patented a detailed method for the production of polymer filaments using electrostatic force in more practical terms. Recently, electrospinning has gained momentum as a viable process that creates submicrometer-to-nanoscale fibers through an electrically charged jet of a polymer solution/melt. A schematic diagram of electrospinning is shown in Figure 1.

The process makes use of electrostatic and mechanical force to spin fibers from the tip of a fine orifice or spinneret. The spinneret is maintained at a positive or negative charge by a direct-current (dc) power supply. When the electrostatic force overcomes the surface tension force of the polymer solution, the liquid spills out of the spinneret and forms an extremely fine continuous filament. These filaments are collected onto a rotating or stationary collector with an electric charge opposite that of the spinneret. The filaments accumulate and bond together to form a nanofiber fabric at the collector. The distance between the spinneret nozzle and the collector generally varies from 15 to 30 cm. An enormous amount of research has been conducted to understand the process for better control of fiber formation.<sup>16–20</sup> Electrospinning is a process by which high voltage is used to produce an interconnected

membranelike web of small fibers (10–1000 nm in diameter). This novel fiber spinning technique provides the capacity to lace together various types of polymers, fibers, and particles to produce ultrathin layers.<sup>21</sup> A number of scientific articles on nanofibers have appeared in the literature. Ramakrishna et al.<sup>22</sup> wrote a book entitled "An Introduction to Electrospinning and Nanofibers." Grafe and Graham<sup>23</sup> discussed the electrospinning process for making nanofibers and nonwoven nanofiber webs from synthetic fiber-forming polymers, and they also mentioned ideas about new applications of nanofibers. The Ultra-Web nanofiber filter medium from Donaldson Co. has become available to the nonwoven and filtration industries for a broad range of filtration applications. Sill and von Recum<sup>10</sup> wrote a review of the applications of electrospun fibers in drug delivery and tissue engineering. Liang et al.<sup>24</sup> wrote a review entitled "Functional Electrospun Nanofibrous Scaffolds for Biomedical Applications."

These electrospun fibers have shown potential for applications in high-performance air filters,<sup>25</sup> protective textiles,<sup>26–28</sup> sensors,<sup>29,30</sup> advanced composites,<sup>31–33</sup> photovoltaic cells,<sup>34</sup> medicine,<sup>35,36</sup> scaffolds in tissue engineering,<sup>37–41</sup> and membranes in separation technology.<sup>42–47</sup> Graham et al.<sup>48</sup> discussed a process for making nanofibers as well as the benefits, limitations, construction, and performance of filters using nanofiber media. In particular, nanofibers provide marked increases in filtration efficiency with relatively small (and in some cases immeasurable) decreases in permeability. Nanofiber filter media have enabled new levels of filtration performance in several diverse applications with a broad range of environments and contaminants. The possibility of applying nanofiber media to a wide range of applications has also been discussed. Recently, Feng et al.<sup>49</sup> reported that polymeric nanofiber membranes have great potential for the desalination of sea water.

Because of the thermal transfer properties, high-loft nanofibers composed of carbon fibers and various polymeric fibers such as polyacrylonitrile (PAN), nylon, and polyurethane (PU) have shown potential for thermal insulation.<sup>50</sup>

Significant progress has been made in areas related to polymeric nanofiber preparation in the past few years and in this technology (the electrospinning of polymer solutions and melts) and its applications for a wide range of polymeric nanofibers.

The list of uses of polymer nanofibers has grown to include applications in filtration, biomedicine, the growth of artificial organs, reinforced composites, lightweight structures in space, precursors of carbon and ceramic nanofibers, and energy conversion devices. Weik et al.<sup>51</sup> and Chung et al.<sup>52</sup> disclosed

improved polymer materials from which fine fibers could be made.

### PROPERTIES AND CHARACTERIZATION OF NANOFIBERS

Nanofibers exhibit special properties because of the extremely high surface-to-weight ratio in comparison with conventional nonwovens. The low density, large surface area with respect to the mass, high pore volume, and tight pore size make nanofiber nonwovens appropriate for a wide range of filtration applications.<sup>53</sup> Polymeric micrometer fibers have unique and remarkable properties, such as ultraviolet (UV) resistance, electrical conductivity, and biodegradability, in comparison with the bulk properties of the materials.<sup>54</sup>

The morphology of fibers depends on the process parameters, including the solution concentration, applied electric field strength, deposition distance, and deposition time.<sup>55</sup> Nonwoven fabrics composed of electrospun fibers have a large specific surface area and a small pore size in comparison with commercial textiles, and this makes them excellent candidates for use in filtration and biomedical materials<sup>44</sup> and membrane applications.<sup>55</sup> The nonstructural and elastic properties of single-polymer [poly(L-lactic acid) (PLLA)] nanofibers extracted from a nanofibrous scaffold were studied with atomic force microscopy (AFM).<sup>56,57</sup> AFM imaging of the nanofibers revealed a shish-kebab structure. A nanoscale three-point bending test was performed to obtain the elastic modulus. This elastic modulus was found to be  $1.0 \pm 0.2$  GPa for fibers less than 350 nm but decreased with an increase in the fiber diameter in excess of 350 nm. The elastic spin modulus of a single electrospun poly(ethylene oxide) (PEO) nanofiber was measured ( $\approx 45$  MPa) with AFM.<sup>58</sup>

Currently, there are no data standards for the systemization of the criteria that are necessary for the characterization of nanofibers and nanofibrous materials prepared by electrospinning.<sup>59</sup> Spasova et al.<sup>59</sup> systemized the main characteristics necessary for a complex evaluation of the morphology of electrospun microfibers and nanofibers. Spasova et al. also fabricated microfibers and nanofibers from polyoxyethylene, polyacrylamide, chitosan, *N*-carboxyethylchitosan (CECh), poly(vinyl alcohol) (PVA), PLLA, and poly(ethylene glycol) (PEG). They discussed the characterization of the morphology and the alignment of various microfibers and nanofibers. Microfibers and nanofibers prepared by electrospinning are usually monolithic with cylindrical shapes.<sup>7,13</sup> However, under some specific conditions, other shapes are formed.<sup>60</sup> Fibers might be hollow and cylinder-like<sup>61</sup> or hollow and ribbonlike.<sup>60,62,63</sup> The

main characteristics of the defect-free cylindrical monolithic fibers are the mean diameter, minimum diameter, maximum diameter, fiber diameter distribution, and standard deviation of the diameter. Depending on the process conditions, the average diameter of electrospun fibers varies from 10 to 3500 nm, whereas their length may be several meters or more.<sup>64</sup> Under certain conditions, they can break up into droplets and thus unconnected and noninterconnected formations. Ring-shaped buns and cups have been obtained in this way. These formations often remain connected to the fibers, and beaded fibers are obtained. The main parameters that influence fiber production are spinning solution parameters (concentration, viscosity, surface tension, and electrical conductivity) and process parameters (applied field strength and feeding rate). Semiconductor quantum dots have been incorporated as integrated light sources into polymer fibers to produce subwavelength-diameter optical wave guides.<sup>65</sup>

Arinstein and Zussman<sup>66</sup> discussed possible macrostate modifications of nanofibers (polymeric) such as radial buckling. A theoretical model describing the kinetics of solvent evaporation was found to be in good agreement with experimental observations. Thus, the physical parameters of the system in question can be estimated, and conditions of fiber-shell instability that produce buckling of the tubular form can also be predicted.

It has been observed that although a poly(vinylidene fluoride) (PVDF)/dimethylformamide (DMF) solution yields fibers approximately 500 nm in diameter, the addition of tetramethylammonium chloride (an organosoluble salt) at a very low concentration (0.01%) produces uniform and ultrathin fibers ( $\approx 40$  nm).<sup>67</sup> It has also been observed that the fiber diameter can be tuned from 40 nm to hundreds of nanometers through a change in the viscosity of the solution, which depends on the polymer concentration and molecular weight and multiwalled carbon nanotube (MWCNT) loading content.

Gomes et al.<sup>68</sup> performed an extensive characterization of an electrospinning process to evaluate how the process parameters and precursor solution characteristics affect the fiber morphology. The work was conducted with precursor solutions with different concentrations of PAN diluted in a fixed amount of DMF. The characteristics of the electrospun fibers were analyzed as a function of the solution viscosity, applied voltage, and distance between the needle tip (positive electrode) and collector plate (grounded electrode). The diameter of the fibers increased with increasing viscosity and applied voltage. The number of deposited fibers also increased with the applied voltage. Moreover, the viscosity and applied voltage strongly affected the shape, length, and morphology of the fibers. The distance between the tip

and collector plate determined the way in which the fibers arrived on the collector plate.

By the use of vapor phase polymerization at a high relative humidity and under ambient conditions, poly(ethyl 2-cyanoacrylate) nanofibers with a high aspect ratio (>500) were obtained.<sup>69</sup> Different nanofiber morphologies of the polymer could be obtained with appropriate initiation and with variation of the reaction conditions. This technique could be used for the preparation of nanofibers from other polymers.

Collagen-blended poly(lactic-co-glycolic acid) (PLGA) nanofibers were obtained with electrospinning techniques.<sup>70</sup> Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) verified the nanoscale and smooth morphology of the blended nanofibers and revealed that 8% was the best concentration for preparing the polymer solution. Mechanical tests of their tensile properties showed that the ultimate strain value and tensile modulus of the blended nanofibers were comparable to those of human skin. A contact angle assessment showed decreased hydrophobicity in comparison with pure PLGA nanofibers and suggested an improved capacity for cell attachment.

The diameter of nanofibers obtained from a polyaniline (PANi)/PEO blend was below 30 nm. Fiber diameters near 5 nm were obtained by optimization of the process parameters. A scanning conductance microscopy study revealed that fibers with a diameter of 15 nm were electrically insulating: the small diameter may allow complete dedoping in air or may be smaller than phase-separation grains of PAN and PEO.<sup>71</sup> The electrical resistance of synthesized hollow PANi nanotubes doped with 2-acrylamid-2-methyl-1-propenesulfonic acid was measured as a function of temperature. The average length of the nanofibers was in the range of 2–5  $\mu\text{m}$ , and the average diameter was in the range of 200–400 nm. The polymer nanotubes did not exhibit metallic characteristics.<sup>72</sup>

A novel method for performing nanoscale mechanical characterization of highly deformable nanofibers was developed.<sup>73</sup> A microelectromechanical system test platform with an on-chip leaf-spring load cell, which was tuned with the aid of a focused ion beam, was built for fiber gripping and force measurements, and it was actuated with an external piezoelectric transducer. Submicrometer-scale tensile tests were performed under ambient conditions with an optical microscope. Engineering stresses and strains were obtained directly from images of the microelectromechanical system platform by extraction of the relatively rigid body displacements of the device components by digital image correlation. The accuracy in determining displacements by this optical method was shown to

be better than 50 nm. With the application of this method, the mechanical behavior of electrospun PAN nanofibers with diameters ranging from 300 to 600 nm was investigated.

Moel et al.<sup>74</sup> demonstrated, using one particular shape (nanorods or nanofibers), a facile concept for preparing nano-objects on self-organized polymeric supermolecules (supramolecular block copolymers). Cylindrical aggregates consisting of a polystyrene (PS) core and a thin corona of poly(4-vinylpyridine) (P4VP) chains were prepared from P4VP(PDP)-*block*-PS comb-coil supramolecules (where PDP is 3-*n*-pentadecylphenol). P4VP-*block*-PS diblock copolymers were stoichiometrically (with respect to the number of pyridine groups) hydrogen-bonded to PDP amphiphiles to yield P4VP(PDP)-*block*-PS comb-coil supramolecules. By the selection of appropriate relative block lengths for P4VP(PDP) and PS, a macrophase-separated cylindrical morphology of PS cylinders inside a P4VP matrix was obtained. The advantages of this concept versus the existing procedures were discussed.

It was noticed that PANi nanofiber films had a faster response when used as conductometric sensors of neutral gas molecules in comparison with conventional PANi thin films. However, high-surface-area nanofibril structures in PANi films did not appear to effectively enhance sensor sensitivity because of the relatively open structure.<sup>75</sup>

TEM images of electrospun PAN-derived carbon nanofibers showed a skin-core structure in a fiber cross section.<sup>76</sup> The skin region contained layered planes oriented predominantly parallel to the surface, but there were some crystals in the skin region misoriented with respect to the fiber long axis. Zussman et al.<sup>77</sup> reported the failure mode of electrospun polymer nanofibers. The nanofibers had diameters in the range of 80–400 nm and lengths greater than several centimeters. The nanofibers failed by a multiple-necking mechanism, which was sometimes followed by the development of a fibrillar structure. This phenomenon was attributed to strong stretching of solidified nanofibers by the tapered accumulating wheel (electrostatic lens) when its rotation became too high. Necking was not observed in the nanofibers collected on a ground plate.

By experimental investigation of the governing parameters in the electrospinning of polymer solutions, it was observed that nanofibers with submicrometer-scale diameters were formed when a droplet of a viscoelastic polymer was subjected to a high-voltage electrostatic field.<sup>78</sup> The influence of different process parameters on the electric current and volume and surface charge density in the polymer jet was also reported. The shear viscosity, surface tension, relaxation time, and electric conductivity and permittivity were measured as well. For this purpose,

different polymer solutions [PEO, poly(acrylic acid), PVA, PU, and polycaprolactone (PCL) in different solvents] were used in the electrospinning of polymer nanofibers. The parameters were the applied voltage, solution flow rate, polymer weight concentration, polymer molecular weight, nozzle-to-ground distance, and, in some solutions, ethanol concentration. The volume charge density followed power-law dependences for the applied voltage, flow rate, polymer weight concentration, polymer molecular weight, and ethanol concentration and depended exponentially on the nozzle-to-ground distance. In addition, the volume charge density decreased with an increasing flow rate for all the solutions tested. The dependence of the surface charge density on the applied voltage and flow rate was similar to that for the volume charge density. In contrast to this, the electric current in the jet increased with the flow rate for some solutions. For a solution of poly(acrylic acid) with a molecular weight of  $4.5 \times 10^5$ , it appeared as if the electric current was not affected at all by the volumetric flow rate. A decrease in the volume charge density at higher values of the volumetric flow rate was attributed to a low residence time of the solution near the electrode.

Aligned nanofibers were prepared from a conducting polymer (with a diameter of 100 nm or 1  $\mu\text{m}$ ) with a rotating disc collector to induce molecular orientation in the electrospun fibers.<sup>79</sup> The effect of electrospinning processes on the optical properties was discussed in terms of the fiber diameter and molecular orientation.

Theron et al.<sup>80</sup> also described the results of experimental investigations and modeling of multiple jets during the electrospinning of polymer solutions. The results demonstrated how the external electric fields and the mutual electric interaction of multiple charge jets influenced their path and evolution during electrospinning.

Nonwoven poly(ethylene terephthalate) (PET) nanofiber mats (NFMs) were prepared via electrospinning, and surfaces were modified to mimic the fibrous proteins in native extracellular matrix (ECM) for constructing a biocompatible surface for endothelial cells (ECs).<sup>81</sup> The electrospun PET NFMs were first treated in formaldehyde to yield hydroxyl groups on the surface, and this was followed by grafting polymerization of methacrylic acid initiated by Ce(IV). Finally, the poly(methacrylic acid)-grafted PET NFMs were grafted with gelatin with water-soluble carbodiimide as a coupling agent. A plain PET film was also surface-modified and characterized for a basic understanding of the surface modification process. The grafting of poly(methacrylic acid) and gelatin on the PET surface was confirmed with X-ray photoelectron spectroscopy and quantitatively analyzed with colorimetric methods. ECs were

cultured on the original and gelatin-modified PET NFMs, and the cell morphology, proliferation, and viability were studied. Three characteristic surface markers expressed by ECs were studied with immunofluorescent microscopy. The gelatin grafting method could obviously improve the spreading and proliferation of ECs on PET NFMs and, moreover, could preserve the EC phenotype.

Wu et al.<sup>82</sup> studied the evolution mechanism of surface rippling in PAN nanofibers under axial stretching. It was detected during single-fiber tension tests and in electrospun polyimide nanofibers after imidization.

The ability of nanostructures to elicit altered cell behaviors, including cell adhesion, proliferation, orientation, motility, integrin expression, cytoskeletal organization, and modulation of intracellular signaling, has raised interest in these materials for various biomedical applications.<sup>83</sup>

Nanomaterials based on silver nanoparticles have received significant attention. Apart from their unique wound-healing ability, silver nanoparticles also exhibit antibacterial properties, and this makes them potential candidates for use in infection-resistant biomaterials.

Hajra et al.<sup>84</sup> fabricated polyamide nanofibers and added them to glass media (fibers) and binders; they studied the effect of the nanofibers on drop coalescence during oil and water filtration. The coalescence performance of the media improved significantly when nanofibers were added to the glass-fiber media.

It was reported that the mechanical properties of collagen-chitosan complex nanofibers varied with the collagen content in the complex. The biodegradability of poly(L-lactic acid-co- $\eta$ -caprolactone) [P(LLA-CL)] nanofibers was faster than that of the membrane, and smooth muscle cells grew faster on collagen nanofibers than on P(LLA-CL) nanofibers.<sup>85</sup>

Katta et al.<sup>86</sup> demonstrated continuous electrospinning of aligned polymer nanofibers onto a wire-drum collector. As the fibers were produced, they were usually spun and collected in a random mat lacking structural orientation. It was claimed by Katta et al. that aligned nanofiber sheets could be easily made without disturbance of the aligned structure, and the method was robust.

Electrospun nanofibrous membranes possess several attractive properties, such as high porosity, pore sizes ranging from submicrometer to several micrometers, interconnected open pore structures, high permeability to gases, and large surface areas per unit of volume, that make them very attractive in separation technology. Polymer fibers are fabricated by a number of processes, including wet, dry, and melt spinning.

Schreder-Gibson et al.<sup>27</sup> reviewed electrospinning processes and their status (up to 2002) as

manufacturing methods. They also reported data and properties of electrospun membranes, including structural effects on the moisture transport, air convection, aerosol filtration, porosity, tensile strength, and enhanced chemical activity of these membranes (nanofibers), and they demonstrated the potential of these nanofiber layers in laminates for specialty textiles.

Moon et al.<sup>87</sup> fabricated flame-resistant electrospun polymer nanofibers from deoxybenzoin-based polymers. The electrospinning of 4,4-bishydroxydeoxybenzoin polyphosphonate was conducted with the variation of the polymer concentration, flow rate, and distance between the charged electrode and grounded target. The nanofibers were unimodal in distribution and uniaxially aligned. Electrospun nanofiber mats of 4,4-bishydroxydeoxybenzoin polyphosphonate with high flame-retarding properties had good mechanical strength and modulus.

Thus, the properties of hollow fibers depend on a number of factors, such as the methods of fabrication and processing, polymers, concentration of the polymeric solution, and temperature.

### PREPARATION OF NANOFIBERS

There are many methods for the preparation of synthetic polymeric nanofibers. Many nanofibers are either electrospun or made during polymerization. However, there are other methods for fabricating nanofibers. Electrospinning is a cost-effective technique that is exponentially evolving because of its simplicity and efficiency in producing fibers down to the nanorange. Details of the electrospinning method have been described earlier.

Electrospinning is a process by which polymer nanofibers (with a diameter less than 100 nm and lengths up to kilometers) can be produced with an electrostatically driven jet of a polymer solution (or polymer melt). The simple alignment of electrospun nanofibers constructs unique functional nanostructures such as nanotubes and nanowires. In an electrospinning process, an electric field is used to create a charged jet of a polymer solution. As this jet travels in air, the solvent evaporates behind a charged fiber, which can be electrically deflected or collected on a metal screen. Fibers with a variety of cross-sectional shapes and sizes can be produced from different polymers.<sup>17</sup> Recently, Andradý<sup>88</sup> wrote a book entitled *Science and Technology of Polymer Nanofibers* and showed how electrospinning is unique among nanofiber fabrication techniques in terms of process control, material combinations, and the potential for scale-up.

Yu et al.<sup>89</sup> developed a new and simple electrospinning method for producing aligned helical PCL polymer nanofibers. The morphology and loop

diameters of the helical structures were dependent on the PCL solution concentration. The three-dimensional helical structures were obtained at the high solution concentration of 10%. The converging electrical field generated by a tip collector played an important role in the alignment of the helical structure.

Yeo and Friend<sup>90</sup> demonstrated a powerful method for synthesizing carbon nanotube (CNT) polymer composite nanofibers by applying an electric stress to draw out a thin nanometer-dimension fiber from the tip of a sharp conical meniscus. Particular attention was paid to the theoretical modeling of these fiber systems and particularly to the electrohydrodynamic modeling of electrospinning polymer jets.

### Polymeric nanofibers prepared by electrospinning

Electrospinning is at least 75 years old,<sup>15</sup> but it is only in recent years that it has been rapidly developed because of the interesting properties of nonstructured materials.<sup>19,20</sup>

The polymer is usually dissolved in a suitable solvent and spun from solutions. Nanofibers in the diameter range of 10–2000 nm can be achieved by the choice of the appropriate polymer–solvent system.<sup>91</sup> Table I lists some polymer–solvent systems used in electrospinning.<sup>92</sup>

Electrospinning methodologies have been known for a number of years, but historically none of these methodologies have offered a meaningful industrial dimension with sufficient manufacturing capacity and stability. This changed in 2003 when Elmarco's exclusive partner, the Technical University of Liberec, patented a novel technology for the industrial production of nanofiber materials. This revolutionary technology is called Nanospider.

Revolutionary thoughts can be very simple. This is the case with Elmarco's Nanospider technology. On the basis of this discovery, it is possible to create a Taylor cone and a subsequent flow of matter not only from the tip of a capillary but also from a thin film of a polymer solution. Nanospider uses a rotating drum partially submerged in a polymer solution for the production of fibers rather than jets or nozzles. Elmarco's Nanospider technology allows nature to define the distance between Taylor cones, creating optimized conditions for the formation of high-quality nanofibers. The main advantages of this technology are as follows:

- Mechanical simplicity. Without nozzles, nanofiber production equipment is much simpler and easier to operate. No clogging or fouling of nozzles results in lower operating costs and dramatically improved nanofiber quality,
- A significant increase in production capacity.

**TABLE I**  
**Polymers and Solvents Used To Prepare Spinning Dopes**

Polymer	Solvent
Nylon-6 and nylon-66	Formic acid
PAN	Dimethyl formaldehyde
PET	Trifluoroacetic acid/ dimethyl chloride
PVA	Water
PS	DMF/toluene
Nylon-6-co-polyamide	Formic acid
Polybenzimidazole	DMAc
Polyaramide	Sulfuric acid
Polyimides	Phenol

A novel method has been developed for the electrospinning of multiple polymer jets into nanofibers. In this novel technique, a 20 wt % nylon-6 solution is electrified and pushed by air pressure through the walls of a porous polyethylene tube. Multiple jets are formed on the porous surface and electrospun into nanofibers. The length-weighted fiber diameters have a mean similar to those from a single jet and are broader in distribution.<sup>93</sup> Under some conditions, a sequence of secondary jet branches emanates from the primary jet during the electrospinning of a PCL solution.<sup>94</sup>

Shin et al.<sup>95</sup> described a simple procedure for fabricating single polymeric helical nanofibers and converting these helical nanofibers into linearly oriented nanofibers with a modified electric field in an electrospinning system. Helical structures were made from a solution of poly(2-acrylamido-2-methyl-1-propane-sulfonic acid) in water and ethanol through the bending instability of electrospinning. By the introduction of parallel subelectrodes that changed an ordinary electric field into a slitting electric field, it was elucidated that the tensional electrostatic forces caused by the modified electric field had an important effect on the transformation of the helical structures.

Xie and Hsieh<sup>96</sup> demonstrated a direct method for fabricating fibrous membranes containing proteins by electrospinning an aqueous solution containing a protein and a water-soluble organic polymer.

Herricks et al.<sup>97</sup> fabricated nanofibers consisting of enzyme-polymer composites by directly electrospinning a solution of a surfactant-stabilized enzyme and polymer in toluene. An additional treatment with glutaraldehyde greatly stabilized the enzyme activity of the fibers. These stable and catalytically active nanofiber-based mats were highly durable and could be ideal candidates for large-scale applications.

Different polymers have been used to make nanofibers with electrospinning techniques. Nanofibers made of the following polymers are widely used in different areas.

#### Cellulose acetate (CA)

A CA nonwoven mesh with fiber diameters ranging from 200 nm to 1  $\mu\text{m}$  was prepared by an electrospinning technique.<sup>42</sup> Heating the mesh under 208°C for 1 h resulted in a significant improvement in its structural integrity and mechanical strength. The CA nanofiber mesh was alkaline-treated to obtain a regenerated cellulose (RC) nanofiber mesh. The RC membrane showed higher water permeability than a conventional microporous membrane. The BSA-adsorbed membrane could be regenerated by rinsing with an elution buffer. The novel RC nanofiber membrane was observed to have potential as an alternative tool for affinity membrane applications.<sup>42</sup> Son et al.<sup>98</sup> fabricated ultrafine oxidized cellulose mats by the oxidation of ultrafine cellulose mats produced by electrospinning and subsequent deacetylation of CA for potential applications in nonwoven adhesion barriers.

#### Cellulose

Cellulose nonwoven mats of submicrometer-sized fibers (150–500 nm in diameter) were produced by the electrospinning of a cellulose solution.<sup>99</sup> A solvent system based on lithium chloride (LiCl) and *N,N*-dimethylacetamide (DMAc) was used, and the effects of (1) the temperature of the collector, (2) the type of collector (aluminum mesh and cellulose filter media), and (3) the postspinning treatment, such as coagulation with water, on the morphology of electrospun fibers were investigated. The SEM and X-ray diffraction studies of as-spun fibers at room temperature revealed that the morphology of cellulose fibers evolved with time because of moisture absorption and swelling caused by the residual salt and solvent. Although heating the collector greatly enhanced the stability of the fiber morphology, the removal of salt by coagulation and of DMAc by heating of the web was necessary for the fabrication of dry and stable cellulose fibers with limited moisture absorption and swelling. When cellulose filter media were used as collectors, dry and stable fibers were obtained without the coagulation step, and the resulting electrospun fibers exhibited good adhesion to the filter media.

Nonwoven mats of submicrometer-sized cellulose fibers (250–750 nm in diameter) were also fabricated through the electrospinning of cellulose from two different solvent systems: LiCl/DMAc and *N*-methylmorpholine oxide/water.<sup>100</sup> SEM images of electrospun fibers revealed that applying coagulation with water right after the collection of fibers was necessary to obtain submicrometer-scale, dry, and stable cellulose fibers for both solution systems. X-ray studies showed that cellulose fibers obtained

from LiCl/DMAc were mostly amorphous, whereas the degree of crystallinity of cellulose fibers from *N*-methylmorpholine oxide/water could be controlled by various process conditions, including the spinning temperature, flow rate, and distance between the nozzle and collector.

#### Polysulfone (PSf)

Jiang et al.<sup>101</sup> fabricated a superhydrophobic PSf film (weight-average molecular weight = 220,000) with a novel composite structure consisting of porous microspheres and nanofibers by a versatile electrohydrodynamic technique. The morphologies of the electrohydrodynamic products could be controlled by adjustments of the concentration of the starting solution. They reported that the hydrophobicity of the spin-coated films depended on the network structure. The contact angle of the film produced by the electrohydrodynamic method was  $160.4 \pm 1.2^\circ$ , whereas the contact angle of the film prepared by spin coating was  $95.1 \pm 0.3^\circ$ .

#### PVDF

PVDF nanofibers were electrospun into membranes and characterized to relate their structural properties to the membrane separation properties (liquid) and performance.<sup>47</sup> The characterization of these electrospun membranes revealed that they had properties similar to those of conventional microfiltration membranes. The electrospun membranes were successful in rejecting more than 90% of the microparticles from solution. These membranes also showed potential as prefilters before ultrafiltration or nanofiltration to minimize the possibility of fouling and contamination from microorganisms or microparticles and also to separate cells. To control the diameter, morphology, and structure of PVDF nanofibers, some parameters were investigated, such as the polymer concentration, nozzle-to-ground collector distance, feeding rate of the polymer solution, and applied voltage.<sup>102</sup> It was found that an increase in the polymer concentration caused an increase in the polymer viscosity and the fiber diameter. At a low polymer concentration (5 wt %), polymer nanoparticles were formed. An increase in the applied voltage resulted in an increase in the fiber diameter. Variations in the nozzle-to-ground collector distance did not result in significant changes in the fiber diameter. An increase in the feeding rate of the polymer solution reduced the fiber diameter. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction measurements showed that the melting point and total crystallinity were reduced. Fourier transform infrared spectroscopy measurements revealed that an electrostatic discharge process

induced the formation of an oriented  $\beta$  phase. However, Nasir et al.<sup>103</sup> did not study the contact angles.

Ren and Dzenis<sup>104</sup> fabricated ultrafine, submicrometer-diameter continuous PVDF nanofibers by an electrospinning method. Fourier transform infrared analysis indicated that the initial  $\alpha$  phase of the raw material was converted to  $\beta$ -phase PVDF during electrospinning.

#### PU

An isotropic fiber mat of PU nanofibers with diameters ranging from 100 to 500 nm was fabricated from a solution (or melt).<sup>14</sup> The electrospun PU produced a stress-strain response characteristically different from that of the material from which the mat was spun. Electron microscopy and vibrational spectroscopy were used to illustrate the morphological changes upon stretching and molecular orientation in the electrospun fibers, respectively. The apparent molecular orientation in the electrospun fibers also led to a pronounced reduction in the elongation to the failure of the electrospun mat with respect to the bulk.

Verreck et al.<sup>105</sup> used an electrostatic spinning technique for the preparation of drug-laden nonbiodegradable nanofibers for potential use in topical drug administration and wound healing. The specific aim of these studies was to assess whether these systems might be of interest as delivery systems for poorly water-soluble drugs. Itraconazole and ketanserin were selected as model compounds, whereas segmented PU was selected as the nonbiodegradable polymer. The collected nonwoven fabrics were shown to release the drugs at various rates and with various profiles based on the nanofiber morphology and drug content. The release phases were temporally correlated with (1) drug diffusion through the polymer and (2) drug diffusion through formed aqueous pores. Because of the unique properties of electrospun PU membranes, they have potential applications for wound dressing.<sup>36</sup>

#### Silk fibroin (SF)

Min et al.<sup>40</sup> used an electrospinning method to fabricate SF nanofiber nonwovens for cell cultures of normal human keratinocytes and fibroblasts. The electrospinning of regenerated SF was performed with formic acid as a spinning solvent. As-spun SF nanofibers exhibited a circular cross section with a smooth surface. According to image analysis, they had an average diameter of 80 nm with a range of 30–120 nm. It was demonstrated by Min et al. that SF nanofibers may be good candidates for biomedical applications, such as wound dressing and scaffolds for tissue engineering.



## PVA

PVA fibers with various diameters (50–250 nm) were obtained by changes in the solution concentration, voltage, and tip-to-collector distance via electrospinning.<sup>106</sup> The major factor was the concentration of the PVA solution, which evidently affected the fiber diameter. With an increase in the concentration, the fiber diameter increased, and the amount of beads was reduced even to 0%. The fibers were found to be efficiently crosslinked by glyoxal during the curing process. After electrospinning, the morphology of PVA was greatly changed. SEM and DSC techniques were employed to characterize the morphology and crosslinking of PVA fibers. It was found that the primary factor affecting the crosslinking density was the content of the chemical crosslinking agent.

Son et al.<sup>107</sup> studied the effect of pH on the electrospinning of PVA and reported that electrospun PVA fibers became straighter and finer with increasing pH under basic conditions, whereas the electrospinning of PVA solutions was not continuous, and PVA fibers with bead-on-string structures were obtained because of the protonation of PVA under acidic conditions.

PVA/ferritin/CNT composite nanofibers with smooth surfaces and a good dispersion of ferritin and CNTs are applicable to artificial muscles requiring enhanced physical properties.<sup>108</sup>

## Collagen

Matthews et al.<sup>37</sup> described how electrospinning could be adapted to produce tissue-engineering scaffolds composed of collagen nanofibers. Optimizing conditions for calfskin type I collagen produced a matrix composed of 100-nm fibers that exhibited the 67-nm banding pattern characteristic of native collagen. The structural properties of electrospun collagen varied with the origin of the tissue (type I from skin vs type II from placenta), the isotype (type I vs type III), and the concentration of the collagen solution used to spin the fibers. They suggested that electrospun collagen may represent a nearly ideal tissue engineering scaffold because of its structural, material, and biological properties.

## Block copolymers

Aligned nanofibrous scaffolds from a solution of the block copolymer P(LLA-CL) (75:25 copolymer in acetone) were fabricated by an electrospinning process.<sup>39</sup> The diameter of the generated fibers was around 500 nm with an aligned topography. The results suggested that this synthetic aligned matrix incorporates the advantages of synthetic biodegradable polymers, its nanometer-scale dimensions mimicking the natural ECM and its defined architecture

replicating the *in vivo* like structure, and it may represent an ideal tissue engineering scaffold, especially for blood vessel engineering.

Block copolymer fibers from a solution of the copolymer poly(styrene-*block*-dimethylsiloxane) in tetrahydrofuran or DMF via electrospinning were obtained.<sup>109</sup> Contact angle measurements indicated that the nonwoven fibrous mats were superhydrophobic with a contact angle of 163° and contact angle hysteresis of 15°. The superhydrophobicity was attributed to the combined effects of surface enrichment in siloxane, as revealed by X-ray photoelectron spectroscopy, and surface roughness of the electrospun mat itself. Calorimetric studies confirmed the strong segregation between PS and poly(dimethylsiloxane) blocks.

Jia et al.<sup>110</sup> investigated the electrospinning behavior of a block copolymer of trimethylene carbonate and  $\epsilon$ -caprolactone dissolved in DMF and methylene chloride. SEM was used to study the effects of the blended solvent volume ratio, the concentration, the voltage, and the tip-to-collector distance on the morphology of the electrospun fibers. The results indicated that the diameter of the electrospun fibers decreased with a decreasing molar ratio of methylene chloride to DMF, but beads formed gradually. The results of DSC and X-ray diffraction showed that the crystallinity and melting point of the electrospun fibers decreased with the trimethylene carbonate content increasing in the polymer. In comparison with the corresponding films, the crystallinity and melting point of the electrospun fibers obviously increased.

## PCL

Microporous, nonwoven PCL scaffolds were fabricated by electrospinning. The data obtained by the culturing of mesenchymal stem cells (derived from the bone marrow of neonatal rats) suggested that electrospun PCL is a potential candidate for bone tissue engineering.<sup>38</sup> He et al.<sup>111</sup> fabricated collagen-coated random and aligned P(LLA-CL) nanofiber meshes by using an electrospinning technique to maintain functions of ECs.<sup>8</sup> A mixture of PCL and PCL-PEG block copolymers was electrospun to prepare amine-terminated block copolymers. The number of surface-exposed amine groups increased as the blend ratio of the block copolymer increased. Fluorescent proteins were immobilized on the surfaces of nanofibers by the conjugation of activated carboxylic groups of the protein to the surface-exposed amine groups of nanofibers in an aqueous environment.<sup>112</sup>

## PEO

Dotti et al.<sup>113</sup> produced nanofibers from polymer solutions of PEO, PVA, and polyamide-6 by using

an electrospinning technique. Fibers were directly deposited in the form of random fiber webs with a high area-to-volume ratio and a small pore size onto ordinary nonwoven filters of PET microfibers. The electrospun fibers had diameters ranging from 70 to 500 nm and were interconnected with one another to form thin webs that had very small pore sizes. After the electrospinning treatment, the air permeability of the filter media decreased 6–17 times, and they showed a significant change in flow resistance that could be controlled by the thickness of the nanofiber layer and the pore size. Dotti et al. suggested that high-efficiency nano/microfiber composite filters could be used in a wide range of applications ranging from air cleaning for automobiles to environmental conditioning or liquid filtration. Single-walled CNTs embedded in a PEO matrix, forming composite nanofibers, have been reported,<sup>114</sup> as well as MWCNTs.<sup>116</sup> The initial dispersion of MWCNTs in water was achieved with amphiphiles [either small molecules such as sodium dodecyl sulfate (SDS) or a high-molecular-weight, highly branched polymer such as gum arabic]. A high degree of alignment of PEO crystals was found in electrospun nanofibers containing only PEO as well as PEO/SDS. The latter also exhibited a high degree of alignment of the SDS layers. The axial orientation of PEO and SDS was significantly reduced in MWCNT-containing nanofibers. TEM images revealed that the MWCNTs embedded in the nanofibers as individual elements, mostly aligned along the fiber axis. Nevertheless, there were also many cases in which the nanotubes were twisted, bent, or had other irregularities. A theoretical model was presented by Dror et al.<sup>115</sup> for the behavior of rodlike particles representing CNTs in electrospinning.

#### Other polymers

There are hundreds of polymers that have been used to make nanofibers. The following are a few polymers that have been mainly used recently for making nanofibers.

Ruotsalainen et al.<sup>116</sup> demonstrated hierarchical self-assembly and mesoporosity in electrospun fibers using selected PS-*b*-P4VP diblock copolymers with hydrogen-bonded PDP, which rendered distorted spherical P4VP(PDP)<sub>10</sub> domains within the PS matrix and an internal lamellar order within the P4VP(PDP)<sub>10</sub> domains and allowed distorted spherical pores by the removal of PDP. In another article, Ruotsalainen et al.<sup>117</sup> presented the tailoring of the hierarchical structure within electrospun fibers due to supramolecular comb-coil block copolymers (PS-*block*-P4VP plasticized by hydrogen-bonded PDP).

Qi et al.<sup>118</sup> described the novel preparation of three kinds of nanofibers [poly(styrene-*co*-methacrylic acid), poly(styrene-*co*-*p*-styrene sulfonate), and PS] and investigated solid-phase extraction sorbents to extract six compounds (nitrobenzene, 2-naphthol, benzene, *n*-butyl-*p*-hydroxybenzoate, naphthalene, and *p*-dichlorobenzene) from environmental water by high-performance liquid chromatography. Parameters affecting the extraction efficiency were investigated in detail to explore the extraction mechanism of the nanofibers. It was suggested by Qi et al. that this new method could be a viable and environmentally friendly technique for analyzing pollutants in environmental samples.

Wan and Xu<sup>119</sup> directly electrospun poly[acrylonitrile-*co*-(*N*-vinyl-2-pyrrolidone)] onto a dense membrane surface and studied the behaviors of blood platelets on the nanostructure surface. The nanostructure surface promoted the activation, adhesion, and orientation of platelets. The promotion of the activation and adhesion of platelets was due to the presence of nanofibers, which induced changes in the surface topography and charge.

Baumgarten<sup>120</sup> fabricated acrylic resin fibers less than 1 μm in diameter by using an electrostatic spinning technique. Electric field maps and other theoretical considerations showed that electric conductivity played an important role in the spinning mechanism. The effects on the fiber diameter and jet length of the solution viscosity, surrounding gas, flow rate, voltage, and geometry were determined.

Fischer and Hampp<sup>121</sup> demonstrated beaded nanofibers containing a purple membrane via the electrospinning of polymer solutions (the purple membrane was an isolated material known as *Halobacterium salinarum* from bacteriorhodopsin, which is a biological photochromic pigment).

McClure et al.<sup>122</sup> fabricated nanofibers from a blend of crosslinking polydioxanone and soluble elastin via electrospinning and characterized them. The material properties of the electrospun polydioxanone/soluble elastin blend nanofibers changed over a period of 1 day.

Bishop et al.<sup>123</sup> prepared polymer-based composites by electrospinning hydroxyapatite with a biocompatible polymer for the development of a structurally stable casing for prosthetic devices.

Sun et al.<sup>124</sup> described the processing of core-shell nanofibers/mesofibers by the co-electrospinning of two materials.

González and Pinto<sup>125</sup> reported the fabrication of an electrospun region-regular poly(3-hexylthiophene) fiber field effect transistor and proposed an easy one-step process to fabricate one-dimensional polymer field effect transistors.

Tan et al.<sup>126</sup> synthesized polymer nanofibers containing magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles from commercially available poly(hydroxyethyl methacrylate) and PLLA for drug delivery by an electrospinning technique. Nanofibers with diameters ranging from 50 to 300 nm were obtained.

Drew et al.<sup>34</sup> fabricated photovoltaic cells from PAN fibers fused with an azo dye (Congo red). The cell performance of the electrospun cells compared favorably to that of cells made from spin-coated thin films of PAN and Congo red.

Kameoka et al.<sup>127</sup> used the scanning electrospinning method to extrude polymeric nanofibers from a blended polymeric solution and deposited oriented nanofibers onto patterned surfaces to form suspended structures. The deposited polymeric nanofibers were converted into silicon oxide by calcination without changes in their morphologies. With this technique, a suspended nanofiber with a diameter of 120 nm was fabricated with a resonant frequency of 10.8 MHz and a mechanical quality factor of 1600.

Prilutsky et al.<sup>128</sup> fabricated hybrid nanofibers with different concentrations of MWCNTs in PAN by using an electrospinning technique and subsequently carbonization. The morphology of the fabricated carbon nanofibers at different stages of the carbonization process was characterized with TEM and RS. The polycrystalline nature of the carbon nanofibers was shown, with the content of ordered regions with enhanced orientation increasing as the content of MWCNTs increased. The results indicated that embedded MWCNTs in the PAN nanofibers promoted the growth of carbon crystals during PAN carbonization.

Gorantia et al.<sup>129</sup> presented a wet-spinning technique capable of producing continuous polymer nanofibers by injecting a solvated polymer into a highly viscous moving medium through a microaperture. The extruded fiber moved in a predictable spiral path and was collected around a spinning mandrel, which also served to pull the extruded fiber away from the aperture. Semicontinuous solid nanofibers of poly(vinyl butyral) were produced with diameters ranging from 10  $\mu\text{m}$  to 400 nm. Electron microscopy indicated submicrometer fibers exhibiting a ribbon-like morphology. The effects of different parameters on the fiber size and shape were discussed.

Tomezak et al.<sup>130</sup> produced light-emitting polymer nanofibers by electrospinning polymer solutions containing either fluorescent organic dye molecules or luminescent semiconductor nanoparticles (quantum dots). The average fluorescence lifetime of single molecules embedded in poly(methyl methacrylate) (PMMA) fibers appeared independent of the fiber diameter. On the other hand, the single-molecule approach revealed a significant broadening of the fluorescence lifetime distribution for fibers with diameters below the wavelength of light.

### Other techniques for making nanofibers with special structures

Several novel approaches for electrospinning techniques have been introduced.

Yarin and Zussman<sup>131</sup> developed a unique electrostatic field-assisted assembly technique with the aim of positioning and aligning individual conducting and light-emitting nanofibers in arrays, crossbars, and ropes.

Suryavanshi et al.<sup>132</sup> demonstrated direct-write manufacturing of nanofibers that exploits the concept of a nanoscale liquid meniscus to confine and sustain the fast and continuous growth of nanofibers of unlimited length in an ambient environment with low humidity.

Recently, a specialized tool was developed for the reproducible and controlled fabrication of micro/nanopolymer (PMMA) fibers using micro/nanopipettes. Nain et al.<sup>133</sup> claimed that their method would facilitate the controlled deposition and shaping of polymer materials at the subscale in precisely determined locations.

An et al.<sup>134</sup> produced a polymer nanofiber ion exchanger via electrospinning from solutions of dissolved PS followed by sulfonation processes. A PS nanofiber cation exchanger was developed for a high ion-exchange capacity and a rapid ion-exchange velocity. The ion-exchange capacity and water uptake of the polymer nanofiber ion exchanger depended on the sulfonation time.

Direct-write, based on near-field electrospinning, is a versatile top-down fabrication technique that can be used to fabricate solid nanofibers with diameters ranging from 50 to 800 nm, such as organic materials or biomaterials, or thin films with line widths ranging from 1 to 20  $\mu\text{m}$  from viscous solutions.<sup>135</sup> There are other techniques such as dip-pen nanolithography,<sup>135</sup> inkjet printing,<sup>135</sup> matrix-assisted pulsed evaporation direct-write,<sup>135</sup> and laser chemical vapor deposition.<sup>135</sup> Direct-write technology based on near-field electrospinning is cheaper in comparison with other methods and can fabricate micro/nanostructures directly and fast on pattern substrates; this is difficult for other direct-write technologies.

Carbon nanofiber assemblies in the form of nonaligned films, arrays of vertically aligned nanofibers, aligned nanofiber mats, and composite coatings were fabricated by laser-assisted catalytic vapor deposition.<sup>136</sup> A visible argon-ion laser was used to thermally decompose pure ethylene over alumina-supported nickel catalysts. Straight, vermicular, beaded, branched, and coiled nanofibers were formed. Ways to control nanofiber characteristics such as shape and internal structure were discussed.

Kameoka et al.<sup>137</sup> described a technique for the formation of oriented single nanofibers, using an arrow-shaped scanning tip. The tip was dipped in a polymeric solution to gather a droplet as a deposition source. A sufficiently high potential, applied between the droplet and a counter electrode, initiated the electrospray deposition of nanofibers onto the counter electrode. By using this technique, Kameoka et al. demonstrated the control of nanofiber fabrication and the nanofiber cross junction for the application of nanofiber-based nanodevices.

Lim and Tan<sup>57</sup> were the first to fabricate a PLLA nanofibrous scaffold from a polymer solution using the phase-separation technique, and they studied the surface structure and elastic properties.

Correa et al.<sup>138</sup> prepared SiC nanofibers by using the polymer blend and melt-spinning technique.

Theron et al.<sup>139</sup> described an approach for aligning nanofibers on a conductive substrate using electrostatic forces. The alignment process was combined with an electrospinning process that yielded polymer-based nanofibers.

Reneker et al.<sup>140</sup> noticed that electrospinning a solution of PCL in acetone caused a dramatic appearance of fluffy, columnar networks of fibers that moved slowly in large loops and long curves.

Rein et al.<sup>141</sup> used an electrospinning method to fabricate ultrafine nanofibers of ultrahigh-molecular-weight polyethylene with a mixture of solvents of different dielectric constants and conductivities. The possibility of producing highly oriented nanofibers from ultrahigh-molecular-weight polymers suggested new ways of fabricating ultrastrong, porous, and single-component nanocomposite fibers with improved properties.

Bellan et al.<sup>142</sup> electrospun blended PEO and DNA. The embedded DNA molecules were imaged with fluorescence microscopy and found to be stretched to lengths approaching the full dyed contour length. Thus, direct observation of the degree to which these molecules had been stretched could give information on the fluid dynamic behavior of the jet and the mechanical properties of the nanofiber.

Zussman et al.<sup>143</sup> reported a technique for the hierarchical assembly of nanofibers (prepared by electrospinning) into crossbar nanostructures. An electrospinning process was used to create polymer-based nanofibers with diameters ranging from 10 to 180 nm and lengths of up to several centimeters. By control of the electrostatic field and the polymer rheology, the nanofibers were assembled into parallel periodic arrays, and they also proposed a theoretical model for the process.

Yarin and Zussman<sup>144</sup> devised a technique for the formation of upward needleless electrospinning of multiple nanofibers. A two-layer system, with the

lower layer being a ferromagnetic suspension and the upper layer being a polymer solution, was subjected to a normal magnetic field provided by a permanent magnet or coil. As a result, steady and vertical spikes of the magnetic suspension perturbed the interlayer interface as well as the free surface of the uppermost polymer layer. When a normal electric field was applied in addition to the system, the perturbations of the free surface became sites of directly upward jetting. Multiple electrified jets underwent strong stretching by the electric field and bending instability, the solvent evaporated, and solidified nanofibers were deposited onto the upper counter electrode, as in an ordinary electrospinning process. However, the production rate was higher.

Bashouti et al.<sup>145</sup> described a promising route for the unidirectional alignment of freestanding cadmium sulfide one-dimensional quantum wires and the formation of semiconductor-polymer core-shell fibers by the electrospinning of quantum wire colloids with a polymer solution.

Silver polymer nanofibers have been applied to various research fields such as biomaterials, medical devices, and electronics.<sup>146,147</sup> In the preparation of silver-polymer nanofibers, silver nanoparticles can be deposited onto the electrospun polymer nanofibers by sputter coating, or polymeric solutions containing silver ions can be electrospun.<sup>148</sup> Jin et al.<sup>148</sup> used two methods to prepare polyvinylpyrrolidone (PVP) nanofibers containing silver nanoparticles. First, they electrospun PVP nanofibers containing silver nanoparticles directly from PVP solutions containing silver nanoparticles. DMF was used as a solvent for PVP and as a reducing agent for the Ag<sup>+</sup> ions in the PVP solutions. In the second method, PVA aqueous solutions were electrospun with 5 wt % PVP containing silver nanoparticles. The silver nanoparticles were evenly distributed in the PVA nanofibers. PVP containing silver nanoparticles could be used to introduce silver nanoparticles into other polymer nanofibers miscible with PVP.

Son and coworkers<sup>149,150</sup> reported for the first time that polymer nanofibers containing silver nanoparticles on their surface could be produced by UV irradiation of polymer nanofibers electrospun with small amounts of silver nitrate (AgNO<sub>3</sub>). The silver nanoparticles with an average size of 22 nm exhibited strong antimicrobial activity.

Hong et al.<sup>151</sup> prepared antimicrobial PVA nanofibers containing silver nanoparticles by the electrospinning of PVA/AgNO<sub>3</sub> aqueous solutions followed by a short heat treatment. After the heat treatment at 155°C for 3 min, the PVA/AgNO<sub>3</sub> nanofibers became insoluble in water, whereas Ag<sup>+</sup> ions therein were reduced to produce a large number of silver nanoparticles situated preferentially on their surface. The average diameter of the silver

nanoparticles after the heat treatment was 5.9 nm, and this value increased slightly to 6.3 nm after UV irradiation.

Jin et al.<sup>152</sup> studied two practical methods for the facile and controlled preparation of PVA nanofibers containing silver nanoparticles for antimicrobial applications. In the first method, PVA nanofibers containing silver nanoparticles were successfully electrospun from PVA/AgNO<sub>3</sub> aqueous solutions after they were first refluxed. Refluxing was required to generate silver nanoparticles in the PVA/AgNO<sub>3</sub> aqueous solutions. Silver nanoparticles were also spontaneously generated during the electrospinning process. In the second method, silver nanoparticles were generated by the annealing of PVA nanofibers electrospun from PVA/AgNO<sub>3</sub> aqueous solutions. Residual Ag<sup>+</sup> ions and the silver nanoparticles generated during the electrospinning process were diffused and aggregated into larger silver nanoparticles in the PVA nanofibers during the annealing process. All the silver nanoparticles were spherical and evenly distributed in the PVA nanofibers prepared by both methods.

Wei et al.<sup>146</sup> prepared electrospun polyamide nanofibers coated with functional silver nanofilms. dc was used to sputter coatings to deposit functional silver nanofilms onto the surfaces.

He and coworkers<sup>153,154</sup> designed an NFM that facilitated viability, attachment, and phenotypic maintenance of human coronary artery ECs. A collagen-coated P(LLA-CL) (70:30) NFM with a porosity of 64–67% and a fiber diameter of 470 ± 130 nm was fabricated by electrospinning followed by plasma treatment and collagen coating. The P(LLA-CL) NFM showed potential as a material for tissue-engineered vascular grafts and blood-vessel-engineered scaffolds.

Berry et al.<sup>155</sup> used a novel method for fabricating interconnected three-dimensional structures with micrometer and submicrometer features. They fabricated PMMA microscale and submicroscale fiber suspended bridges at room temperature by drawing from pools of the solvated polymer with a nanostylus that was precisely positioned by an ultrahigh-precision micromilling machine. Fibers were found to increase in diameter from 450 nm to 50 μm, and this roughly corresponded to the increase in the concentration of PMMA. It was also observed that the fiber diameter increased significantly as the solution concentration and polymer molecular weight increased.

Mincheva and coworkers<sup>156,157</sup> obtained polymer-stabilized magnetic nanoparticles obtained with two biocompatible polyelectrolytes: CECh and poly(α-acrylamido-2-methylpropanesulfonic acid). The size of the particles (mean diameter of 10 or 30 nm, respectively) and the stability of the dispersions

could be effectively controlled, depending on the nature of the polyelectrolyte. Depending on the nature of the polyelectrolyte, the magnetic nanoparticles existed in different magnetic states: a supermagnetic state or an intermediate state between supermagnetic and ferromagnetic states. The fabrication of nanocomposite magnetic fibers with a mean diameter in the range of 100–500 nm was achieved by the electrospinning of a CECh/ferrofluid/ionogenic polymer system.

### Nanofibers by interfacial polymerization

There are other methods beside electrospinning for the fabrication of nanofibers, such as chemical polymerization and copolymerization. However, the length of nanofibers obtained by these methods is less than 1 μm. Block copolymerization has been investigated by several authors.<sup>158–162</sup>

Lee and Liao<sup>158</sup> fabricated polymeric nanofibers by living free-radical (2,2,6,6-tetramethyl-1-piperidinyloxy) polymerization. Living free-radical polymerization was employed to synthesize the PS copolymer. It involved the copolymerization of styrene with 2-hydroxyethyl methacrylate. The copolymers were reacted with cinnamoyl chloride and then irradiated with UV light. The polymeric nanofibers were formed by copolymerization.

Mallick et al.<sup>163</sup> demonstrated a facile route for the synthesis of poly(3,5-dimethyl aniline) nanofibers by the polymerization of 3,5-dimethyl aniline with palladium acetate as the oxidant. The reduction of the palladium ion was accompanied by the oxidative polymerization of 3,5-dimethyl aniline, leading to a metal-polymer composite material.

Huang<sup>164</sup> studied the morphological evolution of PANi during its chemical polymerization and observed that it preferentially formed as nanofibers in aqueous solutions. A high-quality nanofibrous product was obtained by two facile approaches, that is, interfacial polymerization and a rapidly mixed reaction. Huang demonstrated the advantages of nanostructures plus conducting polymers. Conducting polymers have an important role to play in the emerging field of nanoscience. Dong et al.<sup>165</sup> fabricated nanopolyethylene fibers and floccules via ethylene extrusion polymerization *in situ* with an MCM-41-supported metallocene catalytic system under atmospheric pressure. The nanofibers and floccules were the major morphological units in the resultant samples, and the nanofibers aggregated uniformly into aggregates and bundles. The diameter of a single fiber was 80–100 nm. The DSC results showed that the resultant samples had higher melting points in comparison with polyethylene prepared with homogeneous metallocene.

Shang et al.<sup>166</sup> demonstrated a method to obtain parallel polymer nanofibers and hierarchically organized the parallel nanofibers into a crossed system.

Zussman et al.<sup>167</sup> produced hollow CNTs by co-electrospinning two-polymer (PAN/PMMA) solutions. The process was carried out in two stages. In the first stage, the nonsolvent effect was applied to one of the polymers to facilitate the creation of a solid interface between the nanofiber core and shell. In the second stage, the nanofiber was subjected to heat treatment to degrade the core polymer and carbonize the polymer shell.

Organic-dye-embedded polymer nanocomposites have attracted much attention because of their biocompatibility, facile preparation, and diverse functionality.<sup>168–173</sup> Lee et al.<sup>168</sup> for the first time reported the fabrication of PMMA nanotubes and PMMA nanofibers embedded with an organic dye by vapor deposition polymerization and a sequential dye-dipping method.

Srivastava et al.<sup>174</sup> described a method to fabricate hollow and core–sheath nanofibers by electrospinning. Hollow PVP–titania composites and core–sheath polypyrrole–PVP nanofibers of the order of 100 and 250 nm, respectively, were fabricated with elastomeric microfluidic devices.

Kong and Jang<sup>175</sup> fabricated silver-nanoparticle-embedded PVA–PMMA nanofibers via one-step radical-mediated dispersion polymerization using 2,2'-azobis(isobutyronitrile) to reduce the silver ions. In this methodology, PVA acted both as a gelator to form the nanofibers and as a stabilizer to protect the silver clusters from sintering.

Aussawasathein et al.<sup>176</sup> prepared lithium perchlorate doped PEO electrospun nanofibers for humidity sensing and camphor sulfonic acid doped PANI/PS electrospun fibers for sensing hydrogen peroxide and glucose. The diameters of these as-prepared polymeric nanofibers were in the range of 400–1000 nm.

Drew et al.<sup>177</sup> reported a novel method for the fabrication of tin oxide and titanium oxide coated PAN fibers. In this method, the nanofiber membranes were subsequently immersed in an aqueous solution of metal halide salts and halogen scavengers at room temperature to apply the metal oxide coating.

Duvail et al.<sup>178</sup> fabricated nanofibers of poly(3,4-ethylenedioxythiophene) and polypyrrole using the template method and studied the electronic and mechanical properties of those nanofibers. Strong variations of the estimated conductivity, the resistivity ratio (1.5 K/300 K), and the elastic modulus were observed when the diameter was reduced from 200 to 20 nm. These variations were discussed in terms of changes in the conformation of the polymer chains and/or doping level due to confinement.

Dhanote et al.<sup>179</sup> prepared nylon fibers (average diameter = 80–200 nm) embedded with ferrite nanoparticles. The nickel–ferrite particles with a diameter range of 20–30 nm were used to prepare composite electrospun nanofibers. A DSC analysis of the neat nylon polymer fibers and ferrite-filled nanofibers showed an increase in the glass-transition temperature from 55 to 72°C. The melting temperature showed a decrease from 226 to 201°C. The TEM images revealed the presence and some alignment of particles in the polymer. The electron diffraction pattern of ferrite nanoparticles confirmed its crystalline nature.

Kaner et al.<sup>180</sup> patented a synthetic method. The method consists of the following steps.

1. Forming a catalysis aqueous solution comprising an acid and an oxidizer.
2. Forming an organic monomer solution comprising a monomer and an organic solvent.
3. Placing the catalysis aqueous solution in the monomer organic solution to form an interface between the catalysis aqueous solution and the monomer organic solution (this leads to the generation of organic polymer nanofibers).

Polymeric nanofibers such as PANi nanofibers with uniform diameters less than 500 nm can be made in bulk quantities through a facile aqueous and organic interfacial polymerization method under ambient conditions. Thin-film nanofiber sensors can be made of the PANi nanofibers with superior performance with respect to both sensitivity and time response to a variety of gas vapors, including acids, bases, redox active vapors, alcohols, and organic chemicals.

Chuangchote et al.<sup>181</sup> fabricated ultrafine poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]/poly(vinyl pyrrolidone) (PVP) composite fibers for conductive nanofibers, with average diameters ranging from 43 nm to 1.7  $\mu\text{m}$ , by electrospinning blended solutions in a mixed solvent of chlorobenzene and methanol. The average diameter of the as-spun fibers was found to decrease to the nanometer scale with the reduction of the PVP concentration and/or the addition of a volatile organic salt, pyridium formate.

Weiller et al.<sup>182</sup> fabricated PANi nanofibers with uniform diameters less than 500 nm in bulk for conducting sensors by a facile aqueous organic interfacial polymerization method under ambient conditions. The nanofibers had lengths varying from 500 nm to 10  $\mu\text{m}$  and formed interconnected networks in a thin film.

Meziani et al.<sup>183</sup> used a supercritical fluid technique; that is, the rapid expansion of a supercritical solution into a liquid solvent (Resolv) was used to

process polymers into nanofibers (<100 nm in diameter). The polymer concentration in the pre-expansion supercritical solution was found to play a critical role in determining the dominant product morphology between nanoparticles and nanofibers. In the case of carbon dioxide soluble poly(heptadecafluorodecyl acrylate), for example, the rapid expansion of polymer solutions in critical carbon dioxide with low and high poly(heptadecafluorodecyl acrylate) concentrations into ambient aqueous sodium chloride solutions exclusively produced nanoparticles and nanofibers, respectively.

Li et al.<sup>184</sup> fabricated polyethylene and PS nanofibers by combining the template method with extrusion technology. The molten polymer was forced through the pores of an anodic aluminum membrane and cooled to complete the nanofiber formation process. The microstructures of the nanofibers were determined with SEM, TEM, X-ray diffraction, and DSC. The results suggested that the polyethylene nanofibers consisted of extended-chain crystals and a transition from an orthorhombic phase to a hexagonal phase.

Trofin and LeDuc<sup>185</sup> developed a simple and efficient method to produce polydimethylsiloxane nanofibers with controlled aspect ratios that could be used in biological studies. A template synthesis technique was used to create the fibers by molding a polymer solution into an alumina membrane. The pressure and the template surface chemical characteristics were controlled to enable the easy creation of a geometric configuration with up to a 30-fold range of aspect ratios through the use of the same porous alumina template.

Cai et al.<sup>186</sup> synthesized nanostructured conducting polymers by a dilute chemical polymerization method to obtain nanofibers of PANi.

## APPLICATIONS

Dubrow et al.<sup>187</sup> patented applications of nanofiber surfaces in medical devices and methods involving nanofibers. Ma et al.<sup>70</sup> suggested that collagen-blended PLGA nanofibers have great potential to facilitate wound healing.

Conducting polymer nanofibers have tremendous potential in electronic, optoelectronic, and biological applications as sensors, drug delivery devices, and electronic textiles, among other applications.

Gibson et al.'s work<sup>21</sup> on experimental measurements and theoretical calculations showed electrospun fiber mats to be extremely efficient at trapping aerosol particles. The high filtration efficiency is a direct result of the submicrometer-size fibers generated by the electrospinning process. Electrospun fiber coatings can produce an exceptionally lightweight multifunctional membrane for protective

clothing applications, which exhibits high breathability, elasticity, and filtration efficiency. Nanofibers, because of their high surface area and porosity, find applications as filter media and adsorption layers in protective clothing.<sup>188</sup> Ren and Dzenis<sup>104</sup> demonstrated that novel continuous PVDF fibers can be used in nanostructured active textiles and composites and can lead to unusual new designs for actuators and sensors. The following are possible commercial uses of nanofibers described by Ren and Dzenis:

1. Medicine: artificial organ components, tissue engineering, implant materials, drug delivery, wound dressings, and medical textile materials.
2. Protective materials: sound absorption materials, protective clothing for use against chemical and biological warfare agents, and sensor applications for detecting chemical agents.
3. Energy: batteries, photovoltaic cells, polymer electrolytes, and membrane fuel cells.
4. Textiles: sport apparel, sport shoes, climbing gear, rainwear, outerwear garments, and baby diapers.
5. Filtration: heating, ventilating, and air conditioning system filters; high-efficiency particulate air and ultralow particulate air filters; air, oil, and fuel filters for automobiles; and filters for beverage, pharmacy, and medical applications.
6. Napkins with nanofibers containing antibodies against numerous biohazards and chemicals that signal by changing color (potentially useful in identifying bacteria in kitchens).
7. Wound healing: the assembly of nanofibers at the injury site that draw the body's own growth factors to the injury site.

Other applications include industrial and high-tech applications for aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, and information technology.

Wang et al.<sup>45</sup> demonstrated a novel high-flux filtration medium consisting of a three-tier composite structure, that is, a top layer made of a nonporous, hydrophilic nanocomposite coating, a mid-layer made of an electrospun nanofiber (PVA) substrate, and a conventional nonwoven microfibrinous support, for oil/water separation.

Nanofibers have high potential in the fields of affinity membranes, filter media, tissue scaffolds, wound dressing, drug release, chemical and biological protective clothing, sensors, composite reinforcements, and energy and electrical applications.

Ma et al.<sup>189</sup> reported that a polymeric nanofiber matrix is similar to nanoscale, nonwoven, fibrous ECM proteins and thus can be used as an ECM-mimetic material. A review<sup>64</sup> covered the preparation

and modification of a polymeric nanofiber matrix in the development of future tissue-engineering scaffolds. The potential application of polymer nanofibers extends far beyond tissue engineering. Because of their high surface area, functionalized polymer nanofibers will find broad applications as drug delivery carriers, biosensors, and molecular filtration membranes in the future.

Feng et al.<sup>190</sup> wrote a brief review of progress in superhydrophobic surfaces. The article is based on studies of the surfaces of plant leaves and provides a novel approach to constructing superhydrophobic surfaces like those in the natural world. They suggested that nanostructures are essential in fabricating superhydrophobic surfaces with high contact angles and multiscale structures.

Kumbar et al.<sup>191</sup> wrote a review about recent patents on electrospun biomedical nanostructures. In the article, they reported that polymeric nanofibers in the form of nonwoven cloth, membranes, braids, and tubes are extensively used for daily needs and in addition are used as filters, in protective clothing, and for a variety of industrial and biomedical applications.

Kwoun et al.<sup>192</sup> prepared nanofiber films made of poly(lactic acid-co-glycolic acid) and successfully used them as novel sensor interfaces.

Laurencin et al.<sup>193</sup> patented polymeric nanofibers useful in a variety of medical and other applications, such as filtration devices, medical prostheses, scaffolds for tissue engineering, wound dressing, controlled drug delivery systems, cosmetic skin masks, and protective clothing. These could be fabricated from any of a variety of polymers, including nondegradable polymers [nylon, PU, polycarbonate, PAN, PEO, PANi, poly(vinyl carbazole), PS, and poly(vinyl phenol)] and biodegradable polymers (polyhydroxyacids, PCL, polyanhydrides, polyhydroxyalkanoates, PUs, collagen, chitosan, and hyaluronic acids), as well as blends and copolymers.

Ma et al.<sup>70</sup> reported that a collagen-blended biodegradable polymer nanofiber substrate has great potential to facilitate wound healing in skin tissue engineering when it is loaded with necessary growth factors and ECM molecules.

Stasiak et al.<sup>194</sup> designed polymer (PS) nanofiber systems for the immobilization of homogeneous catalysts.

Verreck et al.<sup>195</sup> assessed the application of water-soluble polymer-based nanofibers prepared by electrostatic spinning as a means of altering the dissolution rate of the poorly water-soluble drug intracozazole.

Sundarrajan and Ramakrishna<sup>196</sup> mixed magnesium oxide nanoparticles with various polymer solutions [poly(vinyl chloride), poly(vinylidene fluoride-co-hexafluoropropylene), and PSf] and

produced nanocomposite membranes by an electrospinning technique. The hydrolysis of paraoxon in the presence of these membranes was studied. The fabricated composite membrane (containing 5% magnesium oxide) was tested for the chemical warfare agent stimulant paraoxon and was found to be about 2 times more reactive than currently used charcoal.

Duan et al.<sup>197</sup> prepared PLGA by electrospinning for tissue engineering applications. The PLGA nanofibers had an interwoven and highly porous structure.

Araujo et al.<sup>198</sup> reported that PANi nanofibers could be used as new  $\gamma$ -radiation stabilizer agents for PMMA. PMMA is widely used for manufacturing medical and dental supplies.

Li et al.<sup>199</sup> reported electrospun poly(lactic acid) nanofibers as substrates for biosensor assemblies.

Chen et al.<sup>200</sup> fabricated biodegradable nanofiber membranes from PLLA for use as scaffolds in cartilage tissue engineering.

DuPont Co.<sup>201</sup> announced the production of air-filtration bags from hybrid membrane fibers. Based on nanofiber science, the Hybrid Membrane Technology fiber is produced by a spinning process that delivers continuous filaments with diameters ranging from 200 to 600 nm. Incumbent polyester felt bags are commonly used at production facilities that generate particulates and dust from wood, cement, asphalt, paint, minerals, and powders. Hybrid Membrane Technology also adds breathability and protection to bedding products as well as energy storage.

Lee et al.<sup>202</sup> reported a new method for the creation of a smaller dialyzer by incorporating into a poly(dimethylsiloxane)-based microplatform a polymeric [poly(ether sulfone) and PU] nanofiber (electrospun) web known to have good filtration efficiency for broad particle sizes.

### Nanofibers in membrane separation processes

Very few articles have appeared in the literature concerning the use of nanofibers in membrane separation science and technology. Gibson et al.<sup>28</sup> and Graham et al.<sup>48</sup> demonstrated first the use of nanofibers for air-filtration applications.

Ma et al.<sup>42</sup> reported an electrospun cellulose nanofiber mesh (alkaline-treated RC) as an affinity membrane. The water-filtration properties of the novel RC membrane were studied and compared with those of a commercial microfiltration membrane. The RC membrane showed higher water permeability than the conventional microporous membrane. The BSA-adsorbed membrane could be regenerated by rinsing with an elution buffer. They demonstrated the potential of the novel RC film nanofiber



membrane as an alternative tool for affinity membrane applications.

Feng et al.<sup>49</sup> prepared PVDF nanofibers by electrospinning and demonstrated for the first time how a PVDF nanofiber mat can be used for the production of drinking water from saline water via membrane distillation. This new approach may eventually enable the membrane distillation process to compete with conventional seawater desalination processes such as distillation and reverse osmosis.

Wang et al.<sup>203</sup> demonstrated for the first time a new kind of high-flux ultrafiltration membrane based on a PVA electrospun nanofibrous scaffold support and a PVA hydrogel coating. The filtration study involved the separation of an oil/water emulsion containing soybean oil (1350 ppm) and a non-ionic surfactant (Dow Corning 193 fluid; 150 ppm) at a 100 psi feed pressure and 30–35°C. The ultrafiltration test indicated that the flux rate of the PVA nanofibrous composite membranes was at least several times better than that of existing (commercial) thin-film composite membranes, and its performance could be further optimized by a reduction of the thickness of the top layer or changes in the layer composition. However, the rejection rate or filtration efficiency was similar to that observed in commercial membranes (rejection rate > 99.5%).

Yoon et al.<sup>204</sup> demonstrated high-flux ultrafiltration and nanofiltration composite membranes containing a thin layer of a hydrophilic but water-resistant chitosan coating, an asymmetric electrospun PAN nanofibrous mid-layer support, and a nonwoven PET substrate. The feed solution was prepared via the mixing of vegetable oil (1350 ppm), a surfactant (150 ppm, Dow Corning 193 fluid), and deionized water. Thus, the three-tier composite membranes exhibited flux rates that could be over an order of magnitude higher than that of the commercial nanofiltration filter (e.g., NF 270 from Dow) after 24 h of operation, and they maintained good filtration efficiency with rejection ratios better than 99.9% (i.e., <1 ppm in the permeate). However, these composite membranes had not been fully optimized for further improvement.

Maly and Petrik<sup>205</sup> deposited cellulose nanofibers onto regular cellulose filter media and noticed that the air-filtration parameters improved significantly. A very fine nanofiber web with a basis weight of 0.01–0.1 g<sup>-2</sup> improved the filtration efficiency for submicrometer particles by hundreds of percent, while lowering air permeability by only tens of percent. It was observed that the morphology of nanofibers usually plays a more important role than the basis weight.

Sang et al.<sup>206</sup> reported a novel chloridized poly (vinyl chloride) nanofiber membrane for heavy-metal-contaminated groundwater treatment. The

membrane was prepared from chlorinated poly (vinyl chloride) by a high-voltage electrospinning process. The removal of divalent metal cations, including Cu<sup>+2</sup>, Pb<sup>+2</sup>, and Cd<sup>+2</sup>, from the simulated groundwater was investigated. The experimental results showed that the rejection of copper in the simulated groundwater could reach more than 73%, the rejection of lead could reach more than 82%, and the rejection of cadmium could reach more than 90%.

Qin and Wang<sup>207,208</sup> fabricated nanoscale cross-linked PVA by electrospinning and studied its structure and filtration applications. The fibers were found to be efficiently crosslinked by maleic acid. Vitriolic acid was used as a catalyst activator during crosslinking. The morphology and structure of cross-linked PVA fibers were studied with SEM and differential calorimetry techniques as well as infrared reflection-absorption spectroscopy (Fourier transform infrared). Electrospun nanofibers had good adsorbability and excellent filtration properties because of their smaller diameter (ca. 200 nm) and the very high surface area to volume ratio. During the experiments, crosslinked PVA nanofiber layers with different area weights were placed on the spin-bonded or melt-blown sublayers. The results revealed that the filtration efficiency increased sharply when crosslinked PVA nanofibers layers were added to the sublayers.

## SUMMARY

Electrospun continuous polymer and carbon nanofibers have considerable advantages in comparison with discontinuous carbon nanotubes or other nanotubes in terms of cost, health concerns, and the possibility of integrated one-step manufacturing of assemblies.<sup>198</sup> However, a fundamental experimental and theoretical analysis of the process is needed to develop flexible and reliable fabrication methods for nanofibers and their assemblies and composites. In the past 5 years, a large amount of work has been reported on this new method for the preparation of nanofibers and new blended or unblended polymers and its applications in medicine, sensors, and so forth. However, very little work or a negligible amount has been reported on the application of nanofibers in membrane separation (filtration), even though nanofibers have great potential for membrane science and technology.

## NOMENCLATURE

AFM	atomic force microscopy
AgNO <sub>3</sub>	silver nitrate
BSA	bovine serum albumin
CA	cellulose acetate

CECh	<i>N</i> -carboxyethylchitosan
CNT	carbon nanotube
dc	direct current
DMAc	<i>N,N</i> -dimethylacetamide
DMF	dimethylformamide
DSC	differential scanning calorimetry
EC	endothelial cell
ECM	extracellular matrix
Fe <sub>3</sub> O <sub>4</sub>	magnetite
LiCl	lithium chloride
MWCNT	multiwalled carbon nanotube
NFM	nanofiber mat
P4VP	poly(4-vinylpyridine)
PAN	polyacrylonitrile
PANi	polyaniline
PCL	polycaprolactone
PDP	3- <i>n</i> -pentadecylphenol
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
PLGA	poly(lactic- <i>co</i> -glycolic acid)
PLLA	poly(L-lactic acid)
P(LLA-CL)	poly(L-lactic acid- <i>co</i> -ε-caprolactone)
PMMA	poly(methyl methacrylate)
PS	polystyrene
PSf	polysulfone
PVA	poly(vinyl alcohol)
PVDF	poly(vinylidene fluoride)
PVP	polyvinylpyrrolidone
PU	polyurethane
RC	regenerated cellulose
SDS	sodium dodecyl sulfate
SF	silk fibroin
SEM	scanning electron microscopy
TEM	transmission electron microscopy
UV	ultraviolet

## References

- Burger, C.; Hsiao, B. S.; Chu, B. *Annu Rev Mater Res* 2006, 36, 333.
- Greiner, A.; Wendroff, J. H.; Yarin, A. L.; Zussman, E. *Appl Microbiol Biotechnol* 2006, 71, 387.
- Liao, S.; Li, B.; Ma, Z.; Wei, H.; Chan, C.; Ramakrishna, S. *Biomed Mater* 2006, 1, R45.
- Lutolf, M. P.; Hubbel, J. A. *Nat Biotechnol* 2005, 23, 47.
- Hawker, C. J.; Wooley, K. L. *Science* 2005, 309, 1200.
- Kaur, S.; Gopal, R.; Jern, N. W.; Ramakrishna, S.; Matsuura, T. *MRS Bull* 2008, 33, 21.
- Frenot, A.; Chronakis, I. S. *Curr Opin Colloid Interface Sci* 2003, 8, 64.
- Venugopal, J.; Ramakrishna, S. *Appl Biochem Biotechnol* 2005, 125, 147.
- Saw, S. H.; Wang, Y. P.; Yong, T.; Ramakrishna, S. In *Nanotechnologies for Life Sciences—Tissue, Cell and Organ Engineering*; Kumar, C. S. S. R., Ed.; Wiley-VCH: Weinheim, 2006; Vol.9, Chapter 2, p 66.
- Sill, T. J.; von Recum, H. A. *Biomaterials* 2008, 29, 1989.
- Kumbar, S. G.; Nair, L. S.; Bhattacharyya, S.; Laurencin, C. T. *J Nanosci Nanotechnol* 2006, 6, 2591.
- Chronakis, I. *J Mater Process Technol* 2005, 167, 283.
- Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos Sci Technol* 2003, 63, 223.
- Pedicini, A.; Farris, R. J. *Polymer* 2003, 44, 6857.
- Formhals, A. U.S. Pat. 1,975,504 (1935).
- Fong, H.; Reneker, D. H. In *Structure Formation in Polymeric Fibers*; Salem, D. R., Ed.; Hanser: Munich, 2001; p 225.
- Yarin, A. L.; Koombhongse, S.; Reneker, D. H. *J Appl Phys* 2001, 89, 3018.
- Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. *J Appl Phys* 2002, 87, 4531.
- Reneker, D. H.; Chun, I. *Nanotechnology* 1996, 7, 216.
- Doshi, J.; Reneker, D. H. *J Electrostatics* 1995, 35, 151.
- Gibson, P.; Gibson, S.; Rivin, D. *Colloids Surf A* 2001, 187, 469.
- Ramakrishna, S.; Fuzihara, K.; Teo, W.; Lim, T.; Ma, Z. *An Introduction to Electrospinning and Nanofibers*; World Scientific: Singapore, 2005.
- Grafe, T.; Graham, K. Presented at the International Nonwovens Technical Conference, Atlanta, GA, Sept 24, 2002.
- Liang, D.; Hsiao, B. S.; Chu, B. *Adv Drug Delivery Rev* 2007, 59, 1392.
- Hajra, M. G.; Mehta, K.; Chase, G. G. *Sep Purif Technol* 2003, 3, 79.
- Gibson, P. W.; Schreuder-Gibson, H.; Rivcen, D. *AIChE J* 1999, 45, 190.
- Schreuder-Gibson, H.; Senecal, P. G. K.; Sennett, M.; Walker, J. E.; Yeomans, W.; Ziegler, D.; Tsai, P. P. *J Adv Mater* 2002, 34, 44.
- Gibson, P.; Schreuder-Gibson, H.; Rivin, D. *Colloids Surf A* 2001, 187, 469.
- Wang, X.; Drew, C.; Lee, S. H.; Senecal, K. J.; Kumar, J.; Samuelson, L. A. *Nano Lett* 2002, 2, 1273.
- Wang, X.; Kim, Y. G.; Drew, C.; Ku, B. C.; Kumar, J.; Samuelson, L. A. *Nano Lett* 2004, 4, 331.
- Kim, J. S.; Reneker, D. H. *Polym Compos* 1999, 20, 124.
- Bergshoef, M. M.; Vancso, G. J. *Adv Mater* 1999, 11, 1362.
- Fong, H. *Polymer* 2004, 45, 2427.
- Drew, C.; Wang, X.; Senecal, K.; Schreuder-Gibson, H.; He, J.; Kumar, J.; Samuelson, L. A. *J Macromol Sci Pure Appl Chem* 2002, 39, 1085.
- Verreck, G.; Chun, I.; Rosenblatt, J.; Peeters, J.; Dijk, A. V.; Mensch, J.; Noppe, M.; Brewster, M. E. *J Controlled Release* 2003, 92, 349.
- Khil, M. S.; Cha, D. I.; Kim, H. Y.; Kim, I. S.; Bhattarai, N. *J Biomed Mater Res B* 2003, 67, 675.
- Matthews, J. A.; Wnek, G. E.; Simpson, D. G.; Bowlin, G. L. *Biomacromolecules* 2002, 3, 232.
- Yoshimoto, H.; Shin, Y. M.; Terai, H.; Vacanti, J. P. *Biomaterials* 2003, 24, 2077.
- Xu, C. Y.; Inai, R.; Kotaki, M.; Ramakrishna, S. *Biomaterials* 2004, 25, 877.
- Min, B. M.; Lee, G.; Kim, S. H.; Nam, Y. S.; Lee, T. S.; Park, W. H. *Biomaterials* 2004, 2, 1289.
- Shin, M.; Ishii, O.; Sueda, T.; Vacanti, J. *Biomaterials* 2004, 25, 3717.
- Ma, Z.; Kotaki, M.; Ramakrishna, S. *J Membr Sci* 2005, 265, 115.
- Groitzsch, D.; Fahrbach, E. U.S. Pat. 4,618,524 (1986).
- Grafe, T.; Graham, K. Presented at the International Nonwovens Technical Conference, Atlanta, GA, Sept 24, 2002.
- Wang, X.; Chen, X.; Yoon, K.; Fang, D.; Hsiao, B. S.; Chu, B. *Environ Sci Technol* 2005, 39, 7684.
- Shin, C.; Chase, G. G. *AIChE J* 2004, 50, 343.
- Gopal, R.; Kaur, S.; Ma, Z.; Chan, C.; Ramakrishna, S.; Matsuura, T. *J Membr Sci* 2006, 281, 581.
- Graham, K.; Ouang, M.; Raether, T.; Grafe, T.; McDonald, B.; Knauf, P. Presented at the 5th Annual Technical Conference

- and Expo of the American Filtration and Separation Society, Galveston, TX, April 9, 2002.
49. Feng, C. Y.; Khulbe, K. C.; Matsuura, T.; Gopal, R.; Kaur, S.; Ramakrishna, S.; Khayet, M. *J Membr Sci* 2008, 311, 1.
  50. Gibson, P. W.; Lee, C.; Ko, F.; Reneker, D. *J Eng Fibers Fabrics* 2007, 2, 32.
  51. Weik, T. M.; Crofoot, D. G.; Gogins, M. A.; Hall, J. R. B.; Chung, H. Y. U.S. Pat. 7,318,853 (2008).
  52. Chung, H. Y.; Hall, J. R. B.; Gogins, M. A.; Crofoot, D. G.; Weik, T. M. U.S. Pat. 7,270,693 (2007).
  53. Tsai, P. P. Presented at the Annual International TANDEC Nonwoven Conference, Knoxville, TN, Nov 6, 2001.
  54. Gopal, R.; Ma, Z.; Kaur, S.; Ramakrishna, S. *Molecular Building Blocks for Nanotechnology*; Springer: Berlin, 2007; Vol. 109, p 72.
  55. Fong, H.; Chun, I.; Reneker, D. H. *Polymer* 1995, 40, 4585.
  56. Tan, E. P. S.; Lim, C. T. *Appl Phys Lett* 2004, 84, 1603.
  57. Lim, C. T.; Tan, E. P. S. *MRS Proc* 2003, F8.34.
  58. Tan, E. P. S.; Goh, C. N.; Sow, C. H.; Lin, C. T. *Appl Phys Lett* 2005, 86, 073115.
  59. Spasova, M.; Mincheva, R.; Paneva, D.; Manolova, N.; Rashkov, I. *J Bioact Compat Polym* 2006, 21, 465.
  60. Koombhongs, S.; Liu, W.; Reneker, D. H. *J Polym Sci Part B: Polym Phys* 2001, 39, 2598.
  61. Bognitzki, M.; Hou, H.; Frese, M. I. T.; Hellwig, M.; Schwarte, C.; Schaper, A.; Wendroff, J. H.; Greiner, A. *Adv Mater* 2000, 12, 637.
  62. Mincheva, R.; Manolova, N.; Rashkov, I. *Eur Polym J* 2007, 43, 2809.
  63. Koski, A.; Yim, K.; Shivkumar, S. *Mater Lett* 2004, 58, 493.
  64. Jayaraman, K.; Kotaki, M.; Zhang, Y.; Mo, X.; Ramakrishna, S. *J Nanosci Nanotechnol* 2004, 4, 52.
  65. Liu, H.; Edel, J. B.; Bellan, L. M.; Craighead, H. G. *Small* 2006, 2, 495.
  66. Arinstein, A.; Zussman, E. *Phys Rev E* 2007, 76, 056303.
  67. Behler, K.; Havel, M.; Ko, F.; Gogtosi, Y. *MRS Symp B* 2006, B3.3.
  68. Gomes, D. S.; da Silva, A. N. R.; Morimoto, N. I.; Mendes, L. T. F.; Furlan, R.; Ramos, I. *Polimeros* 2007, 17, 206.
  69. Mankidy, P. J.; Rajagopalan, R.; Foley, H. C. *R Soc Chem Chem Commun* 2006, 1139.
  70. Ma, K.; Yong, T.; Chan, K. C.; Ramakrishna, S. In *Proceedings of the Fifth IASTED International Conference on Biomedical Engineering*; Acta Press: Anaheim, California 2007, pp 262–266.
  71. Zhou, Y.; Freitag, M.; Hone, J.; Staii, C.; Johnson, A. T.; Pinto, N. J.; MacDiarmid, A. G. *Appl Phys Lett* 2003, 83, 3800.
  72. Pinto, N. J.; Carrión, P. L.; Ayala, A. M.; Ortiz-Marciales, M. *Synth Met* 2005, 148, 271.
  73. Naraghi, H.; Chasiotis, I.; Kahn, H.; Wen, Y.; Dzenis, Y. *Rev Sci Instrum* 2007, 78, 085108.
  74. Moel, K.; Alberda van Ekenstien, G. O. R.; Nijland, H.; Polushkin, E.; Brinke, G. T.; Mäki-Ontto, R.; Ikkala, O. *Chem Mater* 2001, 13, 4580.
  75. Guofeng, L.; Martinez, C.; Janata, J.; Smith, J. A.; Josowicz, M.; Semancik, S. *Electrochem Solid-State Lett* 2004, 7, H44.
  76. Zussman, E.; Chen, X.; Ding, W.; Calabri, L.; Dikin, D. A.; Quintana, J. P.; Ruoff, R. S. *Carbon* 2005, 43, 2175.
  77. Zussman, E.; Rittel, D.; Yarin, A. L. *Appl Phys Lett* 2003, 82, 3958.
  78. Theron, S. A.; Zussman, E.; Yarin, A. L. *Polymer* 2004, 45, 2017.
  79. Kotaki, M.; Liu, X. M.; He, C. *J Nanosci Nanotechnol* 2006, 6, 3997.
  80. Theron, S. A.; Yarin, A. L.; Zussman, E.; Kroll, E. *Polymer* 2005, 46, 2889.
  81. Ma, Z.; Kotaki, M.; Yong, T.; He, W.; Ramakrishna, S. *Biomaterials* 2005, 26, 2527.
  82. Wu, X. F.; Kostogorova-Beller, Y. Y.; Goponenko, A. V.; Hou, H.; Dzenis, Y. A. *Phys Rev E* 2008, 78, 061804.
  83. Nair, L. S.; Laurencin, C. T. *J Bone Joint Surg* 2008, 90, 128.
  84. Hajra, M. G.; Mehta, K.; Chase, G. G. *Sep Purif Technol* 2003, 30, 79.
  85. Xiumei, M.; Zonggang, C.; Weber, H. J. *Frontiers Mater Sci China* 2007, 1, 20.
  86. Katta, P.; Alssandro, M.; Ramsier, R. D.; Chase, G. G. *Nano Lett* 2004, 4, 2215.
  87. Moon, S. C.; Ku, B. C.; Emrick, T.; Coughlin, B. E.; Farris, R. J. *J Appl Polym Sci* 2009, 111, 301.
  88. Andradý, A. L. *Science and Technology of Polymer Nanofibers*; Wiley: New York, 2008.
  89. Yu, J.; Qiu, Y.; Zha, X.; Yu, M.; Yu, J.; Rafique, J.; Yin, J. *Eur Polym J* 2008, 44, 2838.
  90. Yeo, L. Y.; Friend, J. R. *J Exp Nanosci* 2006, 1, 177.
  91. Grafe, T.; Graham, K. Presented at the International Nonwovens Technical Conference, Atlanta, GA, Sept 24, 2002.
  92. Nano Technics Co., Ltd. <http://nano21c.en.ec21.com> (accessed June 2009).
  93. Dosunmu, O. O.; Chase, G. G.; Varabhas, J. S.; Kataphinan, W.; Reneker, D. H. *Nanotechnology* 2006, 17, 1123.
  94. Yarin, A. L.; Kataphinan, W.; Reneker, D. H. *J Appl Phys* 2005, 98, 064501.
  95. Shin, M. K.; Kim, S. I.; Kim, S. J. *Appl Phys Lett* 2006, 88, 223109.
  96. Xie, J.; Hsieh, Y. L. *J Mater Sci* 2003, 38, 2125.
  97. Herricks, T. E.; Kim, S. H.; Kim, J.; Li, D.; Kwak, J. H.; Grate, J. W.; Kim, S. H.; Xia, Y. *J Mater Chem* 2005, 15, 3241.
  98. Son, W. K.; Youk, J. H.; Park, W. H. *Biomacromolecules* 2004, 5, 197.
  99. Kim, C. W.; Frey, M. W.; Marquez, M.; Joo, Y. L. *J Polym Sci Part B: Polym Phys* 2005, 43, 1673.
  100. Kim, C. W.; Kim, D. S.; Kang, S. Y.; Marquez, M.; Joo, Y. L. *Polymer* 2006, 47, 5097.
  101. Jiang, L.; Zhao, Y.; Zhai, J. *Angew Chem Int Ed* 2004, 43, 4338.
  102. Nasir, M.; Matsumoto, H.; Danno, T.; Minagawa, M.; Irisawa, T.; Shioya, M.; Tanioka, A. *J Polym Sci Part B: Polym Phys* 2006, 44, 779.
  103. Nasir, M.; Matsumoto, H.; Minagawa, M.; Tanioka, A.; Danno, T.; Horibe, H. *Polym J* 2007, 39, 670.
  104. Ren, X.; Dzenis, Y. *MRS Symp Proc* 2006, 920, S03–03.
  105. Verreck, G.; Chun, I.; Rosenblatt, J.; Peeters, J.; Dijk, A. V.; Mensch, J.; Noppe, M.; Brewster, M. E. *J Controlled Release* 2003, 92, 349.
  106. Ding, B.; Kim, H. Y.; Lee, S. C.; Lee, D. R.; Choi, K. J. *Fibers Polym* 2002, 3, 73.
  107. Son, W. K.; Youk, J. H.; Lee, T. S.; Park, W. H. *Mater Lett* 2005, 59, 1571.
  108. Shin, M. K.; Park, S. J.; Yoon, S. G.; Lee, C. K.; Shin, K. M.; Shin, S. R.; Gu, B. K.; Kim, M. S.; Kim, S. J. *MRS Proc* 2006, 0921-T05-12.
  109. Ma, M.; Hill, R. M.; Lowery, J. L.; Fridrikh, S. V.; Rutledge, G. C. *Langmuir* 2005, 21, 5549.
  110. Jia, Y. T.; Kim, H. Y.; Gong, J.; Lee, D. R. *J Appl Polym Sci* 2006, 99, 462.
  111. He, W.; Yong, T.; Ma, Z. W.; Inai, R.; Teo, W. E.; Ramakrishna, S. *Tissue Eng* 2006, 12, 2457.
  112. Choi, J. S.; Yoo, H. S. *J Bioact Compat Polym* 2007, 22, 508.
  113. Dotti, F.; Varesano, A.; Montarsolo, A.; Aluigi, A.; Tonin, C.; Mazzuchetti, G. *J Ind Text* 2007, 37, 151.
  114. Salalha, W.; Dror, Y.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. *Langmuir* 2004, 20, 9852.
  115. Dror, Y.; Salalha, W.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. *Langmuir* 2003, 19, 7012.
  116. Ruotsalainen, T.; Turku, J.; Heikkilä, P.; Ruokolainen, J.; Nykänen, A.; Laitinen, T.; Torkkeli, M.; Serimma, R.; Brinke, G.; Harlin, A.; Ikkala, O. *Adv Mater* 2005, 17, 1048.
  117. Ruotsalainen, T.; Turku, J.; Hiekkataipale, P.; Vainio, U.; Serimaa, R.; Brinke, G. T.; Harlin, A.; Ruokolainen, J.; Ikkala, O. *Soft Matter* 2007, 3, 978.

118. Qi, D.; Kang, X.; Chen, L.; Zhang, Y.; Wei, H.; Gu, Z. *Anal Bioanal Chem* 2008, 390, 929.
119. Wan, L. S.; Xu, Z. K. *J Biomed Mater Res A* 2009, 89, 168.
120. Baumgarten, P. K. *J Colloid Interface Sci* 1971, 36, 71.
121. Fischer, T.; Hampp, N. *IEEE Trans Nanobiosci* 2004, 3, 118.
122. McClure, M. J.; Sell, S. A.; Barnes, C. P.; Bowen, W. C.; Bowlin, G. L. *J Eng Fibers Fabrics* 2008, 3, 1.
123. Bishop, A. S.; Yang, J. H. C.; Balazsi, C.; Gouma, P. I. *MRS Symp B* 2006, B14.
124. Sun, Z.; Zussman, E.; Yarin, A. L.; Wendorff, J. H.; Greiner, A. *Adv Mater* 2003, 15, 1929.
125. González, R.; Pinto, N. *J Synth Met* 2005, 151, 275.
126. Tan, S. T.; Wendorff, J. H.; Pietzonka, C.; Jia, Z. H.; Wang, G. *Q. Chem Phys Chem* 2005, 6, 1461.
127. Kameoka, J.; Verbridge, S. S.; Liu, H.; Czaplewski, D.; Craighead, H. G. *Nano Lett* 2004, 4, 2105.
128. Prilutsky, S.; Zussman, E.; Cohen, Y. *Nanotechnology* 2008, 19, 165603.
129. Gorantia, M.; Boone, S. E.; El-Ashry, M.; Young, D. *Appl Phys Lett* 2006, 88, 073115.
130. Tomezak, N.; Gu, S.; Han, M.; van Hulst, N. F.; Vancso, G. J. *Eur Polym J* 2006, 42, 2205.
131. Yarin, A. L.; Zussman, E. Presented at the 21st International Congress of Theoretical and Applied Mechanics, Warsaw, Poland, Aug 15, 2004.
132. Suryavanshi, A. P.; Hu, J.; Yu, M. F. *Adv Mater* 2008, 20, 793.
133. Nain, A. S.; Amon, C.; Sitti, M. *Proc IEEE Conf Nanotechnol* 2005, 5, 366.
134. An, H.; Shin, C.; Chase, G. G. *J Membr Sci* 2006, 283, 84.
135. Zheng, G.; Wang, L.; Wang, H.; Sun, D.; Li, W.; Lin, L. *Adv Mater* 2009, 60, 439.
136. Longtin, R.; Fauteux, C.; Caigan, L. P.; Therriault, D.; Pegna, J. *Surf Coat Technol* 2008, 202, 2661.
137. Kameoka, J.; Czaplewski, D.; Craighead, H. G. *J Photopolym Sci Technol* 2003, 16, 423.
138. Correa, Z.; Murata, H.; Tomizawa, T.; Tenmoku, K.; Oya, A. *Adv Sci Technol* 2006, 51, 60.
139. Theron, A.; Zussman, E.; Yarin, A. L. *Nanotechnology* 2001, 12, 384.
140. Reneker, D. H.; Kataphinan, W.; Theron, A.; Zussman, E.; Yarin, A. L. *Polymer* 2002, 43, 6785.
141. Rein, D. M.; Shavit-Hadar, L.; Khalfin, R. L.; Cohen, Y.; Shuster, K.; Zussman, E. *J Polym Sci Part B: Polym Phys* 2007, 45, 766.
142. Bellan, L. M.; Cross, J. D.; Strychalski, E. A.; Moren-Marbel, J.; Craighead, H. G. *Nano Lett* 2006, 6, 2526.
143. Zussman, E.; Theron, A.; Yarin, A. L. *Appl Phys Lett* 2003, 82, 973.
144. Yarin, A. L.; Zussman, E. *Polymer* 2004, 45, 2977.
145. Bashouti, M.; Salalha, W.; Brumer, M.; Zussman, E.; Lifshitz, E. *Chem Phys Chem* 2006, 7, 102.
146. Wei, Q. F.; Ye, H.; Hou, D. Y.; Wang, H. G.; Gao, W. D. *J Appl Polym Sci* 2006, 99, 2384.
147. Jang, J. *Adv Polym Sci* 2006, 199, 189.
148. Jin, W. J.; Lee, H. K.; Jeong, E. H.; Park, W. H.; Youk, J. H. *Macromol Rapid Commun* 2005, 26, 1903.
149. Son, W. K.; Youk, J. H.; Park, W. H. *Carbohydr Polym* 2006, 65, 430.
150. Son, W. K.; Youk, J. H.; Lee, T. S.; Park, W. H. *Macromol Rapid Commun* 2004, 25, 1632.
151. Hong, K. H.; Park, J. L.; Sul, I. H.; Youk, J. H.; Kang, T. J. *J Polym Sci Part B: Polym Phys* 2006, 44, 2468.
152. Jin, J. W.; Jeon, H. J.; Kim, J. H.; Youk, J. H. *Synth Met* 2007, 157, 454.
153. He, W.; Ma, Z. W.; Yong, T.; Teo, W. E.; Ramakrishna, S. *Biomaterials* 2005, 26, 7606.
154. He, W.; Yong, T.; Teo, W. E.; Ma, Z.; Ramakrishna, S. *Tissue Eng* 2005, 11, 1574.
155. Berry, S. M.; Harfenist, S. A.; Cohn, R. W.; Keynton, R. S. *J Micromech Microeng* 2006, 16, 125.
156. Mincheva, R.; Stollova, O.; Penchev, H.; Ruskov, T.; Spirov, I.; Monolova, N.; Rashkov, I. *Eur Polym J* 2008, 44, 615.
157. Mincheva, R.; Manolova, N.; Paneva, D.; Rashkov, I. *J Bioact Compat Polym* 2005, 20, 419.
158. Lee, J. H.; Liao, Y. T. *J Appl Polym Sci* 2006, 101, 3550.
159. Liu, G.; Ding, J.; Guo, J.; Herfort, M. *Macromolecules* 1997, 30, 1851.
160. Tao, J.; Guo, A.; Liu, G. *Macromolecules* 1996, 29, 1618.
161. Ding, J.; Tao, J.; Guo, A. A.; Stewart, S.; Hu, N.; Birss, V. I.; Liu, G. *Macromolecules* 1997, 30, 655.
162. Maskos, M.; Harris, L. R. *Macromol Rapid Commun* 2001, 22, 271.
163. Mallick, K.; Witcomb, M. J.; Dinsmore, A.; Scurrili, M. *Langmuir* 2005, 21, 7964.
164. Huang, J. *Pure Appl Chem* 2006, 78, 15.
165. Dong, X.; Wang, L.; Wang, W.; Yu, H.; Wang, J.; Chen, T.; Zhao, Z. *Eur Polym J* 2005, 41, 797.
166. Shang, T. C.; Yang, F.; Wang, C. *Solid State Phenom* 2007, 121, 583.
167. Zussman, E.; Yarin, A. L.; Bazilevsky, A. V.; Avrahami, R.; Feldman, M. *Adv Mater* 2006, 18, 348.
168. Lee, K. J.; Oh, J. H.; Kim, Y.; Jang, J. *Adv Mater* 2006, 18, 2216.
169. He, F.; Tang, Y.; Yu, M.; Wang, S.; Li, Y.; Zhu, D. *Adv Funct Mater* 2006, 16, 91.
170. Gass, J.; Poddar, P.; Almand, J.; Srinath, S.; Srikanth, H. *Adv Funct Mater* 2006, 16, 71.
171. Lellouche, J. P.; Govindaraji, S.; Joseph, A.; Jang, J.; Lee, K. J. *Chem Commun* 2005, 4357.
172. Jang, J.; Ko, S.; Kim, Y. *Adv Funct Mater* 2006, 16, 754.
173. Liu, A.; Wei, M.; Honma, I.; Zhou, H. *Adv Funct Mater* 2006, 16, 371.
174. Srivastava, Y.; Loscertales, I.; Marquez, M.; Thorsen, T. *Microfluid Nanofluid* 2008, 4, 245.
175. Kong, H.; Jang, J. *Chem Commun* 2006, 3010.
176. Aussawasathein, D.; Dong, J. H.; Dai, L. *Synth Met* 2005, 154, 37.
177. Drew, C.; Liu, X.; Ziegler, D.; Wang, X.; Bruno, F. F.; Whitten, J.; Samuelson, L. A.; Kumar, J. *Nano Lett* 2003, 3, 143.
178. Duvail, J. L.; Godon, C.; Marhic, C.; Louran, G.; Chauvet, O.; Cuenot, S.; Nysten, B.; Pra, L. D.; Demoustier-Champagne, S. *Synth Met* 2003, 135, 329.
179. Dhanote, A.; Ugbolue, S. C.; Warner, S. B.; Patra, P. K.; Katar, P.; Mhetre, S. K. *MRS Symp* 2003, 788, 153.
180. Kaner, R. B.; Huang, J.; Weiller, B. H.; Virji, S. U.S. Pat. 7,144,949 (2006).
181. Chuangchote, S.; Sagawa, T.; Yoshikawa, S. *Jpn J Appl Phys* 2008, 47, 787.
182. Weiller, B. H.; Virji, S.; Kaner, R. B.; Huang, J. U.S. Pat. 7,226,530 (2007).
183. Meziari, M.; Pathak, P.; Wang, W.; Desai, T.; Patil, A.; Sun, Y. P. *Ind Eng Chem Res* 2005, 44, 4594.
184. Li, H.; Ke, Y.; Hu, Y. *J Appl Polym Sci* 2005, 99, 1018.
185. Trofin, L.; LeDuc, P. R. *J Appl Polym Sci* 2007, 105, 549.
186. Cai, L.; Kovalev, A.; Mayer, T. S. *Proc Int Conf Inf Technol Appl Biomed* 2008, 5, 196.
187. Dubrow, R. S.; Sloan, L. D.; Kronenthal, R. I.; Collier, M. D.; Rogers, E. J.; Gertner, M. E. U.S. Pat. 0,221,072 (2005).
188. Subbiah, T.; Bhat, G. S.; Tock, R. W.; Parameswaran, S.; Ramakumar, S. S. *J Appl Polym Sci* 2005, 96, 557.
189. Ma, Z.; Kotaki, M.; Inai, R.; Ramakrishna, S. *Tissue Eng* 2005, 11, 101.
190. Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. *Adv Mater* 2002, 14, 1857.
191. Kumbhar, S. G.; Nukavarapu, S. P.; James, R.; Hogan, M. V.; Laurencin, C. T. *Recent Pat Biomed Eng* 2008, 1, 68.

192. Kwoun, S. J.; Lee, R. M.; Han, B.; Ko, F. K. *Nanotechnology* 2001, 1, 338.
193. Laurencin, C. T.; Nair, L. S.; Bhattacharyya, S.; Allcock, H. R.; Bender, J. D.; Brown, P. W.; Greish, Y. E. U.S. Pat. 7,235,295 (2007).
194. Stasiak, M.; Röben, C.; Rosenberger, N.; Schleth, F.; Studer, A.; Greiner, A.; Wendorff, J. H. *Polymer* 2007, 48, 5208.
195. Verreck, G.; Chun, I.; Peeters, J.; Rosenblatt, J.; Brewster, M. E. *Pharm Res* 2003, 20, 810.
196. Sundarrajan, S.; Ramakrishna, S. *J Mater Sci* 2007, 42, 8400.
197. Duan, Y. Y.; Jia, J.; Wang, S. H.; Yan, W.; Jin, L.; Wang, Z. *J US-China Med Sci* 2007, 4, 41.
198. Araujo, P. L. B.; Santos, R. F. S.; Araujo, E. S. *Express Polym Lett* 2007, 1, 385.
199. Li, D.; Frey, M. W.; Baemner, A. J. *J Membr Sci* 2006, 279, 354.
200. Chen, J. P.; Lee, S. F.; Chiang, I. P. *Nanotechnology* 2005, 1, 100.
201. Hybrid Membrane Fiber Targets Air Filtration Bags. <http://news.thomasnet.com/fullstory/543281> (accessed June 2009).
202. Lee, K.; Kim, D.; Min, B.; Lee, S. *Biomed Microdevices* 2007, 9, 435.
203. Wang, X.; Fang, D.; Yoon, K.; Hsiao, B. S.; Chu, B. *J Membr Sci* 2006, 278, 261.
204. Yoon, K.; Kim, K.; Wang, F.; Fang, D.; Hsiao, B. S.; Chu, B. *Polymer* 2006, 47, 2434.
205. Maly, M.; Petrik, S. Presented at Nanotech 2008, Boston, MA, June 1, 2008.
206. Sang, Y.; Li, F.; Gu, Q.; Liang, C.; Chen, J. *Desalination* 2008, 223, 349.
207. Qin, X. H.; Wang, S. Y. *J Appl Polym Sci* 2008, 109, 951.
208. Qin, X. H.; Wang, S. Y. *J Appl Polym Sci* 2006, 102, 1285.