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# Nanometre diameter fibres of polymer, produced by electrospinning

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**Abstract.** Electrospinning uses electrical forces to produce polymer fibres with nanometre-scale diameters. Electrospinning occurs when the electrical forces at the surface of a polymer solution or melt overcome the surface tension and cause an electrically charged jet to be ejected. When the jet dries or solidifies, an electrically charged fibre remains. This charged fibre can be directed or accelerated by electrical forces and then collected in sheets or other useful geometrical forms.

More than 20 polymers, including polyethylene oxide, nylon, polyimide, DNA, polyaramid, and polyaniline, have been electrospun in our laboratory. Most were spun from solution, although spinning from the melt in vacuum and air was also demonstrated. Electrospinning from polymer melts in a vacuum is advantageous because higher fields and higher temperatures can be used than in air.

#### 1. Introduction to nanofibres

Electrospinning provides a straightforward way to produce long polymer fibres with diameters in the range of 40–2000 nm. Expected improvements in the technique of electrospinning from liquid crystal or other disentangled systems may produce even thinner fibres.

The smallest polymer fibre must contain one polymer molecule. A typical polymer molecule has a diameter of a few tenths of a nanometre. Perhaps the record for the thinnest fibre known can be claimed by the recent discovery [1] of a way to make a chain of single carbon atoms. Oligomers of polyethylene, which have a diameter of around 0.4 nm, have been observed in single-layer crystal-like arrays of extended chains [2]. The DNA double helix has two backbone chains, with a diameter of around 2.5 nm. Optical fluorescence microscopy produces images of DNA molecules in a solution, and makes it possible to observe fibre-like properties such as the extension and transport of single molecules through a solution in response to external forces [3,4]. DNA chains can be spread on a substrate and observed by electron microscopy or scanning probe microscopy. Three collagen molecules twist around each other to form a triple helix fibre, and higher levels of organization of collagen occur to form tendons.

Synthetic fibres with diameters in the nanometre range have been overshadowed by the technological development of textile fibres during the past century. Polyoxymethylene polymerized in the solid state [5,6] forms crystal fibres of parallel extended molecules with diameters in the nanometre range. Mechanical deformation of polymer crystals often produces fibres which are observed in electron micrographs of fracture surfaces, for example. Such fibres typically have diameters of a few tens of nanometres and lengths up to a few micrometres.

Many images of polymer nanofibres exist in the literature [7–10] that deals with polymer morphology, but in almost all cases the nanofibres were observed incidentally to other features of the polymer. The ordered arrangements of molecules in the crystals eliminate entanglements and make it possible to convert the folded or extended chains in the crystals into smooth fibres by mechanical drawing. A process called crazing [11, 12] which occurs in glassy polymers such as polystyrene, involves the creation of fibres a few tens of nanometres in diameter with lengths up to a few micrometres.

A 50 nm diameter polymer fibre has about  $10\,000$  molecules crossing any section of the fibre. A typical polymer molecule in such a fibre has an extended length in the range of  $1{\text -}100~\mu\text{m}$ . The degree to which such long molecules are actually extended in a nanofibre depends on the way the fibre is prepared, for example the temperature, the number of entanglements, the draw ratio, and other parameters. About 3% of the polymer molecules in a 50 nm diameter fibre are on the surface of the fibre, if each molecule has a diameter of about  $0.5\,\text{nm}$ .

Commercial processes for manufacture of non-woven fabrics, which involve the expansion of a foam until most of the polymer is converted to fibres, produce large quantities of fibres with diameters around 100 nm mixed with non-fibre particles of a polymer. Experimental melt-blowing processes produce fibres with diameters in the range of 1–50  $\mu$ m [13, 14]. Particles of polytetrafluoroethylene from dispersion polymerization processes, that are pressed together, adhere to each other and small fibres are formed when the particles are pulled apart. Gentle scratching of the surface of moulded polytetrafluoroethylene with coarse sandpaper leaves many fibres with nanoscale diameters on the surface. A commercial process for making air filters by electrospinning has been described [15].

Conventional fibre spinning technology has been extended to produce a suede-like textile, which contains fibres with nanoscale diameters [16]. In this process, a mixture of two polymers which are mutually insoluble are made into a fibre by extrusion and drawing. One of the polymers forms long fibres in a matrix of the other. A cross sectional slice of such a fibre, suitably stained so that the two polymers can be distinguished, has an appearance that has been given the name 'islands in the sea'. The fibres are woven into a textile in the usual way, and then, to create the suede-like texture, the matrix polymer is removed to expose the thin fibres at the surface of the fabric.

Textile fibres, which utilize a significant fraction of all the synthetic polymer produced, are extruded through a spinnerette, elongated by mechanically stretching, subjected to various treatments, and wound on spools for weaving, or handled in a variety of other ways. The smallest fibres that are made by such processes have diameters of 2  $\mu$ m and the largest are around 20  $\mu$ m. Larger diameter fibres made from polymers are also useful and commercially important. They are generally referred to as monofilament, bristles, or rods.

### 1.1. Introduction to electrospinning

The electrospinning process is driven by the electrical forces on free charges on the surface or inside a polymeric liquid. In conventional spinning, the fibre is subject to tensile, rheological, gravitational, inertial, and aerodynamic forces. The action of these forces has been described by Ziabicki [17]. In electrospinning the tensile force is generated by the interaction of an applied electric field with the electrical charge carried by the jet rather than by the spindles and reels used in conventional spinning. Electrical forces in non-axial directions are also important.

When the free charges in the liquid polymer, which are generally ions, move in response to the electric field, they quickly transfer a force to the polymer liquid. The drift velocity of charge carriers through a material is given by the product of the electric field and a parameter called the mobility of the carriers. For the electric fields of around 105 V m<sup>-1</sup> encountered within the polymer jet in electrospinning, the drift velocity of the ions is estimated to be around 0.15 m s<sup>-1</sup> which is much slower than most regions of the jet move. This estimate is based on the observation that charge carriers such as sodium ions in water and water solutions of polyethylene oxide have a mobility of around  $1.5 \times 10^{-7}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Most charge carriers in organic solvents or polymer melts have even lower mobilities. This low mobility creates the interesting situation that charge can move through the liquid for significant distances if enough time is allowed, for example near the base where distances are short and the liquid velocity is low. In places where the polymer is moving at velocities much higher than the drift velocity of the charge, as occurs in the stable jet, the charge moves with the surrounding molecules.

The behaviour of electrically driven liquid jets, and a closely related topic, the stability of electrically charged liquid drops, have been of interest for many years. Bose

[18], in 1745, created an aerosol spray by applying a high potential to a liquid at the end of a glass capillary tube. Lord Rayleigh [19] calculated the maximum amount of charge which a drop of liquid can hold before the electrical forces overcome the surface tension of the drop. Zeleny [20] described and photographed electrospraying phenomena in 1917. Taylor [21] analysed conditions at the point of a droplet that is deformed by an electric field and showed that a conical interface between two fluids is stable if the cone has a semi-angle of 49.3°. Bailey [22] reviewed the electrostatic atomization of liquids, with emphasis on the practical applications, noting that, in many cases, atomization follows from the formation a jet of liquid which then disintegrates into charged droplets. Roth and Kelly [23] described the disruption of a charged, evaporating droplet into a number of smaller droplets which carried away about 5% of the mass and about 25% of the charge.

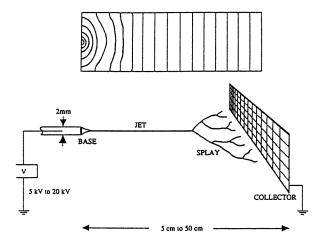
An early patent on electrospinning of polymer fibres was issued to Formhals [24] in 1934, and about 50 other patents on electrospinning processes were found. The electrostatic spinning of acrylic microfibres was described in 1971 by Baumgarten [25]. Fibres with diameters ranging from 500–1100 nm were produced. Larrondo and Manley [26–28] demonstrated the electrospinning of polyethylene and polypropylene fibres from the melt in air. The fibres they obtained had large diameters. The experimental approach used in our laboratory [29, 30] is simple and straightforward. Chun [31] electrospun nanoscale fibres of polyethylene, polypropylene, and polyester from the melt in a vacuum.

#### 1.2. The stable electrospinning jet

A stable electrospinning jet has four distinct regions (see figure 1). The jet emerges from the charged surface at the base region, travels through the jet region, divides into many fibres in the splaying region, and stops in the collection region.

The base is the region where the jet emerges from the liquid polymer. The geometry of the jet, near the base, is a tapered cone in which the axial velocity of the liquid increases as the polymer is accelerated along the axis of the jet. The base may have circular cross sections, or it may have some other shape if surface tension of the liquid anchors the jet to the lip of a hole or some other stationary object. An electric field at the surface of a liquid produces a force that, if the electric field is strong enough, a jet of liquid can be ejected from a surface that was essentially flat before the field was applied.

The electrical charging of the jet occurs in the vicinity of the base. The electrical conductivity of typical molten polymers is large enough to supply the small currents that are required for electrospinning, if the electrode in the melt is close to the base of the jet. Solutions have higher conductivity and form jets readily. It is useful to assume that the charge density in the jet is equal to the charge that flows onto a conducting sphere with a diameter equal to the diameter of the jet, divided by the volume of the sphere. The low mobility of the charge carriers prevents them from flowing a significant distance through the liquid polymer



**Figure 1.** Diagram of an electrospinning apparatus. A polymer solution in a capillary pipette is charged to a high electrical potential. A liquid jet issues from the liquid surface at the tip of the pipette. As the jet stretches and dries, radial electrical forces cause it to splay repeatedly. The dried, solidified fibres are collected on an electrically conducting screen. The diagram at the top shows the equipotential lines in a plane that contains the jet. The electric field vectors, which determine the direction of the electrical forces, are perpendicular to the equipotential lines.

while the jet carries the volume element under consideration to the collector. A nearly equivalent estimate is that the charge per unit area on the surface of a cylindrical element, with length equal to the diameter of the jet, adjacent to the base of the jet is the same as the charge per unit area on a flat surface at the base.

The jet is the region beyond the base where the electrical forces continue to accelerate the polymer liquid and to stretch the jet. In this region, the diameter of the jet decreases and the length increases in a way that keeps constant the amount of mass per unit time passing any point on the axis. A stable electrospinning jet travels from a polymer solution or melt to a collector, for example, a metal screen. The jet is driven by a high electrical potential applied between the solution or melt and the collector. Electrical charges, usually in the form of ions, tend to move in response to the electrical field that is associated with the potential. The charges, which have drift velocities through the liquid polymer that are smaller than the velocity of the jet along its axis, transfer the forces from the electric field to the polymer mass. The electrical forces which stretch the fibre are resisted by the elongational viscosity of the

The acceleration of the polymer in the jet is mediated by the transfer of the forces through the viscoelastic jet, in which the viscoelastic parameters are changing at the same time, as the solvent evaporates from the jet and the temperature of the jet changes. The charges in the jet carry the liquid polymer in which the charge is embedded in the direction of the electric field. This is the mechanism which moves charge from the reservoir of liquid polymer to the collector, and thereby completes an electrical circuit which provides the energy needed to accelerate the polymer, to increase its surface area, and to drive the flow and

deformation processes which change the shape of the liquid into a jet.

If the polymer is in the form of a solution in which the solvent has a high vapour pressure, evaporation of the solvent from the jet may reduce the mass flow velocity. The taper of the jet is also affected by solvent evaporation, since loss of the solvent can have a large effect on the viscoelasticity of the liquid polymer.

The best estimates of the jet velocity come from measurements of the mass of the fibres that are collected in a known time interval, the diameter of the jet, and the concentration of the solution. These observations are limited to jets large enough to measure with a relatively low power optical microscope with a working distance that keeps it far enough from the jet that the electric fields near the jet are not changed by the presence of the microscope. Such measurements of jet velocity yield values of the order of  $10 \text{ m s}^{-1}$ .

Splaying occurs in a region in which the radial forces from the electrical charges carried by the jet become larger than the cohesive forces within the jet, and the single jet divides into many charged jets with approximately equal diameters and charge per unit length.

As the jet progresses from the base toward the collector, the forces from the external electric field accelerate and stretch the jet. Stretching and evaporation of the solvent molecules cause the jet diameter to become smaller. The charge on the fibre tends to expand the jet in the radial directions and to stretch it in the axial direction. As the radius of the jet becomes smaller, the radial forces from the charge can become large enough to overcome the cohesive forces of the fibre and cause it to split into two or more fibres, that is to splay. This jet division process occurs several more times in rapid succession and produces a large number of small electrically charged fibres moving toward the collector.

The divided jets repel each other, thereby acquiring lateral velocities and chaotic trajectories, which gives a bush-like appearance in the region beyond the point at which the jet first splays. Splaying converts a single jet into many much thinner jets. Thin fibres can also be created by elongating a single jet if splaying does not occur. Splaying and elongation appear to occur simultaneously in many cases.

Measurements of the longitudinal fracture behaviour of polymers and elastomers [32] indicate that the surface tension of the jet is a minor component of the fracture surface energy which must be supplied for a fibre to split. Fracture surface energy is a term used to describe the total energy utilized to create a unit area of new surface.

The *collection* region is where the jet is stopped. The polymer fibre that remains after the solvent evaporates may be collected on a metal screen. For polymers dissolved in non-volatile solvents, water or other appropriate liquids can be used to collect the jet, remove the solvent, and coagulate the polymer fibre. Mechanical reels or aerodynamic currents can also be used for collection. If the jet arrives with a high velocity at a stationary collector, the jet tends to coil or fold. Since the jet is charged, a fibre lying on the collector tends to repel fibres that arrive later. The amount

of charge on the fibres can be changed by ions created in a corona discharge and carried to the collection region by air currents. The charge may also be removed by charge migration through the fibre to the conducting substrate, although for dry fibres with low electrical conductivity, this charge migration may be quite slow.

#### 1.3. Initiation of the jet

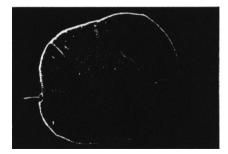
The initiation and formation of the jet is a complex and interesting process with many variations. In electrospinning, initiation is less important than the maintenance of a stable jet, but it is an essential step which deserves separate attention. Much of the literature on electrically driven jets has concentrated on the initiation processes that transform a liquid surface into a jet.

Observations of many single jets show that the surface of the liquid near the base may start as a nearly flat surface across the open tip of the pipette. When a high potential is applied to the liquid in the pipette, the surface is pulled into the approximate shape of a section of a sphere by the electrical forces and surface tension if the base is held as a circle by the lip of the pipette. As this bulge forms, charges move through the liquid and concentrate on the part of the surface that is protruding most. The accumulation of the charge causes the surface to protrude more, and since the charge per unit area is highest near the greatest protrusion, the surface is pulled into a conical shape that was described mathematically by Taylor [33] and often referred to as a Taylor cone. The charge per unit area at the tip of the cone becomes even higher as the radius near the tip of the cone decreases. As the potential is increased, a jet of liquid is pulled from the tip, and electrospinning begins.

As the jet is established, the base of the jet often becomes flatter. The jet may issue from the relatively flat liquid surface at the tip of the pipette, or the base of the jet may move to and become anchored at some point on the perimeter of the tip, in which case spinning can continue even as the meniscus moves inside the capillary.

Sometimes a jet with a base diameter much smaller than that of the tip of the pipette forms without the formation of a Taylor cone. A jet may be established when material is pulled off the liquid surface, for example, after the liquid is touched by an insulating rod, when the rod is pulled away. Jets are sometimes established when a droplet is pulled away from the tip by the electric field and gravity working together.

After the jet is established, force from the interaction of charge with the electric field is transmitted to the base region by the viscous flow and viscoelasticity of the liquid in the jet, as well as by the surface tension. The base region stablizes at a size and shape that is determined by these flow processes and by the rate at which liquid is supplied to the tip. The shape of the base region adjusts to carry charge and mass away from the tip of the pipette at an equilibrium rate. Flow patterns in the base, and parameters such as elongational flow and time dependent elasticity of the liquid affect the diameter and shape of the base.



**Figure 2.** Electrospun polyester fibres collected on a wire frame with a diameter of approximately 15 cm.

#### 2. Example: electrospinning of polyester fibres

The electrospinning of thin fibres of polyethylene terephthalate provides an example of the electrospinning process. More details are in Chun's thesis, which was referred to earlier. The polymer had a molecular weight in the range of 10 000–20 000 g mol<sup>-1</sup> and was of the sort used for spinning textile fibres. The polymer was dissolved in an equal mixture of dichloromethane and trifluoroacetic acid at a concentration of around 4%. Care was taken to avoid contact with the trifluoroacetic acid or inhalation of its vapours. The solution was held in a glass pipette. Spinning occured from the droplet of solution protruding from the 1 mm internal diameter of the tip of the pipette. Electrical contact with the solution was made with a metal wire inserted into the large end of the pipette.

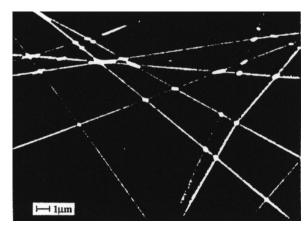
The fibres were collected on a metal frame about 15 cm across shown in figure 2.

The frame was held about 100 cm from the tip. With a potential of 15000 V between the tip and the collector, the electric field in the region near the collector was 150 kV m $^{-1}$ . The electric field at the tip was significantly higher, due to its point-like geometry, but its exact value depends upon details of the shape of the liquid surface which were not measured. The current carried by a typical jet was around 1  $\mu$ A. The high-voltage power supplies used were capable of delivering only 160  $\mu$ A of current, so, although sparks up to a centimetre long and capable of igniting flammable liquids sometimes occurred, the apparatus presented no serious electrical hazards to personnel.

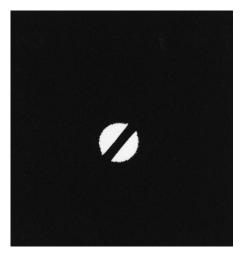
Scanning electron micrographs of the fibres that were produced are shown in figure 3.

The fibres were cylindrical with a diameters of around 300 nm. The diameter of the jet near the base was estimated to be about 10  $\mu$ m. Evaporation of the solvent from a 10  $\mu$ m diameter jet of the 4% solution would leave a fibre with a diameter of about 2  $\mu$ m. To produce the 300 nm fibres observed, the drying jet both splayed and stretched as it approached the collector. Either about five successive splays into two fibres, or elongation of the fibre by a factor of about 1000 would account for the observed reduction in diameter. Both splaying and stretching occurred, so the amount of either was less than if it were acting alone.

The 300 nm fibres were thin enough that the 100 kV beam of a transmission electron microscope penetrated the fibres, and electron diffraction patterns such as that



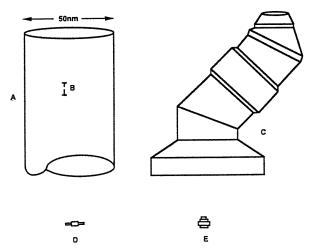
**Figure 3.** Electospun polyester fibres. The mechanical attachment of the fibres to each other at crossing points indicate that the fibres were not completely dry when collected.



**Figure 4.** Electron diffraction pattern from an electrospun polyester fibre similar to those shown in figure 3. The short arcs on the equatorial spot indicate that the polyester molecules were highly oriented along the fibre axis. The fibre was vertical in the plane of the figure. The dark bar across the centre of the pattern is the shadow of a beam stop.

shown in figure 4 were obtained. The diffraction spots on the equator show that the polyethylene terephthlate molecules were aligned along the axis of the fibre. The intermolecular spacings of the molecules ( $d_{010}$  on the meridian equals 0.509 nm, and on the equator,  $d_{\bar{1}10}$  equals 0.393 nm,  $d_{100}$  equals 0.350 nm) which were determined from the diffraction pattern are in close agreement with the intermolecular spacings in larger polyethylene terephthalate fibres which were observed by x-ray diffraction [34].

A model that connects parameters of the jet was made in Chun's thesis, which was referred to earlier. The charge per unit volume at the base of the jet was assumed to be equal to the charge on a sphere of the same diameter as the jet divided by the volume of the sphere. The charge per unit volume was assumed to be conserved. It was assumed that the jet tapers as a cone, splaying was ignored and a range of maximum velocities that the jet might achieve was



**Figure 5.** A. A section of a polymer nanofibre. B. A molecular mechanism that can rotate and translate a polymer molecule as the mechanism moves along the molecule. C. A molecular manipulator that contains 4 million atoms (without the base). D. A bearing made of graphite cylinders for which molecular dynamics calculations have been made. E. A planetary gear made with molecular scale parts.

examined. It was also assumed that the mass and volume of the jet are conserved, that is, evaporation of the solvent was ignored. The diameter of the jet at the base, the diameter at the collector, the mass flow rate, and the charge per unit volume in the base region were specified, as was the velocity of the jet as it arrived at the collector.

For a single, stable jet of polyethylene oxide in water, in an apparatus with 100 cm between the base and the collector, and an applied voltage of around 10 kV, the measured current was around 1  $\mu$ A. The calculated currents carried by a single jet of a 4% solution of polyethylene oxide in water, with a base diameter of 50  $\mu$ m, tapering to a 1  $\mu$ m diameter at the collector, were in the range of 0.1–1  $\mu$ A for average electric fields of 100–250 kV m<sup>-1</sup>, and mass flow rates of 10–50 ng s<sup>-1</sup>, corresponding to velocities at the collector in the range of 10–50 m s<sup>-1</sup>. If splaying occurred, a much lower arrival velocity would be required.

# 2.1. Electrospun nanofibres and nanomachines

Electrospinning makes it relatively easy to spin continuous nanofibres from many different polymers. Here we will deal with potential uses of nanofibres in molecular nanotechnology.

Nanofibres provide a connection between the nanoscale world and the macroscale world, since the diameters are in the nanometre range and the lengths are kilometres. Nanoscale machines will need familiar structural elements. Rods with uniform cross section are widely used in structural design as columns, beams, and cables to maintain tension, and others will be required in many nanoscale structures. Nanoscale wires, ropes, and fabrics have many uses. Belts for transmitting material, force, and charge are also likely to be useful.

An electrospun fibre with a diameter of around 50 nm fits quite nicely into the world of nanomachines. Figure 5 shows a 100 nm length of a polymer nanofibre surrounded by some diagrams of nanomechanisms which have been published. The fibre is about the same diameter as the molecular manipulator (stiff arm design) and about ten times the linear dimensions of a planetary gear designed with molecular scale parts by Drexler [35]. The diameter of the nanofibre shown is about ten times the linear dimensions of a bearing made of cylinders of single layers of graphite modelled by molecular dynamics [36, 37].

The fibre may contain internal mechanisms, such as those described for crystalline polyethylene [38, 39] which can be integrated into nanoscale machinery. Fibres of crystalline polymers contain nanoscale mechanisms which can be predicted and analysed in terms of crystal defects most familiar in metals and inorganic crystals, because these polymers have translational and other kinds of crystallographic symmetry. Defects in the structure and symmetry of the crystal can move within the crystal, and couple to strain fields in the crystal. These defects are, in fact, nanoscale mechanisms that rotate and translate single polymer molecules in a translationally symmetric matrix as the defect travels along the molecule. Polymer crystals are host to a great variety of such nanomechanisms that are potentially useful to designers of nanomechanical devices and systems.

The length of the longest electrospun fibres produced in our laboratory is estimated to be many kilometres. The length is limited by parameters such as the supply of liquid polymer and the time required for the fibre to be spun. Only the transverse dimensions are in the nanometre range. The use of nanofibres as a support for linear arrays of nanomachines is a natural direction for development. Polymer nanofibres are nearly transparent to the electron beam in most transmission electron microscopes, so it is straightforward to observe, at high magnification, arrays of nanomachines attached to a nanofibre. Atomic force microscopy provides a convenient method to measure the diameter of small fibres, and to observe their surface morphology.

Conducting polymers, that are doped with ions to achieve the necessary concentrations of electronic charge carriers, swell when ions are added, and shrink when the ions are removed. The stresses, created by the addition or removal of ions in a process reminiscent of electrode reactions in an electrochemical cell, are very large and have already been demonstrated to be large [40]. Small electrospun fibres of electrically conducting polymers can integrate these forces over their length. The small diameter of the fibres makes it possible for ions to move between the fibres and the surrounding electrolyte in short times, so electromechanical devices that are both powerful and fast can be designed and constructed with nanofibres. Electrical conductivity [41], colour, and rubber elasticity are examples of phenomena in which ions or molecules can produce dramatic changes in polymer properties.

In the high vacuum of space, much higher electrical fields can be attained, so electrospinning becomes capable of creating and handling fibres and yarns with diameters familiar in the textile industry. Electrospinning may be the most economical way to create filaments to carry tensile loads and fabrics for large space structures. It is feasible to design, for production and use in space, a non-woven 'fabric' less than 1000 nm thick that is an interesting candidate for a solar sail.

It is feasible to electrospin one fibre for a special function in a larger system. Some insect larvae use this strategy by spinning a fibre after they emerge from the egg. The fibre carries a larvae on air currents to a location where it can find food. Arrays of nanomachines attached to nanofibres could be dispersed in a similar way.

One interesting aspect of using electrospun fibres is that they are electrostatically charged and can be manipulated by electrical fields. The fibres that are produced by electrospinning are electrically charged. As a result, electrospun fibres can be guided by electrical fields. Weaving, braiding, interlacing, coiling, and similar operations can be performed by using electrical forces, both on fibres of the sort now used in textiles, and on the thinner fibres that can only be made by electrospinning. Thin fibres can be guided electrically in much more straightforward ways than they can by mechanical means. The charge can be removed, when it is not wanted, by exposure to ions carried in air. If the fibres are electrically conducting, the charge can also be adjusted by conduction through the fibre.

# 2.2. The versatility of electrospinning

Many polymers have been spun into thin fibres by electrospinning in our laboratory. Some examples are given in table 1.

# 2.3. Summary and conclusions

Electrospinning provides a straightforward and practical way to produce polymer fibres with diameters ranging from 40–2000 nm. These small fibres can support arrays of nanomachines, and connect integrated arrays of nanomachines to larger scale systems. The ability to examine, with the transmission electron microscope and with the techniques of electron diffraction, nanoscale machines attached to the fibres will provide useful ways for using and observing nanomachines. Nanoscale fibres also contain special arrangements of polymer molecules, often called crystallographic defects, which can themselves function as nanomachines to translate and rotate polymer A nanomachine attached at some point along a polymer molecule can communicate with another nanomachine by the movement of such crystallographic defects between the two machines. Fibres in the nanometre diameter range, which have been largely overshadowed by the development of larger diameter synthetic textile fibres, are likely to find many new applications.

# Acknowledgments

Support from the Edison Polymer Innovation Corporation (EPIC), the National Science Foundation, and the US Army Research Office is greatly appreciated.

Table 1.

| Polymer class                   | Polymer  | Solvent   |
|---------------------------------|--|---|
| High performance Polymers       | Polymides<br>Polyamic acid<br>Polyetherimide                                     | Phenol m-cresol Methylene chloride  |
| Liquid crystalline polymers     | Polyaramid Poly-gamma-benyzyl- glumate Poly( <i>p</i> -phenylene terephthalamide | Sulphuric acid<br>Dimethylformamide<br>Sulphuric acid   |
| Copolymers                      | Nylon 6-Polyimide  | Formic acid   |
| Textile fibre polymers          | Polyacrylonitrile Polyethylene terephthalate Nylon                               | Dimethylformamide<br>Trifluoroacetic acid<br>and dichloromethane<br>Melt in vacuum<br>Formic acid |
| Electrically conducting polymer | Polyaniline  | Sulphuric acid  |
| Biopolymers                     | DNA<br>Polyhydroxybutyrate-<br>valerate  | Water<br>Chloroform   |

#### References

- [1] Rinzler A G, Hafner J H, Nikolaev P, Lou L, Kim S G, Tománek D, Nordlander P, Colbert D T and Smalley R E 1995 Unraveling nanotubes: field emission from an atomic wire *Science* 269 1550–3
- [2] Hentschke R, Schürmann B L and Rabe J P 1992 Molecular dynamics simulations of ordered alkane chains physisorbed on graphite J. Chem. Phys. 96 6213–21
- [3] Perkins T T, Smith D E and Chu S 1994 Direct observation of tube-like motion of a single polymer chain Science 264 819–22
- [4] Perkins T T, Quake S R, Smith D E and Chu S 1994 Relaxation of a single DNA molecule observed by optical microscopy Science 264 822–5
- [5] Colson J P and Reneker D H 1970 Polyoxymethylene crystals grown within irradiated trioxane crystals J. Appl. Phys. 41 4296–312
- [6] Reneker D H and Colson J P 1971 Annealing and melting of polyoxymethylene crystals polymerized within irradiated trioxane crystals J. Appl. Phys. 42 4606–14
- [7] Geil P H 1963 *Polymer Single Crystals* (New York: Interscience)
- [8] Sawyer L C and Grubb D T 1987 *Polymer Microscopy* (New York: Chapman and Hall)
- [9] Bassett D C 1981 *Principles of Polymer Morphology* (Cambridge: Cambridge University Press)
- [10] Wunderlich B 1973 Crystal structure, morphology, defects Macromolecular Physics vol 1 (New York: Academic)
- [11] Berger L L and Kramer E J 1987 Chain disentanglement during high-temperature crazing of polystyrene Macromolecules 20 1980–5
- [12] Yang A C-M, Kramer E J, Kuo C C and Phoenix S L 1986 Craze fibril stability and breakdown in polystyrene Macromolecules 19 2010–19
- [13] Kayser J C and Shambaugh R L 1990 The manufacture of continuous polymeric filaments by the melt-blowing process *Polymer Sci. Eng.* 30 1237–51
- [14] Lee Y and Wadsworth L C 1990 Structure and filtration

- properties of melt blown polypropylene webs *Polymer Sci. Eng.* **30** 1413–19
- [15] Jacobsen M 1991 The nonwovens industry meets the filtration business *Nonwovens Industry* May 36–41; See also: 1989 Chemiefasern/Textilindustrie 39./91. 868
- [16] Baker W R 1992 Microdenier spinning *Int. Fibre J.* April 7–15
- [17] Ziabicki A 1976 Fundamentals of Fibre Formation (New York: Wiley–Interscience)
- [18] Bose G M 1745 Recherches sur la cause et sur la veritable theorie del'electricite (Wittenberg)
- [19] Lord Rayleigh 1882 On the equilibrium of liquid conducting masses charged with electricity *London*, *Edinburgh*, and *Dublin Phil. Mag. J.* 44 184–6
- [20] Zeleny J 1917 Instability of electrified liquid surfaces *Phys. Rev.* 10 1
- [21] Taylor G 1964 Disintegration of water drops in an electric field Proc. R. Soc. A 280 383–97
- [22] Bailey A G 1988 Electrostatic Spraying of Liquids (New York: Wiley)
- [23] Roth D G and Kelly A G 1983 Analysis of the disruption of evaporating charged droplets *IEEE Trans. Ind. Appl.* IA-19 771–5
- [24] Formhals A 1934 Process and apparatus for preparing artificial threads *US Patent 1,975,504*
- [25] Baumgarten P K 1971 Electrostatic spinning of acrylic microfibres J. Colloid Interface Sci. 36 71–9
- [26] Larrondo L and Manley R St J 1981 Electrostatic fibre spinning from polymer melts. I. experimental observations on fibre formation and properties J. Polymer Sci.: Polymer Phys. Edn 19 909–19
- [27] Larrondo L and Manley R St J 1981 Electrostatic fibre spinning from polymer melts. II. examination of the flow field in an electrically driven jet J. Polymer Sci.: Polymer Phys. Edn 19 921–32
- [28] Larrondo L and Manley R St J 1981 Electrostatic fibre spinning from polymer melts. III. electrostatic deformation of a pendant drop of polymer melt J. Polymer Sci.: Polymer Phys. Edn 19 933–40
- [29] Doshi J and Reneker D H 1993 Electrospinning process

- and applications of electrospun fibres *Proc. IEEE Industry Applications Society Meeting Part 3, October 3–8 1993* pp 1698–703
- [30] Doshi J, Srinivasan G and Reneker D H 1995 A novel electrospinning process *Polymer News* 20 206–13
- [31] Chun I 1995 Fine fibres spun by electrospinning process from polymer solutions and polymer melts *Dissertation* The University of Akron
- [32] Cherry B W 1981 *Polymer Surfaces* (Cambridge: Cambridge University Press) ch 4
- [33] Taylor G 1964 Disintegration of water drops in an electric field Proc. R. Soc. A 280 383
- [34] Daubney R P, Bunn C W and Brown C J 1954 Proc. R. Soc. A 226 531
- [35] Drexler K E 1992 Nanosystems: Molecular Machinery, Manufacturing and Computation (New York: Wiley–Interscience) pp 311–12 and 398–403

- [36] Tuzun R E, Noid D W and Sumpter B G 1995 The dynamics of molecular bearings *Nanotechnology* 6 64–74
- [37] Tuzun R E, Noid D W and Sumpter B G 1995 Dynamics of a laser driven molecular motor *Nanotechnology* 6 52–63
- [38] Reneker D H and Mazur J 1988 Small defects in crystalline polyethylene *Polymer* **29** 3–13
- [39] Reneker D H and Mazur J 1990 Crystallographic defects in polymers and what they do Computer Simulation of Polymers ed J Roe (Englewoods Cliffs, NJ: Prentice-Hall) ch 23, pp 332–40
- [40] Smela E, Inganäs O and Lundström I 1995 Controlled folding of micrometer-size structures Science 268 1735–8
- [41] Gokul Srinivasan and Reneker D H 1995 Structure and morphology of small diameter electrospun aramid fibres Polymer Inter. 36 195–201