DOI: 10.1002/anie.200604646

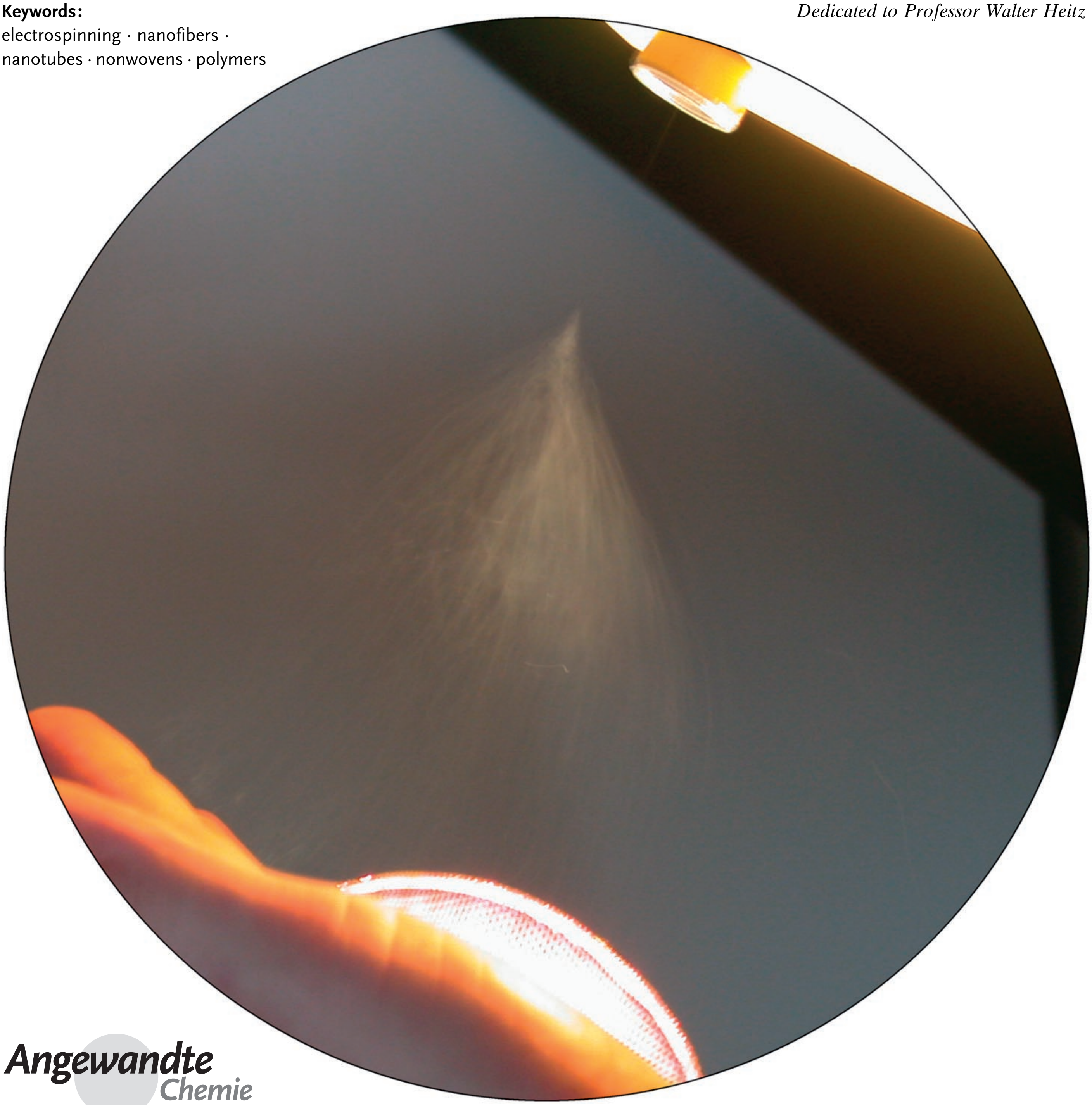
Nanotechnology

Electrospinning: A Fascinating Method for the Preparation of Ultrathin Fibers

Andreas Greiner and Joachim H. Wendorff**

Keywords:
electrospinning · nanofibers · nanotubes · nonwovens · polymers

Dedicated to Professor Walter Heitz



Electrospinning is a highly versatile method to process solutions or melts, mainly of polymers, into continuous fibers with diameters ranging from a few micrometers to a few nanometers. This technique is applicable to virtually every soluble or fusible polymer. The polymers can be chemically modified and can also be tailored with additives ranging from simple carbon-black particles to complex species such as enzymes, viruses, and bacteria. Electrospinning appears to be straightforward, but is a rather intricate process that depends on a multitude of molecular, process, and technical parameters. The method provides access to entirely new materials, which may have complex chemical structures. Electrospinning is not only a focus of intense academic investigation; the technique is already being applied in many technological areas.

From the Contents

1. Introduction

Electrospinning is currently the only technique that allows the fabrication of continuous fibers with diameters down to a few nanometers. The method can be applied to synthetic and natural polymers, polymer alloys, and polymers loaded with chromophores, nanoparticles, or active agents, as well as to metals and ceramics. Fibers with complex architectures, such as core–shell fibers or hollow fibers, can be produced by special electrospinning methods. It is also possible to produce structures ranging from single fibers to ordered arrangements of fibers. Electrospinning is not only employed in university laboratories, but is also increasingly being applied in industry. The scope of applications, in fields as diverse as optoelectronics, sensor technology, catalysis, filtration, and medicine, is very broad.

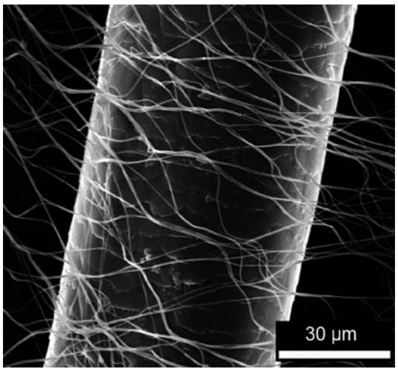


Figure 1. Scanning electron microscope (SEM) image of a human hair surrounded by electrospun fibers of poly(vinyl alcohol) (PVA).

1.1. Nanofibers: A Whiff of Nothing

Tissues made of fibers that are too thin to be observed under the best optical microscope, polymer webs on plants that surpass spiderwebs in fineness, filters covered by a "whiff of nothing" (as once said by J. C. Binzer) that increases their effectiveness immensely, or wound dressings made of gossamer fibers carrying a medical agent, which enable faster healing: these are not fairy tales like "The Emperor's New Clothes" (by H. C. Anderson), but are examples from the rapidly growing domain of electrospinning. Electrospun fibers are considerably thinner than a human hair (Figure 1). To help the imagination, we carry out some example calculations for fibers with diameters on the order of micrometers or nanometers. If the fiber diameter is 10 μm, fibers with a total length of 13 km can be produced from 1 g of polyethylene. In contrast, a diameter of 100 nm leads to fibers with a total length of 130000 km. In the first case, the specific surface area of the fibers is $0.4\,m^2g^{-1}$, while in the second case, it is $40\,m^2g^{-1}$. In fiber technology, the unit denier, which specifies the mass of a fiber with a length of 9000 m, is often used as a measure of fiber fineness. For a fiber of 10 μm in diameter, the fineness is 1 denier, and for a fiber of 100 nm in diameter, it is 10^{-4} denier.

Today, nanofibers from synthetic or natural polymers can be fabricated in a controlled manner with dimensions down to a few nanometers, and functionalized by the addition of drugs, or of semiconductor or catalyst nanoparticles. They can be employed in numerous applications with great benefit.

---

[*] Prof. Dr. A. Greiner, Prof. Dr. J. H. Wendorff
Department of Chemistry
Philipps-Universität Marburg
35032 Marburg (Germany)
Fax: (+49) 6421-282-5785 (A.G.)
Fax: (+49) 6421-282-8916 (J.H.W.)
E-mail: greiner@staff.uni-marburg.de
wendorff@staff.uni-marburg.de

Hybrid fibers composed of metals and ceramics are attainable, as are nanofibers with a solid or liquid core and a solid shell.

Electrospinning, also known as electrostatic spinning, has its basis in early studies. In 1745, Bose described aerosols generated by the application of high electric potentials to drops of fluids.[1] In 1882, Lord Rayleigh investigated the question of how many charges are needed to overcome the surface tension of a drop.[2] Later, the first devices to spray liquids through the application of an electrical charge were patented by Cooley and Morton, in 1902 and 1903.[3–5] In 1929, Hagiwaba et al. described the fabrication of artificial silk through the use of electrical charge.[6] The crucial patent, in which the electrospinning of plastics was described for the first time, appeared in 1934 with Anton Formhals from Mainz as the author (and can be traced back to a German patent filing in 1929).[7] Despite these early discoveries, the procedure was not utilized commercially. In the 1970s, Simm et al. patented the production of fibers with diameters of less than 1 μm.[8] However, this work, which was followed by other patents, also remained unnoticed. Electrospun fibers were first commercialized for filter applications, as part of the nonwovens industry.[9]

Electrospinning gained substantial academic attention in the 1990s, which was partially initiated by the activities of the Reneker group.[10] One reason for the fascination with the subject is the combination of both fundamental and application-oriented research from different science and engineering disciplines. These research efforts usually target complex and highly functional systems, which could certainly be applied on a commercial level. Fiber systems in which the macroscopic properties (that is, specific chemical, physical or biological combinations of properties) can be targeted through modifications on the molecular level are of particular interest.

The scope of possibilities presented by electrospinning encompasses a multitude of new and interesting concepts, which are developing at breakneck speed. This rapid development is reflected by the skyrocketing numbers of scientific publications and patents (Figure 2).

Several expressions are used to describe the electrospinning technique. Among them, the terms "electrostatic spinning" and "electrospinning" are both frequently used. For consistency, we use "electrospinning" as the noun and "electrospin" as the verb.

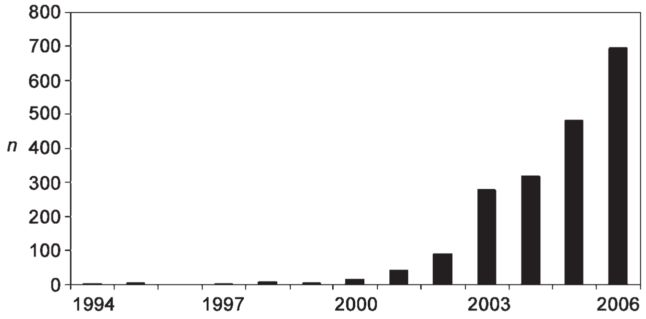


Figure 2. Number (*n*) of scientific publications and patents per year (1994–2006) with the keyword "electrospinning" (source: SciFinder Scholar).

Other techniques for the production of ultrathin polymer fibers include, most notably, melt-blown and multicomponent processes.[11] Both methods make use of thermoplastic polymers and lead to fibers with diameters of less than 500 nm. In the melt-blown technique, polymer melts are pushed, under relatively high pressure, through an array of nozzles. Fibers are formed from the melt under rapid cooling in the countercurrent. Multicomponent fibers, which consist of segments of different polymers, are fabricated by extrusion techniques, for example, by handling with water jets. Though both methods have significantly higher productivity than electrospinning and yield finer fibers from melt, electrospinning is much more flexible in terms of achieving controlled fiber diameters and of processing polymers and additives of all kinds. Therefore, electrospinning provides manifold possibilities for the nanostructuring of materials.

The aim of this Review is not an exhaustive account of the literature, but rather a concise illustration of the various activities and research directions within the subject. It will emphasize trends, but will also highlight gaps requiring further research. We mainly limit our overview to journals articles, and consider patents and conference proceedings only in exceptional cases. Upon reviewing the literature, it is particularly apparent that many sound new studies on

Andreas Greiner studied chemistry at the University of Marburg and earned his doctorate there in 1988. After a postdoctoral stay with D. Pearson and H.-W. Schmidt in Santa Barbara, he returned to Marburg, where he completed his habilitation in macromolecular chemistry in 1995. In the same year, he took up a professorship at the University of Mainz, and in 2000, he became Professor of Macromolecular Chemistry in Marburg. Together with W. Heitz and J. H. Wendorff, he directs the TransMIT Center of Polymer Research and Nanotechnology. His research interests include the classical synthesis of monomers and polymers, the synthesis of functional polymers, nanotechnology, as well as the applications of polymers in optics, electronics, and medicine.

Joachim H. Wendorff received his doctorate from the University of Marburg in 1969 for work in the field of polymer physics with F. H. Müller. After a postdoctoral stay with F. P. Price in Amherst, he became a research assistant with E. W. Fischer at the University of Mainz. In 1982, he completed his habilitation in physical chemistry there. From 1976 to 1991, he headed the Physics Department at the German Polymer Institute (DKI) in Darmstadt. In 1990, he took up a professorship in physics at the TH Darmstadt, and in 1991, he moved to a professorship in physical chemistry at the University of Marburg. His research interests include functional polymers, liquid crystals, polymer alloys, molecular reinforcement, nanostructuring, and electrospinning.

electrospinning have only been published in conference proceedings. The reviews that have been published to date are cited in references [12–23].

1.2. Nanostructuring: New Properties and Applications

The increased interest in electrospinning was initiated in the 1990s by the possibility of producing polymeric nanofibers under laboratory conditions. One principle of nanotechnology is that the reduction of the dimensions of a material leads to new properties. For example, in semiconductor particles or films, new optoelectronic functions (quantum effects) appear, and in magnetic materials, superparamagnetism is observed.[24] In catalytic metal particles, a decrease in the diameter down to a few nanometers is often linked to changes in the crystal structure and the surface topology, as well as the electronic properties: the Fermi level and the reduction potential are shifted.[25] These changes have immediate consequences on the adsorption behavior, the catalytic activity, and the selectivity, for example.

The nanostructuring of surfaces can lead to exceptional effects, for example, the lotus effect (self-cleaning effect).[26] The nanoscale is also particularly relevant for biological systems, because the dimensions of proteins, viruses, and bacteria fall in this size range. Comparison with the diameters of these objects shows that the diameters of electrospun fibers can span a relatively wide range (Figure 3).

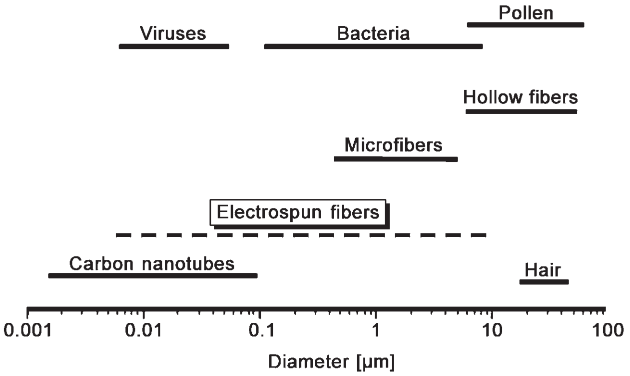


Figure 3. Comparison of the diameters of electrospun fibers to those of biological and technological objects.

Nanostructured systems are promising for diverse applications, such as the transport and targeted release of drugs and active agents in organisms, tissue engineering, the surface modification of implants, and wound healing.[27–29] In almost all these applications, as well as in applications in microelectronics (such as energy storage), nanoparticles and carbon nanotubes are currently in the spotlight. Nanorods of metals, metal oxides, or semiconductors,[30,31] and nanofibers of polymers have only recently gained importance.

2. Electrospinning Processes

2.1. Basic Principles

At first glance, electrospinning gives the impression of being a very simple and, therefore, easily controlled technique for the production of fibers with dimensions down to the nanometer range. First, polymers will be surveyed as fiber-forming materials. Later, materials such as metals, ceramics, and glasses will be considered as fiber precursors. In a typical electrospinning experiment in a laboratory, a polymer solution or melt is pumped through a thin nozzle with an inner diameter on the order of 100 μm (Figure 4). The nozzle simultaneously serves as an electrode, to which a high electric field of 100–500 kV m^{-1} is applied, and the distance to the counter electrode is 10–25 cm in laboratory systems. The currents that flow during electrospinning range from a few hundred nanoamperes to microamperes. The substrate on which the electrospun fibers are collected is typically brought into contact with the counter electrode. The vertical alignment of the electrodes "from top to bottom" is not insignificant with respect to the process, but in principal, electrospinning can also be carried out "from bottom to top" or horizontally.

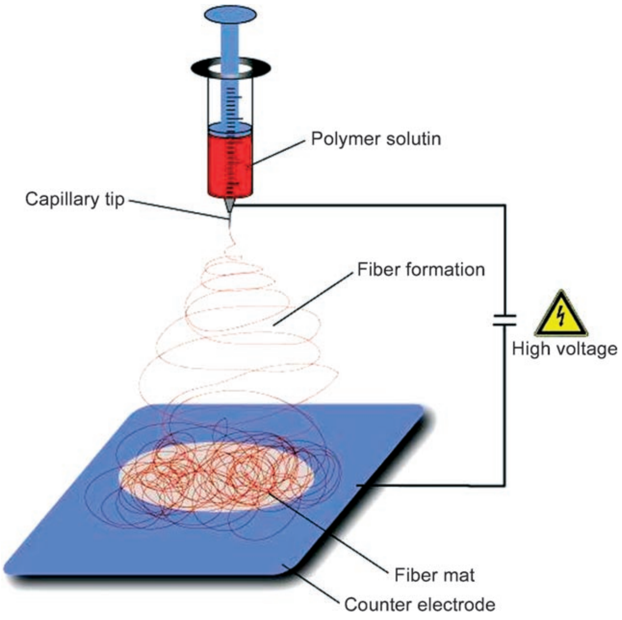


Figure 4. A laboratory setup for an electrospinning experiment with a perpendicular arrangement of the electrodes.

The applied voltage causes a cone-shaped deformation of the drop of polymer solution, in the direction of the counter electrode (Figure 5).[32,33] In electrospinning, the cone angle is about 30°. If higher voltages are applied, a jet is formed from the deformed drop, which moves towards the counter electrode and becomes narrower in the process.[34,35] On the way to the counter electrode, the solvent evaporates (or the melt solidifies), and solid fibers with diameters ranging from micrometers to nanometers are precipitated with high

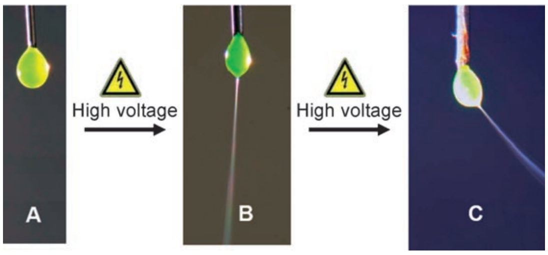


Figure 5. A droplet of a 5% solution of poly(ethylene oxide) (PEO) in water, dyed with fluorescein: A) in the absence of an applied voltage; B) at an applied voltage of 20 kV, with a jet perpendicular to the counter electrode; C) at an applied voltage of 20 kV, with a jet diagonal to the counter electrode.

velocities (of 40 m s^{-1} or more) on the counter electrode (Figure 6).

Upon closer inspection, it becomes clear that the electrospinning process is very complex. The jet, for instance, only follows a direct path towards the counter electrode for a certain distance, but then changes its appearance significantly. The jet is moved laterally and forms a series of coils, the envelope of which has the form of a cone opening towards the counter electrode (Figure 7).[36,37]

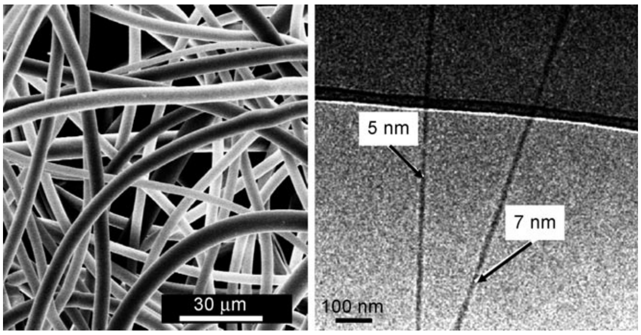


Figure 6. Left: SEM image of fibers of polyamide (PA) produced by melt electrospinning. Right: Transmission electron microscope (TEM) image of fibers of polylactide (PLA) produced by solution electrospinning.

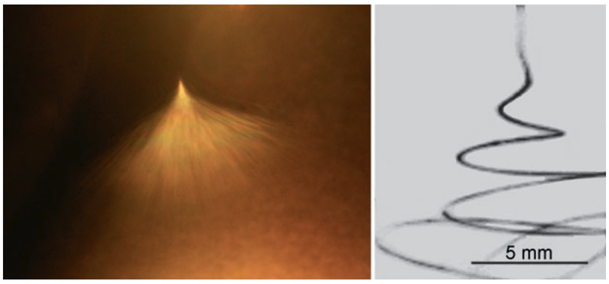


Figure 7. Left: Photograph of a jet of PEO solution during electrospinning. Right: High-speed photograph of jet instabilities.[37]

On occasion, beads, rather than fibers, are formed during electrospinning; fibers with beads arranged like pearls on a string can also be formed. In some cases, the fibers are not round, but are flat ribbons, and in other cases, the distribution of fiber diameters is broad (Figure 8). The shapes and dimensions of the fibers formed depend on a large set of parameters, for example, the properties of the polymer itself (such as molecular weight, molecular-weight distribution, glass-transition temperature, and solubility), as well the properties of the polymer solution (such as viscosity, viscoelasticity, concentration, surface tension, and electrical conductivity). The vapor pressure of the solvent and the relative humidity of the surroundings can also have a significant impact. Furthermore, the properties of the substrate, the feed rate of the solution, and the field strength and geometry of the electrodes (and therefore, the form of the electric field) play a major role in fiber formation.

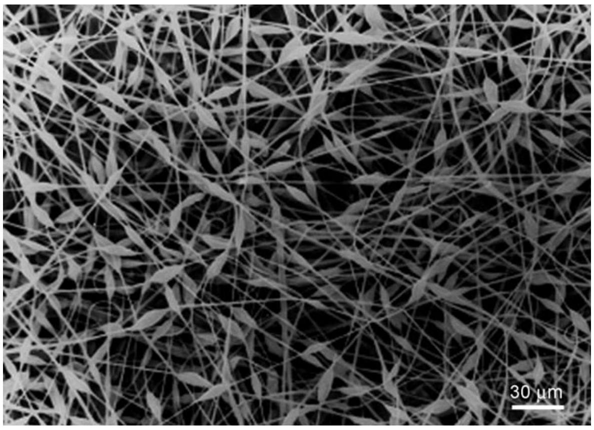


Figure 8. SEM image of the irregularly shaped fibers of polystyrene (PS) produced by electrospinning from THF solution.

2.2. Theoretical Background

As mentioned above, the electrospinning process is very intricate: it can be described as the interaction of several physical instability processes.[36–39] This intricacy is not astounding, considering that a liquid strand (solution or melt) undergoes complex structure-forming processes even in absence of an electric field; the strand is subjected to the so-called Rayleigh instability.[40–43] The final state is a periodic pearl-necklace arrangement of drops of a given radius (Figure 9).

During electrospinning, other instabilities are induced by the coupling of the liquid strand with the electric field (through the field-induced transport of charges into the liquid strand), in particular, the so-called axisymmetrical instability and the bending (or whipping) instability.[36–39]

In the case of the charge-driven axisymmetrical instability, a statistical variance of the jet's radius causes a modulation of the surface charge density. This modulation, in turn, generates tangential forces, which couple to the radius modulation and amplify it. The end result of such a coupling loop is the formation of beads, which are aligned along the fiber like

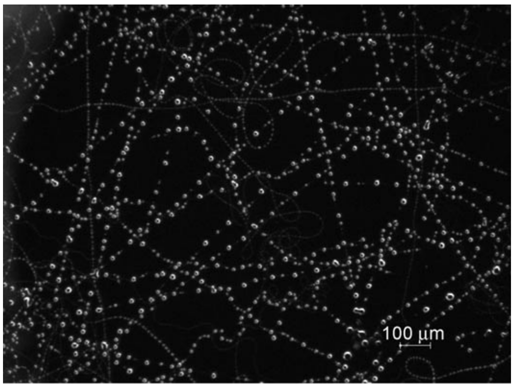


Figure 9. Optical image of the droplets formed from the disintegration of a melt-electrospun fiber.

pearls on a string. By varying the spinning parameters, bead formation can be prevented.

In the actual fiber formation, bending instabilities come into play, the occurrence of which is easily understood. Even a simple linear arrangement of three equal charges elastically fixed along a chain becomes unstable towards lateral deflection.[36] Viscosity and elastic forces counteract these deflections. Bending instabilities occur at high charge densities and fields, and they can typically be enhanced by increasing the electrical conductivity of the polymer solution, for example, by the addition of additives.[43] A straight section of the jet turns sideways and forms loops in the horizontal plane. The loop diameters increase with time during the motion towards the counter electrode (with velocities on the order of meters per second; Figure 10). During this process, the jet is highly stretched and reduced. Along these reduced fibers, bending occurs again and is followed by the formation of a new set of coils. This procedure is repeated until the fibers solidify or become resistant towards these instabilities, owing to their extreme thinness.

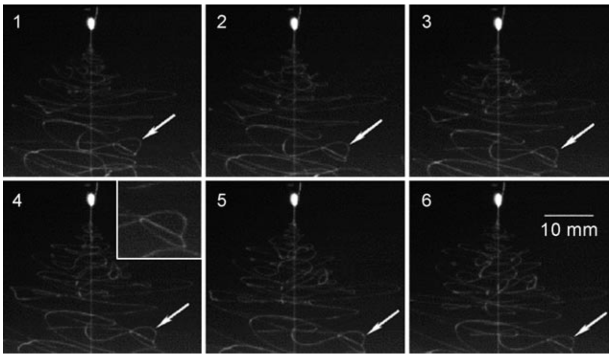


Figure 10. High-speed optical images of the formation of instability loops during electrospinning. The arrows indicate a double loop. Inset in frame 4: enlargement.[44]

Thanks to these instabilities, nanofibers with diameters down to a few nanometers can be generated stably and without decomposition of the jet into droplets. Some numbers are given to illustrate the characteristics of fiber-forming processes during electrospinning: typical stretching ratios are in the range of 10^5, and stretching rates are up to $10^5\ s^{-1}$. Such values are not accessible with other methods, such as fiber extrusion followed by mechanical stretching.[45] The high stretching rates are reflected in the morphologies of the evolving fibers (for example, with a high degree of chain and crystallite orientation), as discussed in Section 4.1. Two other phenomena that are often observed during electrospinning are branching (Figure 11) and the occurrence of undulated fibers.

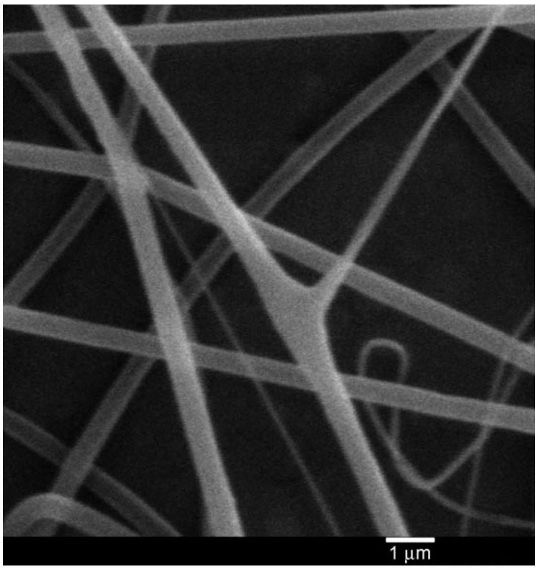


Figure 11. SEM image of a branched fiber formed by the ejection of a secondary jet from the primary jet during electrospinning.

2.3. Core–Shell Nanofibers by Coaxial Electrospinning

In many cases, the functionalization of nanofibers through the integration of functional molecules or objects (in fields such as biosensor technology, tissue engineering, drug delivery, and nanoelectronics) leads to obstacles in conventional electrospinning. An important problem is often the need to keep the functionalizing agents (for example, biomolecules such as enzymes, proteins, drugs, viruses, and bacteria) in a fluid environment to maintain their functionality. Another problem may be that the molecular weight of the material that is to be included in the core fiber is too low for the material to be spun into fibers. In this case, a modified electrospinning process can be applied: coaxial electrospinning.[46–56]

In coaxial electrospinning, two concentrically aligned nozzles are used for spinning (Figure 12). The same voltage is applied to both nozzles, and it deforms the compound droplet. A jet is generated on the tip of the deformed droplet, and in an ideal case, a core–shell nanofiber is created. Upon closer inspection, it becomes clear that coaxial electrospinning involves a set of intricate physical processes, which have only been elucidated experimentally to a certain extent and require mathematical modeling.[53] One common problem during fiber formation is that the outer droplet can be transformed into a jet, while the inner droplet cannot

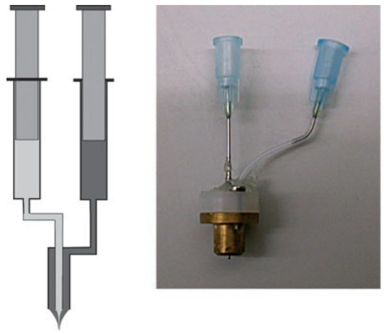


Figure 12. Left: A setup for coaxial electrospinning. Right: The experimental setup for coaxial electrospinning used in our laboratory.

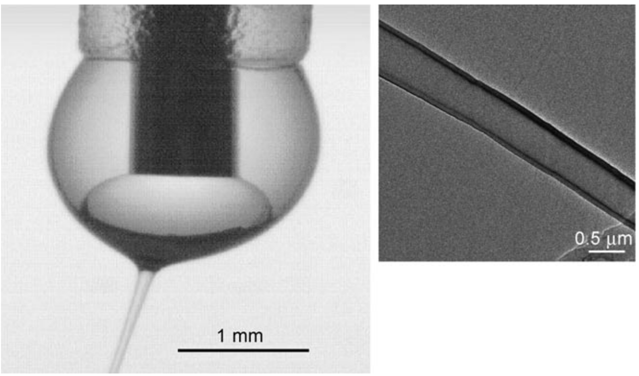


Figure 13. Left: Optical image of core–shell droplets on the nozzles of an apparatus for coaxial electrospinning. Right: SEM image of core–shell fibers of poly(vinylidene fluoride) (PVDF; core) and polycarbonate (PC; shell) produced by coaxial electrospinning.[53]

(Figure 13, left). A major reason for this behavior is that on the inner droplet, contrary to the outer droplet, no surface charges can occur, because of electrostatic forces. The deformation of the inner droplet into the core fiber is left to viscous forces alone. In principal, these viscous forces can be deduced from mathematical modeling, so that general conditions for the experiment are available.

If the appropriate technical parameters are chosen, core–shell fibers can be fabricated with high precision from a huge variety of materials by coaxial electrospinning (Figure 13, right). For example, core–shell fibers can be formed with polystyrene (PS) and poly(ethylene oxide) (PEO), and "nanocables" can be formed with electrically conductive polyhexylthiophene as the core and PEO as the insulating shell.[46]

Coaxial electrospinning is not limited to the production of core–shell fibers with a continuous core. Systems with discontinuous drop-shaped inclusions inside a continuous shell can also be generated. This type of morphology is of interest for the inclusion of biological objects, for example, the green fluorescent protein (GFP), in an aqueous environment, or for the storage and controlled release of drugs. The advantages of coaxial electrospinning in such cases are that the inner droplet is not electrically charged and that the mechanical forces affecting fiber formation are small and theoretically assessable.[53]

With the choice of appropriate solvent combinations, it is possible to produce hollow core–shell fibers. Upon evaporation of the solvent, the core polymer precipitates on the walls of the previously formed shell. Coaxial electrospinning was also used to produce ceramic hollow fibers, for example, by cospinning mineral oil as the core material with polyvinylpyrrolidone and $Ti(O\textit{i}Pr)_4$ (in ethanol) as the shell material. After removal of the oil and calcination, hollow titanium fibers were obtained.[48,49] Non-fiber-forming materials such as oligomers, metal salts, enzymes, and solvents can also be immobilized using this method. Finally, it should be mentioned that studies on electrospraying have played a major role in the development of coaxial spinning.[57]

In an approach similar to coaxial electrospinning, enveloping gas currents were used to stabilize polymer jets during electrospinning.[58] The use of two-phase electrospinning to encapsulate materials that cannot be electrospun (such as water) into fibers is also noteworthy.[59,60]

The use of several syringes in parallel alignment as electrodes in multijet electrospinning allows the fabrication of electrospun tissues consisting of different fiber materials (Figure 14).[61–65] Multijet electrospinning is even more intricate than the single-jet process, because of the repulsion between similarly charged jets, for example. A detailed examination of this matter is particularly important for high efficiencies and complex tissue architectures.

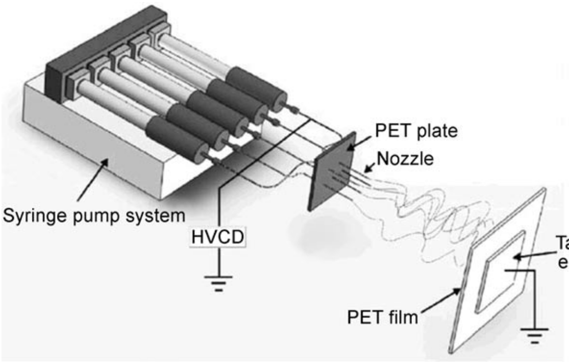


Figure 14. An experimental setup for multijet electrospinning.[65] HVDC = high-voltage direct-current power supply.

3. Choice of System and Parameters

In principal, nearly all soluble or fusible polymers can be processed into fibers by electrospinning, provided that the molecular parameters (such as solubility, glass-transition temperature, melting point, crystallization velocity, molecular weight, molecular-weight distribution, entanglement density, solvent vapor pressure, and pH value) and the process parameters (such as concentration, electrical conductivity, surface tension, feed rate, electrode separation and geometry, temperature, and relative humidity) are correctly adjusted. In this respect, empirical knowledge is crucial, but as mentioned above, theoretical models can increasingly be applied to predict the dimensions and structures of the fibers produced. In the choice of system, the polymer material is generally the first consideration, and it is chosen on the basis of the required properties of the fibers and the necessary spinning parameters. The fibers should be insoluble, electrically conductive, mechanically resilient, adhesive, and should have chemoselective reactivity, for example. With respect to the spinning parameters, the processability in water is often an important criterion. Apart from these purely technical requirements, fundamental aspects can also play a role in the choice of system. For example, the influence of confinement effects (caused by the small dimensions of the nanofibers) on intricate polymer systems with particular conformations, morphologies, and functions are still widely unknown.

For our overview, we have chosen an arbitrary approach that is guided by the discussion of frequently asked questions. In addition to biopolymers and their derivatives, water-soluble polymers, solvent-based polymer systems, and multiphase polymer systems (for example, blends, block, and graft copolymers) will be considered below. However, to gain a first overview of the influence of different parameters on fiber diameter and morphology (for example, cylindrical, ribbon-like, or beaded), in particular, we refer to the work of Fong et al.,[66] Koombhongse et al.,[67] Deitzel et al.,[68] and Shin et al.[69] In these articles, a number of process parameters and their effects on fiber architecture and dimensions are discussed by means of examples such as PEO, PS, and poly(ether imide) (PEI). Further investigations on process parameters were reported for PEO,[70,71] poly(vinyl alcohol) (PVA),[70,72–77] PS,[78–80] polyacrylonitrile (PAN),[78,81–84] polylactide (PLA),[85–87] poly(ε-caprolactone) (PCL),[70,88] polyurethane (PU),[70,89] polyamide (PA),[90–93] cellulose acetate (CA),[94] and poly(vinyl acetate) (PVAc).[95] In general, it is observed that fibers become more uniform and assume a cylindrical shape with increasing polymer concentration in solution; fiber diameters also increase significantly with increasing polymer concentration. At lower concentrations, increasingly thinner fibers are formed, with additional beads along the fiber axis (see Section 2.2); at very high dilution, fiber formation no longer takes place. The formation of beads can be prevented by increasing the electrical conductivity of the solution, so that fibers with diameters down to a few nanometers can be produced. Appropriate solvent viscosities typically range from tens to hundreds of millipascals per second, and electrical conductivities in organic solvents typically range from nano- to microsiemens per centimeter. The surface tension of (organic) solutions is usually about $30\,\mathrm{mN\,m^{-1}}$, and it can be significantly influenced by the addition of surfactants.[96,97] The fiber morphology can also very often be directed to cylindrical by the appropriate choice of solvent mixture (high-boiling/low-boiling solvents).

It is not possible to make a general recommendation for particular concentrations and the resulting viscosities, electrical conductivities, and surface tensions, because the ideal values of these parameters vary considerably with the polymer–solvent system. The polarity of the electrodes and the use of alternating or direct current often do not seem to have much influence, but Kessick et al. observed a significantly higher degree of orientation of PEO fibers and a higher fiber density of carboxymethylcellulose when alternating current was used.[98] Different polarities were reported to result in different morphologies of PA fibers by Supaphol et al.[92] Electrostatic charging of the fibers plays a major role in tissue formation during the deposition on the substrate, but this issue has only been discussed in a few papers.[99]

Though the electrospinning of polymer solutions enables the fabrication of fibers with relatively low diameters, its productivity, in terms of 1–20 wt% solutions, is moderate. Moreover, evaporation of the solvent can substantially impede the electrospinning process and can destroy the evolving fibers by causing filming. An alternative might be electrospinning from the melt, but for all but a few exceptions (low-melting polymers), this method leads to average fiber diameters that are considerably greater than 1 μm and to a broad distribution of diameters, as a result of the high melt viscosities of the polymers.[100]

Levit and Tepper showed that the electrospinning of polymers is also possible using supercritical CO_2 as the solvent.[101] Dalton et al. demonstrated that solvent-free melt electrospinning could be used to electrospin PEO-*b*-PCL block copolymers directly onto living cells, without causing cell death.[102] Because of their high viscosities, the electrospinning of polymer melts requires large electrode separations, which in turn require higher electric fields. Under normal atmosphere, such large electric fields lead to the danger of electric shock. Variation of the atmospheric composition and even variation of the humidity can have a significant impact on the electrospinning process. High-vacuum conditions should allow electrospinning at higher voltages. Kim et al. reported that PCL fibers have significantly better properties when they are electrospun (from solution) under vacuum.[103] Rangkupan and Reneker obtained distinctly thinner fibers from polypropylene (PP) melts when these were electrospun under vacuum rather than under normal pressure.[104] Becker obtained fibers of 900 nm in diameter by melt electrospinning PA mixtures with different molecular weights under an SF_6 atmosphere.[105] This diameter is relatively good for melt-electrospun PA fibers; however, modern melt-blown processes can produce considerably thinner fibers at a higher productivity.

The variety of possible spinning parameters and of resulting new fiber architectures will become even greater with new spinning techniques. Yarin and Zussman developed a two-phase system consisting of a ferroelectric suspension and a polymer solution, which could be multijet electrospun onto the counter electrode through the simultaneous application of magnetic and electric fields.[106] At small electrode separations, the electrospun fibers could be deposited very precisely.[107–109] Either a very fine tip (25 μm in diameter) onto which droplets of the spinning solution were deposited (discontinuous fabrication of fibers) or fine tips that were continuously fed with spinning solution by a microfluidic system were employed. The electrode separations ranged from 500 μm to 2 cm. The counter electrode, onto which the fibers were deposited, was moved with a velocity of up to

150 cm s^{-1}. Thus, nanofibers could be deposited at a given position with a given orientation, as well as according to a predetermined electrode alignment, for example. Similar processes can also be carried out with conventional single-jet electrospinning systems, if the distance between electrodes is reduced to the centimeter range. Further possibilities for the variation of materials are provided by a process reported by Gupta et al. and Kim et al. for the chemical, photoinduced cross-linking of polymethacrylates.[110,111]

As shown by the examples presented above, the variation of process parameters in electrospinning provides diverse possibilities for the targeted adjustment of the chemical and physical properties of the electrospun materials. Further possibilities are provided by the choice of material system, as we discuss below.

3.1. Biopolymers and Modified Biopolymers

Many biopolymers, modified biopolymers, and blends of biopolymers with synthetic polymers have been processed into nanofibers by electrospinning. Very specific conditions are often necessary, such as the use of special solvents or the processing of the materials as blends (for example, with PEO or PVA). Some examples are summarized in Table 1. The electrospinning of collagen for applications in tissue engineering was possible from hexafluoroisopropyl alcohol,[112–114] or as a blend with PEO,[115,116] PCL,[117] or PLA-*co*-PCL.[118] Optimization of the spinning parameters led to collagen fibers with diameters of 200–500 nm. Denatured collagen (gelatin) was electrospun from aqueous solution and 2,2,2-trifluoroethanol, either in pure form or as a blend.[114,116,119] Other proteins and enzymes, such as casein, lipase,[120] cellulase,[121] bovine serum albumin (BSA),[122,123] and luciferase,[122] could only be processed by electrospinning as blends with synthetic polymers.

Fibers containing enzymes are often called bioactive, although this term is actually redundant, because all nanofibers should be bioactive in some way. Surprisingly, an increased enzymatic activity was often reported when enzymes were immobilized in electrospun fibers. The release of enzymes from electrospun fibers of polymer blends is generally very fast (burst release), but can be slowed down considerably by coating the fibers.[122] Enzymes were also immobilized by coupling to electrospun fibers.[124–127]

Fibrinogen, a natural wound-healing material, was processed into fibers with diameters of 0.08–1.2 μm by electrospinning.[128] Several papers describe the electrospinning of silk and silk-like polymers, mainly for biomedical applications.[129–143] Electrospun fibers of artificial spider silk were obtained from hexafluoroisopropyl alcohol.[144] Chitin and chitosan could be electrospun as pure materials and as blends.[145–154] These fibers are of particular interest for wound dressings. Especially noteworthy is the antibacterial activity of fibers produced from quaternized chitosan/PVA blends.[153] Cellulose, a classical fiber material, was electrospun from *N*-methylmorpholine *N*-oxide (NMO)/water systems and *N*,*N*-dimethylacetamide/LiCl systems into fibers with diameters in the submicrometer range.[155,156] CA, a cellulose derivative that is soluble in organic solvents and a well-established filter material, was electrospun without any problem.[94]

Table 1: Electrospun biopolymers.

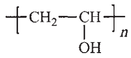
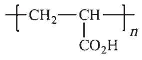
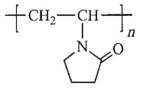
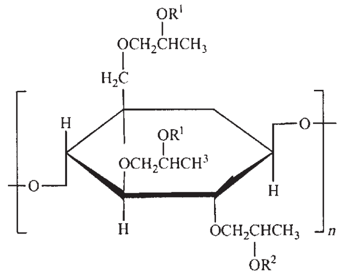
Polymer system	Solvent	Ref.
collagen	hexafluoroisopropyl alcohol	[112–114]
collagen/PEO	aq. HCl	[115]
	water/NaCl	[116]
collagen/PCL	methanol–$CHCl_3$/hexafluoroisopropyl alcohol	[117]
collagen/PLA-*co*-PCL	hexafluoroisopropyl alcohol	[118]
gelatin	hexafluoroisopropyl alcohol	[114]
	2,2,2-trifluoroethanol	[119]
gelatin/PCL	2,2,2-trifluoroethanol	[119]
gelatin/PEO	water/NaCl	[116]
casein/PVA (PEO)	triethanolamine/water	[120]
lipase	bis-tris-propane buffer[a]	[120]
cellulase/PVA	acetic acid	[121]
BSA/PVA	water	[122,123]
luciferase/PVA	water	[122]
α-chymotrypsin	toluene	[124]
fibrinogen	hexafluoroisopropyl alcohol	[128]
regenerated silk (*Bombyx mori*)	hexafluoroacetone	[129,130–132]
Bombyx mori silk/PEO	water	[133,134]
silk fibroin	formic acid	[135–140]
silk fibroin/chitosan	formic acid	[141]
silk fibroin/chitin	hexafluoroisopropyl alcohol	[142]
silk/PEO (coaxial)	water	[143]
artificial spider silk	hexafluoroisopropyl alcohol	[144]
chitin	hexafluoroisopropyl alcohol	[145,146]
chitosan	formic acid	[147]
	trifluoroacetic acid	[147]
	acetic acid	[147]
chitosan/PEO	acetic acid	[148,149]
chitosan/PVA	acetic acid	[150–152]
quaternized chitosan/PVA	water	[153]
hexanoylchitosan/PLA	THF, $CHCl_3$, CH_2Cl_2	[154]
cellulose	NMO/water	[155]
	N,*N*-dimethylacetamide/LiCl	[156]
CA	acetone, *N*,*N*-dimethylacetamide, acetic acid	[94]

[a] 1,3-Bis[tris(hydroxymethyl)methylamino]propane.

3.2. Electrospinning and Cross-Linking of Water-Soluble Polymers

Water-soluble polymers like PEO, PVA, poly(acrylic acid) (PAA), polyacrylamide, polyelectrolytes, polyvinylpyrrolidone (PVP), and hydroxypropylcellulose (HPC) offer a variety of advantages for electrospinning. The solubility properties of water can be adjusted by the pH value, the temperature, or the addition of surfactants or other solvents (for example, alcohols). Electrospun fibers of water-soluble polymers decompose rapidly on contact with water. While this property may be of interest for biomedical applications, additional stabilization of these fibers by cross-linking is necessary for other technical applications (for example, filters and textiles).

Table 2: Electrospun water-soluble polymers.

Polymer system	Chemical formula	Ref.
PEO	$-\!\!\!+\!CH_2-CH_2-O\!+\!\!\!-_n$	[10,36,66,68–71,98,99,157–167]
PVA	 $\left[CH_2-CH(OH)\right]_n$	[70,72–77,96,97,122,123,170–173]
PAA	 $\left[CH_2-CH(CO_2H)\right]_n$	[70,174–176]
PVA/PAA		[178–183]
PVP		[187,188]
PVP composites		[189–213]
PVP, coaxial		[49,214,215]
HPC		[216]

Despite the variety of synthesis possibilities, only a rather small number of water-soluble polymers have been electrospun from water or solvent mixtures containing water. Some examples are summarized in Table 2. The most extensive investigations have been carried out on PEO and PVA, because both these polymers are readily available in different molecular weights. PEO is especially versatile for electrospinning, because it is soluble in many solvents (besides water).[10,36,66,68–71,98,99,157–167] PEO fibers are particularly interesting for biomedical applications, because of their good biocompatibility.[168] However, with increasing degree of polymerization the possibility of the metabolism being influenced must be taken into consideration. The hydrolytic decomposition of physiologically degradable polymer fibers can be affected by the addition of hydrophilic PEO, as shown for the case of PLA.[169] The hydrophilicity and decomposition rate of fiber-forming polymers can also have an impact on their biological activity towards cells.

Compared to PEO, PVA offers an even larger scope of variations,[70,72–77,96,97,122,123,170–173] because its degree of hydrolysis and, hence, its water solubility can be adjusted.[170] The hydroxy groups in PVA can be used for chemical reactions either before or after electrospinning. The crystallinity and, hence, the water resistance of electrospun fibers of PVA can be distinctly increased by treatment with solvents.[96,173] PAA can be electrospun from aqueous solution nearly as well as PVA. Further modifications are possible through the variation of the pH value and the addition of salts.[70,174–176]

The physical stability of PVA/PAA blends towards water can be significantly improved by chemical cross-linking reactions.[177] Correspondingly, the water resistance of electrospun fibers of PVA/PAA blends was increased by esterification reactions[178–183] and by aldol reactions with polyaldehydes.[75] This result is important for a variety of technical applications. However, it must be taken into account that unreacted cross-linking agents can lead to significant changes in the properties of the polymer (for example, toxicity). For instance, the hydrophilicity and, with it, the swelling of PVA fibers in water can be increased through cross-linking with PAA, because of the presence of unreacted carboxy groups.[178] Further disadvantages are the limited hydrolytic stability of the cross-links and, from a technical point of view, the rather poor energy balance of the thermally induced reactions, because the substrate and the electrospun PVA tissue also have to be cross-linked during the cross-linking reactions.

An interesting variation on the cross-linking of PVA with PAA or polyaldehydes was achieved with electrospun PVA/cyclodextrin fibers, which show a largely pH-dependent swelling behavior in water after thermal cross-linking.[174] The functionalization of PVA with photo-cross-linkable substituents leads to electrospun PVA derivatives that can be cross-linked through exposure to light.[184] This procedure results in a better energy balance and also allows site-directed cross-linking. Recently, electrospun polybutadiene fibers were stabilized against cold flow through photo-cross-linking.[185] One noteworthy variation on the cross-linking of electrospun fibers is reactive electrospinning; in a concrete example, 2-hydroxymethyl methacrylate, methacrylic acid, ethylene glycol dimethacrylate, 2,2′-azobis(isobutyronitrile), and a photo-cross-linking agent were first prepolymerized and subsequently photochemically cross-linked during the electrospinning process.[180] Following a similar approach, poly(dicyclopentadiene) fibers could be obtained.[111] The concept of reactive electrospinning offers various possibilities for the dynamic variation of viscosities. However, the electrospinning process becomes technically more complex, and the pot life, in particular, has to be accurately controlled.[186]

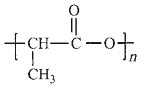
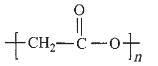
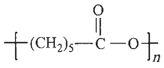
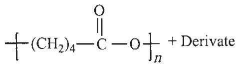
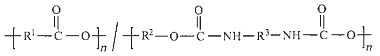
PVP can also be electrospun from aqueous solution.[187] The electrospinning of PVP blends and subsequent selective extraction can be used to produce structured electrospun fibers.[188] A large number of papers have reported the fabrication of electrospun fibers of composites of PVP and metal compounds, viruses, or enzymes.[189–213] Metal compounds are generally used in the form of sol–gel precursors, and the PVP fibers are used as templates. In this way, ceramic fibers with diameters in the submicrometer range can be produced, for example. More complex structures can be prepared through the coaxial electrospinning of PVP.[49,214,215]

Surprisingly, the electrospinning of HPC has only been reported once,[216] although HPC is commercially available, is highly water-soluble, and should, furthermore, be of special interest because of its lyotropic properties in aqueous solution.[217]

3.3. Electrospinning of Bioerodible Polymers

Polymers that are biodegradable or hydrolyzable under physiological conditions (bioerodible polymers), such as aliphatic polyesters, polyanhydrides, and polyphosphazenes, are important for a large variety of applications (Table 3).[218]

Table 3: Electrospun bioerodible polymers.

Polymer system	Chemical formula	Ref.
PLA	 $\left[\mathrm{CH(CH_3)-C(=O)-O}\right]_n$	[85–87, 219–221]
PGA	 $\left[\mathrm{CH_2-C(=O)-O}\right]_n$	[222]
PCL	 $\left[\mathrm{(CH_2)_5-C(=O)-O}\right]_n$	[44, 52, 56, 88, 103, 117, 223–228]
PHB	 $\left[\mathrm{(CH_2)_4-C(=O)-O}\right]_n$ + Derivate	[229–231]
PEU	 $\left[\mathrm{R^1-C(=O)-O}\right]_n / \left[\mathrm{R^2-O-C(=O)-NH-R^3-NH-C(=O)-O}\right]_n$	[232, 233]
blends, composites, copolymers, and block copolymers of PLA, PGA, and PCL		[56, 221, 227, 228, 231, 234–244]

Electrospun fibers of bioerodible polymers are the focus of intense study for pharmaceutical applications and for applications in tissue engineering.

PLA, an aliphatic polyester, is one of the classical bioerodible polymers and has been successfully electrospun.[85,219–221] One reason for the ease with which the different isomers of PLA can be electrospun is their high solubility in halogenated aliphatic solvents. Poly(glycolic acid) (PGA) has only been employed to a limited degree,[222] whereas PCL, which is highly soluble in many solvents, and copolymers of PCL have been used extensively for the fabrication of electrospun tissues.[44,52,56,86,88,103,117,223–228] Polyhydroxybutyrate (PHB) and its versatile derivatives have only been examined in a few studies.[229–231] Poly(ester urethane)s (PEU) have also been infrequently used, which is surprising because these polymers represent a large variety of materials with tailored solution properties; the electrospinning of PEU has been reported in only two papers.[232,233] A large number of papers have been published on blends, composites, copolymers, and block copolymers of various bioerodible polymers.[56,221,227,228,231,234–244] Such systems have also been used for the immobilization and release of functional materials, such as BSA[56] and silver nanoparticles.[244]

3.4. Electrospinning of Organosoluble Polymers and of Polymers Based on Organosoluble Precursors

We already mentioned some bioerodible polymers that can be electrospun from organic solvents in Section 3.3; however, there are, of course, many other organosoluble polymers (Table 4), including PS, PAN, polycarbonate (PC), aliphatic and aromatic PA, polyimides (PI), polybenzimidazole (PBI), poly(ethylene terephthalate) (PET), PU, poly[ethylene-*co*-(vinyl acetate)] (PEV), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), poly(vinyl butyral) (PVB), CA, and poly(vinylidene fluoride) (PVDF). Apart from of the large number of appropriate polymer systems, the main advantage of electrospinning from organic solvents is the availability of a broad range of solvent properties (for example, polarity and vapor pressure). However, the properties of the organic solvents (such as flammability, toxicity, and corrosiveness) can often be disadvantageous. These disadvantages are not an issue in laboratory systems, but may play a major role in industrial production facilities, as the solutions used for electrospinning generally contain 85–95 % solvent. For this reason, melt electrospinning, which requires no solvent and gives quantitative yields, is of great importance, as discussed in Section 3.5.

Table 4: Electrospun organosoluble polymers and polymers based on organosoluble precursors.

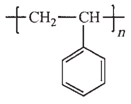
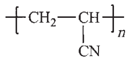
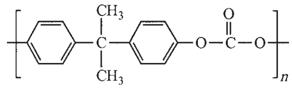
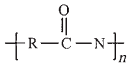
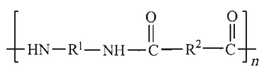
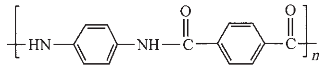
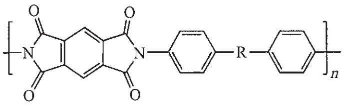
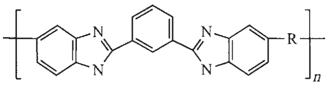
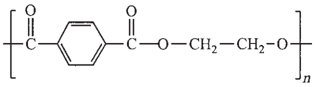
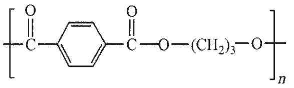
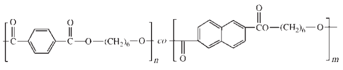
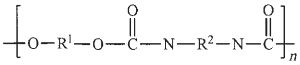
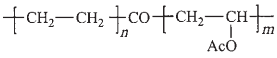
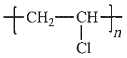
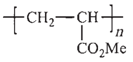
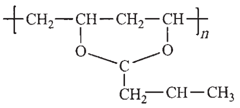
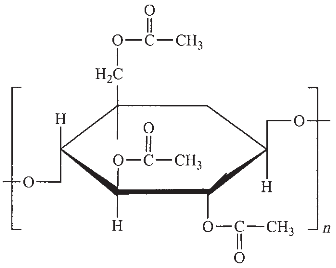
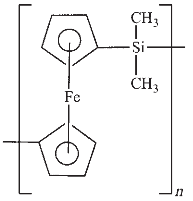
Polymer system	Chemical formula	Ref.
PS		[67, 80, 125, 162, 245–250]
PAN	 $\left[\mathrm{CH_2-CH(CN)}\right]_n$	[81–84, 251–262]
PC		[163, 264]
aliphatic PA	 $\left[\mathrm{R-C(=O)-N}\right]_n$  $\left[\mathrm{HN-R^1-NH-C(=O)-R^2-C(=O)}\right]_n$	[44, 91–93, 265–274]
aromatic PA		[275]

Table 4: (Continued)

Polymer system	Chemical formula	Ref.
PI		[67, 277–279]
PBI		[280, 281]
PET		[12, 273, 282, 283]
PTT		[284]
PHT-*co*-PHN		[285]
PU	 $\left[O-R^1-O-C(=O)-N-R^2-N-C(=O)\right]_n$	[89, 163, 232, 233, 281, 286–293]
PEV	 $\left[CH_2-CH_2\right]_n-CO-\left[CH_2-CH(OAc)\right]_m$	[59, 221]
PVC	 $\left[CH_2-CH(Cl)\right]_n$	[294, 295]
PMMA	 $\left[CH_2-CH(CO_2Me)\right]_n$	[162, 296, 297]
PVB		[298]
ZA		[157]
PVDF	$\left[CH_2-CF_2\right]_n$	[67]
PFDS		[299]

The electrospinning of PS has been extensively studied.[67,80,125,162,245–250] The formation of beads along the fibers typically occurs during the electrospinning of PS, but can be avoided by the appropriate choice of parameters. For example, Supaphol et al. found that bead formation can be prevented by the addition of surfactants.[80] As with most other polymer systems, bead formation can also be prevented by increasing the polymer concentration (which results in larger fiber diameters) or by increasing the electrical conductivity of the spinning solution.

PAN can be electrospun from dimethylformamide (DMF) solution into very thin and uniform fibers.[81–84,251–262] PAN fibers, including electrospun fibers, can be converted into carbon fibers by pyrolysis.[263] Another possibility is the conversion of electrospun PAN fibers by hydrolysis. For example, Liu and Hsieh obtained hydrophilic fibers by the basic hydrolysis of PAN fibers.[261] Vancso et al. studied the mechanical properties of single PAN fibers and found high modulus values, which they attributed to the high degree of molecular orientation of the PAN chains.[256]

The electrospinning of PC usually results in flat ribbonlike fibers,[163,264] or in cylindrical fibers if the electrical conductivity is increased. Because PC fibers can be electrostatically charged, they are suitable as filter materials.[163]

Aliphatic PA (nylon) can be electrospun from organic solutions into very fine and uniform fibers.[44,91–93,265–274] A disadvantage is that some of the solvents required are very corrosive (for example, formic acid). Contrary to the procedure for many other polymers (such as PLA), the electrospinning of PA must often carried out with solutions having high polymer concentrations (10–15%) to obtain continuous fibers. The influence of electrospinning on molecular orientation during fiber formation is of particular interest with respect to the use of PA as a semicrystalline fiber material (see Section 4.1).[268,272] Owing to their relatively high solvent and thermal stability, electrospun PA fibers are of considerable interest for applications in filter media. Suthar and Chase examined the application of electrospun PA fibers in coalescing filters.[267] Electrospun PA fibers were used for the preparation of transparent epoxy composites with improved mechanical properties by Vancso et al.[265] This method has not yet been technologically optimized, possibly because of the relatively low availability of electrospun fibers. Electrospun PA fibers with the smallest diameters to date (1 nm) were obtained by Hou et al.[93] Such fine fibers are currently, for the most part, technologically irrelevant, yet highly interesting from a fundamental point of view because of the possibility of confinement effects resulting from the molecular-level dimensions. Further study of confinement effects in electrospun fibers could yield important results.

Poly(*p*-phenylene terephthalate) (PPTA) is an aromatic PA that melts with decomposition. At sufficient concentrations of PPTA in appropriate solvents, lyotropic solutions are formed, from which fibers with extremely high tensile strength can be produced by solution spinning.[276] Electrospun fibers of PPTA were obtained from sulfuric acid.[275] Two other polymers that have high thermal stability and that melt with decomposition are PI and PBI. The soluble precursors of these polymers can be electrospun from solution and subsequently converted into the target polymers through polymer-analogous reactions (generally thermal).[67,277–281] Note that during the polymer-analogous reaction of the precursors the fiber diameter can shrink considerably, which can cause disintegration of the fiber (however, this problem was not explicitly mentioned in the examples given).

Aliphatic polyesters such as PET are typical construction materials, which are distinguished by their excellent thermal and mechanical properties. However, most are only moderately soluble in rather exotic solvents. This problem could be the reason for the scarcity of studies on the electrospinning of PET.[12,273,282,283] The electrospun PET fibers described in these reports have rather large diameters. Interestingly, derivatives of PET with higher solubilities, poly(trimethylene terephthalate) (PTT) and poly[(hexamethylene terephthalate)-*co*-(hexamethylene 2,6-naphthalate)] (PHT-*co*-PHN)), were employed for electrospinning.[284,285]

The electrospinning of PU, which offers a wide range of possibilities because of its chemical structure, has been considered in several studies.[89,163,232,233,281,286–293] Extensive investigations on the relevant electrospinning parameters of PU systems were carried out by Kidoaki et al.[89] and by Demir et al.,[286] among others. With the appropriate choice of monomers, the resulting electrospun PU tissues are distinguished by very high flexibility[288] or by a strong shape-memory effect.[289] Applications of electrospun PU tissues as wound dressings, for example, have been reported.[287]

PEV is a highly variable polymer system that is commercially available, but it has only attracted moderate interest in the field of electrospinning.[59,221] The situation is similar for PVC.[294] Electrospun fibers with improved hydrolytic resistance towards organophosphates, which are prototypical substances for chemical weapons, were fabricated from mixtures of PVC and modified β-cyclodextrins by Ramakrishna et al.[295]

PMMA is another readily soluble and commercially available polymer that is suitable for electrospinning.[162] PMMA typically forms electrospun fibers with spindlelike beads, but the formation of the beads can be prevented by varying the spinning parameters. The copolymerization of MMA and tetrahydroperfluorooctyl acrylate affords copolymers, which can be electrospun into fibers with a high fluorine content and, hence, a large contact angle with water.[296] In a fundamental study, Zussman et al. obtained coaxially arranged fibers of PAN and PMMA by coaxial electrospinning.[297]

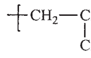
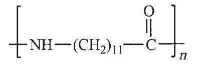
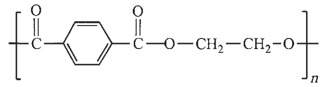
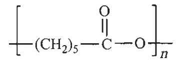
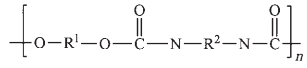
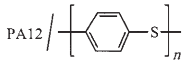
PVB is a readily soluble polymer that has seldom been used for electrospinning, although it forms very uniform fibers with relatively small diameters. The polymer is especially interesting because it is soluble in mixtures of water and ethanol and has a relatively low decomposition temperature. Therefore, PVB is well-suited as a precursor for metal oxide fibers (see Section 3.6).[298]

There have been surprisingly few reports on the electrospinning of CA, although it is readily soluble, can be readily electrospun, and can be chemically modified in diverse ways.[94] The organometallic polymer polyferrocenyldimethylsilane (PFDS) could be electrospun into very fine and highly crystalline fibers.[299]

3.5. Melt-Electrospun Polymers

The electrospinning of polymers from the melt avoids the use of solvents and is, therefore, attractive from the perspective of productivity and environmental considerations. However, the method is limited by the fact that nanofibers with diameters of less than 400 nm and with a narrow diameter distribution cannot yet be fabricated. To date, polyethylene (PE), polypropylene (PP), polyamide 12 (PA12), PET, PCL, and PU have been processed by melt electrospinning (Table 5).[100,102,104,292,300–305] Fiber diameters of less than 300 nm could only be obtained from the low-melting PCL.[102] In this case, PCL was electrospun directly onto the tissue of living cells, without any visible harm to the cells. However, PCL is virtually unfeasible for technical applications, because of its low melting range. As mentioned in Section 3, the electrospinning of PA12 under an SF_6 atmosphere afforded rather thin fibers (average diameters of 900 nm).[105] Coaxially aligned fibers of poly(phenylene sulfide) (PPS) and PET with relatively small diameters were produced by coaxial melt electrospinning (Figure 15).[305]

Table 5: Melt-electrospun polymers.

Polymer system	Chemical formula	Ref.
PE	$\left[\!-CH_2-CH_2-\right]_n$	[300, 301]
PP	 $\left[-CH_2-CH(CH_3)-\right]_n$	[100, 104, 304]
PA12	 $\left[-NH-(CH_2)_{11}-C(=O)-\right]_n$	[105, 302]
PET		[105, 303]
PCL	 $\left[-(CH_2)_5-C(=O)-O-\right]_n$	[102]
PU	 $\left[-O-R^1-O-C(=O)-N-R^2-N-C(=O)-\right]_n$	[292]
PA12/PPS, coaxial		[305]

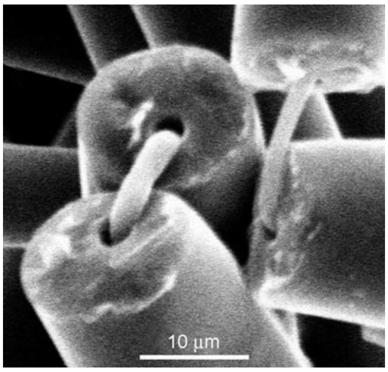


Figure 15. SEM image of core–shell fibers of poly(phenylene sulfide) (PPS; core) and poly(ethylene terephthalate) (PET; shell) produced by coaxial melt electrospinning.[305]

3.6. Complex Polymer Systems and Inorganic Materials

Complex polymer systems are systems that can form supramolecular structures, for example, polymer blends, block and graft copolymers, and polymer composites (mixtures with nonpolymeric compounds). Electrospun fibers of inorganic systems are often obtained through the use of polymer composites with inorganic components or of sol–gel systems. Another broad field of research is the electrospinning of polymer composites with carbon nanotubes, which will also be introduced herein.

Both miscible and immiscible polymer blends can be electrospun. To be able to interpret the properties of the fibers produced by melt electrospinning, it is necessary to determine whether the blend components have undergone a chemical reaction, either during blending or during the electrospinning process. Copolymerization reactions were noted during the melt electrospinning of PET/poly(ethylene naphthalate) blends, for instance.[303] Blend fibers are generally fabricated by electrospinning ternary solutions of two polymers and a solvent. For example, electrospinning PVP and PLA afforded blend fibers with phase-separated domains. Structured PLA fibers were obtained by the selective extraction of PVP.[189] Further examples of blend systems that were electrospun from ternary solutions are polyaniline/PS (or PEO),[253] PVC/PU,[306] poly[(*m*-phenylene vinylene)-*co*-(2,5-dioctyloxy-*p*-phenylene vinylene)]/PEO,[307] poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV)/PS,[308] polyaniline/PS (or PC),[309] PET/PET-*co*-poly(ethylene isophthalate),[282] polysulfone/PU,[310] chitosan/PLA,[154] PGA/chitin,[242] and PLA/poly(lactide-*co*-glycolide).[236] If appropriate dimensions and systems are chosen, the morphologies of the electrospun fibers formed by phase segregation can lead to new property profiles. For instance, Wei et al. observed the formation of core–shell structures in electrospun blends of polyaniline (a conductive polymer when doped) with PS or PC.[309] Kameoka et al. obtained semiconducting wires by the scanning electrospinning of poly[(*m*-phenylene vinylene)-*co*-(2,5-dioctyloxy-*p*-phenylene vinylene)]/PEO blends.[307] The combinational variability of heterogeneous blend systems is virtually inexhaustible. Blends of one and the same polymer may also be of interest. For instance, the electrospinning of blends consisting of PVA with different molecular weights significantly reduced the tendency towards bead formation.[72]

Contrary to blends, block copolymers with physically immiscible segments undergo limited phase separation: typically, microphase separation into domains with sizes of less than 100 nm occurs. The investigation of this type of phase separation in electrospun nanofibers, especially with respect to the dynamics of fiber formation, is of fundamental physical interest. However, it is very difficult to characterize the nanofiber morphologies precisely. Electrospun fibers of block copolymers are of considerable interest for the modification of functional fiber materials. The integration of segments of a hydrophilic block copolymer into bioerodible-polymer fibers can modify the decomposition rate and biocompatibility of the fibers; in water, the hydrophilic segments are not extracted, and the properties of the fibers remain unchanged. Examples of this type of electrospun system are PLA-*b*-PEO block copolymers[311] and poly(lactide-*co*-glycolide)-*b*-PEO block copolymers.[228] Jia et al. observed higher degrees of crystallinity in electrospun fibers of poly[(trimethylene carbonate)-*b*-(ε-caprolactone)] than in films of the same block copolymers.[312] Electrospun fibers with controlled hydrophobicity were fabricated using PS-*b*-polydimethylsiloxane[313] and PS-*b*-PP[314] block copolymers. Phase-separated block copolymer systems were also spun from PS-*b*-polybutadiene-*b*-PS[315] and PS-*b*-polyisoprene.[316] For the PS-*b*-polyisoprene system, phase separation along and perpendicular to the fiber axis of the electrospun fibers was investigated in detail (Figure 16).

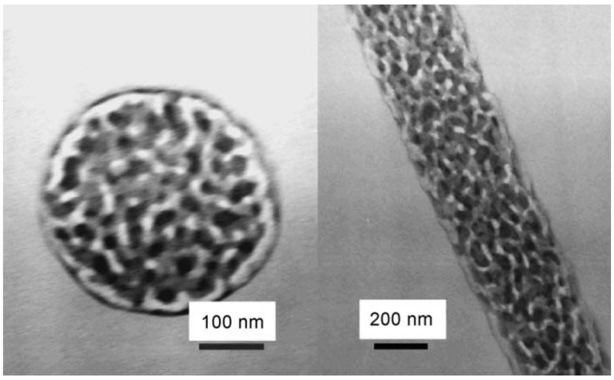


Figure 16. Left: TEM image of an electrospun fiber of a block copolymer of PS and polyisoprene viewed along the fiber axis. Right: TEM image of such a fiber viewed perpendicular to the fiber axis.[316]

For reasons similar to those for block copolymers, graft copolymers are interesting materials for electrospun fibers. The only study on such systems to date concerns the comblike assembly of block-copolymer fibers through amphiphilic interactions.[317] These fibers exhibit microphase separation similar to that detected in classical block copolymers.

A large number of reports describe the electrospinning of polymer composites. Inorganic salts, inorganic and organic

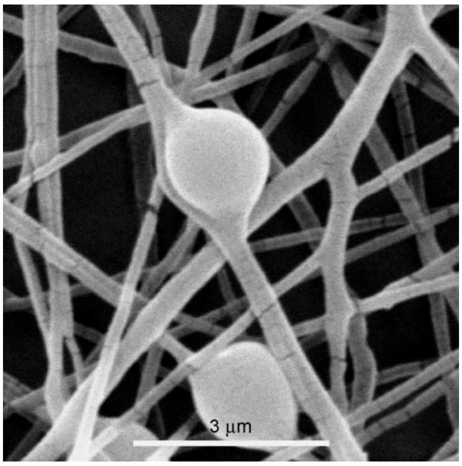


Figure 17. SEM image of electrospun fibers of PS with immobilized PS particles.[318]

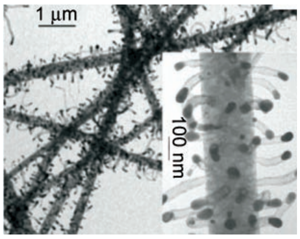


Figure 18. TEM image of carbon fibers with grafted carbon nanotubes (CNTs). The fibers were obtained from electrospun polyacrylonitrile (PAN)/ferrocene composite fibers after pyrolysis of the PAN and catalytic growth. Inset: enlargement.[346]

particles of different forms and dimensions, carbon nanotubes, and similar materials can be immobilized in high concentrations in polymer fibers by electrospinning from ternary solutions (Figure 17).[318] Such composite fibers allow the fabrication of polymer fibers with special functionalities or of precursor fibers. Precursor fibers are usually converted into inorganic fibers by pyrolysis. Electrospun composite fibers containing montmorillonite with polyamide 6 (PA6),[266] polyamide 6,6 (PA66) and PVA,[319] PMMA,[320] or PU[321] as the carrier material have been described. Examples of electrospun polymer-composite fibers containing noble-metal nanoparticles include PAN-*co*-PAA/Pd (by reduction with hydrazine after electrospinning),[322] PEO/Au,[323] PVP/Ag,[203] and PAN/Ag (by UV irradiation of AgNO$_3$).[324] Yu et al. obtained nanofibers of LiMn$_2$O$_4$ from composite fibers of PVA/LiCl/Mn(OAc)$_2$.[325] Electrospun polymer-composite fibers containing magnetic nanoparticles have also been described, for example, PEO (or PVA)/Fe$_3$O$_4$,[326] PCL/FePt (by coaxial electrospinning),[327] PU/MnZnNi,[328] and PMMA/Co.[329]

Carbon nanotubes (CNTs), which were first reported by Oberlin and Endo,[330] and later by Ijima,[331] can be immobilized in electrospun polymer fibers. The goal of most such studies is the functionalization of polymer nanofibers (electrical conductivity or mechanical strengthening) or the orientation of the CNTs along the fiber axis. Examples of polymers that were spun with CNTs into the corresponding composite fibers include PAN,[332–339] PEO,[340–343] PVA,[342] PLA,[332] PC,[344] PS,[345] PU,[345] and PMMA.[336] Very exceptional composite fibers with CNTs arranged in a brushlike manner on carbon fibers were obtained from PAN/ferrocene composite fibers through the synthesis of CNTs and the simultaneous pyrolysis of PAN to carbon fibers (Figure 18).[346]

A large number of polymer/metal oxide (or metal sulfide) composite fibers have been produced by electrospinning in combination with sol–gel processes. In many cases, the composite fibers could be converted into metal oxide (or metal sulfide) fibers by subsequent pyrolysis. Polymer/TiO$_2$ composite fibers were fabricated with PVP,[190,195,197,208,210] PVAc,[347] and PAN.[348] Polymer/ZrO$_2$ composite fibers were produced from PVP,[190,194,199,200] PVAc,[349] and PVA.[350] Further examples of metal oxides and sulfides that have been incorporated into polymer-composite fibers are ZnO,[351–354] CuO,[298,355] NiO,[356,357] CeO$_2$,[358] Mn$_3$O$_4$,[359] Mn$_2$O$_3$/Mn$_3$O$_4$,[360] MoO$_3$,[361,362] BaTiO$_3$,[175,198,207] Y$_2$O$_3$,[199] Gd$_2$O$_3$,[199] Ta$_2$O$_5$,[363] Co$_3$O$_4$,[364] Ba$_{0.6}$Sr$_{0.4}$TiO$_3$,[204] SiO$_2$,[365,366] CdS,[196] PbS,[201] and Ag$_2$S.[202]

The combination of electrospinning and sol–gel processes has also been used for the direct production of fibers of inorganic compounds, for example, SiO$_2$,[367] TiO$_2$,[49,368] SiO$_2$/ZrO$_2$,[369] TiO$_2$/SiO$_2$, and Al$_2$O$_3$.[47] Pure continuous copper nanofibers were obtained from PVB/CuNO$_3$ composite fibers via the reduction of CuO fibers (Figure 19).[298] The copper nanofibers are macroscopically characterized by the typical red color of copper (Figure 19, left). The transmission electron microscope (TEM) image confirms the presence of continuous copper fibers, which do not consist of an alignment of single copper nanoparticles (Figure 19, right).

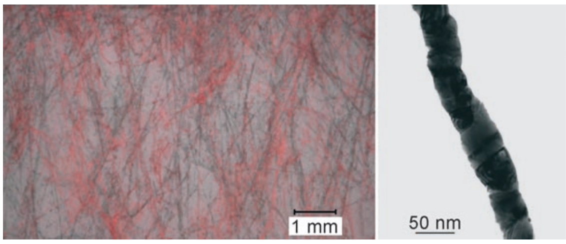


Figure 19. Left: Photograph of copper nanofibers obtained from electrospun poly(vinyl butyral) (PVB)/CuNO$_3$ composite fibers. Right: TEM image of one such fiber.[298]

Electrospun polymer-composite fibers can also be prepared using biological objects, such as active viruses[192] or living bacteria.[370] These types of polymer-hybrid fibers are highly functional fiber tissues with a large scope of variability and are of interest from fundamental and application-oriented points of view.

The abundance of materials that are accessible by the electrospinning process can be increased significantly through self-organization or active structuring during electrospinning, as discussed in Section 4.

4. Structure Formation in Fibers and Nonwovens

4.1. Nanofiber Morphologies

During electrospinning from solution, structure formation within the nanofibers is controlled by the simultaneous processes of the evaporation of the solvent and the extreme elongation of the solidifying fibers.[36] A volume element of the jet travels from the electrospinning nozzle to the counter electrode, where the solid fiber is deposited, in a time frame of 0.1 s. After this time period, both of the processes mentioned above are completed, and the fiber is solid. Therefore, the time limit for structure formation is typically less than 0.01 s. In this respect, electrospinning resembles spincoating, a process in which nanofilms are cast by depositing droplets of a solution onto a rapidly rotating substrate. Below, we distinguish between amorphous glass-forming fibers (of PS, for example) and partially crystallizing fibers (of PA6 or PLA, for example).

For glass-forming systems, states frozen-in by very rapid glass formation differ more significantly from the equilibrium state of the supercooled melt than states frozen-in by slower glass formation.[371] One consequence is the occurrence of a more distinct aging process: in the frozen state, the density and the enthalpy of the fibers change slowly but steadily. This process has immediate consequences for the dynamic and static mechanical properties of the fibers. The verification of such an aging process is usually carried out by calorimetry experiments: upon heating, the step associated with the glass transition is superimposed with maxima and minima in the heat flow.[371] This phenomenon also occurs in semicrystalline polymers, but is concentrated in the amorphous regions. Little has been published on the occurrence of this phenomenon in electrospun fibers. In Figure 20, a differential scanning calorimetry (DSC) curve for nanofibers of semicrystalline PLA is compared to that for a slowly cooled bulk sample of PLA.[372] The curve for the nanofibers shows distinct deviations from the usual steplike changes in heat flow.

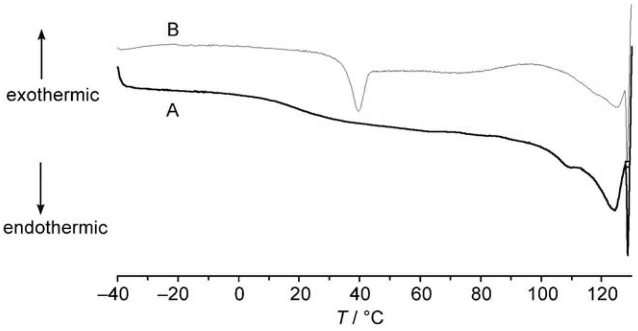


Figure 20. Differential scanning calorimetry (DSC) heating curves for: A) bulk PLA powder; B) electrospun PLA nanofibers.[372]

Of considerably greater significance for the properties of the nanofibers is the frozen-in chain orientation of the fibers, which reveals itself in birefringence. Experimental analysis of the electrospinning process showed that the magnitude of the elongation of the fibers is very high (up to a factor of 10^5), while the rate of elongation is up to $10^5\,\mathrm{s}^{-1}$.[36] According to one estimate, a high degree of chain orientation is probable if the product of the elongation rate and the chain relaxation time exceeds a value of 0.5.[373] For polymer solutions that are suitable for electrospinning (with respect to molecular weight and concentration), relaxation times of 0.1–0.01 s were reported.[36,70] Therefore, chain orientation should always occur during electrospinning. The question of whether the deposited fibers still contain traces of solvent, which would promote chain relaxation, remains open. The answer may depend on the vapor pressure of the solvent.

Actually, the experimental findings on the occurrence of birefringence are rather inconsistent. In some cases, a slight birefringence was reported, for example, for nanofibers of PBI with diameters of about 300 nm and for nanofibers of PS-*b*-polybutadiene-*b*-PS triblock copolymers with diameters of about 100 nm.[374,315] In other cases, nanofibers were obtained that did not show birefringence and, hence, featured no chain orientation.[300] In view of the deformation rates typical of electrospinning and the relaxation times characteristic of the solutions used, it is difficult to understand why amorphous nanofibers do not generally show a high degree of chain orientation. There is clearly a need for systematic investigations. In any case, it must be anticipated that nanofibers will shrink upon heating or upon contact with solvents that cause swelling.

For polymers that can be crystallized, solidification is connected with the formation of crystals. The short crystallization times typical of electrospinning lead to the assumption that the crystallites have a tendency to be small and to contain defects; furthermore, the degree of crystallization may be reduced.[375] Consequences would be low melting points and heats of fusion, but there are no explicit indications in the literature that these effects are significant. For instance, in the cases of nanofibers of PET, poly(ethylene naphthalate), and mixtures of the two, the melting points are not changed by the processing into nanofibers.[303] In contrast, it was reported that the degree of crystallinity, the glass-transition temperature, and the crystallization temperature of these polymers increase. However, the authors did indicate that transesterification processes and, hence, a decrease in chain length must be anticipated during the electrospinning of the mixtures.[303] In the case of PLA, it was observed that the degree of crystallinity and the melting point of the electrospun fibers were very similar to those of macroscopic samples.[268]

There have been several studies on structure formation during the electrospinning of PA.[268,272] It was demonstrated, on the basis of X-ray diffraction and Raman spectroscopy, that nanofibers of PA6 form the less-ordered γ modification. Crystallization from solution, however, affords the ordered α form. It is interesting that crystal formation during the fabrication of conventional fibers by melt extrusion proceeds very similarly to crystal formation during electrospinning (especially when the elongation after extrusion exceeds a certain limit), despite the differences in the fabrication processes.[376,377] The less-ordered γ phase is likewise formed in this case. Therefore, the occurrence of the γ form in the nanofibers is a distinct indication of the mechanical deformations occurring during electrospinning. This phase can be converted into the more ordered α phase by annealing the nanofibers at higher temperatures.[268]

Of greater significance, especially with respect to mechanical properties, are the chain orientation and the orientation of the crystallites in the electrospun fibers. These features can be investigated using Raman spectroscopy, and X-ray or electron diffraction. In this manner, very high degrees of crystallite orientation were confirmed in nanofibers of PFDS by Chen et al.[299] The degree of orientation could be substantially increased by annealing the fibers. Diffraction experiments carried out on single fibers are particularly unambiguous: using selected-area electron diffraction (SAED), the degree of orientation of crystals in a nanofiber of PA6 with a thickness of 50 nm was found to be very high.[268] This high degree of crystallite orientation reveals itself in the inhomogeneous azimuthal distribution of the diffraction intensity (Figure 21).

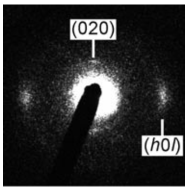


Figure 21. Electron diffraction pattern of an electrospun nanofiber of polyamide 6 (PA6) with a diameter of 50 nm.[268]

In macroscopic fibers produced by melt extrusion, comparable degrees of orientation are only achieved if the extrusion is followed by an extreme elongation.[376,377] In nanofibers of a liquid-crystalline polymer, poly(hexyl isocyanate), it was observed that the degree of orientation can depend significantly on the fiber thickness.[378] Jaeger et al. reported that in PEO fibers, surface layers, in particular, may be highly oriented.[379]

4.2. Surface Structures of Nanofibers

Electrospinning generally affords smooth fibers with a circular cross section; only in exceptional cases does the cross section differ from this form. For a variety of applications, for example, tissue engineering, filtration, catalysis, drug delivery, and nanofiber reinforcement, it could be advantageous if the fiber surfaces were not smooth or were porous. For example, pores function as anchoring points for cells in tissue engineering, increase the surface area in filtration or catalysis, modify the wetting properties and, hence, the matrix–fiber coupling in fiber strengthening, and alter the kinetics of drug release. Pores can also influence the kinetics of biodegradation of bioerodible nanofibers.

In fact, it is now possible to generate different fiber topologies during the electrospinning process by choosing particular solvents or solvent mixtures, by varying the humidity, or by using polymer mixtures. If, for instance, phase separation into polymer-rich and polymer-poor regions occurs upon evaporation of the solvent (this can generally be estimated from phase diagrams), there is a high probability that pores will form in the solid in the polymer-poor region. Thereby, the extent of pore formation is determined by the relative proportions of both phases. The use of solvent mixtures allows the selective adjustment of porosity.[219] Figure 22 shows an example of porous PLA fibers that were fabricated by this method.

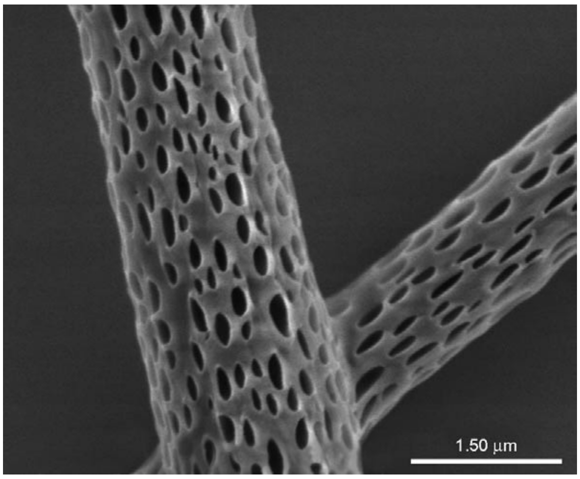


Figure 22. SEM image of electrospun porous PLA fibers.

Another route to porous fibers is through condensation processes during electrospinning in a very humid environment.[78,162] It is imagined that the spinning jet cools because of solvent evaporation, such that tiny droplets of water precipitate onto the jet. These droplets then form the pores in the solidified fiber. The extent of pore formation and the pore size can be tuned by varying the humidity.

Entirely different fiber topologies are obtained if nanofibers of a mixture of immiscible polymers are electrospun from the same solvent.[189] Upon evaporation of the solvent, phase separation occurs, which leads to binodal or spinodal structures in the nanofibers, depending on the system. In the case of binodal structures, one phase is dispersed in a matrix, while in the case of spinodal (cocontinuous) structures, two phases interpenetrate. To generate porous fibers of high overall porosity, two strategies are possible. In the first, the use of a solvent causing a high degree of swelling leads to a significant increase in the fiber diameter. After removal of the swelling agent, a highly porous structure with porosities of 75% and more remains (Figure 23). In the second method, the removal of one of the two phases from the binodal or spinodal mixtures mentioned above by using a specific solvent

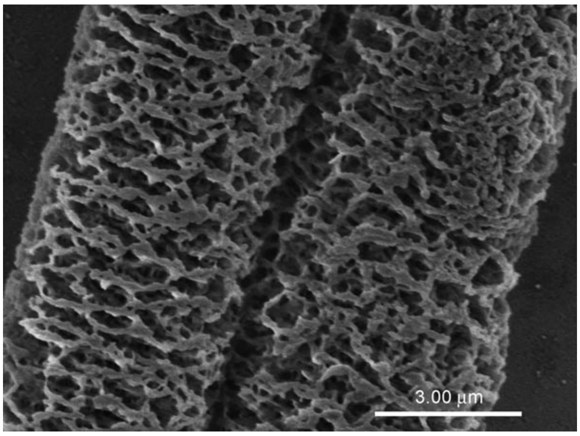


Figure 23. SEM image of electrospun fibers of a PLA/PEO blend after removal of the swelling agent, water.

leads, respectively, to porous fibers or to nanofibers with periodic thickness fluctuations and fractal surfaces (Figure 24). Furthermore, porous fibers can be obtained if the fibers are electrospun in a bath of liquid nitrogen. The consequence is a phase separation of the polymer and the solvent; after the removal of the solvent under vacuum, highly porous fibers remain. This process was demonstrated for PS, PAN, PCL, and PVDF, for example.[260]

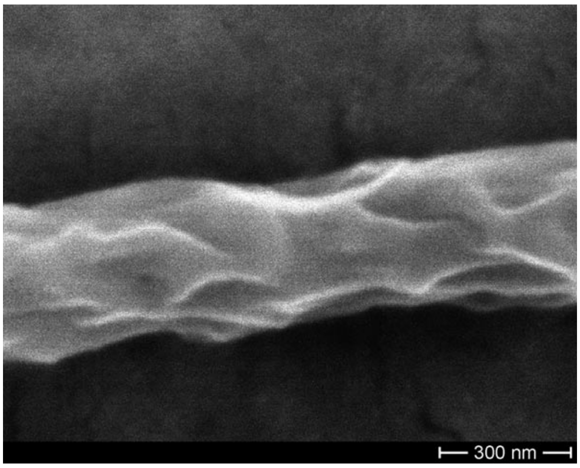


Figure 24. SEM image of electrospun fibers of a PLA/polyvinylpyrrolidone (PVP) blend after the selective extraction of PVP.

Porous fibers allow the enlargement of the inner surface without any change in the flow rate of gases and liquids, which is determined by the mutual alignment of the fibers. This feature could be important for the application of electrospun fibers in filtration or catalysis.

4.3. Fiber Arrangements and Pore Structures in Electrospun Nonwovens

For nonwovens produced by electrospinning, the fiber arrangement (1D, 2D, or 3D) and pore structure are of great importance. Using a standard laboratory apparatus for electrospinning (consisting of circular spin nozzles and a flat counter electrode), the fibers are deposited onto the plane defined by the counter electrode in a statistical orientation. A very open mesh is generated, and the nonwoven is fabricated by the layer-by-layer deposition of such planar arrangements. The developing nonwoven can serve as a surface coating (of porous filtering papers, for example), it can modify the surface of a solid substrate (to alter the wetting properties, for example), or it can also be used as a self-supporting nonwoven (as a template for tissue engineering, for example).

Electrospinning is not limited to the production of nonwovens with a random planar fiber orientation. The orientation of nanofibers along a preferred direction (Figure 25) is of interest for structural reinforcement with nanofibers (see Section 6.4) or for tissue engineering to give the cells a preferred growth direction (see Section 6.5.1).

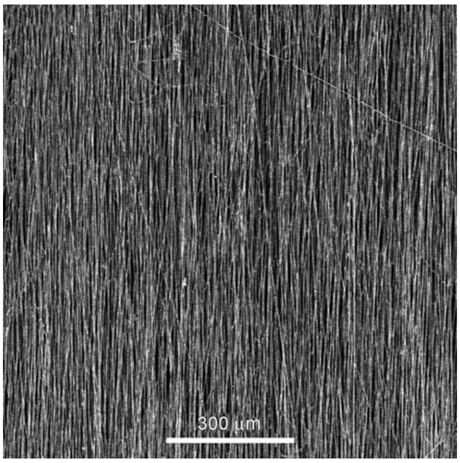


Figure 25. SEM image of a planar nonwoven composed of parallel PLA nanofibers.

Parallel fibers can, for example, be obtained by the use of rapidly rotating cylindrical collectors, which either serve as counter electrode or are combined with an electrode.[112,161,380,381] The collectors usually have the shape of a cylinder, but can also be narrow or wheel-shaped.[116,381] Parallel fibers can also be produced with special electrode arrangements consisting of two parallel flat plates or with frame-shaped electrodes.[13,14,268,191] A very high degree of orientation can be achieved with this method. Another possibility is the use of a quadratic arrangement of four electrodes, which leads to a cross-shaped deposition of nanofibers.[191,382] High degrees of orientation can also be achieved if the distance between the electrodes is reduced to the centimeter or millimeter range and if either the spinning electrode or the counter electrode has the shape of a fine tip.[383,107–109] To obtain fiber arrangements oriented in 3D in nonwovens, the techniques used for the production of conventional nonwovens composed of macroscopic fibers may be applied (needling, water-jet treatment).[384,385] This topic has not yet been discussed with respect to nonwovens made of nanofibers.

Efforts are generally made to assemble nonwovens from fibers of the same material having a uniform thickness. However, it can also be of interest for a variety of applications to construct nonwovens from fibers of non-uniform thickness, for example, to control the pore-size gradients or to modify the transport properties. Experimental[91,386,387] and theoretical[388] studies showed that the fiber diameter of a material can be varied by a factor greater than 10 through the choice of solvent and of concentration of the spinning solution. The use of several nozzles allows the fabrication of heterogeneously structured nonwovens (of PA6, for example) composed of fibers with significantly different diameters (Figure 26).

In a similar manner, chemically inhomogeneous nonwovens (composed of both PA6 and PLA, for example) can be produced with multijet arrangements (Figure 27). For applications in tissue engineering, heterogeneous carrier matrices (with layered or nonlayered structures) composed of micro- and nanofibers (of PEO, collagen, and segmented PU, for example) were fabricated by either sequential or

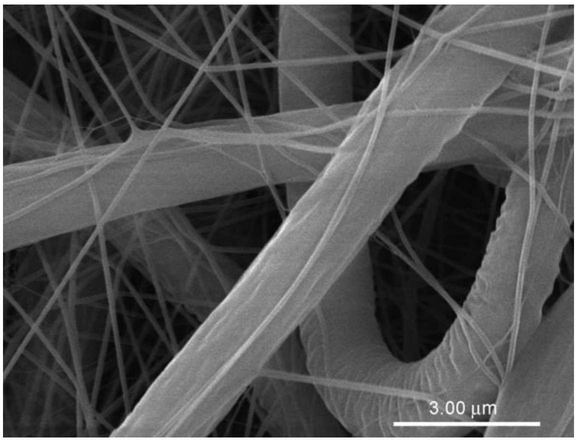


Figure 26. SEM image of a heterogeneously structured nonwoven of PA6.[387]

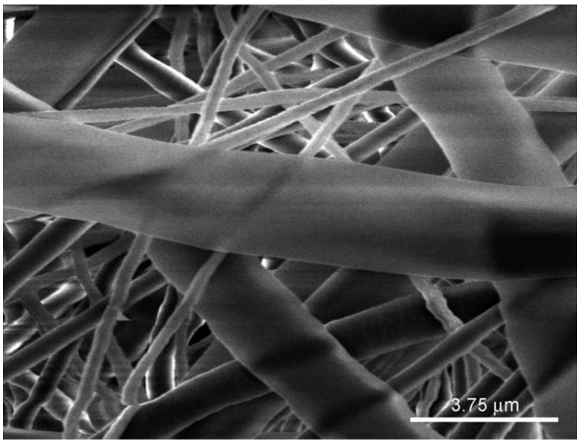


Figure 27. SEM image of a chemically heterogeneous nonwoven of PA6 (thick fibers) and PLA (thin, porous fibers).[387]

simultaneous electrospinning.[389] A cylindrically structured tissue constructed from thin collagen nanofibers as the inner layer and thick PU fibers as the outer layer serves as a good carrier matrix for artificial blood vessels.

The pore structure of these nonwovens determines the diffusion of gas though the fibers, the resistance to airflow, the filter effectiveness, as well as the suitability of the nonwoven as a scaffold for tissue engineering (for example, via stem cells). Experimental results on pore dimensions were obtained using various porosimeter techniques (for example, mercury porosimetry). A broad distribution of pore diameters over the range of 10^2–10^4 nm is typical.[270] However, the pore diameter can be significantly modified by controlling the overall porosity.[281,390] For planar orientations, the porosity is typically around 90%. However, there are methods that allow a significant compaction of the nonwovens to a porosity of less than 60%, namely the use of nanofibers with high flexibilities (for example, elastomers).[281,390]

Many simulations have investigated pore shape and pore density in nonwovens as a function of the number of fibers per layer.[391–393] The average pore diameter ($\bar{d}$) in nonwovens depends on the average fiber radius (r), as well as the overall porosity, that is, the volume fraction of the pores with respect to the overall volume of the nonwoven (Figure 28). For fibers of equal radius, the higher the porosity, the bigger the average pore size. The average pore size typically varies between $\bar{d}=r$ at a porosity of 20% and $\bar{d}=10r$ at a porosity of 80%. At even lower porosities, $\bar{d}$ becomes smaller than r. The specific surface areas of nanofibers typically range from 500–10 m^2 g^{-1} for fiber diameters of 10–500 nm.[281,390–393] Furthermore, Monte Carlo simulations show that the porosity of nonwovens decreases significantly with increasing flexibility of the fibers[394] and that chemical vapor deposition (CVD), which leads to the construction of a shell around the fibers, can also decrease the porosity significantly.[395]

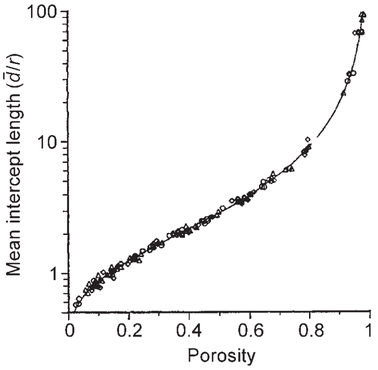


Figure 28. Correlation of the average pore diameter ($\bar{d}$), the average fiber radius (r), and the porosity of nonwovens, as determined by Monte Carlo simulations.[392]

5. Mechanical Properties of Fibers and Nonwovens

5.1. Properties of Nonwovens

The mechanical properties of a nonwoven are important if the nonwoven is used, for example, as a scaffold for stem cells in tissue engineering (see Section 6.5.1). The mechanical properties of the nonwoven should generally be similar those of the tissue that it is supposed to replace. Tissues such as cartilage or skin tissue are typically characterized by a Young's modulus (stiffness) of tens to hundreds of millipascals, by a maximum deformation stress (strength) of tens of millipascals, and by a maximum deformation of about 10–200%.[396] To determine the corresponding values for nonwovens composed of nanofibers, the nonwovens can be mounted in a stress–strain tester that measures the dependence of the deformation stress on the magnitude of the deformation.[112,115,234,268,281,291,294,310,396,397] Figure 29 shows typical results for nonwovens based on copolyamide 6/6T (PA6/6T) nanofibers. For nonwovens composed of electrospun nanofibers of soft elastomers that do not show a preferred orientation in the spinning plane, a Young's modulus of about 3 MPa, a maximum deformation stress of about 9.6 MPa, and a maximum deformation of about 360% were reported.[112] For nonwovens composed of significantly stiffer PA fibers, a Young's modulus of about 100 MPa, a maximum deformation

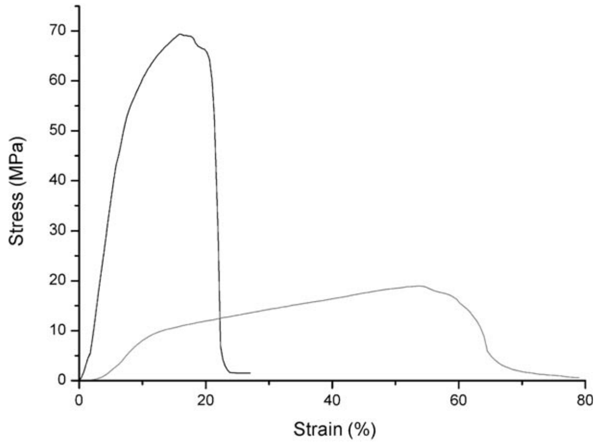


Figure 29. Stress–strain curves for nonwovens composed of copolyamide 6/6T (PA6/6T) nanofibers: black: with a preferred fiber orientation along the elongation direction; gray: with no preferred fiber orientation. The effective polymer cross-section in the nonwoven was considered in the calculation of the stress values.

stress of 20 MPa, and a maximum deformation of 53 % were determined.

It is conceivable that a high degree of fiber orientation along a preferred direction increases the stiffness and strength of the nonwoven. According to Figure 29, the Young's modulus (slope of the stress–strain curve) increases from 100 MPa for nonwovens with no preferred fiber orientation to 900 MPa for nonwovens with fibers oriented along the elongation direction. Similarly, the maximum deformation stress increases from 20 to 70 MPa and the maximum deformation decreases from 53 to 18 %. For tissues of electrospun collagen fibers with diameters of about 100 nm, Young's moduli of 52 and 26 MPa were measured for elongation along and perpendicular to the direction of preferred orientation, respectively. The corresponding maximum deformation stresses were 1.5 and 0.7 MPa.

5.2. Properties of Nanofibers

For materials reinforcement, the strength and stiffness of single nanofibers is particularly important. However, few experimental investigations on the stress–strain behavior of single electrospun nanofibers have been reported. Atomic force microscopy (AFM) was used in most of these cases.[167,256,398] These studies have shown that electrospun nanofibers feature very good mechanical properties. For example, Young's moduli of up to 50 GPa were reported for PAN nanofibers with a high degree of orientation (as determined by X-ray diffraction).[256] For comparison, bulk samples of PAN with no preferred orientation showed moduli of only 1.2 GPa. The Young's moduli measured for PEO nanofibers were distinctly higher than those measured for bulk samples. The orientation induced by electrospinning is again the proposed reason for the increased stiffness.[167] In contrast, Young's moduli of only 0.9 GPa were measured for nanofibers composed of PVP and TiO_2 nanoparticles; however, no information was given regarding the orientation of the fibers.[398] Nevertheless, it is clear that nanofibers feature very high Young's moduli if they have a high degree of crystallite and chain orientation. Such fibers are suitable for application in nanofiber reinforcement (see Section 6.4).

6. Applications of Electrospun Nanofibers

6.1. Templates

Electrospun polymer fibers can be used as templates for the preparation of hollow fibers (tubes by fiber templates (TUFT) process).[90,399–403] In the TUFT process, electrospun fibers of bioerodible or soluble polymers are coated with polymers, metals, or other materials. After selective extraction or degradation of the template fibers, hollow fibers corresponding to negative replicas of the templates are obtained. For example, hollow fibers of poly(*p*-xylylene)s (PPX) were fabricated by CVD of PPX onto electrospun PLA fibers and subsequent pyrolysis of the PLA fibers.[90,399] In an analogous way, hollow fibers of PPA/Al were produced by the sequential coating of PLA fibers with PPX and Al.[400] The fabrication of hollow fibers of PPX with inner diameters of less than 10 nm and outer diameters of about 50 nm (Figure 30, right) was accomplished using extremely thin electrospun fibers of PLA (Figure 30, left).[90]

Coating electrospun fibers of PLA/$Pd(OAc)_2$ with PPX and subsequent pyrolysis of the PLA afforded hollow fibers of PPX with incorporated nanoparticles of Pd (Figure 31).[90,401]

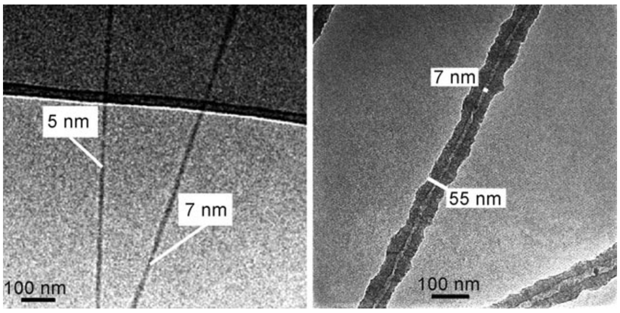


Figure 30. Left: TEM image of electrospun PLA nanofibers. Right: TEM image of hollow fibers of poly(*p*-xylylene) (PPX) prepared from the PLA nanofibers.[90]

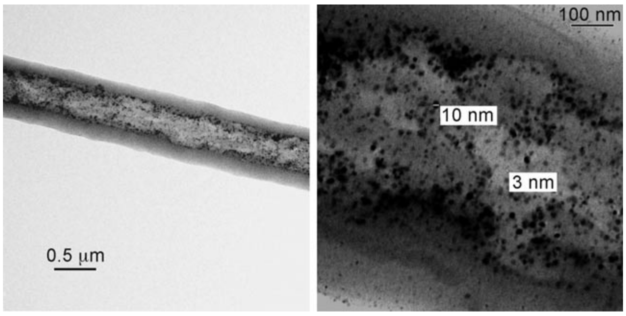


Figure 31. Left: Lower-magnification TEM image of a hollow fiber of PPX with incorporated nanoparticles of Pd. Right: Higher-magnification TEM image of the fiber.[401]

Similarly, hollow fibers of PPX/Cu and PPX/Ag were obtained from functionalized template fibers by the TUFT process.[401] Hollow fibers of TiO_2 were obtained from electrospun PA fibers coated with $Ti(OiPr)_4$ after pyrolysis of the PA and calcination.[400] Hollow fibers of Al were also obtained by CVD of Al onto PLA fibers and subsequent pyrolysis of the PLA.[399] Hollow fibers of Au, Cu, and Ni were fabricated in an analogous way.[402] In a further development of the TUFT process, hollow fibers with intricate architectures were prepared using a layer-by-layer technique.[403]

Hollow fibers could also be produced directly by coaxial electrospinning. Li and Xia[49] and Loscertales et al.[404] employed oils as template liquids for hollow fibers of ceramics.

6.2. Filter and Textile Applications

Both filter and textile applications of nonwovens have the common feature that the pore structure of the material controls its properties and functions. The three most important parameters of nonwovens are the overall porosity (ε; defined as the ratio of the pore volume (V_p) to the overall volume (V)), the average pore size ($\bar{d}$; if necessary, also the pore size distribution), and the inner specific surface area (S; defined as the surface area (O) divided by either the overall volume (V) or the overall mass (M)). These parameters determine the diffusion of gas through the fibers, the resistance to airflow, the filter effectiveness, as well as the suitability of the nonwoven as a carrier for tissue engineering (for example, via stem cells). As discussed in Section 4.3, both theoretical and experimental investigations of these parameters have been carried out.[281,390,392,393]

6.2.1. *Textiles*

Nonwovens composed of nanofibers can be used in combination with conventional textiles (for example, as interlinings) to modify the properties of the textiles. The objective can be to increase the wind resistance, to regulate the water-vapor permeability, to optimize the thermal insulation behavior, or to give the textile a specific functionality (such as the lotus effect, aerosol filtering, or protection against chemical or biological hazards).

The transition from microfiber to nanofiber nonwovens leads to significant changes in the transport processes of the material as a result of the dramatic reduction in the pore dimensions and the large increase in the inner surface area. For example, in the case of gas diffusion, which is important with respect to thermal insulation, there is a transition from the normal diffusion regime (in which the diffusion path is determined by impacts between the gas particles) to the Knudsen regime (in which the diffusion path is mainly determined by impacts between the gas particles and the fibers). This topic has been extensively studied using Monte Carlo simulations.[392,393] The situation is similar for the viscous permeation of liquids through nonwovens: the permeation coefficient is directly correlated to the average fiber radius.

Gas-transport properties are of great importance to textile applications.[163,281,390] Experimental findings have shown that the airflow (wind) resistance of nanofiber nonwovens is increased by up to three orders of magnitude in comparison to conventional textiles, which leads to a significant thermal effect. The wind resistance improves immensely with decreasing pore dimensions (Figure 32) and, given identical pore sizes and fiber dimensions, can be varied over a large range by adjusting the coverage (ρ_m; the mass of deposited nanofibers per unit area). The wind resistance typically increases by a factor 1000 if the coverage is increased from 0.1 to 10 $g\,m^{-2}$. The coverage of 10 $g\,m^{-2}$ corresponds to a nonwoven thickness of up to 20 μm (for a porosity of 60 %). At the same time, the permeability of the nonwovens to water vapor is very high (comparable to that of PTFE membranes) and can be influenced by the chemical nature of the fiber material (for example, hydrophilic or hydrophobic).

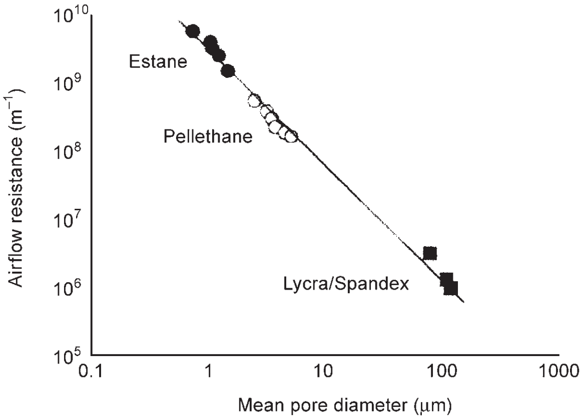


Figure 32. Dependence of the airflow (wind) resistance of different nonwovens on the average pore size.[281]

The thermal insulation of nonwovens is mainly a result of the limited diffusion of air molecules in the materials. The thermal insulation increases significantly with decreasing pore size if the pore diameter of the nonwoven is 10–100 times smaller than the mean free path of the gas molecules (about 70 nm for air at normal pressure).

The aerosol-filtering properties of nanofiber nonwovens have also been investigated. The filter efficiency of a textile increases significantly with increasing coverage by a nanofiber nonwoven. An efficiency of 100 % can be achieved at a coverage of only 1 $g\,m^{-2}$.[281,390] The use of nanofiber nonwovens for protection against chemical and biological hazards has been discussed as well. This application is based on the functionalization of the nonwoven with a catalyst (for example, an enzyme) that can decompose harmful substances.[281,295,390] The large inner surface area that is available for these catalytic processes is a great advantage of nanofiber nonwovens.

6.2.2. *Filters*

To reach high filter efficiencies, it is generally necessary that the sizes of the channels and pores in the filter material be adjusted to the fineness of the particles to be filtered. To filter increasingly finer particles, a transition from fibers with diameters in the micrometer range to fibers with diameters in the nanometer range is required.[9,163,269,405] Coalescing and aerosol filters are characteristic applications for nanofiber nonwovens. Coalescing filters are used to filter tiny water droplets (with dimensions in the nanometer range) from aviation fuel to prevent the formation of ice crystals at high altitudes.[391] Fine aerosol particles can also be very effectively filtered using nanofiber nonwovens of thicknesses that do not cause an unacceptably high flow resistance:[269,281,390] filters with thicknesses in the range of 10 μm and fiber coverages of about 1 $\mathrm{g\,m^{-2}}$ are suitable.

Nanofibers are already used extensively in air filters. Conventional air filters consist of paper mats composed of fibers with diameters in the micrometer range. They function by trapping particles floating in the air deep inside the filter, which means that the whole filter material is involved in the retention of the particle. As the number of particles trapped in the filter material increases, the pressure drop across the filter also increases, and above a certain limit, the filter can no longer be used. The filter is usually partially cleaned with a pressure blast, whereby the particles are pushed out of the filter and collected. With each cleaning process, a higher pressure drop remains, and eventually the filter must be replaced.

One concept for the improvement of filter properties is to coat the crude filter material with a gossamer fleece composed of nanofibers. The particles are, thus, captured at the surface. The pressure drop remaining after each cleaning process is significantly reduced, and the filter lifetime can be prolonged by a factor of about 10. This type of surface filter has achieved great market success.

Further improvement is possible by electrostatically charging the nanofibers.[163,390] The fibers are often already charged during electrospinning, but this charge generally dissipates through contact of the fibers with an electrical ground. A permanent charge can be generated by corona polarization or by triboelectric polarization (for example, by using polymers with different triboelectric properties for the fabrication of the fibers). The filter efficiency could be increased significantly through the use of chemically selective materials, such as the "Smart Dust" reported by Schmedake et al.[406]

6.3. Catalysis

A crucial step in catalysis is the removal and recycling of the catalyst after the reaction. The immobilization of homogeneous or heterogeneous catalysts in nanofibers presents an interesting solution to this problem. In principle, the reaction can be carried out in two ways. The reaction mixture can circulate around the catalyst fibers (as is the case in a continuously operating microreactor),[407] or the fibers can be fixed on a carrier and then immersed repeatedly in the reaction vessel.

The use of polymer nanofibers loaded with monometallic or bimetallic nanoparticles (such as Rh, Pt, Pd, Rh/Pd, and Pd/Pt) has been described.[322,408] These catalyst systems can be applied in hydrogenation reactions, for example. To fabricate such fibrous catalyst systems, polymer nanofibers are typically electrospun from solutions containing metal salts (such as $\mathrm{Pd(OAc)_2}$) as precursors. In the next step, the salts incorporated in the fibers are reduced, either thermally at temperatures around 250 °C or in the presence of a reducing agent (such as H_2 at about 130 °C or hydrazine). The nanoparticles formed have diameters in the range of 5–15 nm, depending on the fabrication method (Figure 33). The catalytic properties of these mono- or bimetallic nanofiber catalysts were investigated in several model hydrogenations, which demonstrated that the catalyst systems are highly effective.

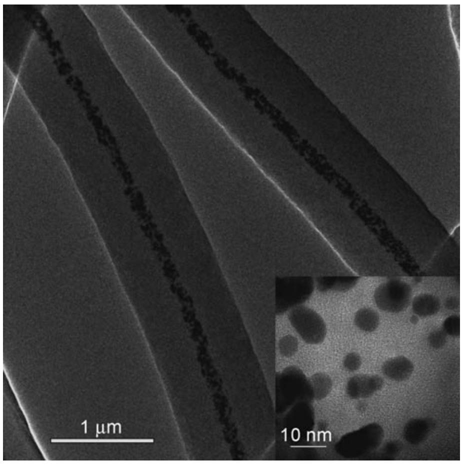


Figure 33. SEM image of nanofibers loaded with bimetallic nanoparticle catalysts. Inset: TEM image of the catalyst nanoparticles.

For homogeneous catalysis, systems consisting of core–shell nanofibers combined with proline and $\mathrm{Sc(OTf)_3}$ ($\mathrm{TfO} = \mathrm{CF_3SO_3}$) catalysts were fabricated by the TUFT method.[409,410] In contrast to conventional catalysis in homogeneous solution or in microemulsions, for which the conversion is 80 %,[411] the fiber systems achieve complete conversion in the same or shorter reaction times. The fibers can be used several times without loss of activity.[409] Furthermore, nanofibers were used as carriers for enzymes, whereby the enzymes either were chemically attached to the electrospun fibers or were directly dispersed in the nanofibers during the electrospinning process.[120,125] High catalyst activities were reported in this case as well.

6.4. Nanofiber Reinforcement

Glass fibers, carbon fibers, and poly(*p*-phenylene terephthalamide) fibers are used for the reinforcement of synthetic materials in many technical products.[412,413] The parameters that dominate the reinforcing effect are the tensile modulus of the fibers, the coupling between the matrix polymer and the fibers, and the axial ratio of the fibers.[414,415] Despite the success, several problems remain in fiber reinforcement: the reinforcement usually leads to an increased brittleness; the macroscopic fibers can cause rough surfaces; and longer fibers are shortened during the processing, such that the reinforced materials can fail under compression. To counteract these problems, the concept of molecular reinforcement, in which the macroscopic fibers are replaced by single stiff-chain molecules, was introduced over 20 years ago.[416,417] In fact, it was shown that molecular reinforcement is possible in special cases.[418] However, the nearly complete immiscibility of the stiff-chain molecules and the flexible-chain molecules of the matrix presented a serious problem. Therefore, the stiff-chain molecules are not dispersed in isolation, but are phase-separated in larger domains and, thus, do not provide any reinforcement. Because of this disadvantage, molecular reinforcement did not gain wide acceptance. Nanofibers offer a new and promising approach.

The rules established for reinforcement by macroscopic fibers should also apply to reinforcement by nanofibers.[419] However, nanofibers have several advantages over macroscopic fibers. Because the reinforcement effect is determined by the axial ratio of the fibers, nanofibers with diameters of 10–100 nm can be 100–1000 times shorter than fibers with diameters of 10–100 μm. Because of their small diameters, nanofibers cause little refraction of light; therefore, transparent matrices reinforced by nanofibers stay transparent, even if the refraction indices of the matrix and the fibers do not match.[265] Furthermore, smaller loadings of nanofibers in the matrix are required to achieve the same reinforcement effect as macroscopic fibers. Thus, material can be saved and the brittleness of the matrix reduced. Finally, the large specific surface area between the nanofibers and the matrix promotes relaxation processes, which improves the impact strength of the reinforced matrix. As discussed in Section 5.2, electrospun nanofibers can have very high Young's moduli.

Given the advantages of nanofibers for reinforcement, the number of investigations on this topic is rather small. The main problems, to which there are no convincing solutions yet, are the dispersion of the electrospun nanofiber webs and the control of the nanofiber orientation in the polymer matrix. The felt-mat structure of the nonwoven is for the most part maintained upon the incorporation of the nanofibers into the matrix. Attempts to disperse single nanofibers from the nonwoven mats using ultrasound, kneaders, or high-speed stirrers have only been marginally successful. Very similar problems occurred in matrix reinforcement with carbon nanotubes and nanofilaments.[420]

The pulverization of nanofibers into shorter fragments is also very difficult, because they are surprisingly resistant to fragmentation. Kim and Reneker were able to incorporate nanofibers into a rubber matrix and to disperse the fibers by repeated grindings, but the resulting homogeneity of the distribution was significantly worse than that of the macroscopic glass fibers or particles that are conventionally used for reinforcement.[280] Furthermore, the application of this method is limited to few materials. The optical or mechanical cutting of nanofibers at low temperatures typically affords fiber fragments of about 100 nm in length, which should facilitate dispersion. However, the amounts of fibers with finite lengths yielded by this method are currently limited. Because of all these problems, current research on nanofiber reinforcement deals with the application of very specific methods to very specific systems.

Epoxide matrices were reinforced with polyamide 4,6 (PA46) nanofibers of about 30 nm in diameter by Bergshoef and Vancso.[265] Fiber mats were dipped into a solution of a two-component epoxide resin, and subsequently dried and cured for 60 h under standard conditions. An increase of the Young's modulus by a factor of 35 and of the breaking load by a factor of 4 was reported for the composites. The loading of the matrix was later determined to be 4–4.5 % by elemental analysis. Kim and Reneker carried out similar experiments with nanofibers of PBI,[280] whereby 8–32 layers of fiber mats were pressed together and immersed in an epoxide resin, which was subsequently thermally cured in several steps. A 25–35 % increase in the Young's modulus was observed for a 3–15 % mass percentage of nanofibers. Similar experiments on the reinforcement of a styrene–butadiene rubber with PBI nanofibers resulted in an increase in the Young's modulus by a factor of 10 and in an increase in the tensile strength by a factor of 2. Another aspect of nanofiber reinforcement is noted in a patent of Dzenis and Reneker: the use of nanofibers to increase the interlamellar toughness of compounds composed of fiber-reinforced lamellar layers.[421]

It is clear that nanofiber reinforcement offers great opportunities for thin films and bulk samples, and for elastomers, thermoplastics, duromers, as well as ceramics, which are accessible by sol–gel processes. However, it is equally clear that research on nanofiber reinforcement is still at its beginnings.

6.5. Medical Applications

Nanostructured polymer systems of natural or synthetic origin—in the form of nanofibers, hollow nanofibers, core–shell nanofibers, nanotubes, or nanorods—have a multitude of possible applications in medicine and pharmacy. A main reason for this wide applicability is that the nanoscale is particularly relevant for biological systems, because proteins, viruses, and bacteria have dimensions on this order. Many viruses, for example, the tobacco mosaic virus or the Marburg virus, have the shape of a nanotube. In the following, we present some current activities in the use of nanosystems in tissue engineering, wound healing, and drug delivery.

6.5.1. Tissue Engineering

One rapidly developing field of application for electrospun polymer nanofibers is regenerative medicine. The tissues that are targets for regeneration include cartilage, bone, skin tissue, blood vessels, lymphatic vessels, lung tissue, and heart tissue.[422,423] One approach in tissue engineering is the use of scaffolds or carrier matrices onto which stem cells or human body cells can be seeded. The job of the matrix is to facilitate the anchorage, migration, and proliferation of the cells, to reproduce the three-dimensional structure of the tissue to be replaced, and to support a differentiation along different cell lines, if stem cells are seeded first.

This type of carrier matrix has to fulfill a diverse range of requirements with respect to biocompatibility, biodegradability, morphology, sterilizability, porosity, ability to incorporate and release drugs, and mechanical suitability. The morphologies of the matrices and materials used are diverse. For instance, powders, foams, membranes, and gels consisting of a variety of natural and synthetic polymers, as well as porous ceramics have been applied.[424–427] The efficiency of these scaffolds is often limited. Biological matrices are usually not available in sufficient amounts, and they can be afflicted with biological-infection problems. Also, powders, foams, and membranes are commonly not open-pored enough to allow cell growth in the depth of the scaffold; consequently, the formation of a three-dimensional tissue structure is frequently impossible. Even loose gel structures (for example, of polypeptides) may fail. Furthermore, smooth walls and interfaces, which occur naturally in membranes and foams, are unfavorable for the adsorption of many cell types.

It is clear that scaffolds mimicking the architecture of the extracellular matrix should offer great advantages for tissue engineering. The extracellular matrix surrounds the cells in tissues and mechanically supports them.[428,429] This matrix has a structure consisting of a three-dimensional fiber network, which is formed hierarchically by nanoscale multifilaments. An ideal scaffold should replicate the structure and function of the natural extracellular matrix as closely as possible, until the seeded cells have formed a new matrix.

The use of synthetic or natural nanofibers to build scaffolds, therefore, seems to be especially promising, and numerous reports on this topic have appeared.[112,115,119,136,137,224,229,234,296,380,389,396,430–444] Electrospinning prevails as the fabrication method for these scaffolds. Biocompatible and biodegradable natural and synthetic polymers (such as polyglycolides, PLA, PCL, various copolymers, segmented PU, polyphosphazenes, collagens, gelatin, chitosans, silks, and alginates) are used as the carrier materials (Figure 34). Mixtures of gelatin and chitosans or synthetic polymers like PCL and PEO are also employed, as are PCL or poly[lactide-*co*-(ε-caprolactone)] modified by grafting, and copolymers coated or grafted with gelatin.[119,442] The aim of such modifications is to provide surfaces suitable for the adsorption and proliferation of cells.

A variety of cells (for example, mesenchymal stem cells, endothelial cells, neural stem cells, keratinocytes, muscle cells, fibroblasts, and osteoblasts) have been seeded onto carrier matrices (Figure 35) for the generation of target tissues (such as skin tissue, bone, cartilage, arteries, and nerve tissue). The diameters of the fibers used generally conform to the structural properties of the extracellular matrix and are on the order of 100 nm; however, in some cases, fibers with diameters of less than 100 nm or on the order of 1 μm were used.[229] In several studies, the proliferation behavior of cells in such fiber structures was compared with that on films cast from the same polymer material.[137,229,436] The results showed that the fiber architecture generally affects cell growth positively. For endothelial cells, however, it was reported that a smoother surface can be beneficial for cell adhesion and proliferation.[436] Another conclusion made was that the biocompatibility of a material improves with decreasing fiber diameter.[439] Porosity also seems to have a favorable influence on cell growth. For instance, it was observed that mesenchymal stem cells form branches to the pores on nanoporous nanofibers.[431]

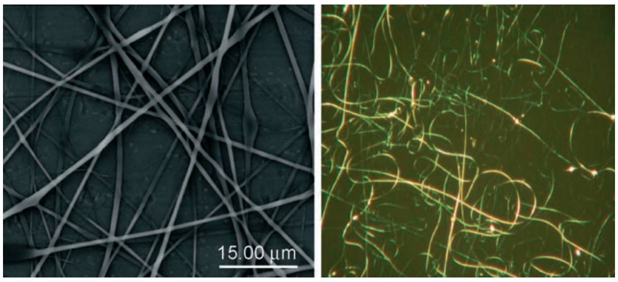


Figure 34. Left: SEM image of electrospun fibers of collagen. Right: Optical image of electrospun fibers of chitosan. Such fibers can be used as scaffolds for tissue engineering.

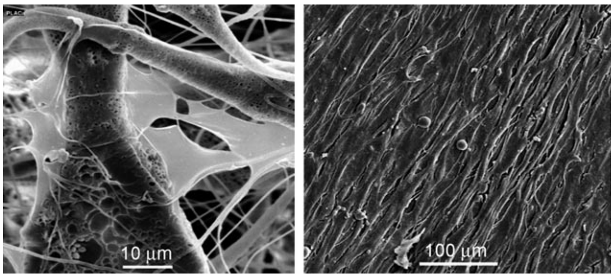


Figure 35. Left: SEM image of stem cells seeded onto a PLA scaffold. Right: SEM image of oriented cell growth on a scaffold of oriented PLA fibers.

Another important requirement is that the scaffolds are porous enough to allow cells to grow in their depths while being provided with the necessary nutrients and growth factors. The degree of porosity and the average pore dimensions are significant factors for cell proliferation and the formation of three-dimensional tissues.[443–445] Depending on the cell type, the optimal pore diameters are 20–100 μm; pore diameters larger than 100 μm are not required for optimal cell growth.[430] For carrier matrices composed of electrospun fibers of 100 nm in diameter, pore diameters of 1–100 μm were reported.[438,439] It was also found that cells can easily migrate to a depth of about 100 μm, but encounter problems at greater depths.[119]

A further prerequisite for a scaffold is a sufficient mechanical compatibility. Cartilage, for example, is characterized by a Young's modulus of about 130 MPa, a maximum deformation stress of about 20 MPa, and a maximum deformation of 20–120%; the corresponding values for skin tissue are 15–150 MPa, 5–30 MPa, and 35–115%.[234] These ranges of values can be achieved with electrospun nanofibers. For instance, for tissues of electrospun collagen fibers with diameters of about 100 nm, a Young's modulus of 170 MPa and maximum deformation stress of 3.3 MPa were measured.[396] However, the maximum elongation is usually less than 10%.

The role of fiber texture has also been investigated. Arrangements of statistically oriented fibers and of parallel fibers were analyzed. It was observed that growing cells tend to follow the orientation of the fibers (Figure 35, right)[431–433,440] and that certain cells (for example, fibroblasts) can assume spindlelike shapes. Another important finding is that the fibers can impart mechanical stress to the collective of growing cells. It was reported that the production of extracellular tissue is greater if oriented rather than non-oriented matrix fibers are employed. This production can be significantly increased by the application of a periodical mechanical deformation (typically 6 %).[440]

Heterogeneously structured carrier matrices composed of micro- and nanofibers (of PEO, collagen, and segmented PU, for example) were fabricated by sequential and simultaneous electrospinning, which yield layered or nonlayered structures, respectively.[440] A cylindrically structured tissue constructed from thin collagen nanofibers as the inner layer and thick PU fibers as the outer layer serves as good carrier matrix for artificial blood vessels.

Early investigations on the cogrowth of different types of cells on scaffolds are very promising. For instance, the cogrowth of fibroblasts, keratinocytes, and endothelial cells[441] was reported; the astonishing result is that cogrowth enhances cell growth.

Scaffolds fabricated from electrospun nanofibers have several clear advantages. However, considerable room for optimization remains with respect to architecture, surface properties, biodegradability, porosity, and mechanical properties, and also with respect to the seeding of cells in the three-dimensional space and the supply of nutrients to the cells. It is often observed that the cells preferentially grow on the surfaces or that they initially adhere to the carrier fibers, but then detach after differentiation.

6.5.2. *Wound Healing*

An interesting application of electrospun nanofibers is the treatment of large wounds such as burns and abrasions.[380,434,435,446] It is found that these types of wounds heal particularly rapidly and without complications if they are covered by a thin web of nanofibers, in particular, of biodegradable polymers. Such nanowebs have enough pores to assure the exchange of liquids and gases with the environment, but have dimensions that prevent bacteria from entering. Mats of electrospun nanofibers generally show very good adhesion to moist wounds.[447] Furthermore, the large specific surface area of up to $100\,m^2g^{-1}$ is very favorable for the adsorption of liquids and the local release of drugs on the skin, making these materials suitable for application in hemostatic wound closure.[14,448] Compared to conventional wound treatment, the advantage is that scarring is prevented by the use of nanofibers.[220,448,449]

The nanofibrillar structure of the nanoweb promotes skin growth, and if a suitable drug is integrated into the fibers, it can be released into the healing wound in a homogeneous and controlled manner. The charging of biodegradable nanofibers with antibiotics was realized with the drugs cefazolin and mefoxin.[28,448] Generally, different drugs with antiseptic and antibiotic effects, as well as growth and clotting factors, are available for wound healing.

PU is widely used as the nanoweb material because of its excellent barrier properties and oxygen permeability. Khil et al. implemented electrospun mats of PU nanofibers as wound dressings, which were successfully tested on pigs.[287] Histological investigations showed that the rate of epithelialization during the healing of wounds treated with nanofiber mats is higher than that of the control group. Another promising and, in contrast to PU, biodegradable material is collagen. Rho et al. investigated the wound-healing properties of mats of electrospun fibers of type I collagen on wounds in mice.[113] It was shown that, especially in the early stages of the healing process, better healing of the wounds was achieved with the nanofiber mats than with conventional wound care. Blends of collagen or silk and PEO were also electrospun into fibers and used in wound dressings.[133] Numerous other biodegradable polymers that can be electrospun can be applied in wound healing, for example, PLA and block-copolymer derivatives, PCL, chitin, and chitosan.[145] Using tetracycline hydrochloride as a model drug, is was shown that the release kinetics can be adjusted by varying the polymer used for the fabrication of the nanofibers. Poly[ethylene-*co*-(vinyl acetate)] (PEVA), PLA, and a 50:50 mixture of the two polymers were investigated.[221,450] With PEVA, faster drug release was observed than with PLA or the blend. With PLA, burst release occurred, and the release properties of the blend are intermediate to those of the pure polymers. The morphology of the fibers and their interaction with the drug are critical factors.[451] The concentration of the drug in the fibers also affects the release kinetics.[451] The higher the concentration, the more pronounced the burst, evidently because of an enrichment of the drug on the surface.

Smith and Reneker describe a process in which a fiber mat is directly electrospun onto the affected skin areas.[452] Handheld electrospinning devices have been developed for the direct application of nanofibers onto wounds (Figure 36). In such a device, a high voltage is generated with the voltage supplied by standard batteries. The device has a modular construction, so that different polymer carriers and drugs can be applied, depending on the type of wound, by exchanging

Figure 36. Handheld device for the electrospinning of wound dressings. Inset: PEO fibers electrospun from aqueous solution onto a hand.

the vials of spinning solution. From a technical point of view, the device has proven itself in continuous use over several months.

6.5.3. *Transport and Release of Drugs*

Nanofiber systems for the release of drugs (or functional compounds in general) are of great interest for tumor therapy, as well as for inhalation and pain therapy. The nanostructured carriers must fulfill diverse functions. For example, they should protect the drugs from decomposition in the bloodstream, and they should allow the controlled release of the drug over a chosen time period at a release rate that is as constant as possible. They should also be able to permeate certain membranes (for example, the blood–brain barrier), and they should ensure that the drug is only released in the targeted tissue. It may also be necessary for the drug release to be triggered by a stimulus (either external or internal) and to continue only as long as necessary for the treatment. For some time, nanoparticles (of lipids or biodegradable polymers, for example) have been extensively investigated with respect to the transport and release of drugs.[453,454] A variety of methods have been used for the fabrication of such nanoparticles, including spraying and sonification, as well as self-organization and phase-separation processes. Such nanoparticles are primarily used for systemic treatment. However, experiments are currently being carried on the targeting and enrichment of particular tissues (vector targeting) by giving the nanoparticles specific surface structures (for example, sugar molecules on the surface).

A very recent approach is based on the use of anisometric nanostructures (that is, nanorods, nanotubes, and nanofibers) for the transport and release of drugs. With this development, the main area of application for nanofibers charged with drugs will shift from systemic to locoregional therapy. In locoregional therapy, the fibers are localized at the spot where the drug should be applied. The applications of nanofibers in wound healing (localization on wounds) and in tissue engineering (localization in cell-proliferation areas) discussed above are typical examples.

Anisometric carriers can be fabricated by electrospinning with simultaneous incorporation of the drugs (or other functional elements).[29,122,221,455,456] Nanofibers with incorporated superparamagnetic Fe_3O_4 nanoparticles serve as an example of a multifunctional carrier. An enrichment of the targeted tissue with the carrier should be possible with the application of an external magnetic field. An interesting property of superparamagnetic systems is that they can be heated by periodically modulated magnetic fields. This feature allows drug release to be induced by an external stimulus.

In in vitro experiments on the release kinetics of functional molecules, it was possible to follow their release from fibers into the environment (by fluorescence microscopy). However, the experiments demonstrated that the release often occurs as a burst, in a process that is definitely nonlinear with respect to time. The release kinetics, including the linearity of the release over time and the release time period, can be influenced by the use of core–shell fibers, in which the core immobilizes the drugs and the shell controls their diffusion out of the fibers.[456] In addition to low-molecular-weight drugs, macromolecules such as proteins, enzymes, growth factors (see Section 6.5.1), and DNA are also of interest for incorporation in transport and release systems. Several experimental studies on this topic have been carried out.[59,77,122,311,457–459] The incorporation of plasmidic DNA into PLA-*b*-PEG-*b*-PLA block copolymers and its subsequent release was investigated, and it was shown that the released DNA was still fully functional.[311] BSA and lysozyme were also electrospun into polymer nanofibers, and their activities after release were analyzed, again yielding positive results.[122,457] In the case of BSA, is was shown that the use of core–shell fibers fabricated by the CVD of PPX onto electrospun nanofibers affords almost linear release over time.[122] Further investigations deal with the incorporation and release of growth factors for applications in tissue engineering.[77,458,459] In the following, some specific applications of nanofibers in drug release are described.

6.5.3.1. *Tumor Therapy*

Nanofibers of biodegradable polymers were investigated with respect to their use in local chemotherapy.[60,460,461] The water-insoluble antitumor drug paclitaxel (as well as the antituberculosis drug rifampin) was electrospun into PLA nanofibers.[461] In some cases, a cationic, anionic, or neutral surfactant was added, which influenced the degree of charging of the nanofibers. Analysis of the release kinetics in the presence of proteinase K revealed that the drug release is nearly ideally linear over time. The release is clearly a consequence of the degradation of the polymer by proteinase. Analogous release kinetics were found when the degree of charging was increased to 50%. Similar investigations were also carried out with the hydrophilic drug doxorubicin.[460] The hydrophilic nature of the drug apparently causes its accumulation on the surface of the nanofibers, which results in burst release.

To obtain nanofibers with linear release kinetics for water-soluble drugs like doxorubicin, water–oil emulsions were electrospun, in which the drug was contained in the aqueous phase and a PLA-*co*-PGA copolymer in chloroform was contained in the oil phase.[60] These electrospun fibers showed bimodal release behavior consisting of burst kinetics for drug release through diffusion from the fibers, followed by linear kinetics for drug release through enzymatic degradation of the fibers by proteinase K. In many cases, this type of bimodal behavior may be desired. Furthermore, it was shown that the antitumor drug retained its activity after electrospinning and subsequent release. The drug taxol was also studied with respect to its release from nanofibers.[461]

6.5.3.2. *Inhalation Therapy*

A promising application for anisometric drug carriers is inhalation therapy. For this type of therapy, the aerodynamic radius of the anisometric particles is adjusted through their shape, such that the drug carriers are deposited at specific positions in the lung. From extensive experimental and theoretical studies relating to the inhalation of asbestos, the way in which fibers are deposited in the lung as a function of their axial ratio, length, radius, density, and surface structure is well-known.[462,463] This knowledge can be used for the development of strategies to place fiber drug carriers at specific positions in the lung for locoregional release. An apparent advantage of anisometric over spherical particles is that a significantly larger percentage of anisometric particles remains in the lung after exhalation. Indications for treatment with nanofiber systems are tumors, metastases, pulmonary hypertension, and asthma. But these systems are also under consideration for the administration of insulin and other drugs through the lung. To control their aerodynamic radius, the electrospun fibers must be shortened to certain axis ratios (for example, by laser or mechanical cutting). The aerodynamic radius can also be controlled through density; highly porous fibers can be used for this purpose. Progress in inhalation therapy mainly depends on finding polymer systems that do not irritate the lung tissue. The polymer systems should be biocompatible and water-soluble (for example, PEO or biodegradable PLA).

Anisometric carrier systems offer manifold possibilities for the transition from systemic to locoregional treatment (for example, the implantation of nanofibers under the skin). Fibers with antimicrobial[464] or antifungal[465] properties are examples of such systems.

7. Outlook

The results described herein demonstrate the great potential of electrospinning in fundamental and application-oriented research. In addition to general investigations on the theory and optimization of the electrospinning process itself, current research has also focused on many specific aspects of electrospinning, for instance, the structure formation of crystallizable polymers, the aging phenomena of amorphous polymers, and the structure formation (for example, crystallization, phase separation, and orientation) and dynamics of multiphase polymer systems (for example, blends and block copolymers), polymer composites, and supramolecular polymer systems (for example, dendrimers, liquid-crystalline polymers, and graft copolymers). Although most of these topics are of fundamental interest, they have, for the most part, been studied only rudimentarily to date. In particular, nanofiber systems with supramolecular structures on scales larger than 10 nm should provide exciting prospects and could afford entirely new structures with new properties. In the area of composite formation, important questions remain with respect to the incorporation of carbon nanotubes (does orientation occur?) and nanoparticles (do gradient structures form?). Mainly technical polymers have used been for electrospinning to date; in only a few cases have polymers synthesized for specific morphologies or properties been employed. Considerable room for experimentation remains.

Many investigations have dealt with the functionalization and application of electrospun polymer fibers, especially in the areas of medicine and pharmacology. Electrospun fibers have been applied very successfully in the improvement of filters for air filtration. Subsequent modification of electrospun fibers (for example, by coating) has led to a significant expansion of the already broad scope of their applications. The electrospinning of materials other than polymers has not yet received much attention, although there have been some promising approaches to this topic.

The sparsity of investigations on the efficiency of the electrospinning process is surprising, because the technological application of electrospun fibers is only possible if they can be produced in sufficient amounts. Although the efficiency of melt electrospinning should generally be much higher than that of solution electrospinning, the melt electrospinning of technologically relevant polymers leads to fiber diameters that are not competitive with those obtained by other established methods (for example, melt blowing). Recently developed methods for the oriented deposition of electrospun fibers, for the fabrication and oriented deposition of single polymer fibers, and for the production of electrospun fibers with defined lengths will offer entirely new opportunities for the realization of new properties and applications.

The authors thank Edith Schmidt, Martina Gerlach, Marianne Schnorr, Uwe Justus, and Dr. Roland Dersch for their valuable support in the preparation of the manuscript, Dr. Olaf Kriha for the tractor photograph, and Dr. Andreas Schaper and Martin Hellwig for the SEM and TEM images. Financial support from the DFG (SPP1165) and the Volkswagen-Stiftung is acknowledged.

Received: November 15, 2006

[1] G. M. Bose, *Recherches sur la cause et sur la véritable théorie de l'électricité*, Wittenberg, **1745**.
[2] Lord Rayleigh, *Philos. Mag.* **1882**, *14*, 184–186.
[3] J. F. Cooley, US 692,631, **1902**.
[4] W. J. Morton, US 705,691, **1902**.
[5] J. F. Cooley, US 745,276, **1903**.
[6] K. Hagiwaba, O. Oji-Machi, K. Ku, Jpn 1,699,615, **1929**.
[7] A. Formhals, US 1,975,504, **1934**.
[8] W. Simm, K. Gosling, R. Bonart, B. von Falkai, GB 1346231, **1972**.
[9] M. Jacobsen, *Chemiefasern/Textilind.* **1991**, 36–41.
[10] J. Doshi, G. Srinivasan, D. Reneker, *Polym. News* **1995**, *20*, 206–207.
[11] J. Hagewood, A. Wilkie, *Nonwovens World* **2003**, 69–73.
[12] D. H. Reneker, I. Chun, *Nanotechnology* **1996**, *7*, 216–223.
[13] H. Fong, D. H. Reneker in *Structure Formation in Polymeric Fibers* (Ed.: D. R. Salem), Hanser, München, **2001**, pp. 225–246.
[14] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, *Compos. Sci. Technol.* **2003**, *63*, 2223–2253.
[15] R. Dersch, A. Greiner, J. H. Wendorff in *Dekker Encyclopedia of Nanoscience and Nanotechnology* (Eds.: J. A. Schwartz, C. J. Contesen, K. Putgern), Marcel Dekker, New York, **2004**, pp. 2931–2938.
[16] D. Li, Y. Xia, *Adv. Mater.* **2004**, *16*, 1151–1170.
[17] N. N. V. Raagavan, P. Karnan, S. Jagadeeswaran, *Synth. Fibres* **2005**, *34*, 16–20.
[18] I. S. Chronakis, *J. Mater. Process. Technol.* **2005**, *167*, 283–293.
[19] J. B. Chiu, Y. K. Luu, D. Fang, B. S Hsiao, B. Chu, M. Hadjiargyrou, *J. Biomed. Nanotechnol.* **2005**, *1*, 115–132.

[20] W.-J. Li, R. L. Mauck, R. S. Tuan, *J. Biomed. Nanotechnol.* **2005**, *1*, 259 – 275.
[21] Y. K. Wang, T. Yong, S. Ramakrishna, *Aust. J. Chem.* **2005**, *58*, 704 – 712.
[22] T. Subbiah, G. S. Bhat, R. W. Tock, S. Parameswaran, S. S. Ramkumar, *J. Appl. Polym. Sci.* **2005**, *96*, 557 – 569.
[23] W. Sigmund, J. Yuh, H. Park, V. Maneeratana, G. Pyrgiotakis, A. Daga, J. Taylor, J. C. Nino, *J. Am. Ceram. Soc.* **2006**, *89*, 395 – 407.
[24] C. P. Bean, J. D. Livingston, *J. Appl. Phys.* **1959**, *30*, S120 – S129.
[25] M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293 – 346.
[26] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1 – 8.
[27] U. Boudriot, R. Dersch, A. Greiner, J. H. Wendorff, *Artif. Organs* **2006**, *30*, 785 – 792.
[28] D. S. Katti, K. W. Robinson, F. K. Ko, C. T. Laurencin, *J. Biomed. Mater. Res. Part B* **2004**, *70*, 286 – 296.
[29] J. Xie, C. H. Wang, *Pharm. Res.* **2006**, *23*, 1817 – 1826.
[30] K.-S. Lee, M. A. El-Sayed, *J. Phys. Chem. B* **2005**, *109*, 20331 – 20338.
[31] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, *Science* **2002**, *295*, 2425 – 2427.
[32] G. Taylor, *Proc. R. Soc. London Ser. A* **1964**, *280*, 383 – 397.
[33] S. N. Reznik, A. L. Yarin, A. Theron, E. Zussman, *J. Fluid Mech.* **2004**, *516*, 349 – 377.
[34] M. Cloupeau, B. Prunet-Foch, *J. Electrost.* **1989**, *22*, 135 – 159.
[35] A. L. Yarin, S. Koombhongse, D. H. Reneker, *J. Appl. Phys.* **2001**, *90*, 4836 – 4846.
[36] D. H. Reneker, A. L. Yarin, H. Fong, S. Koombhongse, *J. Appl. Phys.* **2000**, *87*, 4531 – 4547.
[37] A. L. Yarin, S. Koombhongse, D. H. Reneker, *J. Appl. Phys.* **2001**, *89*, 3018 – 3026.
[38] M. M. Hohman, M. Shin, G. Rutledge, M. P. Brenner, *Phys. Fluids* **2001**, *13*, 2201 – 2220.
[39] M. M. Hohman, M. Shin, G. Rutledge, M. P. Brenner, *Phys. Fluids* **2001**, *13*, 2221 – 2236.
[40] Lord Rayleigh, *Philos. Mag.* **1892**, *34*, 145 – 155.
[41] S. Tomotika, *Proc. R. Soc. London Ser. A* **1935**, *150*, 322 – 337.
[42] F. D. Rumscheidt, S. G. Mason, *J. Colloid Sci.* **1962**, *17*, 260 – 269.
[43] T. Pakula, J. Grebrowicz, M. Kryszewski, *Polym. Bull.* **1980**, *2*, 799 – 804.
[44] D. H. Reneker, W. Kataphinan, A. Theron, E. Zussman, A. L. Yarin, *Polymer* **2002**, *43*, 6785 – 6794.
[45] *High-Speed Fiber Spinning: Science and Engineering Aspects* (Eds.: A. Ziabicki, H. Kawai), Wiley, New York, **1985**.
[46] Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2003**, *15*, 1929 – 1932.
[47] G. Larsen, R. Velarde-Ortiz, K. Minchow, A. Barrero, I. G. Loscertales, *J. Am. Chem. Soc.* **2003**, *125*, 1154 – 1155.
[48] J. H. Yu, S. V. Fridrikh, G. C. Rutledge, *Adv. Mater.* **2004**, *16*, 1562 – 1566.
[49] D. Li, Y. Xia, *Nano Lett.* **2004**, *4*, 933 – 938.
[50] Y. Zhang, Z. M. Huang, X. Xu, C. T. Lim, S. Ramakrishna, *Chem. Mater.* **2004**, *16*, 3406 – 3409.
[51] D. Li, J. T. McCann, Y. Xia, *Small* **2005**, *1*, 83 – 86.
[52] H. Jiang, Y. Hu, Y. Li, P. Zhao, K. Zhu, W. Chen, *J. Controlled Release* **2005**, *108*, 237 – 243.
[53] S. N. Reznik, A. L. Yarin, E. Zussman, L. Bercovici, *Phys. Fluids* **2006**, *18*, 062101.
[54] M. Wang, J. H. Yu, D. L. Kaplan, G. C. Rutledge, *Macromolecules* **2006**, *39*, 1102 – 1107.
[55] X.-J. Han, Z.-M. Huang, C.-L. He, L. Liu, X.-J. Han, Q.-S. Wu, *Polym. Compos.* **2006**, *27*, 381 – 387.
[56] Y. Z. Zhang, X. Wang, Y. Feng, J. Li, C. T. Lim, S. Ramakrishna, *Biomacromolecules* **2006**, *7*, 1049 – 1057.
[57] I. G. Loscertales, A. Barrero, I. Guerrero, R. Cortijo, M. Marquez, A. M. Gañán-Calvo, *Science* **2002**, *295*, 1695 – 1698.
[58] G. Larsen, R. Spretz, R. Velarde-Ortiz, *Adv. Mater.* **2004**, *16*, 166 – 169.
[59] E. H. Sanders, R. Kloefkorn, G. L. Bowlin, D. G. Simpson, G. E. Wnek, *Macromolecules* **2003**, *36*, 3803 – 3805.
[60] X. Xu, L. Yang, X. Xu, X. Wang, X. Chen, Q. Liang, J. Zeng, X. Jing, *J. Controlled Release* **2005**, *108*, 33 – 42.
[61] P. Gupta, G. L. Wilkes, *Polymer* **2003**, *44*, 6353 – 6359.
[62] S. Madhugiri, A. Dalton, J. Gutierrez, J. P. Ferraris, K. J. Balkus, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 14531 – 14538.
[63] B. Ding, E. Kimura, T. Sato, S. Fujita, S. Shiratori, *Polymer* **2004**, *45*, 1895 – 1902.
[64] O. O. Dosunmu, G. G. Chase, W. Kataphinan, D. H. Reneker, *Nanotechnology* **2006**, *17*, 1123 – 1127.
[65] G. Kim, Y.-S. Cho, W. D. Kim, *Eur. Polym. J.* **2006**, *42*, 2031 – 2038.
[66] H. Fong, I. Chun, D. H. Reneker, *Polymer* **1999**, *40*, 4585 – 4592.
[67] S. Koombhongse, W. Liu, D. H. Reneker, *J. Polym. Sci. Part B* **2001**, *39*, 2598 – 2606.
[68] J. M. Deitzel, J. Kleinmeyer, D. Harris, N. C. Beck Tan, *Polymer* **2001**, *42*, 261 – 272.
[69] Y. M. Shin, M. M. Hohman, M. P. Brenner, G. C. Rutledge, *Polymer* **2001**, *42*, 9955 – 9967.
[70] S. A. Theron, E. Zussman, A. L. Yarin, *Polymer* **2004**, *45*, 2017 – 2030.
[71] W. K. Son, J. H. Youk, T. Seung Lee, W. H. Park, *Polymer* **2004**, *45*, 2959 – 2966.
[72] Z. Jun, H. Hou, J. H. Wendorff, A. Greiner, *e-Polymers* **2005**, No. 38.
[73] W. K. Son, J. H. Youk, T. S. Lee, W. H. Park, *Mater. Lett.* **2005**, *59*, 1571 – 1575.
[74] A. Koski, K. Yim, S. Shivkumar, *Mater. Lett.* **2004**, *58*, 493 – 497.
[75] B. Ding, H.-Y. Kim, S.-C. Lee, D.-R. Lee, K.-J. Choi, *Fibers Polym.* **2002**, *3*, 73 – 79.
[76] J. S. Lee, K. H. Choi, H. D. Ghim, S. S. Kim, D. H. Chun, H. Y. Kim, W. S. Lyoo, *J. Appl. Polym. Sci.* **2004**, *93*, 1638 – 1646.
[77] C. Zhang, X. Yuan, L. Wu, Y. Han, J. Sheng, *Eur. Polym. J.* **2005**, *41*, 423 – 432.
[78] C. L. Casper, J. S. Stephens, N. G. Tassi, D. B. Chase, J. F. Rabolt, *Macromolecules* **2004**, *37*, 573 – 578.
[79] K. H. Lee, H. Y. Kim, H. J. Bang, Y. H. Jung, S. G. Lee, *Polymer* **2003**, *44*, 4029 – 4043.
[80] T. Jarusuwannapoom, W. Hongrojjanawiwat, S. Jitjaicham, L. Wannatong, M. Nithitanakul, C. Pattamaprom, P. Koombhongse, R. Rankupan, P. Supaphol, *Eur. Polym. J.* **2005**, *41*, 409 – 421.
[81] S. Y. Gu, J. Ren, G. J. Vancso, *Eur. Polym. J.* **2005**, *41*, 2559 – 2568.
[82] Q.-B. Yang, C. Wang, Y.-L. Hong, Z.-Y. Li, Y.-Y. Zhao, S.-L. Qiu, Y. Wei, *Gaodeng Xuexiao Huaxue Xuebao* **2004**, *25*, 589 – 591.
[83] Y.-S. Kang, H.-Y. Kim, Y.-J. Ryu, D.-R. Lee, S.-J. Park, *Polymer (Korea)* **2002**, *26*, 360 – 366.
[84] T. Wang, S. Kumar, *J. Appl. Polym. Sci.* **2006**, *102*, 1023 – 1029.
[85] J. Zeng, H. Hou, A. Schaper, J. H. Wendorff, A. Greiner, *e-Polymers* **2003**, No. 9.
[86] S.-H. Tan, R. Inai, M. Kotaki, S. Ramakrishna, *Polymer* **2005**, *46*, 6128 – 6134.
[87] S.-Y. Gu, J. Ren, *Macromol. Mater. Eng.* **2005**, *290*, 1097 – 1105.
[88] J. P. Jeun, Y. M. Lim, Y. C. Nho, *J. Ind. Eng. Chem. (Seoul)* **2005**, *11*, 573 – 578.
[89] S. Kidoaki, I. K. Kwon, T. Matsuda, *J. Biomed. Mater. Res. Part B* **2006**, *76*, 219 – 229.
[90] H. Hou, Z. Jun, A. Reuning, A. Schaper, J. H. Wendorff, A. Greiner, *Macromolecules* **2002**, *35*, 2429 – 2431.
[91] C. Mit-uppatham, M. Nithitanakul, P. Supaphol, *Macromol. Chem. Phys.* **2004**, *205*, 2327 – 2338.

[92] P. Supaphol, C. Mit-uppatham, M. Nithitanakul, *J. Polym. Sci. Part B* **2005**, *43*, 3699 – 3712.
[93] C. Huang, S. Chen, C. Lai, D. H. Reneker, H. Qiu, Y. Ye, H. Hou, *Nanotechnology* **2006**, *17*, 1558 – 1563.
[94] I H. Liu, Y.-L. Hsieh, *J. Polym. Sci. Part B* **2002**, *40*, 2119 – 2129.
[95] B. Lee, K. Lee, D. Lee, B. Pak, H. Kim, *J. Korean Fiber Soc.* **2003**, *40*, 341 – 347.
[96] L. Yao, T. W. Haas, A. Guiseppi-Elie, G. W. L. Bowlin, D. G. Simpson, G. E. Wnek, *Chem. Mater.* **2003**, *15*, 1860 – 1864.
[97] Y. H. Jung, H. Y. Kim, D. R. Lee, S.-Y. Park, M. S. Khil, *Macromol. Res.* **2005**, *13*, 385 – 390.
[98] R. Kessick, J. Fenn, G. Tepper, *Polymer* **2004**, *45*, 2981 – 2984.
[99] P. Tsai, H. L. Schreuder-Gibson, *Adv. Filtr. Sep. Technol.* **2003**, *16*, 340 – 353.
[100] J. Lyons, C. Li, F. Ko, *Polymer* **2004**, *45*, 7597 – 7603.
[101] N. Levit, G. Tepper, *J. Supercrit. Fluids* **2004**, *31*, 329 – 333.
[102] P. D. Dalton, K. Klinkhammer, J. Salber, D. Klee, M. Möller, *Biomacromolecules* **2006**, *7*, 686 – 690.
[103] H.-J. Kim, Y.-h. Jung, M.-s. Khil, H.-y. Kim, H.-J. Bang, *J. Korean Fiber Soc.* **2004**, *41*, 424 – 432.
[104] R. Rangkupan, D. H. Reneker, *J. Met. Mater. Miner.* **2003**, *12*, 81 – 87.
[105] M. Becker, Dissertation, Philipps-Universität Marburg.
[106] A. L. Yarin, E. Zussman, *Polymer* **2004**, *45*, 2977 – 2980.
[107] J. Kameoka, R. Orth, Y. Yang, D. Czaplewski, R. Mathers, G. W. Coates, H. G. Craighead, *Nanotechnology* **2003**, *14*, 1124 – 1129.
[108] J. Kameoka, H. G. Craighead, *Appl. Phys. Lett.* **2003**, *83*, 371 – 373.
[109] D. Sun, C. Chang, S. Li, L. Lin, *Nano Lett.* **2006**, *6*, 839 – 842.
[110] P. Gupta, S. R. Trenor, T. E. Long, G. L. Wilkes, *Macromolecules* **2004**, *37*, 9211 – 9218.
[111] S. H. Kim, S.-H. Kim, S. Nair, E. Moor, *Macromolecules* **2005**, *38*, 3719 – 3723.
[112] J. A. Matthews, G. E. Wnek, D. G. Simpson, G. L. Bowlin, *Biomacromolecules* **2002**, *3*, 232 – 238.
[113] K. S. Rho, L. Jeong, G. Lee, B.-M. Seo, Y. J. Park, S.-D. Hong, S. Roh, J. J. Cho, W. H. Park, B.- M. Min, *Biomaterials* **2006**, *27*, 1452 – 1461.
[114] M. Li, M. J. Mondrinos, R. M. Gandi, F. K. Ko, A. S. Weiss, P. I. Lelkes, *Biomaterials* **2005**, *26*, 5999 – 6008.
[115] L. Huang, K. Nagapudi, R. P. Apkarian, E. L. Chaikof, *J. Biomater. Sci. Polym. Ed.* **2001**, *12*, 979 – 993.
[116] L. Buttafoco, N. G. Kolkman, P. Engbers-Buitjenhuijs, A. A. Poot, P. J. Dijkstra, I. Vermes, J. Feijen, *Biomaterials* **2006**, *27*, 724 – 734.
[117] J. Venugopal, L. L. Ma, T. Yong, S. Ramakrishna, *Cell Biol. Int.* **2005**, *29*, 861 – 867.
[118] W. He, T. Yong, W. E. Teo, Z. Ma, S. Ramakrishna, *Tissue Eng.* **2005**, *11*, 1574 – 1588.
[119] Y. Zhang, H. Ouyang, C. T. Lim, S. Ramakrishna, Z.-M. Huang, *J. Biomed. Mater. Res. Part B* **2005**, *72*, 156 – 165.
[120] J. Xie, Y.-L. Hsieh, *J. Mater. Sci.* **2003**, *38*, 2125 – 2133.
[121] L. Wu, X. Yuan, J. Sheng, *J. Membr. Sci.* **2005**, *250*, 167 – 173.
[122] J. Zeng, A. Aigner, F. Czubayko, T. Kissel, J. H. Wendorff, A. Greiner, *Biomacromolecules* **2005**, *6*, 1484 – 1488.
[123] C. Zhang, X. Yuan, L. Wu, L. Wu, J. Sheng, *e-Polymers* **2005**, No. 72.
[124] T. E. Herricks, S.-H. Kim, J. Kim, D. Li, J. H. Kwak, J. W. Grate, S. H. Kim, Y. Xia, *J. Mater. Chem.* **2005**, *15*, 3241 – 3245.
[125] H. Jia, G. Zhu, B. Vugrinovich, W. Kataphinan, D. H. Reneker, P. Wang, *Biotechnol. Prog.* **2002**, *18*, 1027 – 1032.
[126] Y. Wang, Y.-L. Hsieh, *J. Polym. Sci. Part A* **2004**, *42*, 4289 – 4299.
[127] P. Ye, Z.-K. Xu, J. Wu, C. Innocent, P. Seta, *Macromolecules* **2006**, *39*, 1041 – 1045.
[128] G. E. Wnek, M. E. Carr, D. G. Simpson, G. L. Bowlin, *Nano Lett.* **2003**, *3*, 213 – 216.
[129] K. Ogho, C. Zhao, M. Kobayashi, T. Asakura, *Polymer* **2003**, *44*, 841 – 846.
[130] S. Sukigara, M. Gandhi, J. Ayutsede, M. Micklus, F. Ko, *Polymer* **2003**, *44*, 5721 – 5727.
[131] S. Sukigara, M. Gandhi, J. Ayutsede, M. Micklus, F. Ko, *Polymer* **2004**, *45*, 3701 – 3708.
[132] J. Ayutsede, M. Gandhi, S. Sukigara, M. Micklus, H.-E. Chen, F. Ko, *Polymer* **2005**, *46*, 1625 – 1634.
[133] H.-J. Jin, S. V. Fridrikh, G. C. Rutledge, D. L. Kaplan, *Biomacromolecules* **2002**, *3*, 1233 – 1239.
[134] M. Wang, H.-J. Jin, D. L. Kaplan, G. C. Rutledge, *Macromolecules* **2004**, *37*, 6856 – 6864.
[135] S. H. Kim, Y. S. Nam, T. S. Lee, W. H. Park, *Polym. J.* **2003**, *35*, 185 – 190.
[136] B.-M. Min, G. Lee, S. H. Kim, Y. S. Nam, T. S. Lee, W. H. Park, *Biomaterials* **2004**, *25*, 1289 – 1297.
[137] B.-M. Min, L. Jeong, Y. S. Nam, J.-M. Kim, J. Y. Jin, W. H. Park, *Int. J. Biol. Macromol.* **2004**, *34*, 223 – 230.
[138] H. Wang, Y. Zhang, H. Shao, X. Hu, *J. Mater. Sci.* **2005**, *40*, 5359 – 5363.
[139] H. Wang, H. Shao, X. Hu, *J. Appl. Polym. Sci.* **2006**, *101*, 961 – 968.
[140] L. Jeong, K. Y. Lee, J. W. Liu, W. H. Park, *Int. J. Biol. Macromol.* **2006**, *38*, 140 – 144.
[141] W. H. Park, L. Jeong, D. I. Yoo, S. Hudson, *Polymer* **2004**, *45*, 7151 – 7157.
[142] K. E. Park, Y. S. Jung, S. J. Lee, B.-M. Min, W. H. Park, *Int. J. Biol. Macromol.* **2006**, *38*, 165 – 173.
[143] Y. Wang, D. J. Blasioli, H.-Y. Kim, H. S. Kim, D. L. Kaplan, *Biomaterials* **2006**, *27*, 4434 – 4442.
[144] J. S. Stephens, S. R. Fahnestock, R. S. Farmer, K. L. Kiick, D. B. Chase, J. F. Rabolt, *Biomacromolecules* **2005**, *6*, 1405 – 1413.
[145] B.-M. Min, S. W. Lee, J. N. Lim, Y. You, T. S. Lee, P. H. Kang, W. H. Park, *Polymer* **2004**, *45*, 7137 – 7142.
[146] H. K. Noh, S. W. Lee, J.-M. Kim, J.-E. Oh, K.-H. Kim, C.-P. Chung, S.-C. Choi, W. H. Park, B.-M. Min, *Biomaterials* **2006**, *27*, 3934 – 3944.
[147] K. Ohkawa, D. Cha, H. Kim, A. Nishida, H. Yamamoto, *Macromol. Rapid Commun.* **2004**, *25*, 1600 – 1605.
[148] X. Geng, O.-H. Kwon, J. Jang, *Biomaterials* **2005**, *26*, 5427 – 5432.
[149] B. Duan, C. Dong, X. Yuan, K. Yao, *J. Biomater. Sci. Polym. Ed.* **2004**, *15*, 797 – 811.
[150] M. Spasova, N. Manolova, D. Paneva, I. Rashkov, *e-Polymers* **2004**, No. 56.
[151] N. Bhattarai, D. Edmondson, O. Veiseh, F. A. Matsen, M. Zhang, *Biomaterials* **2005**, *26*, 6176 – 6184.
[152] L. Li, Y.-L. Hsieh, *Carbohydr. Res.* **2006**, *341*, 374 – 381.
[153] M. Ignatova, K. Starbova, N. Markova, N. Manolova, I. Rashkov, *Carbohydr. Res.* **2006**, *341*, 2098 – 2107.
[154] M. Peesan, R. Rujiravanit, P. Supaphol, *J. Biomater. Sci. Polym. Ed.* **2006**, *17*, 547 – 565.
[155] P. Kulpinski, *J. Appl. Polym. Sci.* **2005**, *98*, 1855 – 1859.
[156] C.-W. Kim, M. W. Frey, M. Marquez, Y. L. Joo, *J. Polym. Sci. Part B* **2005**, *43*, 1673 – 1683.
[157] V. K. Daga, M. E. Helgeson, E. Matthew, N. J. Wagner, *J. Polym. Sci. Part B* **2006**, *44*, 1608 – 1617.
[158] J. Doshi, D. H. Reneker, *J. Electrost.* **1995**, *35*, 151 – 160.
[159] V. N. Morozov, T. Y. Morozova, N. R. Kallenbach, *Int. J. Mass Spectrom.* **1998**, *178*, 143 – 159.
[160] J. M. Deitzel, J. Kleinmeyer, J. K. Hirvonen, N. C. Beck Tan, *Polymer* **2001**, *42*, 8163 – 8170.
[161] A. Theron, E. Zussman, A. L. Yarin, *Nanotechnology* **2001**, *12*, 384 – 390.
[162] S. Megelski, J. S. Stephans, C. D. Bruce, J. F. Rabolt, *Macromolecules* **2002**, *35*, 8456 – 8466.

[163] P. P. Tsai, H. Schreuder-Gibson, P. Gibson, *J. Electrost.* **2002**, *54*, 333 – 341.
[164] S.-H. Lee, J.-W. Yoon, M. H. Suh, *Macromol. Res.* **2002**, *10*, 282 – 285.
[165] A. Pedicini, R. J. Farris, *J. Polym. Sci. Part B* **2004**, *42*, 752 – 757.
[166] N. Tomczak, N. F. van Hulst, G. J. Vancso, *Macromolecules* **2005**, *38*, 7863 – 7866.
[167] M. L. Bellan, J. Kameoka, H. G. Craighead, *Nanotechnology* **2005**, *16*, 1095 – 1099.
[168] "Poly(ethylene oxide) and Related Hydrogels": N. B. Graham in *Hydrogels in Medicine and Pharmacy*, *Vol. II* (Ed.: N. A. Peppas), CRC, Boca Raton, **1986**, pp. 96 – 97.
[169] S. R. Bhattarai, N. Bhattarai, P. Viswanathamurthi, K. H. Yi, H. P. Hwang, H. Y. Kim, *J. Biomed. Mater. Res. Part A* **2006**, *78*, 247 – 257.
[170] F. L. Marten, C. W. Zvanut in *Polyvinyl Alcohol: Developments* (Ed.: C. A. Finch), Wiley, Chichester, **1992**.
[171] B. Ding, H.-Y. Kim, S.-C. Lee, C.-L. Shao, D.-R. Lee, S.-J. Park, G.-B. Kwag, K.-J. Choi, *J. Polym. Sci. Part B* **2002**, *40*, 1261 – 1268.
[172] N. Ristolainen, P. Heikkilä, A. Harlin, J. Seppälä, *Macromol. Mater. Eng.* **2006**, *291*, 114 – 122.
[173] S. L. Shenoy, W. D. Bates, G. Wnek, *Polymer* **2005**, *46*, 8990 – 9004.
[174] L. Li, Y.-L. Hsieh, *Polymer* **2005**, *46*, 5133 – 5139.
[175] B. Kim, H. Park, S.-H. Lee, S. M. Sigmund, *Mater. Lett.* **2005**, *59*, 829 – 832.
[176] B. Ding, M. Yamazaki, S. Shiratori, *Sens. Actuators B* **2005**, *106*, 477 – 483.
[177] K. Kumeta, I. Nagashima, S. Matsui, K. Mizoguchi, *J. Appl. Polym. Sci.* **2003**, *90*, 2420 – 2427.
[178] J. Zeng, H. Hou, J. H. Wendorff, A. Greiner, *e-polymers* **2004**, No. 78.
[179] X. Jin, Y.-L. Hsieh, *Polymer* **2005**, *46*, 5149 – 5160.
[180] L. Li, Y.-L. Hsieh, *Nanotechnology* **2005**, *16*, 2852 – 2860.
[181] X. Jin, Y.-L. Hsieh, *Macromol. Chem. Phys.* **2005**, *206*, 1745 – 1751.
[182] B. Ding, J. Kim, K. Fujimoto, S. Shiratori, *Chem. Sens.* **2004**, *20 (Suppl. B)*, 264 – 265.
[183] B. Ding, J. Kim, Y. Miyazaki, S. Shiratori, *Sens. Actuators B* **2004**, *101*, 373 – 380.
[184] J. Zeng, H. Hou, J. H. Wendorff, A. Greiner, *Macromol. Rapid Commun.* **2005**, *26*, 1557 – 1562.
[185] S.-S. Choi, J.-P. Hong, Y. S. Seo, S. M. Chung, C. Nah, *J. Appl. Polym. Sci.* **2006**, *101*, 2333 – 2337.
[186] L. M. Bellan, G. W. Coates, H. G. Craighead, *Macromol. Rapid Commun.* **2006**, *27*, 511 – 515.
[187] Q. Yang, Z. Li, Y. Hong, Y. Zhao, S. Qiu, C. Wang, Y. Wei, *J. Polym. Sci. Part B* **2004**, *42*, 3721 – 3726.
[188] M. Bognitzki, T. Frese, M. Steinhart, A. Greiner, J. H. Wendorff, A. Schaper, M. Hellwig, *Polym. Eng. Sci.* **2001**, *41*, 982 – 989.
[189] D. Li, G. Ouyang, J. T. McCann, Y. Xia, *Nano Lett.* **2005**, *5*, 913 – 916.
[190] D. Li, Y. Xia, *Nano Lett.* **2003**, *3*, 555 – 560.
[191] D. Li, Y. Wang, Y. Xia, *Nano Lett.* **2003**, *3*, 1167 – 1171.
[192] S.-W. Lee, A. M. Belcher, *Nano Lett.* **2004**, *4*, 387 – 390.
[193] K. Sawicka, P. Gouma, S. Simon, *Sens. Actuators B* **2005**, *108*, 585 – 588.
[194] N. Jing, M. Wang, J. Kameoka, *J. Photopolym. Sci. Technol.* **2005**, *18*, 503 – 506.
[195] J. Watthanaarun, V. Pavarajarn, P. Supaphol, *Sci. Technol. Adv. Mater.* **2005**, *6*, 240 – 245.
[196] X. Lu, Y. Zhao, C. Wang, Y. Wei, *Macromol. Rapid Commun.* **2005**, *26*, 1325 – 1329.
[197] S. Park, D. Y. Lee, M.-H. Lee, S.-J. Lee, B.-Y. Kim, *J. Korean Ceram. Soc.* **2005**, *42*, 548 – 553.
[198] J. Yuh, J. C. Nino, W. M. Sigmund, *Mater. Lett.* **2005**, *59*, 3645 – 3647.
[199] A.-M. Azad, T. Matthews, J. Swary, *Mater. Sci. Eng. B* **2005**, *123*, 252 – 258.
[200] A.-M. Azad, *Mater. Lett.* **2006**, *60*, 67 – 72.
[201] X. Lu, Y. Zhao, C. Wang, *Adv. Mater.* **2005**, *17*, 2485 – 2488.
[202] X. Lu, L. Li, W. Zhang, C. Wang, *Nanotechnology* **2005**, *16*, 2233 – 2237.
[203] W.-J. Jin, H. K. Lee, E. H. Jeong, W. H. Park, J. H. Youk, *Macromol. Rapid Commun.* **2005**, *26*, 1903 – 1907.
[204] S. Maensiri, W. Nuansing, J. Klinkaewnarong, P. Laokul, J. Khemprasi, *J. Colloid Interface Sci.* **2006**, *297*, 578 – 583.
[205] X. Lu, X. Liu, W. Zhang, C. Wang, Y. Wei, *J. Colloid Interface Sci.* **2006**, *298*, 996 – 999.
[206] R. Ostermann, D. Li, Y. Yin, J. T. McCann, Y. Xia, *Nano Lett.* **2006**, *6*, 1297 – 1302.
[207] J. T. McCann, J. I. L. Chen, D. Li, Z.-G. Ye, Y. Xia, *Chem. Phys. Lett.* **2006**, *424*, 162 – 166.
[208] W. Nuansing, S. Ninmuang, W. Jarernboon, S. Maensiri, S. Seraphin, *Mater. Sci. Eng. B* **2006**, *131*, 147 – 155.
[209] H. Pan, L. Li, L. Hu, X. Cui, *Polymer* **2006**, *47*, 4901 – 4904.
[210] D. Y. Lee, B.-Y. Kim, S.-J. Lee, M.-H. Lee, Y.-S. Song, J.-Y. Lee, *J. Korean Phys. Soc.* **2006**, *48*, 1686 – 1690.
[211] E. Yan, Z. Huang, Y. Xin, Q. Zhao, W. Zhang, *Mater. Lett.* **2006**, *60*, 2969 – 2973.
[212] Y. Wang, Y. Li, S. Yang, G. Zhang, D. An, C. Wang, Q. Yang, X. Chen, X. Jing, Y. Wei, *Nanotechnology* **2006**, *17*, 3304 – 3307.
[213] Z.-G. Wang, J.-Q. Wang, Z.-K Xu, *J. Mol. Catal. B* **2006**, *42*, 45 – 51.
[214] D. Li, A. Babel, S. A. Jehekhe, Y. Xia, *Adv. Mater.* **2004**, *16*, 2062 – 2066.
[215] B. Sun, B. Duan, X. Yuan, *J. Appl. Polym. Sci.* **2006**, *102*, 39 – 45.
[216] S. Shukla, E. Brinley, H. J. Cho, S. Seal, *Polymer* **2005**, *46*, 12130 – 12145.
[217] R. S. Werbowyi, D. G. Gray, *Mol. Cryst. Liq. Cryst. Lett. Sect.* **1976**, *34*, 97 – 103.
[218] *Handbook of Biodegradable Polymers* (Eds.: A. J. Domb, J. Kost, D. M. Wiseman), Harwood, Amsterdam, **1997**.
[219] M. Bognitzki, W. Czado, T. Frese, A. Schaper, M. Hellwig, M. Steinhart, A. Greiner, J. H. Wendorff, *Adv. Mater.* **2001**, *13*, 70 – 72.
[220] X. Zong, K. Kim, D. Fang, S. Ran, B. S. Hsiao, B. Chu, *Polymer* **2002**, *43*, 4403 – 4412.
[221] E.-R. Kenawy, G. L. Bowlin, K. Mansfield, J. Layman, D. G. Simpson, E. H. Sanders, G. W. Wnek, *J. Controlled Release* **2002**, *81*, 57 – 64.
[222] S. Sahoo, H. Ouyang, J. C.-H. Goh, T. E. Tay, S. L. Toh, *Tissue Eng.* **2006**, *12*, 91 – 99.
[223] C.-M. Hsu, S. Shivkumar, *Macromol. Mater. Eng.* **2004**, *289*, 334 – 340.
[224] H. Yoshimoto, Y. M. Shin, H. Terai, J. P. Vacanti, *Biomaterials* **2003**, *24*, 2077 – 2082.
[225] N. Bölgen, Y. Z. Menceloglu, K. Acatay, I. Vargel, E. Piskin, *J. Biomater. Sci. Polym. Ed.* **2005**, *16*, 1537 – 1555.
[226] G. H. Kim, *J. Polym. Sci. Part B* **2006**, *44*, 1426 – 1433.
[227] Z.-M. Huang, C.-L. He, A. Yang, Y. Zhang, X. -J. Han, J. Yin, Q. Wu, *J. Biomed. Mater. Res. Part A* **2006**, *77*, 169 – 179.
[228] T. G. Kim, T. G. Park, *Biotechnol. Prog.* **2006**, *22*, 1108 – 1113.
[229] I. S. Lee, O. H. Kwon, W. Meng, I.-K. Kang, Y. Ito, *Macromol. Res.* **2004**, *12*, 374 – 378.
[230] J. S. Choi, S. W. Lee, L. Jeong, S.-H. Bae, B. C. Min, J. H. Youk, W. H. Park, *Int. J. Biol. Macromol.* **2004**, *34*, 249 – 256.
[231] Y. Ito, H. Hasuda, M. Kamitakahara, C. Ohtsuki, M. Tanihara, I.-K. Kang, O. H. Kwon, *J. Biosci. Bioeng.* **2005**, *100*, 43 – 49.
[232] S. A. Riboldi, M. Sampaolesi, P. Neuenschwander, G. Cossu, S. Mantero, *Biomaterials* **2005**, *26*, 4606 – 4615.

[233] J. J. Stankus, J. Guan, K. Fujimoto, W. R. Wagner, *Biomaterials* **2006**, *27*, 735 – 744.
[234] W.-J. Li, C. T. Laurencin, E. J. Caterson, R. S. Tuan, F. K. Ko, *J. Biomed. Mater. Res.* **2002**, *60*, 613 – 621.
[235] X. Zong, S. Ran, D. Fang, B. S. Hsiao, B. Chu, *Polymer* **2003**, *44*, 4959 – 4967.
[236] K. Kim, M. Yu, X. Zong, J. Chiu, D. Fang, Y.-S. Seo, B. S. Hsiao, B. Chu, M. Hadjiargyrou, *Biomaterials* **2003**, *24*, 4977 – 4985.
[237] C. Y. Xu, R. Inai, M. Kotaki, S. Ramakrishna, *Biomaterials* **2004**, *25*, 877 – 886.
[238] B.-M. Min, Y. You, J.-M. Kim, S. J. Lee, W. H. Park, *Carbohydr. Polym.* **2004**, *57*, 285 – 292.
[239] I. K. Kwon, S. Kidoaki, T. Matsuda, *Biomaterials* **2005**, *26*, 3929 – 3939.
[240] X. Zong, H. Bien, C.-Y. Chung, L. Yin, D. Fang, B. S. Hsiao, B. Chun, E. Entcheva, *Biomaterials* **2005**, *26*, 5330 – 5338.
[241] D. Liang, Y. K. Luu, K. Kim, B. S. Hsiao, M. Hadjiargyrou, B. Chu, *Nucleic Acids Res.* **2005**, *33*, e170.
[242] K. E. Park, H. K. Kang, S. J. Lee, B.-M. Min, W. H. Park, *Biomacromolecules* **2006**, *7*, 635 – 643.
[243] H.-J. Jin, M.-O. Hwang, J. S. Yoon, K. H. Lee, I.-J. Chin, M.-N. Kim, *Macromol. Res.* **2005**, *13*, 73 – 79.
[244] X. Xu, Q. Yang, Y. Wang, H. Yu, X. Chen, X. Jing, *Eur. Polym. J.* **2006**, *42*, 2081 – 2087.
[245] J. S. Stephens, S. Frisk, S. Megelski, J. F. Rabolt, D. B. Chase, *Appl. Spectrosc.* **2001**, *55*, 1287 – 1290.
[246] T. Lin, H. Wang, H. Wang, X. Wang, *Nanotechnology* **2004**, *15*, 1375 – 1381.
[247] G.-T. Kim, Y.-J. Hwang, Y.-C. Ahn, H.-S. Shin, J.-K. Lee, C.-M. Sung, *Korean J. Chem. Eng.* **2005**, *22*, 147 – 153.
[248] C. Shin, G. G. Chase, D. H. Reneker, *Coll. Surf. Physicochem. Eng. Aspects* **2005**, *262*, 211 – 215.
[249] K. Kim, M. Kang, I.-J. Chin, H.-J. Jin, *Macromol. Res.* **2005**, *13*, 533 – 537.
[250] S. C. Baker, N. Atkin, P. A. Gunning, N. Granville, K. Wilson, D. Wilson, J. Southgate, *Biomaterials* **2006**, *27*, 3136 – 3146.
[251] P. K. Baumgarten, *J. Colloid Interface Sci.* **1971**, *36*, 71 – 79.
[252] I. Chun, D. H. Reneker, X. Fang, H. Fong, J. Deitzel, N. Beck, K. Kearns, *Int. SAMPE Symp. Exhib.* **1998**, *43*, 718 – 729.
[253] A. G. MacDiarmid, W. E. Jones, I. D. Norris, J. Gao, A. T. Johnson, N. J. Pinto, J. Hone, B. Han, F. K. Ko, H. Okuzaki, M. Llaguno, *Synth. Met.* **2001**, *119*, 27 – 30.
[254] H. L. Schreuder-Gibson, P. Gibson, P. Tsai, P. Gupta, G. Wilkes, *Int. Nonwovens J.* **2004**, *13*, 39 – 45.
[255] C. Kim, K.-S. Yang, W.-J. Lee, *Electrochem. Solid-State Lett.* **2004**, *7*, A397 – A399.
[256] S.-Y. Gu, Q.-L. Wu, J. Ren, G. J. Vancso, *Macromol. Rapid Commun.* **2005**, *26*, 716 – 720.
[257] Q. B. Yang, D. M. Li, Y. L. Hong, Z. Y. Li, C. Wang, S. L. Qiu, Y. Wei, *Synth. Met.* **2003**, *137*, 973 – 974.
[258] P. P. Tsai, W. Chen, J. R. Roth, *Int. Nonwovens J.* **2004**, *13*, 17 – 23.
[259] S.-Y. Gu, J. Ren, Q. L. Wu, *Synth. Met.* **2005**, *155*, 157 – 161.
[260] J. McCann, M. Marquez, Y. Xia, *J. Am. Chem. Soc.* **2006**, *128*, 1436 – 1437.
[261] H. Liu, Y.-L. Hsieh, *Macromol. Rapid Commun.* **2006**, *27*, 142 – 145.
[262] Y. Kim, D. Y. Lee, M.-H. Lee, S.-J. Lee, *J. Korean Ceram. Soc.* **2006**, *43*, 203 – 206.
[263] L. E. Peebles, *Carbon Fibers: Formation, Structure, and Properties*, CRC, Boca Raton, **1995**, p. 7.
[264] R. V. N. Krishnappa, K. Desai, C. Sung, *J. Mater. Sci.* **2003**, *38*, 2357 – 2365.
[265] M. M. Bergshoef, G. J. Vancso, *Adv. Mater.* **1999**, *11*, 1362 – 1365.
[266] H. Fong, W. Liu, C.-S. Wang, R. A. Vaia, *Polymer* **2002**, *43*, 775 – 780.
[267] A. Suthar, G. Chase, *Tce* **2001**, *726*, 26 – 28.
[268] R. Dersch, T. Liu, A. K. Schaper, A. Greiner, J. H. Wendorff, *J. Polym. Sci. Part A* **2003**, *41*, 545 – 553.
[269] M. G. Hajara, K. Metha, G. G. Chase, *Sep. Filtr. Technol.* **2003**, *30*, 79 – 88.
[270] Y. Ryu, H. Y. Kim, K. H. Lee, H. C. Park, D. R. Lee, *Eur. Polym. J.* **2003**, *39*, 1883 – 1889.
[271] P. Katta, M. Alessandro, R. D. Ramsier, G. G. Chase, *Nano Lett.* **2004**, *4*, 2215 – 2218.
[272] J. S. Stephans, D. B. Chase, J. F. Rabolt, *Macromolecules* **2004**, *37*, 877 – 881.
[273] K. H. Hong, T. J. Kang, *J. Appl. Polym. Sci.* **2006**, *100*, 167 – 177.
[274] Y. Li, Z. Huang, Y. Lǚ, *Eur. Polym. J.* **2006**, *42*, 1696 – 1704.
[275] G. Srinivasan, D. H. Reneker, *Polym. Int.* **1995**, *36*, 195 – 201.
[276] S. L. Kwolek, US 3600350, **1971**.
[277] S.-G. Lee, S.-S. Choi, C. W. Joo, *J. Korean Fiber Soc.* **2002**, *39*, 1.
[278] C. Nah, S. H. Han, M.-H. Lee, J. S. Kim, D. S. Lee, *Polym. Int.* **2003**, *52*, 429 – 432.
[279] C. Huang, S. Wang, H. Zhang, T. Li, S. Chen, C. Lai, H. Hou, *Eur. Polym. J.* **2006**, *42*, 1099 – 1104.
[280] J.-S. Kim, D. H. Reneker, *Polym. Compos.* **1999**, *20*, 124 – 131.
[281] H. L. Schreuder-Gibson, P. Gibson, K. Senecal, M. Sennett, J. Walker, W. Yeomans, D. Ziegler, P. P. Tsai, *J. Adv. Mater.* **2002**, *34*, 44 – 55.
[282] K. W. Kim, K. H. Lee, B. S. Lee, Y. S. Ho, S. J. Oh, H. Y. Kim, *Fibers Polym.* **2005**, *6*, 121 – 126.
[283] Z. Ma, M. Kotaki, T. Yong, W. He, S. Ramakrishna, *Biomaterials* **2005**, *26*, 2527 – 2536.
[284] M. S. Khil, H. Y. Kim, M. S. Kim, S. Y. Park, D.-R. Lee, *Polymer* **2004**, *45*, 295 – 301.
[285] Y. K. Kim, W. H. Park, S. C. Lee, Y. G. Jeong, W. H. Jo, *J. Korean Fiber Soc.* **2004**, *41*, 30 – 36.
[286] M. M. Demir, I. Yilgor, B. Erman, *Polymer* **2002**, *43*, 3303 – 3309.
[287] M.-S. Khil, D.-I. Cha, H.-Y. Kim, I.-S. Kim, N. Bhattarai, *J. Biomed. Mater. Res. Part B* **2003**, *67*, 675 – 679.
[288] G. M. McKee, T. Park, S. Unal, I. Yilgor, T. E. Long, *Polymer* **2005**, *46*, 2011 – 2015.
[289] D. I. Cha, H. Y. Kim, K. H. Lee, Y. C. Jung, J. W. Cho, B. C. Byung, *J. Appl. Polym. Sci.* **2005**, *96*, 460 – 465.
[290] T. Matsuda, M. Ihara, H. Inoguchi, I. K. Kwon, K. Takamizawa, K. Keiichi, S. Kidoaki, *J. Biomed. Mater. Res. Part A* **2005**, *73*, 125 – 131.
[291] K. Lee, B. Lee, C. Kim, H. Kim, K. Kim, C. Nah, *Macromol. Res.* **2005**, *13*, 441 – 445.
[292] S. B. Mitchell, S. B. Sanders, *J. Biomed. Mater. Res. Part A* **2006**, *78*, 110 – 120.
[293] S. Thandavamoorthy, N. Gopinath, S. S. Ramakumar, *J. Appl. Polym. Sci.* **2006**, *101*, 3121 – 3124.
[294] K. H. Lee, H. Y. Kim, Y. M. La, D. R. Lee, N. H. Sung, *J. Polym. Sci. Part B* **2002**, *40*, 2259 – 2268.
[295] R. Ramaseshan, S. Sundarrajan, Y. Liu, R. S. Barhate, N. L. Lala, S. Ramakrishna, *Nanotechnology* **2006**, *17*, 2947 – 2953.
[296] J. M. Deitzel, W. Kosik, S. H. McKnight, N. C. Beck Tan, J. M. Desimone, S. Crette, *Polymer* **2002**, *43*, 1025 – 1029.
[297] E. Zussman, A. L. Yarin, A. V. Bazilevsky, R. Avrahami, M. Feldman, *Adv. Mater.* **2006**, *18*, 348 – 353.
[298] M. Bognitzki, M. Becker, M. Graeser, W. Massa, J. H. Wendorff, A. Schaper, D. Weber, A. Beyer, A. Gölzhäuser, A. Greiner, *Adv. Mater.* **2006**, *18*, 2384 – 2386.
[299] Z. Chen, M. D. Foster, W. Zhou, H. Fong, D. H. Reneker, R. Resendes, I. Manners, *Macromolecules* **2001**, *34*, 6156 – 6158.
[300] L. Larrondo, R. St. John Manley, *J. Polym. Sci. Polym. Phys. Ed.* **1981**, *19*, 909 – 920.
[301] L. Larrondo, R. St. John Manley, *J. Polym. Sci. Polym. Phys. Ed.* **1981**, *19*, 933 – 940.

[302] L. Larrondo, R. St. John Manley, *J. Polym. Sci. Polym. Phys. Ed.* **1981**, *19*, 921 – 932.
[303] J.-S. Kim, D.-S. Lee, *Polym. J.* **2000**, *32*, 616 – 618.
[304] S. Lee, S. K. Obendorf, *J. Appl. Polym. Sci.* **2006**, *102*, 3430 – 3437.
[305] M. Becker, A. Greiner, unpublished results.
[306] K. H. Lee, H. Y. Kim, Y. J. Ryu, K. W. Kim, S. W. Choi, *J. Polym. Sci. Part B* **2003**, *41*, 1256 – 1262.
[307] J. Kameoka, R. Ilic, D. Czaplewski, R. T. Mathers, G. W. Coates, H. G. Craghead, *J. Photopolym. Sci. Technol.* **2004**, *17*, 421 – 425.
[308] P. Wutticharoenmongkol, P. Supaphol, T. Srikhirin, T. Kerdcharoen, T. Osotchan, *J. Polym. Sci. Polym. Phys. Ed.* **2005**, *43*, 1881 – 1891.
[309] M. Wei, J. Lee, B. Kang, J. Mead, *Macromol. Rapid Commun.* **2005**, *26*, 1127 – 1132.
[310] D. I. Cha, K. W. Kim, G. H. Chu, H. Y. Kim, K. H. Lee, N. Bhattarai, *Macromol. Res.* **2006**, *14*, 331 – 337.
[311] Y. K. Luu, K. Kim, B. S. Hsiao, B. Chu, M. Hadjiargyrou, *J. Controlled Release* **2003**, *89*, 341 – 353.
[312] Y.-T. Jia, H.-Y. Kim, J. Gong, D.-R. Lee, *J. Appl. Polym. Sci.* **2006**, *99*, 1462 – 1470.
[313] M. Ma, R. M. Hill, J. L. Lowery, S. V. Fridrikh, G. C. Rutledge, *Langmuir* **2005**, *21*, 5549 – 5554.
[314] A. Alli, B. Hazer, Y. Menceloglu, S. Süzer, *Eur. Polym. J.* **2006**, *42*, 740 – 750.
[315] H. Fong, D. H. Reneker, *J. Polym. Sci. Part B* **1999**, *37*, 3488 – 3493.
[316] V. Kalra, P. A. Kakad, S. Mendez, T. Ivannikov, M. Kamperman, Y. L. Joo, *Macromolecules* **2006**, *39*, 5453 – 5457.
[317] T. Ruotsalainen, J. Turku, P. Heikkilä, J. Ruokolainen, A. Nykänen, T. Laitinen, M. Torkkeli, R. Serimaa, G. ten Brinke, A. Harlin, O. Ikkala, *Adv. Mater.* **2005**, *17*, 1048 – 1052.
[318] Photograph by R. Dersch.
[319] N. Ristolainen, P. Heikkila, A. Harlin, J. Seppala, *Macromol. Mater. Eng.* **2006**, 291, 114 – 122.
[320] G.-M. Kim, R. Lach, G. H. Michler, Y.-W. Chang, *Macromol. Rapid Commun.* **2005**, *26*, 728 – 733.
[321] J. H. Hong, E. H. Jeong, H. S. Lee, D. H. Baik, S. W. Seo, J. H. Youk, *J. Polym. Sci. Part B* **2005**, *43*, 3171 – 3177.
[322] M. M. Demir, M. A. Gulgun, Y. Z. Menceloglu, B. Erman, S. S. Abramchuk, E. E. Makhaeva, A. R. Khokhlov, V. G. Matveeva, M. G. Sulman, *Macromolecules* **2004**, *37*, 1787 – 1792.
[323] G.-M. Kim, A. Wutzler, H.-J. Radusch, G. H. Michler, P. Simon, R. A. Sperling, W. J. Parak, *Chem. Mater.* **2005**, *17*, 4949 – 4957.
[324] Z. Li, H. Huang, T. Shang, F. Yang, W. Zheng, C. Wang, S. K. Manohar, *Nanotechnology* **2006**, *17*, 917 – 920.
[325] N. Yu, C. Shao, Y. Liu, H. Guan, X. Yang, *J. Colloid Interface Sci.* **2005**, *285*, 163 – 166.
[326] M. Wang, H. Singh, T. A. Hatton, G. C. Rutledge, *Polymer* **2004**, *45*, 5505 – 5514.
[327] T. Song, Y. Zhang, T. Zhou, C. T. Lim, S. Ramakrishna, B. Liu, *Chem. Phys. Lett.* **2005**, *415*, 317 – 322.
[328] P. Gupta, R. Asmatulu, R. Claus, G. Wilkes, *J. Appl. Polym. Sci.* **2006**, *100*, 4935 – 4942.
[329] O. Kriha, M. Becker, M. Lehmann, D. Kriha, J. Krieglstein, M. Yosef, S. Schlecht, R. Wehrspohn, J. H. Wendorff, A. Greiner, *Adv. Mater.*, in press.
[330] A. Oberlin, M. Endo, *J. Cryst. Growth* **1976**, *32*, 335 – 349.
[331] S. Iijima, *Nature* **1991**, *354*, 56 – 58.
[332] F. Ko, Y. Gogotsi, A. Ali, N. Naguib, H. Ye, G. Yang, C. Li, P. Willis, *Adv. Mater.* **2003**, *15*, 1161 – 1165.
[333] C. Kim, S.-H. Park, J.-I. Cho, D.-Y. Lee, T.-J. Park, W.-G. Lee, K.-S. Yang, *J. Raman Spectrosc.* **2004**, *35*, 928 – 933.
[334] H. Ye, H. Lam, N. Titchenal, Y. Gogotsi, F. Ko, *Appl. Phys. Lett.* **2004**, *85*, 1775 – 1777.
[335] J. J. Ge, H. Hou, Q. Li, M. J. Graham, A. Greiner, D. H. Reneker, F. W. Harris, S. D. Cheng, *J. Am. Chem. Soc.* **2004**, *126*, 15754 – 15761.
[336] J. Liu, T. Wang, T. Uchida, S. Kumar, *J. Appl. Polym. Sci.* **2005**, *96*, 1992 – 1995.
[337] H. Hou, J. J. Ge, J. Zeng, Q. Li, D. H. Reneker, A. Greiner, S. Z. D. Stephen, *Chem. Mater.* **2005**, *17*, 967 – 973.
[338] S. Kedem, J. Schmidt, Y. Paz, Y. Cohen, *Langmuir* **2005**, *21*, 5600 – 5604.
[339] E. J. Ra, K. H. An, K. K. Kim, S. Y. Jeong, Y. H. Lee, *Chem. Phys. Lett.* **2005**, *413*, 188 – 193.
[340] Y. Dror, W. Salalha, R. L. Khalfin, Y. Cohen, A. L. Yarin, E. Zussman, *Langmuir* **2003**, *19*, 7012 – 7020.
[341] W. Salalha, Y. Dror, R. L. Khalfin, Y. Cohen, A. L. Yarin, E. Zussman, *Langmuir* **2004**, *20*, 9852 – 9855.
[342] W. Zhou, Y. Wu, F. Wie, G. Luo, W. Qian, *Polymer* **2005**, *46*, 12689 – 12695.
[343] J. Y. Lim, C. K. Lee, S. J. Kim, I. Y. Kim, S. I. Kim, *J. Macromol. Sci. Pure Appl. Chem.* **2006**, *43*, 785 – 796.
[344] G.-M. Kim, G. H. Michler, P. Pötschke, *Polymer* **2005**, *46*, 7346 – 7351.
[345] R. Sen, B. Zhao, D. Perea, M. E. Itkis, H. Hu, J. Love, E. Bekyarova, R. C. Haddon, *Nano Lett.* **2004**, *4*, 459 – 464.
[346] H. Hou, D. H. Reneker, *Adv. Mater.* **2004**, *16*, 69 – 73.
[347] B. Ding, C. K. Kim, H. Y. Kim, Y. Hak, M. K. Seo, J. P. Soo, *Fibers Polym.* **2004**, *5*, 105 – 109.
[348] Y. Hong, D. Li, J. Zheng, G. Zou, *Nanotechnology* **2006**, *17*, 1986 – 1993.
[349] N. Dharmaraj, C. Kim, H. Kim, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2006**, *36*, 29 – 32.
[350] C. Shao, H. Guan, Y. Liu, J. Gong, N. Yu, X. Yang, *J. Cryst. Growth* **2004**, *267*, 380 – 384.
[351] P. Viswanathamurthi, N. Bhattarai, H. Y. Kim, D. R. Lee, *Nanotechnology* **2004**, *15*, 320 – 323.
[352] X. Yang, C. Shao, H. Guan, X. Li, J. Gong, *Inorg. Chem. Commun.* **2004**, *7*, 176 – 178.
[353] X. M. Sui, C. L. Shao, Y. C. Liu, *Appl. Phys. Lett.* **2005**, *87*, 113115.
[354] H. Wu, W. Pan, *J. Am. Ceram. Soc.* **2006**, *89*, 699 – 701.
[355] H. Guan, C. Shao, B. Chen, J. Gong, X. Yang, *Inorg. Chem. Commun.* **2003**, *6*, 1409 – 1411.
[356] H. Guan, C. Shao, S. Wen, B. Chen, J. Gong, X. Yang, *Inorg. Chem. Commun.* **2003**, *6*, 1302 – 1303.
[357] C- L. Shao, H. Y. Guan, S. B. Wen, B. Chen, X. H. Yang, J. Gong, *Chin. Chem. Lett.* **2004**, *15*, 365 – 367.
[358] X. Yang, C. Shao, Y. Liu, R. Mu, H. Guan, *Thin Solid Films* **2005**, *478*, 228 – 231.
[359] C. L. Shao, H. Y. Guan, S. B. Wen, B. Chen, X. H. Yang, J. Gong, *Chin. Chem. Lett.* **2004**, *15*, 471 – 474.
[360] C. Shao, H. Guan, Y. Liu, X. Li, X. Yang, *J. Solid State Chem.* **2004**, *177*, 2628 – 2631.
[361] P. I. Gouma, *Rev. Adv. Mater. Sci.* **2003**, *5*, 147 – 154.
[362] S. Li, C. Shao, Y. Liu, S. Tang, R. Mu, *J. Phys. Mater. Res.* **2006**, *67*, 1869 – 1872.
[363] N. Dharmaraj, H. C. Park, C. H. Kim, P. Viswanathamurthi, H. Y. Kim, *Mater. Res. Bull.* **2006**, *41*, 612 – 619.
[364] C. L. Shao, Y. H. Guan, S. B. Wen, B. Chen, X. H. Yang, J. Gong, Y. C. Liu, *Chin. Chem. Lett.* **2004**, *15*, 492 – 494.
[365] C. Shao, H.-Y. Kim, J. Gong, B. Ding, D.-R. Lee, S.-J. Park, *Mater. Lett.* **2003**, *57*, 1579 – 1584.
[366] T.-J. Shi, Y.-B. Zhou, R.-G. Liao, H.-L. Wang, *Gaodeng Xuexiao Huaxue Xuebao* **2005**, *26*, 2373 – 2376.
[367] S.-S. Choi, S. G. Lee, S. S. Im, S. H. Kim, Y. L. Joo, *J. Mater. Sci. Lett.* **2003**, *22*, 891 – 893.
[368] S. Zhan, D. Chen, X. Jiao, C. Tao, *J. Phys. Chem. B* **2006**, *110*, 11199 – 11204.

[369] J.-B. Ko, S. W. Lee, D. E. Kim, Y. U. Kim, G. Li, S. G. Lee, T.-S. Chang, D. Kim, Y. L. Joo, *J. Porous Mater.* **2006**, *13*, 325–330.
[370] W. Salalha, J. Kuhn, Y. Dror, E. Zussman, *Nanotechnology* **2006**, *17*, 4675–4681.
[371] L. C. E. Struik, *Polym. Eng. Sci.* **1977**, *17*, 165–173.
[372] S. Agarwal, M. Puchner, A. Greiner, J. H. Wendorff, *Polym. Int.* **2005**, *54*, 1422–1428.
[373] P. de Gennes, *J. Chem. Phys.* **1974**, *60*, 5030–5042.
[374] J. S. Kim, D. H. Reneker, *Polym. Eng. Sci.* **1999**, *39*, 849–854.
[375] B. Wunderlich, *Macromolecular Physics*, *Vol. 1*, Academic Press, New York, **1973**.
[376] J. M. Samon, J. M. Schultz, B. Hsiao, *Polymer* **2000**, *41*, 2169–2182.
[377] J. M. Samon, J. M. Schultz, J. Wu, B. Hsiao, F. Yeh, R. Kolb, *J. Polym. Sci. Part B* **1999**, *37*, 1277–1287.
[378] D. Y. Lin, D. C. Martin, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2003**, *44*, 70–71.
[379] R. Jaeger, H. Schönherr, G. J. Vancso, *Macromolecules* **1996**, *29*, 7634–7636.
[380] E. D. Boland, G. E. Wnek, D. G. Simpson, K. J. Palowski, G. L. Bowlin, *J. Macromol. Sci. Pure Appl. Chem.* **2001**, *38*, 1231–1243.
[381] E. Zussman, A. Theron, A. L. Yarin, *Appl. Phys. Lett.* **2003**, *82*, 973–975.
[382] D. Li, Y. Wang, Y. Xia, *Adv. Mater.* **2004**, *16*, 361–366.
[383] B. Sundaray, V. Subramanian, T. S. Natarajan, R.-Z. Xiang, C.-C. Chang, W.-S. Fann, *Appl. Phys. Lett.* **2004**, *84*, 1222–1224.
[384] G. Egbers, *Angew. Makromol. Chem.* **1974**, *40*, 219–237.
[385] S. Y. Yeo, O. S. Kim, D. Y. Lim, S. W. Byun, S. H. Jeong, *J. Mater. Sci.* **2005**, *40*, 5393–5398.
[386] C. Mit-uppatham, M. Nithitanakul, P. Supaphol, *Macromol. Symp.* **2004**, *216*, 293–300.
[387] A. Holzmeister, Diplomarbeit, Philipps-Universität Marburg **2006**.
[388] S. V. Fridrikh, J. H. Yu, M. P. Brenner, G. C. Rutledge, *Phys. Rev. Lett.* **2003**, *90*, 144502.
[389] S. Kidoaki, I. K. Kwon, T. Matsuda, *Biomaterials* **2005**, *26*, 37–46.
[390] P. Gibson, H. Schreuder-Gibson, D. Rivin, *Colloids Surf. A* **2001**, *187–188*, 469–481.
[391] M. S. Abdel-Ghani, G. A. Davies, *Chem. Eng. Sci.* **1985**, *40*, 117–129.
[392] M. M. Tomadakis. S. V. Sotirchos, *AIChE J.* **1991**, *37*, 74–86.
[393] M. M. Tomadakis, S. V. Sotirchos, *AIChE J.* **1993**, *39*, 397–412.
[394] E. K. O. Hellen, M. J. Alava, K. J. Niskanen, *J. Appl. Phys.* **1997**, *81*, 6425–6431.
[395] M. M. Tomadakis, S. V. Sotirchos, *J. Chem. Phys.* **1993**, *99*, 9820–9827.
[396] K. J. Shields, M. J. Beckman, G. L. Bowlin, J. S. Wayne, *Tissue Eng.* **2004**, *10*, 1510–1517.
[397] G. Mathew, J. P. Hong, J. M. Rhee, D. J. Leo, C. Nah, *J. Appl. Polym. Sci.* **2006**, *101*, 2017–2021.
[398] S.-H. Lee, C. Tekmen, W. M. Sigmund, *Mater. Sci.* **2005**, *398*, 77–81.
[399] M. Bognitzki, H. Hou, M. Ishaque, T. Frese, M. Hellwig, C. Schwarte, A. Schaper, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2000**, *12*, 637–640.
[400] R. Caruso, J. H. Schattka, A. Greiner, *Adv. Mater.* **2001**, *13*, 1577–1579.
[401] Z. Sun, J. Zeng, H. Hou, H. Wickel, J. H. Wendorff, A. Greiner, *Prog. Colloid Polym. Sci.* **2005**, *130*, 15–19.
[402] F. Ochanda, W. E. Jones, Jr., *Langmuir* **2005**, *21*, 10791–10796.
[403] K. Müller, J. F. Quinn, A. P. R. Johnston, M. Becker, A. Greiner, F. Caruso, *Chem. Mater.* **2006**, *18*, 2397–2403.
[404] I. G. Loscertales, A. Barrero, M. Marquez, R. Spretz, R. Valarde-Ortiz, G. Larsen, *J. Am. Chem. Soc.* **2004**, *126*, 5376–5377.
[405] X.-H. Qin, S.-Y. Wang, *J. Appl. Polym. Sci.* **2006**, *102*, 1285–1290.
[406] T. A. Schmedake, F. Cunin, J. R. Link, M. J. Sailor, *Adv. Mater.* **2002**, *14*, 1270–1272.
[407] G. Emig, E. Klemm, *Technische Chemie. Einführung in die Chemische Reaktionstechnik*, Springer, Berlin, **2005**.
[408] M. Graeser, Diplomarbeit, Philipps-Universität Marburg, **2004**.
[409] M. Stasiak, A. Studer, A. Greiner, J. H. Wendorff, *Eur. Polym. J.*, in press.
[410] M. Stasiak, A. Studer, A. Greiner, J. H. Weendorff, *Polymer*, submitted.
[411] S. Kobayashi, R. Akiyama, *Chem. Commun.* **2003**, 449–460.
[412] *Fibre Reinforcements for Composite Materials* (Ed.: A. R. Bunsell), Elsevier, Amsterdam, **1988**.
[413] "Structure and Properties of Composites": *Material Science and Technology*, *Vol. 13* (Eds.: T. W. Chou, R. W. Cahn, P. Haasen, E. J. Kramer), VCH, Weinheim, **1993**.
[414] J. C. Halpin, J. L. Kardos, *Polym. Eng. Sci.* **1976**, *16*, 344–352.
[415] S. Wu, *Polymer Interfaces and Adhesion*, Marcel Dekker, New York, **1982**.
[416] P. J. Flory, *Macromolecules* **1978**, *11*, 1138–1141.
[417] M. Ballauff, *Angew. Chem.* **1989**, *101*, 261–276; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 253–267.
[418] J. Wendling, J. H. Wendorff, *Macromol. Theory Simul.* **1996**, *5*, 381–391.
[419] S. J. V. Frankland, D. W. Brenner, *Mater. Res. Soc. Symp. Proc.* **2000**, *593*, 199–204.
[420] D. D. L. Chung, *Carbon* **2001**, *39*, 1119–1125.
[421] Y. A. Dzenis, D. H. Reneker, US 626,533, **2001**.
[422] R. Langer, J. P. Vacanti, *Science* **1993**, *260*, 920–926.
[423] C. J. Koh, A. Atala, *J. Am. Soc. Nephrol.* **2004**, *15*, 1113–1125.
[424] J. L. Pariente, B. S. Kim, A. Atala, *J. Biomed. Mater. Res.* **2001**, *55*, 33–39.
[425] B. S. Kim, D. J. Mooney, *Trends Biotechnol.* **1998**, *16*, 224–230.
[426] S. Li, *The Biomedical Engineering Handbook*, CRC, Boca Raton, **1995**, p. 627.
[427] J. Kohn, R. Langer in *Biomaterials Science: An Introduction to Materials in Medicine*, Academic Press, New York, **1996**, p. 64.
[428] B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, J. D. Watson, *Molecular Biology of the Cell*, Garland, New York, **1994**, p. 971.
[429] W. Tan, R. Krishnaraj, T. A. Deasi, *Tissue Eng.* **2001**, *7*, 203–210.
[430] S. R. Bhattarai, N. Battarai, H. K. Yi, P. H. Hwang, D. I. Cha, H. Y. Kim, *Biomaterials* **2004**, *25*, 2595–2602.
[431] U. Boudriot, R. Dersch, B. Goetz, P. Griss, A. Greiner, J. H. Wendorff, *Biomed. Tech.* **2004**, *49*, 242–247.
[432] U. Boudriot, B. Goetz, R. Dersch, A. Greiner, J. H. Wendorff, *Macromol. Symp.* **2005**, *225*, 9–16.
[433] R. Dersch, M. Steinhart, U. Boudriot, A. Greiner, J. H. Wendorff, *Polym. Adv. Technol.* **2005**, *16*, 276–282.
[434] L. S. Nair, S. Bhattacharyya, C. T. Laurencin, *Expert Opin. Biol. Ther.* **2004**, *4*, 659–668.
[435] M.-S. Khil, S. R. Bhattarai, H.-Y. Kim, S.-Z. Kim, K.-H. Lee, *J. Biomed. Mater. Res. Part B* **2004**, *72*, 117–124.
[436] C. Xu, F. Yang, S. Wang, S. Ramakrishna, *J. Biomed. Mater. Res. Part A* **2004**, *71*, 154–161.
[437] L. A. Smith, P. X. Ma, *Colloids Surf. B* **2004**, *39*, 125–131.
[438] F. Yang, C. Y. Xu, M. Kotaki, S. Wang, S. Ramakrishna, *J. Biomater. Sci. Polym. Ed.* **2004**, *15*, 1483–1497.
[439] E. D. Boland, T. A. Telemeco, D. G. Simpson, G. E. Wnek, G. L. Bowlin, *J. Biomed. Mater. Res. Part B* **2004**, *71*, 144–152.
[440] C. H. Lee, H. J. Shin, I. H. Cho, Y.-M. Kang, I. A. Kim, K.-D. Park, J.-W. Shin, *Biomaterials* **2005**, *26*, 1261–1270.
[441] W.-J. Li, R. Tuli, X. Huang, P. Laquerriere, R. S. Tuan, *Biomaterials* **2004**, 26, 5158–5166.
[442] Z. Ma, W. He, T. Yong, S. Ramakrishna, *Tissue Eng.* **2005**, *11*, 1149–1158.

[443] A. F. Recum, C. E. Shannon, C. E. Cannon, K. J. Long, T. G. van Kooten, *Tissue Eng.* **1996**, *2*, 241 – 253.
[444] P. X. Ma, J.-W. Choi, *Tissue Eng.* **2001**, *7*, 23 – 33.
[445] A. Itälä, H. O. Ylänen, C. Ekholm, K. H. Karlsson, H. T. Aro, *J. Biomed. Mater. Res. Part B* **2001**, *58*, 679 – 683.
[446] "Next Generation Applications for Polymeric Nanofibers": T. C. Lim, S. Ramakrishna in *Nanotechnology: Global Strategies, Industry Trends and Applications* (Ed.: J. Schulte), Wiley, Chichester, **2005**.
[447] J. Venugopal, S. Ramakrishna, *Appl. Biochem. Biotechnol.* **2005**, *125*, 147 – 158.
[448] R. A. Coffee, PCT/GB97/01968, **1998**.
[449] D. Martindale, *Sci. Am.* **2000**, *282*, 34 – 36.
[450] E. R. Kenawy, G. L. Bowlin, K. Mansfield, J. Layman, D. G. Simpson, E. H. Sanders, G. E. Wnek, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2002**, *43*, 457 – 458.
[451] K. Kim, Y. K. Luu, C. Chang, C. D. Fang, B. S. Hsiao, B. Chu, B. M. Hadjiargyrou, *J. Controlled Release* **2004**, *98*, 47 – 56.
[452] D. Smith, D. H. Reneker, PCT/US00/27737, **2001**.
[453] R. H. Müller, K. Mäder, S. Gohla, *Eur. J. Pharm. Biopharm.* **2000**, *50*, 161 – 177.
[454] K. S. Soppimath, T. M. Aminabhavi, A. R. Kulkarni, W. E. Rudzinski, *J. Controlled Release* **2001**, *70*, 1 – 20.
[455] G. Verreck, I. Chun, J. Rosenblatt, J. Peeters, A. Van Dijck, J. Mensch, M. Noppe, M. E. Brewster, *J. Controlled Release* **2003**, *92*, 349 – 360.
[456] A. Greiner, J. H. Wendorff, A. L. Yarin, E. Zussman, *Appl. Microbiol. Biotechnol.* **2006**, *71*, 387 – 393.
[457] H. Jiang, D. Fang, B. S. Hsiao, B. Chu, W. Chen, *Biomacromolecules* **2004**, *5*, 326 – 333.
[458] C. L. Casper, N. Yamaguchi, K. L. Klick, J. F. Rabolt, *Biomacromolecules* **2005**, *6*, 1998 – 2007.
[459] S. Y. Chew, J. Wen, E. K. F. Yim, K. W. Leong, *Biomacromolecules* **2005**, *6*, 2017 – 2024.
[460] J. Zeng, L. Yang, Q. Liang, X. Zhang, H. Guan, X. Xu, X. Chen, X. Jing, *J. Controlled Release* **2005**, *105*, 43 – 51.
[461] J. Zeng, X. Y. Xu, X. S. Chen, Q. Z. Liang, X. Bian, L. Yang, X. Jing, *J. Controlled Release* **2003**, *92*, 227 – 231.
[462] V. Timbrell, *Ann. N. Y. Acad. Sci.* **1965**, *132*, 255 – 273.
[463] T. M. Crowder, J. A. Rosati, J. D. Schroeter, A. J. Hickey, T. B. Martonen, *Pharm. Res.* **2002**, *19*, 239 – 245.
[464] A. A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier, W. J. Youngs, *J. Am. Chem. Soc.* **2005**, *127*, 2285 – 2291.
[465] K. E. Brewster, G. Verreck, I. Chun, J. Rosenblatt, J. Mensch, A. Van Dijck, M. Noppe, A. Ariën, M. Bruining, J. Peeters, *Pharmazie* **2004**, *59*, 387 – 391.