

Nanoprocessing of polymers: applications in medicine, sensors, catalysis, photonics[†]

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Nanofibers and nanotubes based on polymers offer a broad range of applications in areas such as photonics, sensorics, catalysis or medicine and pharmacy. A set of preparation techniques which allow to introduce simultaneous specific functions into such nanoobjects has been developed recently. These include electrospinning and co-electrospinning of nanofibers as well as template methods utilizing eletrospun nanofibers or porous substrates. These techniques yield infinitively long nanofibers and nanotubes with well defined aspect ratios respectively with diameters down to a few ten nanometers. These nanofibers and nanotubes can be functionalised, among others by using biodegradable materials or via the incorporation of nanoparticles or precursor molecules, in such a way that applications for tissue engineering, for catalysis, photonics and sensorics become available. Copyright © 2005 John Wiley & Sons, Ltd.

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INTRODUCTION

Polymer nanofibers and nanotubes may serve as a highly versatile platform for a broad range of applications in widely different areas such as nanoreinforcement and nanofluidics, catalysis, sensors, photonics or medicine and pharmacy. Depending on the particular area of applications the required properties of the polymer material will have to be optimized. It might, for instance, be necessary that the polymer is hydrophobic or hydrophilic, biocompatible and biodegradable, that it possesses a high stiffness and strength or that it displays piezo- and pyro-electrical properties, to name just a few examples. Often a combination of properties is asked for which cannot be achieved by a single synthetic material. Nanotubes or nanofibers then have to be made from polymers of biological origin, from polymer blends or block copolymers, from polymers with additives or fillers. It is, thus, highly advantageous to have preparation techniques at hand to process commercially available polymer systems to nanofibers and nanotubes. Established methods for the preparation of nanotubes and nanofibers based on self-organization or on templating^{1–4} fail, in general, in this respect.

In addition, the particular application of interest may require fibers or tubes with complex architectures such as core/shell fibers, fibers or tubes with porous topology or

hybrid systems, characterized by a combination of different materials such as polymer and semiconductor or metal particles. Again, the preparation methods mentioned earlier are not able to meet this task. Herein, this article will introduce four different methods; namely electrospinning,^{5–17} the recently developed co-electrospinning,¹⁸ tubes by fiber templates—the TUFT-process,^{19,20} and finally wetting assisted templating—the WASTE-process.^{21–24} All are able to yield nanoobjects with complex architectures based on commercial polymers, and extending well beyond these materials. In addition, applications of such nanofibers and nanotubes in medicine, sensors, catalysis and photonics will be discussed briefly.

ELECTROSPINNING OF NANOFIBERS

Until now, electrospinning is the only technique available for the production of fibers with extremely small diameters. Melt blowing, which basically is a process in which a high velocity stream of gases or fluids (steam, air or other fluids), blows molten thermoplastic resins from an extruder die tip. This was invented close to 50 years ago, and provides a very fine fiber web yet the dimensions are still well above the 100 nm range.

In electrospinning, a strong electrical field is applied to a droplet formed from a polymer solution or polymer melt at the tip of a die acting as one of the electrodes. The counter electrode is typically located at a distance of several 10 cm. The charging of the fluid leads, as shown by Taylor, to a conical deformation of the droplet (the well known Taylor cone), and eventually to the ejection of a jet from the tip of the

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cone.^{25,26} The equilibrium state for higher electrical fields corresponds to a cone with a jet emerging continuously from the cone. The charged jet is accelerated towards the counter electrode, and thins rapidly during this period due to elongation and evaporation of the solvent until solid fibers are deposited in a random fashion onto the substrate located on top of the counter electrode.

The detailed experimental and theoretical analysis reveals that the electrospinning process is highly complex since it is controlled by various types of instabilities such as the Rayleigh instability, an axisymmetric instability, and finally by a so called whipping or bending instability.^{13,27–29} It is in particular the whipping instability which has been identified as the one controlling elongation and thinning of the electrospun fibers. The other types of instability give rise to fluctuations of the radius of the jet and may eventually result in droplet formation.

The whipping mode corresponds to long wavelength oscillations of the centerline of the jet, i.e. the jet is subjected to bending modes. The strong thinning of the jet as well as the strong elongational deformation taking place during electrospinning has been attributed to this mode of instability. For large static charge densities the whipping mode tends to dominate since high charge densities at the surface simultaneously tend to suppress both the Rayleigh and the axisymmetric modes of instability.

Today, a broad range of polymers is known which can be spun to nanofibers either from solution or from the melt³⁰ (Fig. 1). One advantage of electrospinning is that water can be used as solvent. Water-soluble polymers such as polyethyleneoxide (PEO) or polyvinylalcohol (PVA) are examples. Polylactide (PLA), polystyrene (PS), poly(methylmethacrylate) (PMMA), polyamides, polyimides, polycaprolactone, and polyvinylidene fluoride are examples for the case where organic solvents are used for spinning. Electrospinning can also be achieved for blends or composites and polymer nanofibers loaded with drugs or other biologically active molecules are obtained by spinning of polymers from ternary solutions containing the reagent.

Based on these experimental studies it has become apparent that the control of the fiber diameter, the presence or absence of drop formation, the control of the surface morphology, and the control of the texture of the web, produced by electrospinning, depends on a broad range of parameters. These parameters include thermodynamic properties of the solvent and the polymer, such as vapor pressure, crystallization and glass transition temperature, solubility of the polymer in the solvent or mixture of solvents, molecular weight, and the molecular weight distribution. The most important set of parameters to control fiber formation obviously are the surface free energy, concentration, and viscosity as well as the electric conductivity.

The critical field for the onset of fiber formation is controlled by the surface tension. An increase of the conductivity leading to an increase of the surface charge density leads to a stabilization of the whipping modes giving rise to fiber extension. Furthermore, bead formation arising from other modes of instability tends to be suppressed. Experiments performed on solutions of PLA in dichloromethane, doped with various amounts of pyridinium formate, showed that, in fact, an increasing concentration of the dopant leads to a reduction of bead formation and to smaller diameters of the fibers. There is a direct correlation between concentration and fiber diameter. A decrease, for instance, of the concentration gives rise to a corresponding reduction of the fibers. Provisions have to be made in many cases to reduce bead formation, i.e. electrospinning from diluter solutions requires a certain degree of conduction. Electrospinning is basically a simple method, yet it is a demanding task to adjust the parameters for a given system to be able to spin nanofibers in a controlled way.

The electrospinning process is characterized by rapid evaporation of the solvent in the case of solution spinning and a rapid temperature decrease in the case of spinning from the melt. Structure formation happens on a millisecond scale and the nucleation and growth of crystals should therefore be modified compared with bulk materials. Yet the finding is that the degree of crystallinity as well as the perfection of the

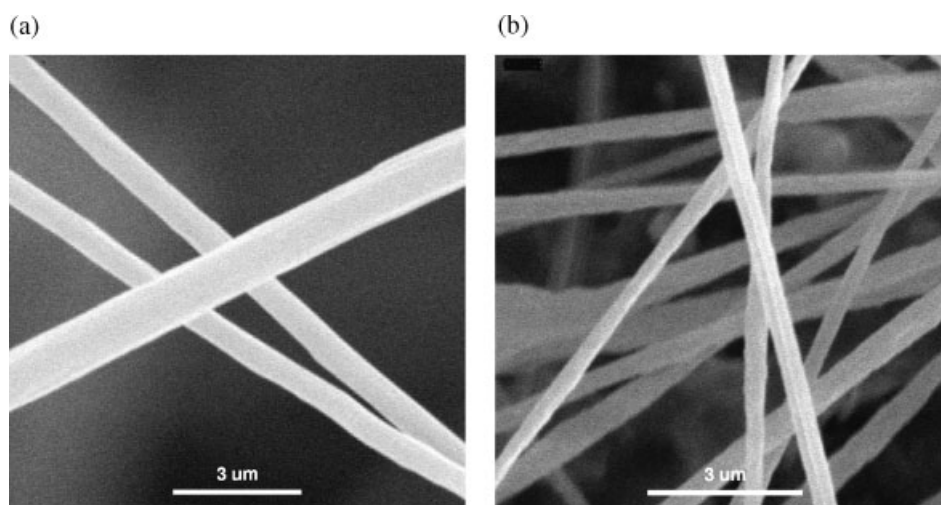


Figure 1. Electrospun nanofibers from different polymers. (a) Cellulose acetate from 5% solution in dichloromethane/ethanol, 9:1, (b) polyvinylidene difluoride from 15% solution in dimethylformamide/tetrahydrofuran, 1:1.

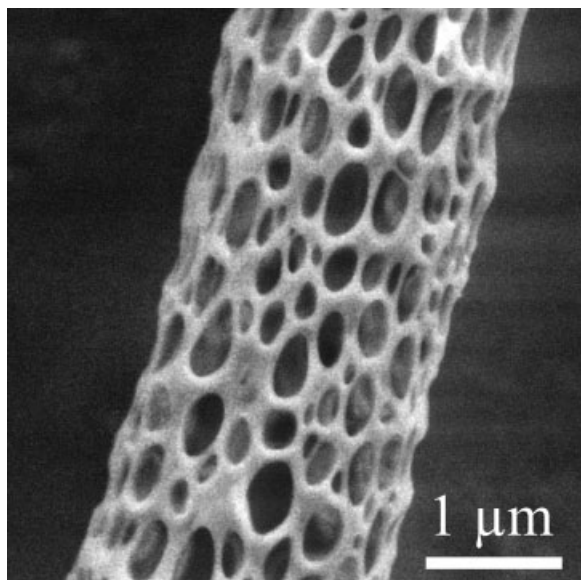


Figure 2. PLA fiber with porous surface spun from dichloromethane.

crystals which grow within the fibers are similar to those observed for thicker fibers as obtained, for instance, from melt-extrusion. A second feature is the strong deformation taking place during the whipping mode which tends to give rise to orientational processes within the fibers. High degrees of crystal orientation have been observed for various electrospun polymers including polyethyleneoxide and polyamide.^{31,32} Upon performing selected area electron diffraction studies on polyamide-6 nanofibers, it was shown that the degree of orientation obtained directly by electrospinning corresponded to the one obtained for melt-extruded fibers only after considerable stretching.³¹ However, no crystal orientation has been reported for electrospun fibers made from other polymers such as PLAs.

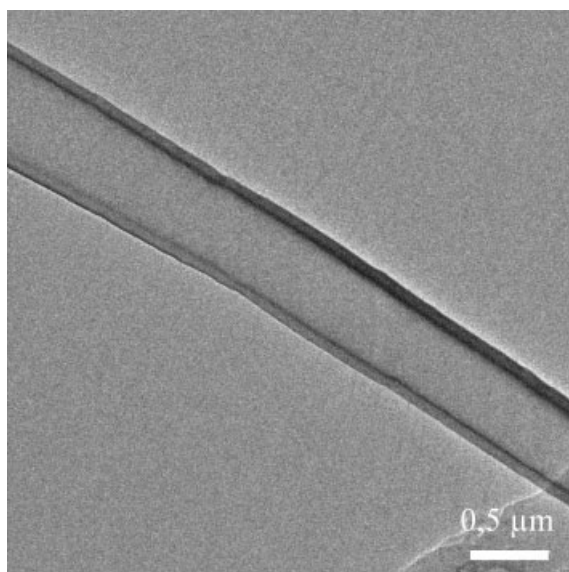


Figure 3. Core-shell nanofibers obtained via electrospinning (core: polyvinylidene difluoride; shell: polycarbonate).

The properties and functionality of electrospun nanofibers can be also modified by their surface morphology.^{15,16} One approach considers electrospinning of ternary systems composed of two incompatible polymers and a solvent. The concept is to use binodal or spinodal phase separation processes during electrospinning and to remove one of the phases selectively. Yet one might also induce phase separation processes in binary systems composed of one polymer and a solvent during electrospinning. PLA spun from dichloromethane is an example where fibers result that are characterized by nanopores (Fig. 2).

More recently, a new version of electrospinning, namely co-electrospinning aimed at compound core-shell nano/meso fibers has been developed.¹⁸ In this approach, two liquids of different chemical composition emerge from a core and the surrounding concentric annular nozzles. The compound droplet sustained at the edge of such compound nozzles undergoes transformation into a compound jet co-electrospun from its tip. The jet is pulled by the electric field, and stretched by the bending instability far enough from the droplet, the solvent evaporates, and the compound jet solidifies resulting in compound core-shell nanofibers (Fig. 3). The co-electrospinning process is, in principle, fast enough to prevent any mixing of the core and shell polymers. Co-electrospinning is of particular interest for those core materials that will not form fibers via electrospinning by themselves, such as dispersions of drugs. Here, the shell polymer serves as a template for the core material leading to compartment-type structures. In fact, it was shown that the original polymer systems can be loaded in such a way that complex hybrid tubes, metal tubes, or tubes with semiconductor particles result. Core-shell fibers of this type will certainly foster applications, e.g. in the field of microelectronics, optics, and medicine.

NANOTUBES

Approaches towards nanotubes

To manufacture nanotubes two fundamentally different approaches have been reported: self-assembly or the use of templates.^{1–4} Self-assembly of carbon or boron nitride, with surfactants, and of polypeptides have been reported in the literature.^{3,33–35} Self-assembly is limited to specific precursor materials. Polymerization within the pores of nanoporous matrices offers a second route towards nanotubes. The polymerization starts at the walls of the pores resulting in tubes with a given wall thickness or compact nanofibers that reproduce the pore size, depending on the polymerization time. In a second step, the template material is removed.

Tubes by fiber templates^{19,20}

To produce nanotubes which, in principle, are not restricted in length, nanofibers accessible by electrospinning are used as templates. Well established deposition methods, such as chemical or physical vapor deposition, spincoating or spraying, are employed to cover the template fibers with a thin layer of wall material. A particular example is the chemical vapor deposition of polyparaxylylene (PPX) using paracyclophane as precursor material. Commercial set-ups are available which allow for a highly controlled deposition in this case.

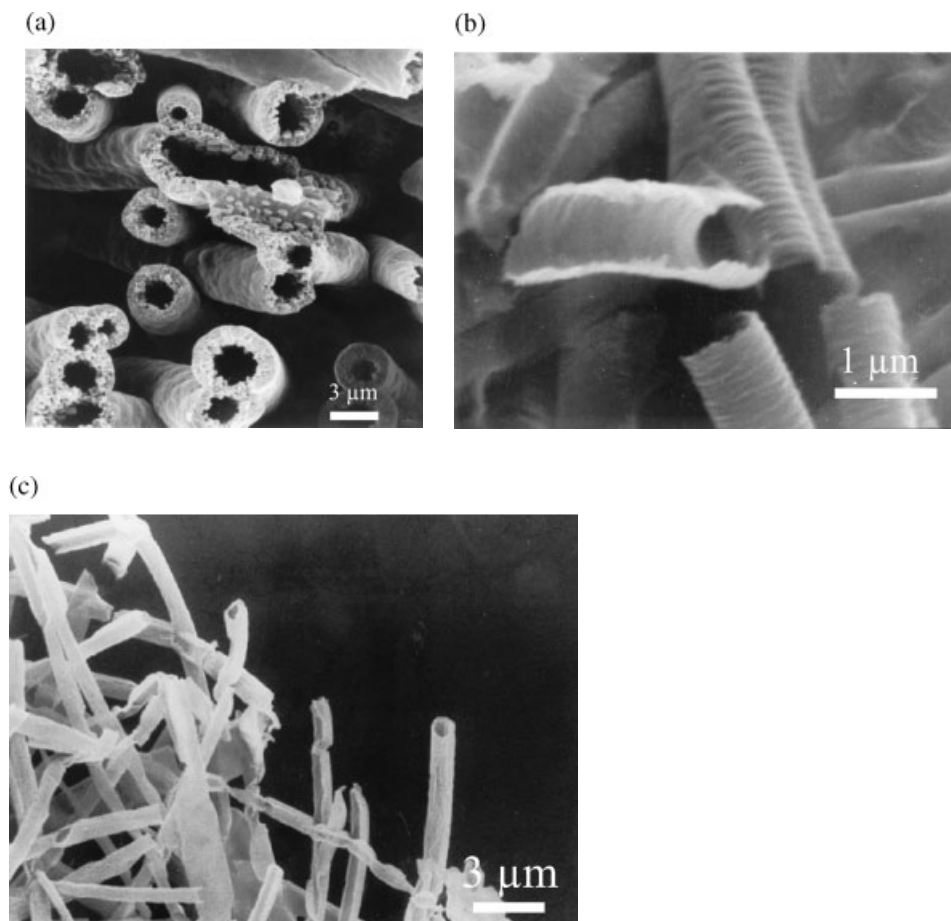


Figure 4. Nanotubes produced by TUFT. (a) PPX tubes, (b) chromium tubes and (c) glass tubes.

The template fibers are subsequently selectively removed either by thermal decomposition or by choosing a selective solvent. The requirement is that the wall material is stable both against the annealing temperature and the applied solvent. PPX, for example, is insensitive to temperatures as high as 300°C and insoluble in most common solvents.

Using this approach, nanotubes with inner diameters down to 5 nm have been prepared, approaching the dimensions characteristic for carbon nanotubes. Polymer nanotubes, metal nanotubes obtained via physical vapor deposition of metals, and glass nanotubes resulting from the deposition of SiO₂ have been prepared (Fig. 4). By the stepwise deposition of different materials, one is able to prepare multilayer nanotubes either from different polymers or from polymers in combination with other materials such as metals. Metal/polymer nanotubes serve as nanocables and metal/polymer/metal nanotubes as nanocapacitors.

Certain applications actually do not require the removal of the template fibers or at least not the complete removal. Template fibers loaded with metal nanoparticles, which have either been grown *in situ* from precursor materials or which have been mixed in during electrospinning, can be transformed into nanocables by a selective removal of just the polymer part of the template fiber. Template fibers spun from water solutions containing enzymes have been covered with a thin wall layer. The total composite fiber can be used for controlled catalytic processes, with the wall material controlling the release rate of the enzyme into the reaction vessel.

A particularly interesting aspect is that one can use template fibers with specific surface topologies (see section on electrospinning), such as porous fibers, to produce nanotubes with similar features. The increase of the total amount of surface available as well as the corresponding modulations of the wall thickness, allow the control of, for instance, the catalytic activity as well as the release rates.

Polymer nanotubes by wetting^{21–24}

A further type of template method will be described as follows. It has the advantage that it uses commercially available structural polymers as well as functional polymers, that it does not require a polymerization or vapor deposition process, which may impose restrictions to the kind of polymers that can be used, and that it does not require the use of solvents. Polymers containing additives, polymer blends, even polymers which are molecularly reinforced can be processed to nanotubes based on the approach described later. It is based on wetting processes.

A phenomenon, described in the literature namely the formation of a so-called “precursor film” of submicron-size thickness, is exploited in this method. This process takes place if liquid droplets spread on flat substrates. This happens even in the case of viscous liquids. The precursor film, with a typical thickness from less than 100 nm down to few Ångströms, emanates from the macroscopic droplet of the wetting liquid and covers the substrate. Its spatial extension can approach the millimeter range.

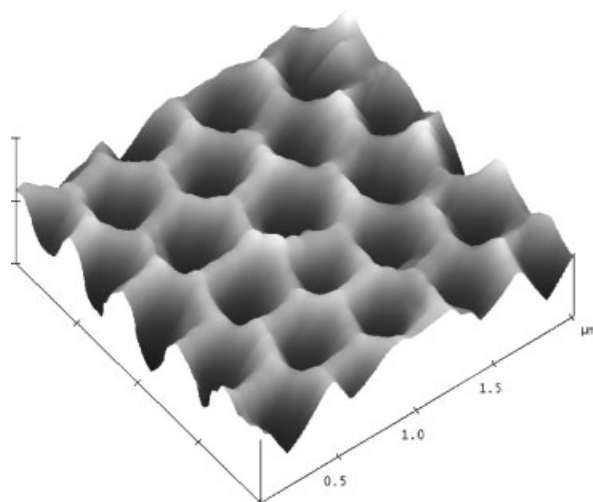


Figure 5. Nanoporous silicon as template.

It is apparent that it should be possible to prepare polymer nanotubes via the wetting of an array of cylindrical submicrometer nanopores by polymers in the molten state. Common templates possess pore walls consisting of aluminum oxide or silicon oxide, which are high-energy surfaces (Fig. 5). One thus expects a complete wetting of the pore walls by polymers, the thickness of the polymer wetting layer being controlled by the polymer–wall material interaction. The driving forces for complete filling are much weaker than for the coating of the pore walls by a thin wetting film. The two processes of wall wetting and complete filling will thus take place on different time scales. Polymer nanotubes can be expected to result if the flow of the polymer is quenched after the wall is wetted prior to the complete filling.

The diameter of the nanotubes, the distribution of the diameter and the homogeneity along the tubes as well as their length are all controlled by the template matrix.

To prepare the polymer nanotubes, one places the polymer material as a powder or even as pellets on the top of a pore array within a thermostated cell. The whole set-up is heated up to a temperature well above the glass temperature or the melting point, in the case of partially crystalline polymers. The polymer then flows along the pore walls into the pores until the entire pore surface is covered. This process takes

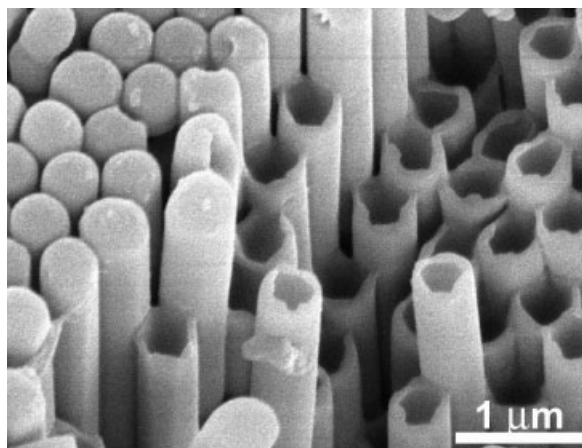


Figure 6. PS nanotubes produced by wetting.

place on a time scale of some minutes if the molecular weight of the polymer is sufficiently low.

Polymer melts thus invade the porous templates and wet the pore walls so that the shape of the pores is reproduced. The polymer nanotubes possess walls with a typical thickness of around 10 nm while the diameter of the tubes might be in a range from several less than 100 nm up to a few microns depending on the template (Fig. 6). Their length is controlled by the depth of the template pores, and can be adjusted up to 100 microns and more. If the template is removed selectively, arrays of free standing polymer nanotubes can be obtained. The advantage of this approach is that one can prepare a large amount of polymer nanotubes from any polymer that is processible from the melt. Further investigation will aim at a better understanding of the underlying wetting processes. It is obvious that polymer nanotubes manufactured by pore wetting will be of considerable interest for a broad range of applications in nanotechnology.

APPLICATIONS IN MEDICINE, SENSORS, CATALYSIS AND PHOTONICS

Medicine

In a recent report,³⁶ business opportunities for nanostructured materials in biotechnology and medicine were estimated to be of the order of 180 billion US\$ in 2015.

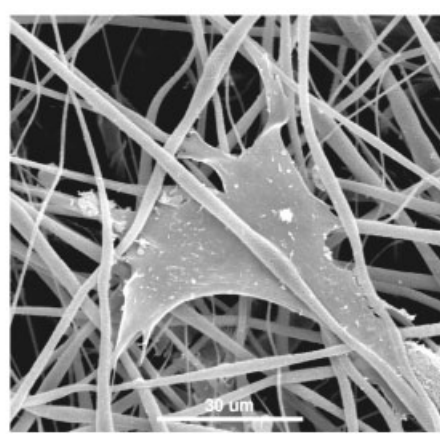
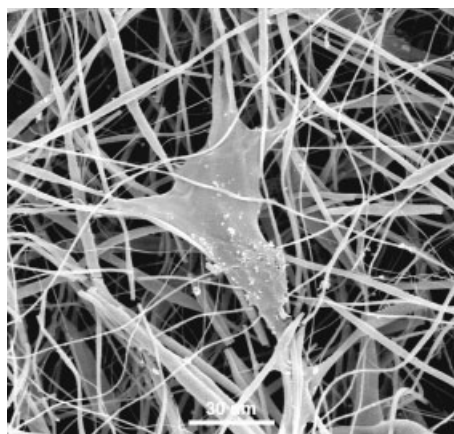


Figure 7. Mesenchymal stem cells on a matrix of PLA spun from dichloromethane.

Particular examples which were highlighted were drug release systems, nanofibers for wound healing obtained by electrospinning as well as nanostructured materials for tissue engineering, where bone tissue engineering was one important aspect. In the following, some examples for the application of nanostructured materials in medicine are presented. Several materials, e.g. poly(glycolic acid),³⁷ poly(epsilon-caprolactone),³⁸ poly(D,L-lactide-co-glycolide),³⁹ collagen type II,⁴⁰ or PLA have been used for tissue engineering applications.

PLA nanofibers, electrospun from dichloromethane solution, were used for growing bone cells and mesenchymal stem cells. These fibers consisted either of pure polylactide or of PLA into which tricalcium phosphate was incorporated. The findings are that the cells attach strongly to the fibers and grow along the fibers, as shown in Fig. 7. Further studies are concerned with the impact of mechanical loadings on the growth of bone tissue.

Another aspect is the inclusion of drugs or other functional materials in medicine and pharmacy into polymer nanofibers and polymer nanotubes.⁴¹ The nanoobjects then serve both as drug carrier and drug release system. It is the particular shape and size of the nanoobjects as well as their internal architecture which control where the nanoobjects will attach in the body, and in which manner the release will take place. To test the release characteristics nanofibers loaded with bovine serum albumine, with and without a thin wall material, were investigated.⁴² The finding is that the release rate can be strongly controlled by the fiber architecture.

Sensors

Nanotubes were grown from polyvinylidene fluoride, known to exhibit piezo-, pyro-, and ferro-electric properties if one of the polar crystal modifications can be induced.²² Wetting, in fact, yields perfect nanotubes from polyvinylidene fluoride. A further finding is that the orientation of the axis of the unit cell (α -modification: a , 4.96 Å; b , 9.64 Å; c , 4.62 Å) are well defined within the tubes. The b -axis is along the length of the tubes, the c -axis points radially and the a -axis is tangentially oriented. The curvature obviously controls the crystal orientation. The disadvantage so far is that only the non-polar crystal form is exhibited. The authors are currently

modifying the crystal growth conditions in order to obtain a polar crystal form. Yet, starting from precursor systems, it has been possible to obtain lead zirconate titanate nanotubes actually displaying piezo-electric properties and showing ferro-electric switching hysteresis.²¹ This approach can be used to obtain various kinds of nanotubes of interest in the area of sensors and actuators.

Catalysis

Nanotubes composed of palladium and nanotubes composed both of a polymer and palladium nanoparticles may serve as an example of catalytic materials. The procedure to prepare such nanotubes is straightforward. Mixtures of a polymer, such as PLA with palladium acetate in a common solvent such as dichloromethane, are used to wet the pores of a porous template. Heating to a temperature of about 150°C leads to a reduction of the palladium acetate to palladium and to the formation of nanoparticles the size of which can be controlled by annealing time and annealing temperature. Heating to even higher temperature, of the order of 250°C, leads to a complete removal of the polymer, affording pure palladium tubes to result (Fig. 8). Similarly other types of metal tubes designed for catalysis can be prepared (23).

Photonics

A regular array of objects such as nanotubes with diameters in the range corresponding roughly to the wavelength of the light are known to display the properties of photonic crystals. Photonic crystals are characterized, for example, by energy ranges (wavelength ranges) which are allowed and for which light can propagate through the material or by energy ranges for which light can not propagate. The regular arrangements of nanotubes accessible by the wetting methods may serve, in principle, as a photonic crystal. Yet more interesting effects result according to recent theoretical considerations if semiconductor quantum structures such as quantum dots are incorporated in such structures.⁴³ In a preliminary study PS nanotubes via the wetting method containing HgSe and HgTe quantum dots emitting light very effectively have been produced.⁴⁴ The next step will consist of placing these nanotubes into a photonic crystal arrangement.

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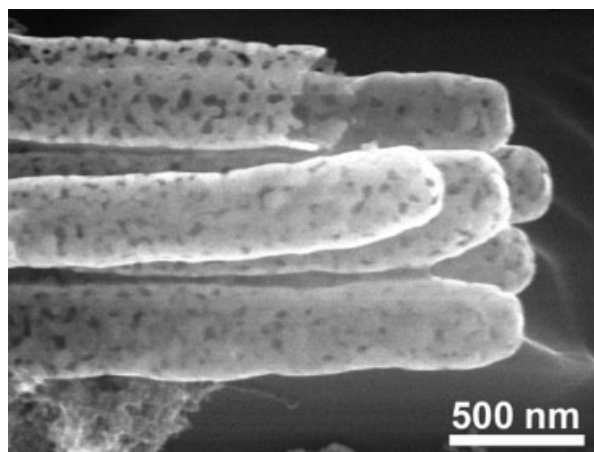


Figure 8. Nanotubes from Palladium.

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