SCIENCE AND TECHNOLOGY OF POLYMER NANOFIBERS

Anthony L. Andrady

Research Triangle Institute

A JOHN WILEY & SONS, INC., PUBLICATION

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To my wife Lalitha

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PREFACE

Since its inception six years ago, federal R&D investment in the national nanotechnology initiative focused on exploring the "inner space" has been well over $6.5 billion, matched by about the same amount from private industry. It is an impressive budget, but one that still pales in comparison to the hundreds of billions of dollars spent on outer-space exploration, our most visible science project. In terms of rewards, however, the few billions spent have opened the portals of nanoscale phenomena to hundreds if not thousands of researchers worldwide (as opposed to the few fortunate astronauts who trod the lunar soil or enjoyed the breathtaking view of Earth from outer space.) In terms of pure science and educational dividends, the investment is already a resounding success. In Feynman's words, there certainly "is plenty of room at the bottom" to accommodate all those curious minds and those yet to follow. Rewards in terms of products reaching the marketplace, however, have been slower to come. The relatively young nanotechnogy effort appears to be paying off in terms of the emerging nano-enabled products already entering the marketplace. If the projections are correct, the estimated market value of "nano-goods" resulting from the R&D effort in the near future is indeed staggering. The National Science Foundation estimates a market of US$240 billion per year for nanomaterials. If there were unambiguous definitions of what constitutes "nano" or "nano-enabled," then one might even be able to count and trend these technologies. Therein lies a fundamental and very practical question: what constitutes a nanomaterial and specifically a nanofiber?

One can conveniently invoke the familiar and accepted technical criterion: "nano" being 10^{-9}th of a meter, an object that is 100 nm or smaller in at least one of its dimensions is a nanomaterial. It is an arbitrary size range in any event, and reliable techniques to even assess if a particle is slightly over or under this limit do not exist. Real-world materials with particle sizes that are several hundred nanometers, a micron, or even several microns are loosely referred to as "nanomaterials." Textile fibers that are as large as 500 nm in diameter are by convention referred to as nanofibers in the industry. The marketplace boasts of hundreds of nanomaterials and nano-products

ranging from the familiar inorganic reinforcing fillers, composites, and coatings to the exotic quantum dots. A less-rigorous working definition of what constitutes a nanomaterial can be particularly useful given the wide range of products in the marketplace claiming to be nano-enabled. Also, there is the issue of macro-scale objects carrying nanoscale features that provide them with functionality (nanoporous polymer foams); certainly they are nano-enabled materials, but are they distinct from nanomaterials?

Going by the restrictive scientific definition, one can envision classes of nanomaterials based on their dimensionality, counting the non-nanoscale dimensions associated with an object. A nanoparticle such as a quantum dot where all dimensions fall within a defined nano regime (say $<100\,\text{nm}$ for the sake of discussion) is clearly a zero-dimension (0-D) nanomaterial. A material where two of the dimensions are not nanoscale (only a single nano-dimension) will then be a two-dimensional (2-D) nanomaterial, and would include ultrathin coatings or plate-like fillers. Nanofibers or nanowires where a single dimension falls outside the nano regime will be classified as one-dimensional (1-D) material according to this scheme. Electrospun nanofibers are 1-D nanomaterials based on this taxonomy. However, in the electrospinning literature, nanofibers (along with nanorods, nanowires, and nanobelts) are sometimes referred to as 2-D structures. This is based on the alternative convention of counting only the nanoscale dimensions of a material. The length scale of 1-D nano-object can take any value outside the nano regime and therefore includes fibers, nanotubes, most nanoribbons, and high-aspect-ratio particles.

Reducing the size of a particle will eventually force its characteristics to change. The classical paradigms that apply in macro-world will cease to describe its behavior and will need to be replaced by quantum mechanical descriptions. The size scale where the gradual change from the classical to quantum behavior occurs encompasses classical nanomaterials, with their unexpected, unusual characteristics. Even at dimensions where classical rules continue to apply, particle size reduction and the ensuing increased fraction of atoms at the interface (based on dimensionality) will bring about dramatic changes in material properties. It is the exploitation of these two sets of tunable materials characteristics that the nanotechnologists typically work with. The so-called “molecular Lego set” of nano-engineering is nothing more than an exceptionally economical, bottom-up approach to engineering design that replaces the convention of turning out devices (and waste) from large chunks of materials.

Nature was the first nanomaterials foundry, producing nanoparticles in natural geological phenomena, mainly in volcanic eruptions and in forest fires. As the human population density increased along with their increasingly energy-intensive lifestyles, nanoparticles from the burning of fossil fuel, dust

from industrial processes, and fines exhausted into the environment from transportation also increased. Ultrafines and their negative impact were identified as far back as the mid-1970s with an appreciation of the particularly damaging effects of the smallest of these ultrafine particles. The PM-10, PM 2.5, and PM-1 program focus by the United States Environmental Protection Agency (USEPA) in the 1980s and 1990s did not quite encompass the nano regime, but that was mainly because of limitations in the available monitoring equipment at the time.

THE PRESENT

Interest in producing smaller-diameter textile fibers came about long before interest in engineered nanomaterials surfaced in recent years. The first microdenier fibers (denier <1) in the United States were spun in 1989 by the DuPont Company. Several ingenious textile techniques such as the spinning of bicomponent polymer fibers through islands-in-the-sea dies followed by extraction of the soluble component, melt-spinning of splittable bicomponents, and melt-blowing have since been used to obtain fibers with average diameters in the range of hundreds of nanometers (even sub-100 nm fibers have been claimed) and commercial fibers that are considerably finer than silk. Electrospinning, however, introduces a new level of versatility and a wider range of materials into the micro/nanofiber range. An old technology rediscovered, refined, and expanded into nontextile applications in recent years, electrospinning is unique among nanofiber fabrication techniques in terms of process control, materials combinations, and the potential for scale-up. This has led to it being recognized as a key platform technology that will yield products for a broad range of uses including electronics, drug delivery, chemical sensors, tissue scaffolding, filtration, and solid-state lighting applications.

This renaissance is partly a result of the availability of key tools such as scanning probe microscopy and high-resolution electron microscopy to enable facile exploration of the size-scale involved. However, it is mainly the rediscovery of the nanoscale nature of electrospun fiber and an appreciation of the unique behavior typical of nanomaterials that has spearheaded the resurgence of electrospinning. It is this same expectation that encourages research on nanofibers in nontextile uses (as the process is hardly cost competitive with conventional spinning in comfort-fiber applications) such as in sensors, scaffolds, and electronic devices. High-value applications, mainly biomedical applications, account for the majority of patents associated with the technology. A consideration in scaling up the process comprises the environmental and safety attributes of electrospinning.

With the solvent-electrospun mats (as opposed to the melt-electrospun fibers) having more controllable and finer morphologies, the environmental issues of scaled-up electrospinning in a textile setting can be as prohibitive as with conventional dry spinning. In nontextile applications, however, the volumes of material processed can be small by comparison and the same concerns can be better addressed. In filter applications, for instance, commercial electrospinning operations processing moderate volumes of nanofiber are already in commercial operation; for example, multiple-needle spin heads for pilot plant and scale-up operations are beginning to be advertised. The sole high-volume application for nanofibers at the present time is in the area of air filtration. With the present emphasis on homeland security, effective filtration is indeed a critical application.

Ultimately, however, the value of the technology lies in the smallest fiber diameters that can be fabricated and manipulated under practical conditions. Research literature claims 1–2 nm nanofibers electrospun from solution.[1] These, however, are very small samples, which can be imaged microscopically, but these cannot as yet be consistently electrospun as large homogeneous mats of fiber to be used in practical applications. The high degree of process and material control needed to fabricate these is not compatible with high-speed manufacturing environments. Yet, mats comprising nanofibers that are a few hundred nanometers in diameter and of consistent variability appear to be achievable even in large-scale electrospinning. With improvements in rapid characterization technologies for mats, more robust stable power supplies and tighter process control, innovative scale-up possibilities for the technology should definitely increase.

THE FUTURE

Future advancements in nanofiber technology will be fueled primarily by (1) improvements in electrospinning technology and process control to allow consistent production of nanofiber mats with single-digit fiber diameters, and (2) the potential to combine several physical, chemical, and biological functionalities into a single fiber to make multipurpose fiber mats and smart materials a reality. The functionalities considered need to move well beyond the simple passive effects of biocidal effectiveness (for instance by incorporating nanosilver), superhydrophobicity by surface

[1]Nanofibers that are only 1.6 nm diameter, electrospun from nylon-4,6 in 99% formic acid (2% nylon with 0.44% pyridine) have been reported (Huang, C. B., et al. 2006a). A 1.2-nm diameter cylinder theoretically accommodates only 6–7 nylon molecules!

texturing, or simple breathable biodegradable wound dressings. Future nanofibers are likely to deliver far more advanced multiple functionalities, and will likely be active devices that perhaps enable impressive disruptive technologies. These will include fabric-based computing/communications capabilities (integration of circuitry and transponders into nanofibers), disposable physiology/environment monitoring in apparel (disposable sensors, alarms, and on-demand countermeasures integrated into fabric), rapid physiological testing arrays (automated or on-demand bedside clinical testing), fibrous photovoltaic technologies (solar sails for space exploration and batteries in nanofiber geometry); they will also provide tunable highly efficient photo- and electroluminescent solid-state illumination. The enabling base technologies for all these are already on the horizon as far as material choices go, but design, integration, and productization has yet to be carried out. Refinements in electrospinning technology that will support these innovations broadly fall into two categories: innovations in process/materials and the recognition of new cross-disciplinary applications for electrospun materials.

Recent electrospinning of phospholipids, genetic materials, and biomimetic proteins into electrospun fibers, as well as the potential of nanofibers as controlled delivery vehicles for plasmid DNA or large protein drugs, and, autologous stem-cell scaffolding studies also suggest exciting directions for future advances. Recent fiber-level innovations include core–shell bicomponent fibers that can be used in drug delivery, nanoparticle-reinforced nanoscale fibers for composite applications, nanofibrous scaffolding for complex tissue replacement, and the development of inorganic oxide nanofibers for efficient sensors or catalysis. Also, the adoption of nanofibers as composites containing quantum dots, the fabrication of semiconductor "quantum fibers," the use of conducting polymer nanofibers with quantum confinement properties (see FET studies[2]), and nanowire circuitry show great future promise. A significant breakthrough that will overcome the limitations in temperature sensitivity and aging issues in organic polymers is the recent advancement in sol–gel spinning to yield inorganic nanofibers. Catalysis and some mechanical application often require the nanofibers to be exposed to high temperatures and solvents, which affect the organic polymer nanofibers.

As an integral and key component of the nanomaterials revolution, organic and inorganic nanofibers remain an increasingly versatile class of nanomaterials that promises to touch upon and improve different aspects of the

[2]The fabrication of an electrospun regio-regular poly(3-hexylthiophene-2,5-diyl) nanofiber-based field effect transistor (FET) was reported (González and Pinto 2005).

human condition, from the improvement human health to playing a key role in the drive for energy production.

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A. L. A.

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INTRODUCTION

Fueled by the promise of lucrative returns, nanotechnology has enjoyed unprecedented global research and development support over the last few years. Among the many facets of this unique technology, nanomaterials appear to be the first, albeit relatively low-technology, product to have reached commercialization. Nanomaterials enjoy the advantage of an existing sophisticated microscale technology for producing bulk micropowders, fibers, and thin film in enhancing their utility as high-performance smart materials in a myriad of applications. Their unusual physicochemical characteristics are primarily governed by their very high surface area to volume ratio (or the ratio of surface atoms to the interior atoms in the cluster). Material characteristics that determine catalysis, optical properties, certain mechanical properties, and even biological phenomena generally have a length scale in the 100 nm range. Nanomaterials can have very different geometries — they might be nanoparticles or clusters, nanolayers or nanofilms, nanowires, and nanodots. Building on existing robust fine-powder technology, nanoparticle materials have been among the first nanoscale products to be commercialized and are already creating a significant impact in diverse industries. These include their use in catalytic converters, oxides in sunscreens, nanoclay reinforcing fillers, abrasion-resistant oxides (e.g., alumina or zirconia-based oxides) coatings, ferrofluids, and conductive inks.

Furthermore, those materials that fall into the strict nano-regime (where one of their dimensions is <100 nm) may display unique and controllable

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properties governed by quantum constraint effects (He, J. H., et al. 2007b). For instance, nanoparticles of semiconductor CdSe behave as pseudo-atoms with molecular orbitals delocalized over the entire cluster. The associated quantized energy levels[1] allow these (quantum dots) to display, on excitation, well-defined size-dependent fluorescence emissions at visible wavelengths. The bandgaps of the semiconductor nanoparticles vary with particle size. As the particle sizes of the quantum dots vary from 2 nm to 6 nm, the emission wavelength changes from blue to red when excited at $\lambda = 290$ nm. Other properties such as the ionization potential, melting temperature, catalytic activity, glass transition temperature, magnetic susceptibility are all size-dependent properties of nanomaterials.

Nanofibers, especially organic nanofibers, constitute a particularly interesting and versatile class of one-dimensional (1-D) nanomaterial. The more exotic of the conventional textile fiber technologies include "microdenier fibers" (0.2–1.5 denier per filament), produced using multistep fabrication techniques such as melt spinning using "islands at sea" type extrusion dies. Further refinement of these textile industry techniques to obtain nanoscale fibers (that are several orders of magnitude smaller in diameter) is not practical, cost-effective, or scalable. Several techniques unrelated to electrospinning were reported in early literature for the laboratory preparation of nanofibers. Self-assembly of polymers under certain conditions and drawing of polymer melts can produce small samples of polymer nanofibers.

Electrostatic spinning or electrospinning, however, remains the most convenient and scalable technique for nanofiber production. The process has been successfully scaled up and is already used in the production of industrial products such as air filter media. Fibers with a diameter in the range $d = 50–900$ nm can readily be electrospun into mats; at $d \sim 50$ nm about 10,000 polymer chains, each up to a length of 100 μm, pass through the cross-section of the nanofiber (Reneker and Chun 1996). Electrospun nanofibers are orders of magnitude smaller in diameter compared to synthetic textile fibers and common natural fibers (Table 1.1). Electrospun nanofibers with diameters as small as 3–5 nm have been reported (Zhou et al. 2003); however, these cannot be generated consistently in quantity, even at the laboratory scale. The smallest of the nanofibers, with diameters of only several nanometers, can be selected for imaging from an ensemble of nanofibers electrospun usually from dilute solutions of a high-molecular-weight polymer under carefully controlled conditions.

[1]Small nanoparticles with quantized energy levels are sometimes referred to as "artificial atoms." Although there is no central nucleus holding the electrons, a parabolic potential well holds the electrons, which can move in a two-dimensional plane in the well.

TABLE 1.1 Comparison of natural and textile fibers

Fiber	Diameter (μm)	Coefficient of Variation (%)
Spider silk	3.57	14.8
Bombyx mori silk	12.9	24.8
Merino wool	25.5	25.6
Human hair	89.3	17.0
Cotton	10–27	2.5
Polyester	12–25	4–5
Nylon	16–24	3–6

1.1 HISTORICAL BACKGROUND

The first documented accounts of electrostatic spinning of a polymer solution into nanofibers were described in 1902 by J. F. Cooley and by W. J. Morton (see Table 1.2). Figure 1.1 shows Cooley's diagram of the electrospinning equipment as it appears in his 1902 U.S. patent # 692,631 (note that the

TABLE 1.2 Chronological development of electrospinning patents

Year	Persons	Description
1902	Cooley, J. F.	U.S. pat. # 692,631
1902	Morton, W. J.	U.S. pat. # 705,691
1903	Cooley, J. F.	U.S. pat. # 745,276
1934–1944	Formhals, A.	U.S. pat. #s 1,975,504; 2,077,373; 2,109,333; 2,116,942; 2,123,992; 2,158,415; 2,158,416; 2,160,962; 2,187,306; 2,323,025; 2,349,950
1929	Hagiwara, K.	U.S. pat. # 1,699,615
1936	Norton, C. L.	U.S. pat. # 2,048,651
1939	Gladding, E. K.	U.S. pat. # 2,168,027
1943	Manning, F. W.	U.S. pat. # 2,336,745
1966	Simons, H. L.	U.S. pat. # 3,280,229
1976	Simm, W., et al.	U.S. pat. # 3,944,258
1977/1978	Martin, G. E., et al.	U.S. pat. # 4,043,331; 4,044,404; 4,127,706
1978	Simm, W., et al.	U.S. pat. # 4,069,026
1980	Fine, J., et al.	U.S. pat. # 4,223,101
1980/1981	Guignard, C.	U.S. pat. # 4,230,650; 4,287,139
1982	Bornat, A.	U.S. pat. # 4,323,525
1985	How, T. V.	U.S. pat. # 4,552,707
1987	Bornat, A.	U.S. pat. # 4,689,186
1989	Martin, G. E., et al.	U.S. pat. # 4,878,908
1991	Berry, J. P.	U.S. pat. # 5,024,789
2000	Scardino, F. L. and Balonis, R. J.	U.S. pat. # 6,106,913
2004	Chu, B., et al.	U.S. pat. # 6,713,011

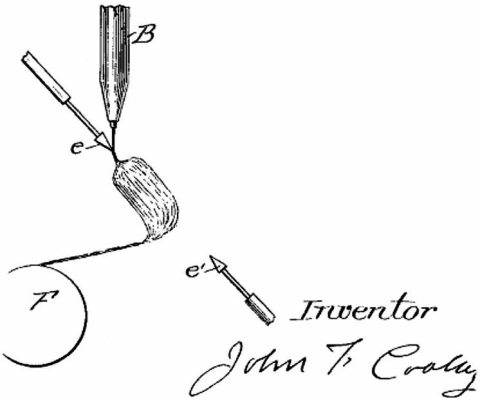

Figure 1.1 A solution of polymer (e.g., collodion or cellulose nitrate in ether or acetone) delivered into the high-voltage direct current (DC) electric field via tube *B* to form electrospun nanofibers collected on a drum *F*. (*Source*: Cooley 1902, Fig. 5 of U.S. patent 692, 631.)

static electricity generator connected to the electrodes is not shown).[2] These patents teach the deposition of a viscous polymer solution on a positively charged electrode (a roughened brass sphere) held close to an electrode of opposite charge to obtain electrostatic spinning. The spun fibers were collected as "a cob-web like mass" on the negatively charged electrode. The process was described as being the result of "electrical disruption of the fluid." A closely related patent issued a year later in 1903 to Cooley also addressed electrospinning. The claims in the latter patent included the introduction of the viscous polymer solution near the terminus of a charged electrode, but not necessarily in contact with it, to yield electrospun fibers. These early patents emphasize the need for the polymer solution to be of adequate viscosity and used, as a specific example, the electrospinning of nitrocellulose. Interestingly, the fundamental features of the process, as described in these century-old patents, have changed little with time.

Anton Formhals, a quarter century later in 1934, patented an improved version of the electrospinning process and apparatus. His first patents on electrospinning of cellulose acetate from acetone used a fiber collection system that could be moved, allowing some degree of fiber orientation during spinning. He recognized the importance of adequate drying of the fibers prior to the nanofibers being collected on a grounded surface. By 1944, he had filed four more patents on improved processes and claimed methods to electrospin even multi-component webs that contained more than one type of nanofiber.

[2]The first reported electrostatic spraying of a liquid was described by Jean-Antoine Nollet in 1750, long before the term electrospraying was even coined.

In 1936, C. L. Norton (see Table 1.2) used a plate collector electrode in conjunction with a static electricity generator in his design to provide a "transverse intermittent electromotive force" to improve fiber quality and collection.

Sir Geoffrey Taylor's contribution in the 1960s towards the fundamental understanding of the behavior of droplets placed in an electric field helped further develop the technique (Taylor 1964, 1969). In 1966, H. L. Simons (see Table 1.2) described the production of nonwoven nanofiber mats of a variety of thermoplastics including polycarbonate and polyurethane using metal grids to obtain a variety of patterned mats with uneven fiber density. His patent identifies viscosity, dielectric constant, conductivity, and volatility of the solvent as the key process parameters. His work explicitly identified the role of viscosity of the polymer solution in obtaining finer continuous fibers. Peter Baumgarten, working with an acrylic copolymer/dimethylformamide (DMF) system, described the dependence of fiber diameter on viscosity (and hence on concentration) of the solution as well as on the magnitude of the electric field (Baumgarten 1971). His experiment included a high-voltage power supply as well as a positive displacement pump.

Similar data for electrospinning polyolefins in the melt were reported by Larrondo and St. John Manley (1981a, 1981b, 1981c), with obtained fiber diameters being somewhat larger than those of solvent-spun nanofibers. Increasing the melt temperature and therefore decreasing melt viscosity resulted in smaller fiber diameters. Melt electrospinning can be an important approach, especially with common thermoplastics such as polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), and nylon (PA), which do not dissolve in common solvents (Dalton et al. 2006; Larrondo and St. John Manley 1981a, 1981b, 1981c; Lyons et al. 2004). Melt spinning, however, has to be carried out at high temperatures (usually $>200^{\circ}C$), requires larger electric fields (compared to electrospinning solutions), and is usually carried out in a vacuum.

Although this early work laid down the basic technique of electrostatic spinning, the present understanding of the process is mainly due to more recent work, especially that carried out within the last 10–15 years. Recent contributions towards understanding fluid dynamics (Hohman et al. 2001a, 2001b) and electrostatics (Shin et al. 2001a, 2001b; Spivak and Dzenis 1999) associated with electrospinning were fundamental to the resurgence of interest in the technique. Doshi and Reneker (1995), Jaeger et al. (1998) and Reneker et al. (2000) in the 1990s quantified the reduction in electrospun jet diameter as a function of distance away from the Taylor's cone for poly(ethylene oxide) (PEO) in water. In a systematic study, Doshi and Reneker (1995) established a viscosity window for successful electrospinning of PEO solutions (applicable of course to the particular average molecular

weight of polymer used). Hayati et al. (1987) recognized the relationship between the solution conductivity and the whipping instability (as well as the likelihood of electrospray behavior). Early attempts at electrospinning polymers were beset with experimental difficulties, the most important among them being "bead" formation. Deitzel et al. (2001a), as well as Doshi and Reneker (1995), studied bead formation in nanofibers, relating their frequency of occurrence to the applied voltage and recognizing the influence of the changes in shape of droplet with electric field in yielding beaded fibers.

Present-day laboratory electrospinning equipment is quite similar to that used in the approaches described above. The basic hardware components remain the same, especially in research electrospinning apparatus. However, the availability of more stable power supply units and pulse-free pumps to regulate the delivery of polymer solution to the charged electrodes now allows for better nanofiber quality. Minor modifications to the basic experimental setup have been described. Controlling the nonlinear whipping instability during electrospinning by modifying the geometry of the applied electric fields has been attempted. Warner et al. (1999) and others (Shin et al. 2001a, 2001b), for instance, claimed to improve the uniformity of the electric field by using a disc electrode of about the same diameter as the collector at the capillary tip resulting in a parallel-plate electrode design. Others have used a second ring electrode (Jaeger et al. 1998) or auxiliary plate electrodes to control and focus the electrospun fiber on the collector plate. Using a ring electrode at the same potential as the main electrode improved stability in the initial part of the jet (close to the droplet); however, the whipping instability, which occurs closer to the fiber collection region, was not substantially improved. Most of these innovations, however, can be traced back to aspects of the very early disclosures on the technique; auxiliary electrodes and rotating collectors, and solid tips were all featured in the very earliest patents on electrospinning. For example, several early patents such as U.S. patents # 4,043,331 (1977, Martin, G. E., et al.), # 4,127,706 (1978, Martin, G. E., et al.), # 4,878,908 (1989, Martin, G. E., et al.) and # 3,994,258 (1976, Simm, W., et al.) described rotating or moving-belt type collectors for the electrospun fiber mats.

The bulk of the reported early research on electrospinning focused on a limited number of polymer/solvent combinations. Naturally, these were the polymers that were easy to electrospin under laboratory conditions. These likely included those polymers that dissolved in common solvents that are "good solvents" for the polymer, where the chain-like polymer molecules adopt open, extended macromolecular conformations (as opposed to compact globular geometries) that allow adequate entanglement of polymer chains. With potential for future scale-up in mind, solvents that are both economical and also environmentally acceptable were preferred.

These considerations encouraged water-soluble polymers such as PEO to be popularly studied in early research on electrospinning. Only limited work on electrospinning of polymers such as polyamides was reported in the early literature because of the requirement for expensive and/or hazardous solvents (e.g., formic acid for nylon-6,6).

1.2 BASIC EXPERIMENTAL APPROACH

The minimum equipment requirements for demonstration of simple electrospinning in the laboratory are as follows:

1. A viscous polymer solution or a melt.
2. An electrode (hollow tubular or solid) that is maintained in contact with the polymer solution.
3. A high-voltage DC generator connected to the electrode.[3]
4. A grounded or oppositely charged surface to collect the nanofibers.

Figure 1.2 is a schematic representation of the equipment generally used in laboratory electrospinning of polymer solutions.

A simple experimental setup may consist of a glass pipette drawn into a capillary at one end, carrying a few milliliters of a viscous solution of a high polymer (for example a 20% w/w solution of polystyrene (PS) dissolved in methylene chloride). The viscosity of the solution is high enough to prevent it dripping from the vertical pipette under gravity. The tube is mounted vertically a few inches (6–10 inches) above a grounded metal (e.g., aluminum) plate or drum. A metal wire electrode that dips into the solution in the tube is connected to the positive terminal of a high-voltage DC power supply unit.[4]

The power is switched on and the voltage increased to 10–20 kV using the controls on the power supply. At a certain threshold voltage (depending on a number of factors to be discussed later), a droplet of the liquid is drawn out of the tube into a cone-shaped terminus and sprays downwards

[3] Alternating current (AC) potentials can also be used in electrospinning. He and colleagues developed a mathematical model for electrospinning using an AC potential (He and Gong 2003; He, J.-H., et al. 2005a). A comparison of PEO mats spun from DC and AC potentials showed the latter to suppress whipping of the jet and result in better alignment of the nanofibers (Kessick et al. 2004). The charge build-up on the collector is likely to be less of a problem with AC voltage compared to DC voltage.

[4] All that is needed is a strong enough electric field, not necessarily an electrode in contact with the polymer solution. Electrospinning an 8 wt% solution of poly(acrylonitrile) (PAN) in dimethylformamide (DMF) using ionized field charging with a noncontacting ring electrode was recently reported (Kalayci et al. 2005).

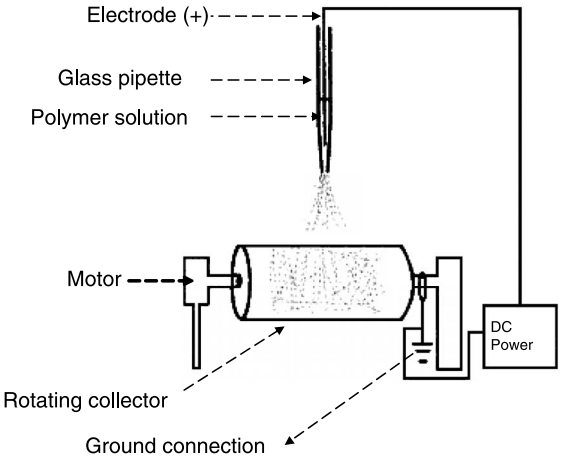

Figure 1.2 A schematic of a simple electrospinning experiment. Reprinted with permission from J.-S. Kim and Reneker (1999b). Copyright 1999. John Wiley & Sons.

as a jet towards the grounded plate as a barely visible nanoscale fiber. The high charge density on the surface of the fine jet leads to electrical instability of the electrospinning fiber, making it whip about rapidly. This splaying of the nanofiber often gives the appearance of a multiplicity of nanofibers being sprayed from the single droplet suspended from the capillary tip of the glass tube. High-speed photography, however, has demonstrated that, in general, a single nanofiber is spun out of the droplet, and its rapid movement generates the appearance of a multiplicity of fibers (Reneker et al. 2000). Consistent with this observation, one rarely observes fiber ends in high-resolution microscopic images of the nanofiber mats collected on the grounded surface. The mat is generally composed of a single long fiber arranged randomly on the collector surface. The solvent, which often accounts for more than 80% of the solution, evaporates rapidly from the surface of the spinning jet. It is desirable to select a solvent, gap distance, and temperature that would ensure that the electrospun fiber is completely dry by the time it reaches the grounded plate. Any residual surface charge on the nanofiber is rapidly dissipated on contact with the grounded metal plate, and the nanofiber mat can be peeled off it. Samples of nanofiber for microscopic examination are conveniently obtained by placing a sample collection stub over the grounded surface.

Shenoy et al. (2005a) pointed out the similarities between conventional pressure-driven dry spinning and electrospinning. Although both fiber-forming processes use polymer solutions and rely on rapid removal of the solvent to generate the fiber, the mechanisms responsible for the initial formation of the cylindrical fiber geometry and the subsequent "drawing" or thinning of the fiber are too different in the two processes to consider