CHAPTER 1

Introduction

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1.1 Polymer Fibres

The generation of materials with elongation in the form of fibres is a commercially important aspect of polymer science. The act of stretching a macromolecular system into a fibre orients the polymer chains and increases intermolecular interactions; thus, while the diameter of a fibre is much reduced by the drawing process, this is offset by the increased modulus of the fibres which can produce some of the strongest materials known. For example, weight for weight, spider silk is 5 times as strong as steel; many of the applications of nylon rely on the strength provided by the structures that develop on drawing; and another polyamide, Kevlar is well known for its high strength induced by virtue of the hydrogen bonding and phase structure. Less obviously, polyethylene can be made into an ultra-high strength material by drawing.[1]

Fibres are involved in a number of products, most notably textiles, but also in applications as diverse as paper and tyre cord. Fibres also play a crucial role in biology, with materials such as cellulose forming fibrils which provide much-needed strength to plant walls or, on the negative side, the development of amyloid fibrils has been linked with a range of human diseases (Figure 1.1(a)).[2] In a commercial or laboratory setting the process of fibre formation can be done in a number of ways, but all rely on the polymer

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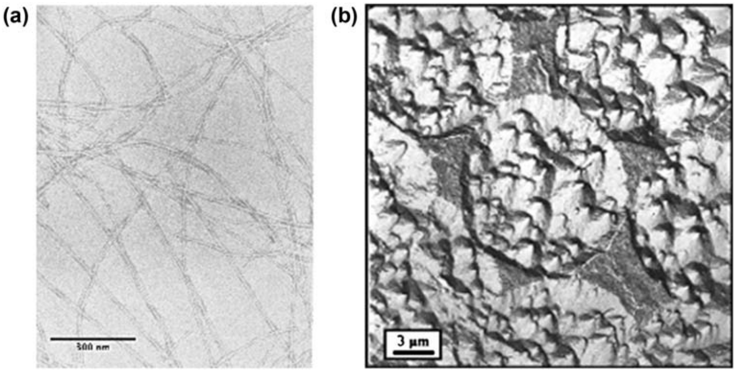

Figure 1.1 (a): Amyloid fibrils formed from the peptide sequence YTIAALLSPYSGGRADS. Reproduced from ref. 2. (b): Internal morphology of a composite based on high strength polyethylene fibres. From ref. 3. (Photo provided by R. H. Olley.)

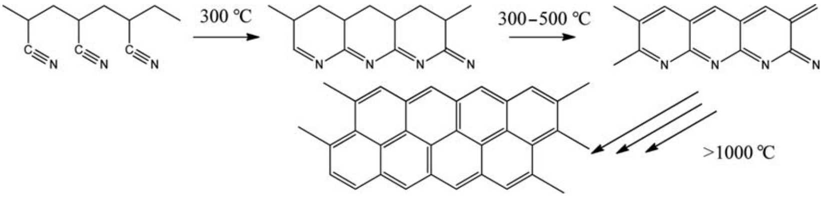

Figure 1.2 Thermal degradation of polyacrylonitrile, leading to the generation of carbon fibres.

initially being present in a molten or a solution state. The production of fibres from synthetic polymers is a major industrial activity. In a typical process to produce a textile fibre, the polymer is passed through a spinneret, and then elongated by the application of a mechanical force. This process requires, firstly, that the polymer is able to flow prior to processing, *i.e.* it must be in a molten or a solution state; secondly, that the material solidifies in the region post spinning. For melt spinning the requirement is simply one of reducing the temperature; for solution spinning the solvent must be removed by evaporation (known as dry spinning) or by precipitation into a solvent bath (termed wet spinning).[4] Many commercial applications require post processing, for example, in the viscose process cellulose is modified to produce a processable material and subsequently regenerated in sulphuric acid post processing.[5] Famously, carbon fibres are generated from thermal treatment of polyacrylonitrile in a process involving cyclisation, as shown in Figure 1.2.[6]

In general, spinning processes such as those described above result typically in threads with diameters between 1 and 20 µm.[†] Recently, interest

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[†] Typically, the fineness of fibres is denoted by the denier number, which is the mass of material in grams needed to produce 9000 metres for a polyester sample with a density of 1.4 g cm^{-3} the diameter of approximately 10 µm results in ~1 g of material required.

in developing materials at the nanoscale has resulted in a surge of activity in the production of fibres with submicron diameters. Whilst such materials are largely inaccessible to melt spinning, there are alternative processes such as melt blowing, which are clearly capable of producing fibres with diameters smaller than 500 nm.[7] The possibility of such top-down methods of producing nanofibres has attracted huge interest in such technology[8] and, in particular, the technique which is the focus of this book: electrospinning, a techniques that produce fibres with diameters ranging from a few microns to a few nanometres.[9]

1.2 Principles of Electrospinning

In electrospinning, an electrostatic force produced by a high voltage supply is used to drive the spinning process. This field is applied to droplets of polymer solution (or a melt) passed from the tip of a fine orifice.[10] The technique has its origin in the studies on electric fields initiated by Lord Rayleigh in the nineteenth century, and was originally patented in 1902,[11] although it was in 1934 that Formhals considered the procedure as a means for processing textile yarns.[12] It was Taylor who, in his work, developed the theoretical understanding of the influence of an electric field on a small volume of liquid.[13] Thus, when an electric field is applied to a liquid droplet, an electrostatic charge accumulates at the tip of this droplet. Consequently, charge repulsion works against the surface tension, causing the shape to change from a broadly spherical surface to an elongated cone shape (known later as a Taylor Cone), a jet then is released from the capillary spinneret. This jet may take a complex path and is subjected to instabilities induced by electric charges, but in the absence of a viscous polymer solute, the liquid will ultimately atomise into tiny droplets; this is the origin of the important process of electrospraying.[14] However, when the liquid contains a polymer as a solute, the viscosity must also be considered; if sufficiently large,[15] the polymer viscosity will oppose the breaking up of the jet into droplets. This produces a thread of polymer solution which will be subjected to the electrical instabilities also seen in the pure liquid. These whipping or bending instabilities[16] mean that the polymer solution may take a complex path, as shown in Figure 1.3, and as a result of the motion and stretching, solvent is removed and the polymer thread elongated. This is crucial to the development of fibres with sub-micron diameters. The whipping process, while crucial to the development of the extreme elongation of the fibres, distinguishes this technique from other fibre producing technologies, where the fibre orientation is easily controlled. As a consequence of this controlled deposition of fibres to form organised structures, a basic requirement for developing nanomaterials requires some modification to the techniques, as discussed below. The physics of the polymer jet is discussed further in Chapter 5.

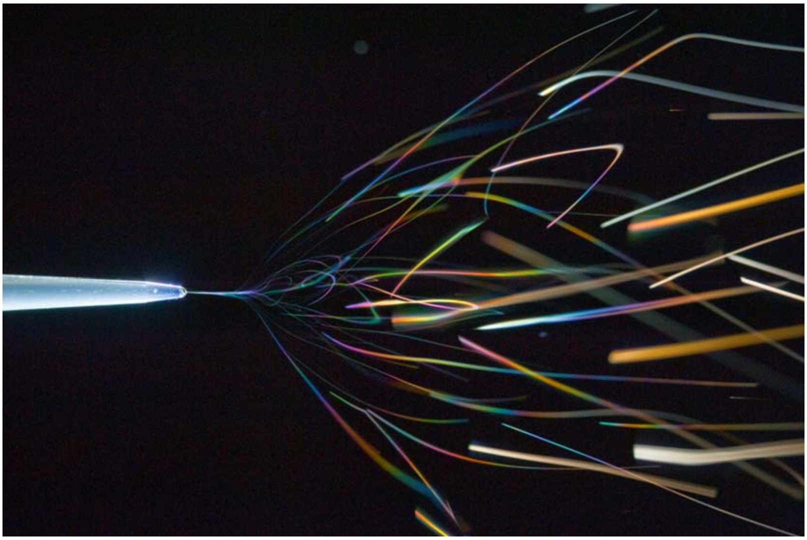


Figure 1.3 Path of jet formed by electrical instabilities.
Picture by Robert Lamberts, Senior Science Photographer at Plant and Food Research Ltd. (www.plantandfood.co.nz)

1.3 Equipment for Electrospinning

The equipment needed for electrospinning on a laboratory scale is relatively simple; in the basic setup there are three main components: the high voltage power supply, a syringe pump and the collector, which can be simply a sheet of aluminium foil. A schematic of the equipment used for electrospinning is shown in Figure 1.4. In this simple arrangement the fibres are deposited as a random mat, as shown in Figure 1.5(a). There may, however, be alternative arrangements, for example, the New Zealand company *Electrospinz* produces an elegantly designed apparatus that uses a constant pressure header tank rather than the syringe pump and needle arrangement represented by Figure 1.4. An interesting variation of needle electrospinning is coaxial electrospinning, which in some cases[17] uses two concentric needles with different diameters. In this way, fibres can be obtained with an inner core that differs from the external part of the fibre (core–shell fibres). In general, the design of electrospinning systems has been subject to numerous technological advances in recent years.[18]

For many applications, and indeed for certain characterisation techniques, a random mat is not suitable, and an array of aligned fibres is required.[19] There are a number of ways this problem can be addressed; one simple means of doing this is via the use of a rotating collector which produces aligned fibres, as shown in Figure 1.5(b).[20] The preparation of aligned fibres is one important area of control, but there is also a demand

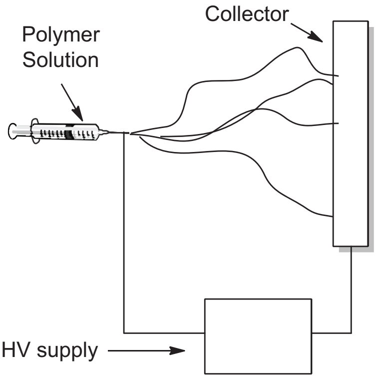


Figure 1.4 Schematic of electrospinning setup.

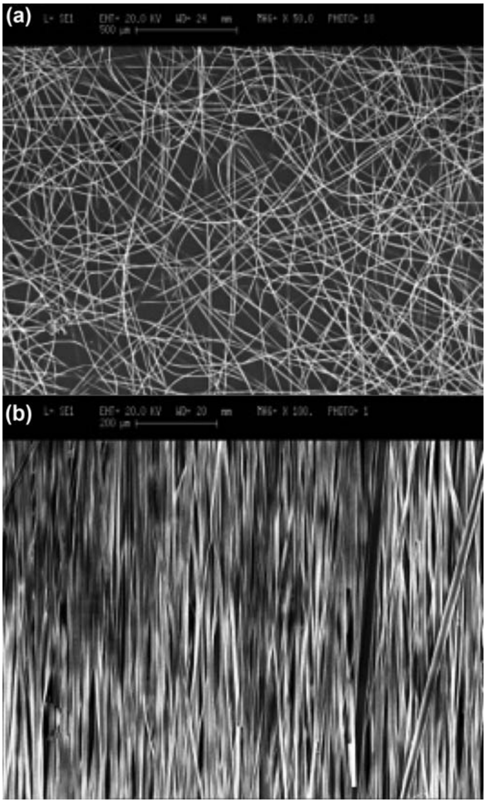


Figure 1.5 (a) Unaligned (b) Aligned polystyrene fibre spun from MEK.

for precision deposition of nanofibres to provide patterned nanostructures. A range of techniques can be used for this. For example, near-field electrospinning uses a reduced distance between the collector combined with a solid probe to produce patterns,[21] though the limitations of dip-pen methodology mean modifications must be made if the method is to be used to form continuous fibres.[22] Further details on the control of electrospinning are provided later in the book (Chapter 9).

The system shown in Figure 1.4 is not suitable for the large-scale production of fibres, which for many applications is necessary if significant commercialisation is to be achieved. One simple approach is the multi-needle system, but this requires the needles to be spaced such that the neighbouring fields do not interact, and the needles are subject to blocking. Such difficulties have prompted the investigation of needleless approaches,[23] whereby the use of a rotating cylinder partially immersed in a polymer solution produces multiple jets, and this is an approach patented by Elmarco in the device known commercially as the Nano spider; a more recent development of this uses a stationary wire electrode system (see Figure 1.6).[24] Other approaches include using compressed air to generate bubbles on the surface, from which multiple jets can be formed (see Figure 1.7),[25] and the use of a rotating cone.[26]

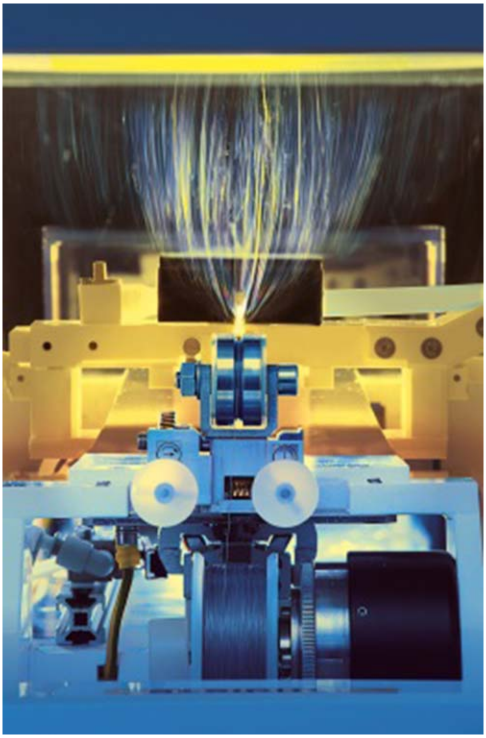


Figure 1.6 NS 1WS500U model equipment for multiple jet formation (photo by permission of Elmarco).[24]

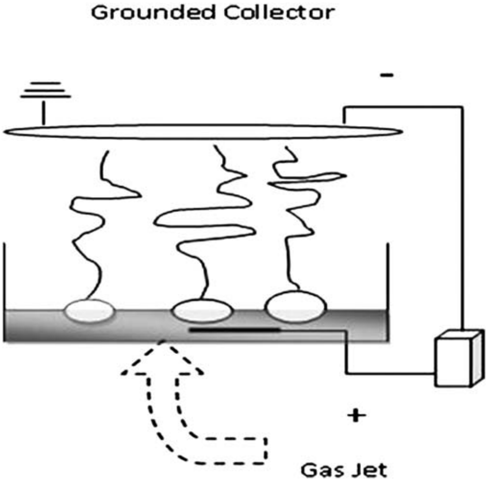


Figure 1.7 Schematic of bubble electrospinning.

1.4 Processing Parameters

The need for fibres with controlled diameters and morphology has prompted many studies of the relationship between the fibre properties and the variable parameters.[27] It is helpful to classify these parameters into three categories: solution or material parameters such as viscosity and/or concentration, operation parameters which consider the main critical factors in theoretical and applied studies such as voltage, working distance, flow rate *etc.* and finally the ambient parameters such as humidity and temperature. These factors may influence the fibre morphology individually in some way, or they may all work in harmony with one another (see Chapter 4 for specific examples). Table 1.1 provides a summary of some of the most important parameters and their effect on fibre diameter and/or morphology.

Most electrospinning is carried out in a suitable solvent. Though many of the crucial parameters (such as viscosity) depend on the properties of the polymer, the solvent is also important in the electrospinning process. Particularly important factors are, firstly, the vapour pressure, which can have a major effect on polymer morphology; secondly, the polarity which will influence the conductivity and hence interaction with the electric field; thirdly, the surface tension, which is a force to be overcome by the electric field. Of course, the addition of the polymer will further modify the properties and there are a range of additives which can also affect the behaviour of the solution. For example, the viscosity can be increased by the addition of dibenzyl sorbitol[35] and the surface tension can be modified by the addition of surfactants.[36] The solvent properties, such as those listed in Table 1.2, provide a guide to the limitations of a particular system. It is particularly important to note that there are substantial hazards involved with the use of many solvents, as shown in Table 1.2, many of the solvents listed below are

Table 1.1 Parameters in electrospinning and their influence on fibre morphology.

Parameter	Effected property	Reference
Solution properties		
Viscosity	Fibre diameter	28
	Bead formation in competition with surface tension	
Molecular weight	A factor in the viscosity (*vide supra*)	28
Concentration of polymer	Increases the viscosity and increases the amount of polymer deposited	
Electric conductivity	The fibre diameter decreases with increasing conductivity; addition of ionic materials may reduce beading	28 and 29
Solvent properties		
Surface tension	Small unless becomes significant compared to viscosity, in which case beading occurs	30
Permittivity	Conductivity seems more influenced by the properties of the solvent and traces of ionic impurities	31
Vapour pressure	May cause problems with solvent evaporation before spinning; if too low solvent may not evaporate. Solvent evaporation may influence the formation of non-cylindrical morphologies	32
Operation conditions		
Applied voltage	Fibre diameter in principle reduced as the forces on the fibre increase; however, rate of production increased, which may increase fibre production	31
Distance of collector from the spinneret	Fibre solidification deposition over an increased area	33
Feeding rate	Too small a flow rate stops Taylor cone developing; too fast and there may be pulsing	28
Surrounding conditions		
Temperature	Fibre diameter through changes in viscosity (largely decreases with temperature) may affect many solution properties	33
Humidity	Porosity may influence solvent evaporation	34

flammable and/or may have the potential to produce cancer, or are hazardous to unborn children. On that basis, the possibility of residual solvent may be a restriction in many applications. In such circumstances, melt electrospinning offers an alternative route to fibres but, by virtue of the intrinsically higher viscosity, the fibre diameters are likely to be larger. However, some improvements have been made in this direction.[37] In contrast, for conventional fibre production, melt spinning is the default technique; solution spinning might be used, for example, when the polymer degrades in the melt. In this case the advantages, both in terms of economics, safety and the environment, are considerable and in many cases the fibres can be produced at a faster rate.[4]

Table 1.2 Properties of solvents used for electrospinning.[38]

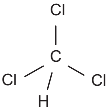
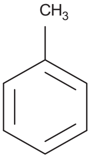
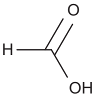
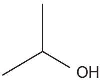
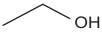
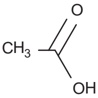
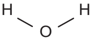
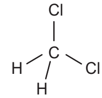
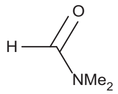
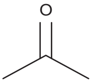
Solvent	Boiling Point	Surface Tension/ m Nm^{-1}	Dielectric Constant	Dipole Moment/D	Other (*e.g.* example hazards)[a]
 (hexane)	69	18.43	2.0	0.00	F[b] Terat[c]
 (Chloroform)	61	27.14	4.8	1.04	Carc[d]
 (Toluene)	111	28.5	2.4	0.36	F[b] P[e] Terat[c]
 (Formic acid)	101	37.6	58	1.41	F Corr[f]
 (propan-2-ol)	82	21.7	18	1.66	F Toxic
 (ethanol)	79	22.75	30	1.69	F
CH_3 - OH (Methanol)	65	22.61	33	1.70	F Toxic
 (acetic acid)	118	27.8	6.2	1.74	Corr
 (water)	100	73.05	80	1.85	
 (dichloromethane)	40	26.52	9.1	1.6	Carc

Table 1.2 (*Continued*)

Solvent	Boiling Point	Surface Tension/ m Nm^{-1}	Dielectric Constant	Dipole Moment/D	Other (*e.g.* example hazards)[a]
 (Dimethyl formamide)	158	37.1	38	3.82	F Terat
 (acetone)	56	23.70	21	2.88	F
CH_3 - CN acrylonitrile	82	29.30	37	3.92	F Toxic

[a] Selected safety data listed on Aldrich website.
[b] Highly flammable or extremely flammable.
[c] May cause defects in unborn children.
[d] Known or potential carcinogen.
[e] Prolonged exposure damages organs.
[f] Corrosive.

Of the solution parameters, the viscosity is probably the most important and several studies on this have been conducted (see Chapter 4). Long *et al.*[15] have shown that, for a range of polymers, the diameter of the fibres produced can be related to the ratio of the concentration of the solution used to the critical concentration required for entanglements *via* a power law. Similarly, Wang *et al.* have related the viscosity to the fibre diameter *via* the relationship shown in eqn (1). The viscosity can be increased by changing the concentration of polymer or by changing the molecular weight. In both cases, as the viscosity increases there is a transition from a regime where spinning fibres is not possible, to one where fibres are formed with a diameter increasing with the viscosity. In the intermediate range the transition from electrospraying to electrospinning is shown by the presence of fibres interspersed with polymer droplets (beaded fibres), as shown in Figure 1.9. In general, the fibre diameter increases with increasing viscosity (and hence molecular weight and concentration) and this can be an important factor in determining if a particular material can be electrospun. On this basis, it might be expected that fibres generated in the melt would be less likely to be nanoscale, but note that while this is often the case as, for example, with the poly(caprolactone) samples shown in Figure 1.8, with good experimental control, excellent results have been found with melt spun fibres, particularly in the medical field (see Chapters 6 and 11).[39]

$$d \sim \eta^{0.41} \tag{1}$$

Though the viscosity supplies some control of the fibre parameters, other factors need to be considered. Surface tension is important in control of the

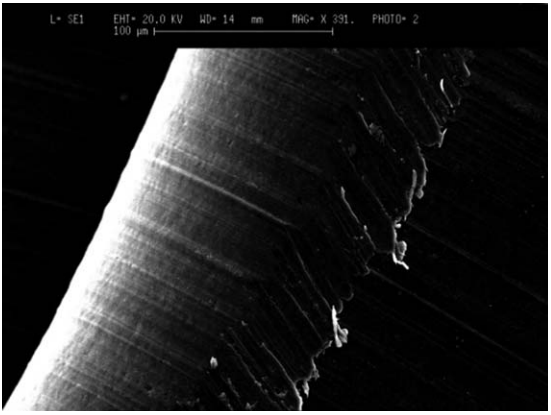


Figure 1.8 Polycaprolactone Melt 14 kV 90 °C.

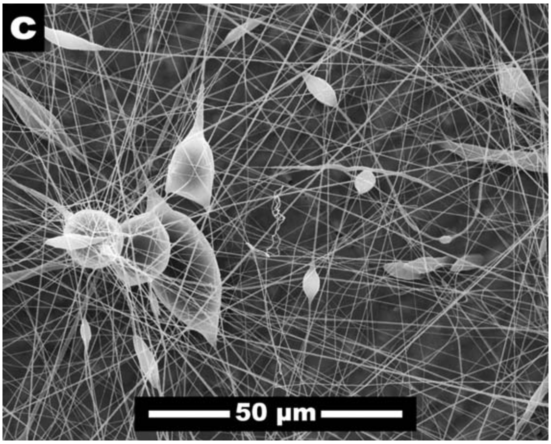


Figure 1.9 Polycaprolactone DCE-MeOH from ref. 40.

Taylor cone, but it may not contribute hugely to the tunability of the system in normal circumstances, but when the viscosity is low then, importantly, this will start to influence the fibres in terms of the beading discussed above;[41] conductivity increases the charge separation and increases elongation and thus it would seem an increase in conductivity will result in a decrease in fibre diameter.

1.5 Materials

Most common soluble and tractable polymers have been processed as nanofibres *via* electrospinning. Some typical examples are included in Table 1.3, and in several excellent reviews on the subject.[8,9,42] The important features are the solubility or the ability to melt the polymer, and that the molecular weight is sufficiently high to allow entanglements between

Table 1.3 Examples of polymer systems used for electrospinning.

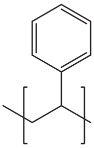
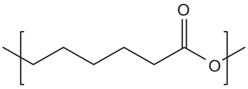
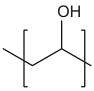
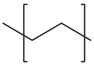
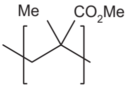
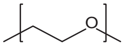
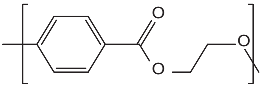
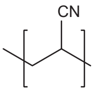
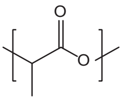
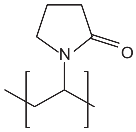
Polymer	Solvent	Comment	Reference
 (Polystyrene)	DMF[a] MEK[b]	High molecular weights needed to electrospin effectively. Parameters controlling fibre diameters are well studied	28 34
 [Poly(caprolactone)]		Particularly of interest in medical applications; can be spun from melt or solution	46
 [Poly(vinylalcohol)]	H_2O	Used as a carrier polymer with many biopolymers	9
 [Polyethylene]	Melt	Early experiments involved blending with paraffin and melt spinning the composite	47
 [Poly(methyl methacrylate)]	CH_2Cl_2	Typically forms fibres with beads	9
 [Poly(ethylene oxide)]	H_2O	Particularly of interest for medical uses due to biocompatability	9
 [Poly(ethylene terephthalate)]	Melt	Electrospinning of PET from recycled material has been explored	39
 [Poly(acrylonitrile)]	DMF	Single fibres have high modulus due to crystallinity	48
 [Poly(lactic acid)]		Can be spun from solution or the melt	9 and 39

Table 1.3 (*Continued*)

Polymer	Solvent	Comment	Reference
 [Poly(vinyl pyrrolidone)]	H_2O	Water-soluble polymer which can be cospun with a range of inorganic materials	9
Gelatin	H_2O Acetic acid	Can be spun in water at temperatures above the gel point.	49
Chitosan	Trifluoroacetic acid	Can be spun on its own or as a blend	9

[a] Dimethyl formamide.
[b] Methylethylketone.

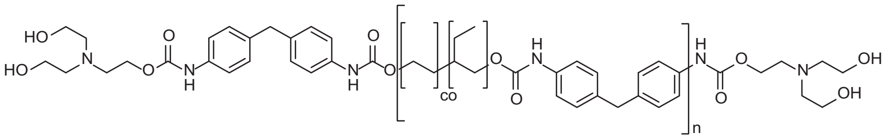


Figure 1.10 Urethane.

polymer chains (*vide supra*). However, it should be noted that there are examples where low molecular weight polymers can be spun by virtue of the presence of associative interactions as is the case in the urethane systems shown in Figure 1.10.[43]

As can be seen in Table 1.3, many of the polymers electrospun have been water soluble materials these include polyethylene oxide, poly(vinylalcohol) and poly(*N*-vinyl pyrrolidone). Water has a great advantage in terms of potential commercialisation and it is particularly advantageous when the proposed application is medical, since alternative solvents may introduce problems such as toxicity; even though the removal of the majority of the solvent is integral to the process. Biopolymers and even more complex entities such as active viruses and bacteria are not destroyed by electrospinning and so there is much interest in these fibres in the medical field. However, many polymer systems, including many of those that may have potential medical applications, are not water-soluble. Melt electrospinning offers an alternative for applications where the use of water-soluble polymers is not an option (see Chapter 6).

Electrospinning has been used to prepare more complex systems than simple polymers; for example, block copolymers and polymer blends. In such systems the development of the morphology may occur in a complex fashion. Inorganic materials can be produced by electrospinning; for example, a metal oxide/polymer mixture followed by pyrolysis. Interestingly, copper nanofibres have been prepared from poly(vinylbutyral)/$CuNO_3$

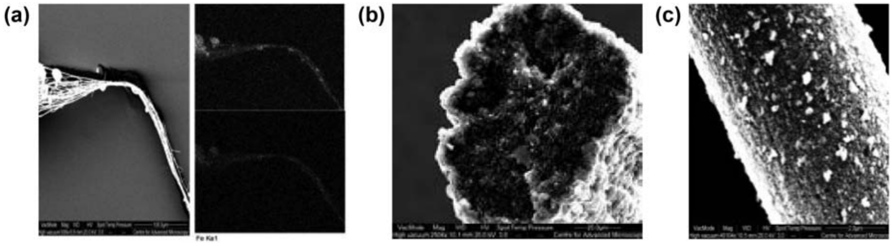


Figure 1.11 (a): PVA containing poly(pyrrole) particulates and elemental mapping (top chlorine, below iron).[44] (b): Polystyrene fibre cospun with $FeCl_3$, after exposure to pyrrole vapour at 60 °C for 1 hour. (c): Polystyrene fibre cospun with glucose and reacted with silver nitrate.

composite fibres.[45] In addition, composite fibres have been prepared, incorporating a range of particles *e.g.* carbon nanotubes have been incorporated into poly(acrylonitrile) which on pyrolysis produce carbon fibres. In a similar fashion a range of particulate materials can be incorporated into a carrier polymer; for example, Figure 1.11(a) shows polypyrrole particulates spun into fibres of polyvinyl alcohol. A variety of reagents can also be incorporated for post processing *e.g.* ferric chloride can be incorporated into polystyrene and nanofibres produced – this, post processing can be treated with pyrrole vapour to produce a material with a polypyrrole surface; similarly, inclusion of glucose and post treatment with ammonical silver nitrate produces silver coated fibres [Figure 1.11(b) and (c), respectively].

1.6 Characterisation of Fibres

Optical microscopy is particularly important in the characterisation of conventional polymer fibres; in particular, when used in conjunction with polarised light, the birefringence, which relates to directional differences in the refractive index,[50] can be used to measure levels of orientation.[51] In the case of electrospun fibres, where diameters as small as 10 s of nanometers may be obtained, there may be problems with the resolution of optical microscopy, related to light diffraction, particularly for fibres with diameters in the submicron range. However, with special adaptations to the technique, fibres with diameters as low as 300 nm may be studied.[52] The method of choice for studying nanofibres is generally SEM, this comfortably provides a route to visualisation of fibres with diameters of a few 10 s of nanometres; the use of this technique in conjunction with image analysis software provides information on the distribution of fibre diameters. In addition, this can be used to study the internal structure of fibres; for example, Figure 1.12 shows pores found in the internal structure of electrospun polystyrene. For many fibres, diameters are sufficiently narrow to allow the use of TEM; this has been exploited in diffraction experiments, as described below.

X-ray scattering techniques are particularly helpful in understanding the structure of polymer fibres. Often, collections of fibres need to be gathered

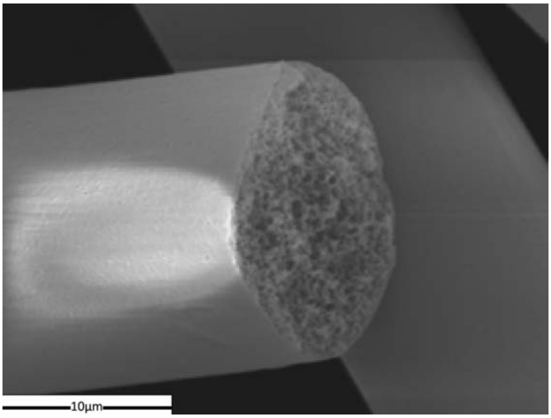


Figure 1.12 Internal structure of an electrospun polymer fibres.

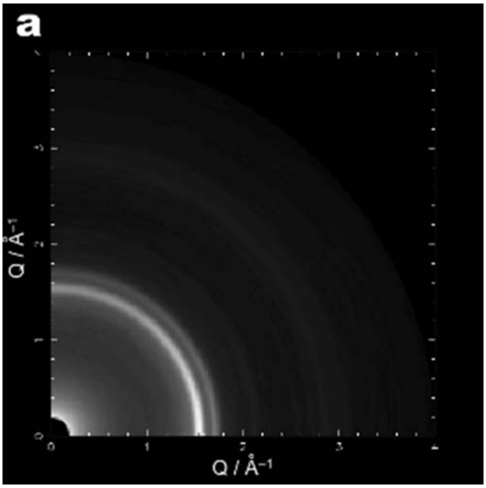


Figure 1.13 X-ray pattern of polycaprolactone fibres revealing a significant level of crystallinity.

with a common fibre axis to provide sufficient scattering to gauge, for example, levels of anisotropy, even using powerful synchrotron sources. X-ray studies are particularly useful to gauge levels of crystallinity, for example, in random mats such samples may produce sharp bands reflecting crystalline regions, as shown in Figure 1.13 for polycaprolactone. Orientation may also be measured by polarised infrared spectroscopy, and this has been used, for example, to monitor bundles of electrospun poly(acrylonitrile) fibres; here, the distinctive peak at 2240 cm^{-1} is an effective probe of the trajectory of the polymer chain. Diffraction from single fibres can, however, be obtained using selected-area electron diffraction and this can be used to probe the uniformity within individual fibres.[53]

Thermal analysis, particularly differential scanning calorimetry (DSC), gives further details of crystallisation behaviour; in particular, it can pick up and quantify non-equilibrium behaviour. In addition, for glass-forming systems the glass from a material cooled slowly from the melt may differ significantly from that from an electrospun fibre. In both cases, these will show significant features in the DSC traces.[9]

Neutron scattering, when combined with isotopic substitution of the polymer backbone, can give an indication of the radius of gyration of the polymer backbone. Studies of such samples can be complicated if the fibres form pores, which add significantly to the scattering obtained, but such effects can be removed by careful analysis of the data.[54] Results obtained from polystyrene show the presence of anisotropy, though a component of this is induced by the drawing caused by the rotating collector, which is necessary to produce macroscopic alignment of the fibres; the inherent anisotropy induced by electrospinning is around 5%. It should also be noted that the radius of gyration is greater than the bulk, suggesting the polymer conformation present in solution is partially retained (for more information see Chapter 8).

The mechanical properties of conventional polymer fibres may be readily measured using tensile testing machines with the scale adapted to the particular sample under consideration; with nanoscale fibres there are difficulties with this methodology including observation and manipulation of the fibres and accurate measurement of the applied force. These difficulties have led to several inventive solutions,[55] but a particularly attractive one is the use of atomic force microscopy (AFM) in conjunction with SEM (for more details on property measurements see Chapter 10).[56]

1.7 Health and Safety

Perhaps the most well-publicised risk of nanofibres concerns the effect of high aspect ratio fibres on the lungs. Asbestosis is a major health concern and is known in part to be due to the high length to radius ratio of asbestos fibres. In 2012, Donaldson *et al.*[57] published data showing a threshold length for fibre-induced pleural inflammation from silver nanowires and this prompted considerable concern over the use and production of nanofibres. However, it should be noted that there are some suggestions that the measurements of Donaldson's team are not fully applicable to electrospinning. This is for a number of reasons. Firstly, although high aspect fibres are generally harmful, electrospun fibres are sufficiently long, so that inhalation is unlikely; secondly, the high electric fields involved in the production of fibres appear to reduce dispersion into the atmosphere; thirdly, the use of electrospun fibres in medical applications has produced no evidence of harmful inflammation. That being said, there are many different types of fibres and the potential hazards are likely to vary significantly. On that basis, the minimum precautions should eliminate the possibility of fibre inhalation by production in an enclosed system. Particular care should of course be taken when manipulating electrospun fibres to avoid fragmentation and the production of fine particles.

Solution electrospinning involves the use of solvents which vary in the severity of harm caused to human health, depending upon the solvent used in the process. For example, in the case of water there is no health concern, however, many polymers are not water soluble. In this case, organic solvents have to be used, which vary in the effects they have on human health, ranging from mild irritation (acetone) to toxic effects (DMF), corrosiveness to human tissue (acetic acid) and potential carcinogenic effects (chloroform and 1,2-dichloroethane). Exposure to these chemicals must be avoided as far as reasonably possible and certainly should not exceed the exposure limits noted on the manufacturer's data sheets. To a large extent, this can be achieved by working under a fumehood/extractor system and the use of personal protective equipment. The fibres themselves may be contaminated (particular where less volatile solvents such as DMF are used). The flammability of solvents in the presence of high voltages (and thus potential sources of ignition) must be a consideration, particularly if scale-up is required.

Additional health and safety concerns revolve around the use of high voltage in order for the electrospinning process to occur. In most electrospinning setups the current is kept to a minimum as currents of a few tens of microamps are sufficient. The low current will reduce the chances of a severe or potentially fatal electric shock (generally *ca.* 0.1–0.2 Amps are viewed as being sufficient to induce ventricular fibrillation); however, the potential difference of several thousand volts would still be sufficient to give a mild but painful electric shock. The risk can be reduced by having an isolated system or interlock system where either the high voltage must be disengaged before accessing the high voltage probe, or an automatic cut off is present, so that when the door to the isolated environment opens, the high voltage power supply is automatically switched off. The capacitance of the equipment should also be considered. Grounding will help reduce additional risks so that there is no potential current flow to other systems, such as the syringe pump or residual charge built up on the collector. Additional monitoring devices such as a digital multimeter can be set up and checked and a grounding probe can be used on the high voltage probe before handling for additional safety. The advantage of an isolated system also ensures that there are no additional dangers from spillages of solution, which can also conduct the charge.

Finally, one other health concern that is sometimes overlooked is the use of a needle and syringe as a spinneret for the polymer solution. Care should be taken to minimise contact with the needle tip and it should be covered unless in use. If some general setup of equipment is needed then the syringe and needle containing polymer solution would be best put into the pump as one of the last stages before the high voltage is engaged.

1.8 Applications

Much of the intense research effort that has surrounded the production of nanofibres by electrospinning has been driven by their potential for applications. The most obvious factor here is that the smaller the diameter of the fibre, the greater the ratio of surface area to volume. Thus, reducing diameters from a few microns to a few nanometres increases the surface available by 1000 times. Examples of areas where electrospun fibres have potential include a range of biomedical applications[58] such as drug delivery[59] and the use of scaffolds to provide a framework for tissue regeneration in both soft[60] and hard[61] tissue Other areas include filtration,[62] protective clothing,[63] conducting composites[64] and hydrogen storage.[65] Selected applications will be discussed in later chapters (see Chapters 11 and 12).

1.9 Summary

Nanofibres produced by electrospinning offer a unique opportunity to develop nanostructures using a top-down approach. In most ways, the systems resemble rather larger fibres. Where differences and challenges arise, these are in most instances reflections of the different length-scale; for example, probing the internal structure of single fibres may be prevented by limitations in instrument resolution. In such cases, alternative techniques must be used, or multiple fibres studied. One significant difference is that due to the whipping motion induced in the jet collection of aligned fibres modifications to the simple system are required. Not only do techniques such as rotating collectors allow the collection of fibres with their axes aligned, but methodology such as near-field electrospinning allows direct writing with nanofibres.

In the remainder of the book, the electrospinning process is described in sequence from the hardware, through the solutions or polymer melts through to the nature of the electrospinning jet. Subsequently, the alignment and physical properties of the fibres are described. Finally, selected applications are considered and the future outlook discussed.

References

1. G. Capaccio and I. M. Ward, *Polymer*, 1974, **15**, 233.
2. J. C. Rodríguez-Pérez, I. W. Hamley, S. L. Gras and A. M. Squires, *Chem. Commun.*, 2012, **48**, 11835–11837.
3. D. C. Bassett, *Polymer*, 2006, **47**, 5221–5227.
4. V. B. Gupta and V. K. Kothari, *Manufactured Fibre Technology*, Chapman and Hall, London, 1997.
5. M. P. Stevens, *Polymer chemistry an introduction*, OUP, NY, 1990.
6. E. Fitzer, *Carbon*, 1989, **27**, 621.
7. C. J. Ellison, A. Phatak, D. W. Giles, C. W. Macosko and F. S. Bates, *Polymer*, 2007, **48**, 3306.
8. C. J. Luo, S. D. Stoyanov, E. Stride, E. Pelan and M. Edirisinghe, *Chem. Soc. Rev.*, 2012, **41**, 4708–4735.
9. A. Greiner and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2007, **46**, 5670–5703.

10. D. H. Reneker, A. L. Yarin, H. Fong and S. Koombhongse, *J. Appl. Phys.*, 2000, **87**, 4531–4547.
11. J. F. Cooley, *US Pat.*, 692,631, 1902; W. J. Morton, *US Pat.*, 0,705,691, 1902.
12. A. Formhals, *US Pat.*, 1,975,504, 1934.
13. G. I. Taylor, *Proc. R. Soc. London, Ser. A*, 1969, **313**, 453.
14. A. Jaworek, *J. Mater. Sci.*, 2007, **42**, 266–297.
15. M. G. McKee, G. L. Wilkes, R. H. Colby and T. E. Long, *Macromolecules*, 2004, **37**, 1760.
16. Y. M. Shin, M. M. Hohman, M. P. Brenner and G. C. Rutledge, *Appl. Phys. Lett.*, 2001, **78**, 1149.
17. H. Qu, S. Wei and Z. Guo, *J. Mater. Chem., A*, 2013, **1**, 11513.
18. W.-E. Teo1, R. Inai and S. Ramakrishna, *Sci. Technol. Adv. Mater.*, 2011, **12**, 013002.
19. Z.-M. Huang, Y.-Z. Zhang, M. Kotaki and S. Ramakrishna, *Compos. Sci. Technol.*, 2003, **63**, 2223–2253.
20. M. D. Edwards, G. R. Mitchell, S. D. Mohan and R. H. Olley, *Eur. Polym. J.*, 2010, **46**, 1175–1183.
21. G. Zheng, W. Li, X. Wang, D. Wu, D. Sun and L. Lin, *J. Phys. D: Appl. Phys.*, 2010, **43**, 415501.
22. C. Chang, K. Limkrailassiri and L. Lin, *Appl. Phys. Lett.*, 2008, **93**, 123111.
23. H. Niu and T. Lin, *J. Nanomater.*, 2012, 725950.
24. For further information see the company website at http://www.elmarco.com/.
25. Y. Liu, J. He and J. Yu, *J. Phys.: Conf. Ser.*, 2008, **96**, 012001.
26. B. Lu, Y. Wang, Y. Liu, H. Duan, J. Zhou, Z. Zhang, Y. Wang, X. Li, W. Wang, W. Lan and E. Xie, *Small*, 2010, **6**, 1612–1616.
27. S. R. Coles, D. K. Jacobs, J. O. Meredith, G. Barker, A. J. Clark, K. Kirwan, J. Stanger and N. Tucker, *J. Appl. Polym. Sci.*, 2010, **117**, 2251.
28. C. Wang, C.-H. Hsu and J.-H. Lin, *Macromolecules*, 2006, **39**, 7662–7672.
29. S. Ramakrishna K. Fujihara, W.-E. Teo, T.-C. Lim and Z. Ma, *An Introduction to Electrospinning And Nanofibers*, World Scientific Publishing, Singapore, 2005.
30. H. Fong, I. Chun and D. H. Reneker, *Polymer*, 1999, **40**, 4585–4592.
31. S. A. Therona, E. Zussman and A. L. Yarin, *Polymer*, 2004, **45**, 2017–2030.
32. S. Koombhongse, W. Liu and D. H. Reneker, *J. Polym. Sci., Part B: Polym. Phys.*, 2001, **39**, 2598.
33. C. J. Thompson, G. G. Chase, A. L. Yarin and D. H. Reneker, *Polymer*, 2007, **48**, 6913.
34. C. L. Casper, J. S. Stephens, N. G. Tassi, D. B. Chase and J. F. Rabolt, *Macromolecules*, 2004, **37**, 573.
35. M. Y. Kariduraganavar, F. J. Davis, G. R. Mitchell and R. H. Olley, *Polym. Int.*, 2010, **59**, 827–835.
36. L. Yao, T. W. Haas, A. Guiseppi-Elie, G. W. L. Bowlin, D. G. Simpson and G. E. Wnek, *Chem. Mater.*, 2003, **15**, 1860–1864.
37. P. D. Dalton, D. Grafahrend, K. Klinkhammer, D. Klee and M. Möller, *Polymer*, 2007, **48**, 6823.

38. *Handbook of Chemistry and Physics*, ed. W. M. Haynes, CRC Press, Boca Raton, 95th edn, 1991.
39. D. W. Hutmacher and P. D. Dalton, *Chem. – Asian J.*, 2011, **6**, 44–56.
40. M. Y. Kariduraganavar, F. J. Davis, G. R. Mitchell and R. H. Olley, *Polym. Int.*, 2010, **59**(6), 827–835.
41. C. J. Thompson, G. G. Chase, A. L. Yarin and D. H. Reneker, *Polymer*, 2007, **48**, 6913.
42. N. Bhardwaj and S. C. Kundu, *Biotechnol. Adv.*, 2010, **28**, 325–347.
43. D. Hermida-Merino, M. Belal, B. W. Greenland, P. Woodward, A. T. Slark, F. J. Davis, G. R. Mitchell, I. W. Hamley and W. Hayes, *Eur. Polym. J.*, **48**(7), 1249–1255.
44. S. Sen, F. J. Davis, G. R. Mitchell and E. Robinson, *J. Phys.: Conf. Ser.*, 2009, **183**, 012020.
45. M. Bognitzki, M. Becker, M. Graeser, W. Massa, J. H. Wendorff, A. Schaper, D. Weber, A. Beyer, A. Gölzhäuser and A. Greiner, *Adv. Mater.*, 2006, **18**, 2384–2386.
46. A. Cipitria, A. Skelton, T. R. Dargaville, P. D. Dalton and D. W. Hutmacher, *J. Mater. Chem.*, 2011, **21**, 9419.
47. L. Larrondo and R. St. John Manley, *J. Polym. Sci. Part B*, 1981, **19**, 909.
48. S.-Y. Gu, Q.-L. Wu, J. Ren and G. J. Vancso, *Macromol. Rapid Commun.*, 2005, **26**, 716.
49. D. E. Elliott, F. J. Davis, G. R. Mitchell and R. H. Olley, *J. Phys.: Conf. Ser.*, 2009, **183**, 012021.
50. P. H. Hermans and P. Platzek, *Kolloid-Z.*, 1939, **88**, 68–72.
51. A. A. Hamza, T. Z. N. Sokkar, K. A. El-Farahaty and H. M. El-Dessouky, *Polym. Test.*, 2004, **23**, 203–208.
52. D. Kołbuk, P. Sajkiewicz and T. A. Kowalewski, *Eur. Polym. J.*, 2012, **48**, 275–283.
53. R. Dersch, T. Liu, A. K. Schaper, A. Greiner and J. H. Wendorff, *J. Polym. Sci., Part A: Polym.Chem.*, 2003, **41**, 545–553.
54. S. D. Mohan, G. R. Mitchell and F. J. Davis, *Soft Matter*, 2011, **7**, 4397–4404.
55. E. P. S. Tan and C. T. Lim, *Compos. Sci. Technol.*, 2006, **66**, 1102–1111.
56. F. Hang, D. Lu, R. J. Bailey, I. Jimenez-Palomar, U. Stachewicz, B. Cortes-Ballesteros, M. Davies, M. Zech, C. Bödefeld and A. H. Barber, *Nanotechnology*, 2011, **22**, 365708.
57. A. Schinwald, F. A. Murphy, A. Prina-Mello, C. A. Poland, F. Byrne, D. Movia, J. R. Glass, J. C. Dickerson, D. A. Schultz, C. E. Jeffree, W. MacNee and K. Donaldson, *Toxicol. Sci.*, 2012, **128**, 461–470.
58. T. J. Sill and H. A. von Recum, *Biomaterials*, 2008, **29**, 1989–2006.
59. E.-R. Kenawy, G. L. Bowlin, K. Mansfield, J. Layman, D. G. Simpson, E. H. Sanders and G. E. Wnek, *J. Controlled Release*, 2002, **81**, 57–64.
60. E. J. Chong, T. T. Phan, I. J. Lim, Y. Z. Zhang, B. H. Bay, S. Ramakrishna and C. T. Lim, *Acta Biomater.*, 2007, **3**, 321–330.

61. F. Yang, J. G. C. Wolke and J. A. Jansen, *Chem. Eng. J.*, 2008, **137**, 154–161.
62. R. S. Barhate and S. Ramakrishna, *J. Membr. Sci.*, 2007, **296**, 1–8.
63. P. Gibson, H. Schreuder-Gibson and D. Rivin, *Colloids Surf., A*, 2001, **187–188**, 469–481.
64. I. D. Norris, M. M. Shaker, F. K. Ko and A. G. MacDiarmid, *Synth Met*, 2000, **114**, 109–114.
65. Z. Kurban, A. Lovell, S. M. Bennington, D. W. K. Jenkins, K. R. Ryan, M. O. Jones, N. T. Skipper and W. I. F. David, *J. Phys. Chem. C*, 2010, **114**, 21201–21213.