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Nanostructured Fibers via Electrospinning**

By Michael Bognitzki, Wolfgang Czado, Thomas Frese, Andreas Schaper, Michael Hellwig, Martin Steinhart, Andreas Greiner, and Joachim H. Wendorff*

Structured polymer fibers with diameters in the range from several micrometers down to tens of nanometers are of considerable interest for various kinds of applications. Examples are thin fibers for filter applications,^[1,2] fiber mats serving as reinforcing component in composite systems,^[3,4] biomedical applications^[5] or fiber templates for the preparation of functional nanotubes.^[6,7] Electrospinning has been shown to be an effective method for the production of such thin fibers.^[8–19]

The electrospinning process involves the application of a strong electrostatic field to a capillary connected with a reservoir containing a polymer solution. Under the influence of the electrostatic field, a pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape (Taylor cone).^[20] If the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a fine charged jet is ejected. The jet moves towards a ground plate acting as counter electrode. Due to the viscosity of the polymer solution and the presence of entanglements, the jet remains stable and does not transform into spherical droplets as expected for a liquid cylindrical thread.^[21] The solvent begins to evaporate immediately after the jet is formed. The result is the deposition of a thin polymer fiber on a substrate located above the counter electrode.

The electrospinning process, invented by Formhals in 1934,^[8] was studied in detail particularly by Reneker and co-workers^[13,17,19] as well as by Vancso and co-workers^[16] during the last decade. It has been found that the fiber diameter can be controlled within a broad range down to a few tens of nanometers by proper selection of the processing parameters.^[6,13,14] A sharp decrease of the jet diameter immediately after its formation is observed.^[17] Occasionally branching of the jet occurs leading to a further decrease in diameter.^[19] The obtained fibers may show anisotropic structure patterns as described by Vancso et al.^[22]

For selected applications it is desirable to control not only the fiber diameter, but also the internal morphology. Porous fibers are of interest for applications such as filtration or the preparation of functional nanotubes by fiber templates.^[6,7] A given surface topology will affect, for instance, the wetting behavior as well as specific adsorption processes. We found that electrospinning will directly yield porous fibers provided that the spinning parameters and the solvent are chosen appropriately. The basic concept was to control the formation of the fiber morphology in such a way that phase separation processes take place during electrospinning. This leads to spinodal or binodal types of phase morphologies within the fibers. This article describes this approach in detail as well as experimental results on the morphology of electrospun fibers.

As polymers we selected partially crystalline poly-L-lactide (PLLA) and the amorphous polymers polycarbonate (PC) and polyvinylcarbazole. As a common solvent we used dichloromethane, which evaporates rapidly during electrospinning at room temperature (boiling point 40 °C, vapor pressure 475 mbar at 20 °C^[23]). The total polymer concentration in solution was in the range of 5–15 % (PLLA: 5 wt.-%, PC: 15 wt.-%, polyvinylcarbazole: 7.5 wt.-%).

Electrospinning of polymer solutions involves, to a first approximation, a rapid evaporation of the solvent. In fact it has been reported that the deposition rate of the fibers is in the order of several meters per second.^[9,13] Furthermore, the jet is strongly elongated during electrospinning due to the acceleration in the direction of the counter electrode.^[17] This leads to a dramatic increase of the jet surface within milliseconds. The evaporation of the solvent thus will happen on a time scale well below the second-range. As a result, phase boundaries may be crossed and structure formation by phase separation sets in.^[24,25] Therefore, the tendency towards a spinodal phase separation will be enhanced since nucleation phenomena require in general more time than the initial growth of instable concentration fluctuations. A second consequence is that the phase-separated regions are not able to coarsen strongly prior to a vitrification. As a result very fine phase morphologies are preserved. The solidification will be controlled by the onset of a glass transition process as the concentration of the solvent is further reduced^[26] or by the onset of crystallization.

The experiments revealed that all three polymers could be spun to fibers with diameters in the range from several micrometers down to 100 nm without problems. Figure 1 represents

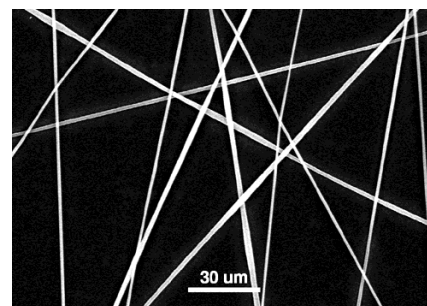


Fig. 1. Scanning electron microscopy (SEM) micrograph of electrospun PLLA fibers.

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a set of PLLA-fibers with a well-controlled thickness. X-ray studies as well as calorimetric studies revealed that the PC and polyvinylcarbazole fibers are amorphous as expected, whereas the PLLA fibers are partially crystalline.

Figure 2 displays differential scanning calorimetry thermograms obtained for as-spun PLLA-fibers (first heating run) and for an isotropic PLLA-sample, quenched from the melt

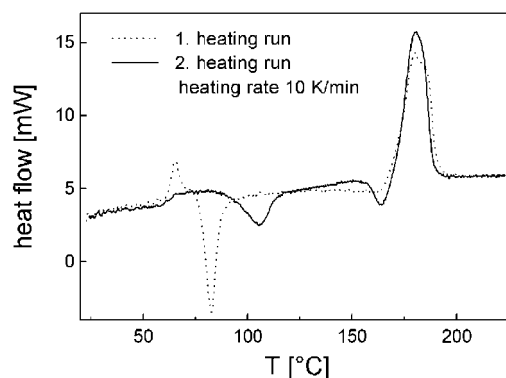


Fig. 2. Differential scanning calorimetry (DSC) thermogram obtained for electrospun PLLA fibers (first heating run) and for a sample cooled down from melt with 10 K/min (second heating run).

with 10 K/min (second heating run). 10 K/min were also chosen as common heating rates. The first heating run is characterized by a stepwise increase of the specific heat at the glass transition of PLLA at 63 °C followed by a distinctive aging peak and an exothermic crystallization peak with a maximum at 83 °C. These features occurring in the electrospun fibers on heating are a signature of the rapid structure formation taking place during the electrospinning process. The second heating run does not show an aging peak adjacent to the glass point and the exothermic crystallization peak is shifted to a 20 K higher temperature. This may result from a certain alignment of the polymer chains in the as spun fibers allowing crystallization to occur at a lower temperature than in an isotropic sample. The melting endotherm occurs both for the first and the second heating run at 180 °C. In contrast to the first heating run in the second heating run a small exothermic peak at 164 °C appears. We are not able to explain this finding so far.

A comparison of the melting endotherms with the crystallization exotherms reveals that the original degree of crystallinity of the PLLA-fibers is of the same order of magnitude than for the sample cooled down at 10 K/min. One obtains degrees of crystallinity of 35 % and 40 %, respectively, as judged from the absolute heat of fusion.^[27] These values are well below the ones obtained for crystallization from melt (60 %^[28,29]) and from diluted solutions (90 %^[27]) if a slow structure formation process takes place.

The interesting finding is that the use of volatile solvents such as dichloromethane yields polymer fibers with a regular pore structure as shown in Figure 3 for PLLA-fibers. The average pore size is in the order of 100 nm in width and 250 nm in length with the long axis being oriented along the fiber axis. Our interpretation is that the regular phase morphology is generated by rapid phase separation during the

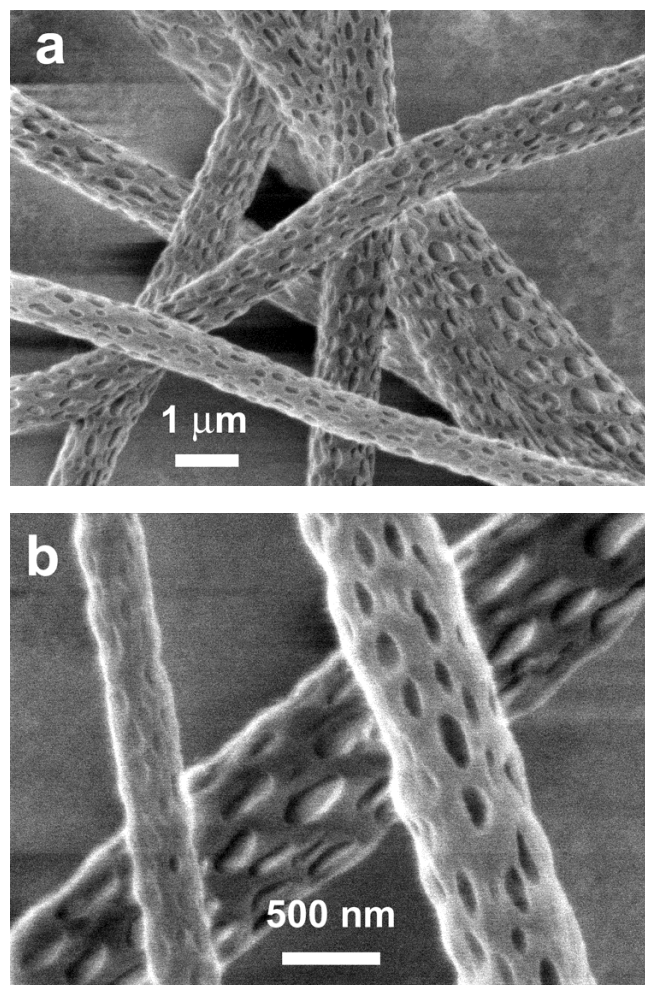


Fig. 3. SEM micrographs of porous PLLA fibers obtained via electrospinning of a solution of PLLA in dichloromethane. a) Survey. b) Magnification.

electrospinning process. The solvent rich regions are apparently transformed into pores. The replacement of dichloromethane by solvents with lower vapor pressure such as chloroform reduces the tendency towards pore formation significantly. The elongation of the pores along the fiber axis which is apparent from Figure 3 is the result of a uniaxial extension of the jet in the electric field.

One obtains similar results by electrospinning of the amorphous materials PC and polyvinylcarbazole using dichloromethane as solvent. This is obvious from Figure 4. The polycarbonate fibers have pores with a circular shape and a narrow size distribution. The pore diameters are in the range of 200 nm. Regular pits on the surface rather than pores penetrating the core of the fiber are observed for polyvinylcarbazole fibers. The pits have an ellipsoidal shape with the long axis oriented into the direction of the fiber axis.

Our conclusion is that electrospinning of polymers from solution may yield fibers in the micrometer range and below which are characterized by a regular structure: pores or pits in the 100 nm range. The structure formation is apparently controlled by a rapid phase separation induced by the evaporation of the solvent and a subsequent rapid solidification. Such

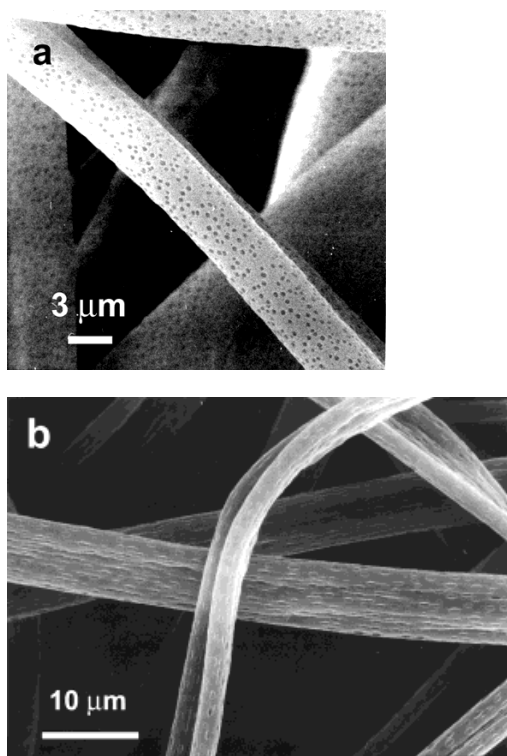


Fig. 4. SEM micrographs of fibers with regular surface and pore structures obtained by electrospinning of solutions in dichloromethane. a) PC fibers. b) Polyvinylcarbazole fibers.

fibers are of interest for a broad range of applications in areas such as sensor or filter technologies not only due to their enhanced surface to volume or surface to weight ratio. Specific surface topologies can be used to control wetting processes or the adsorption behavior. So far we are not able to describe the structure formation leading to such highly structured fibers in detail. This is the goal of current investigations.

Experimental

PLLA was obtained from Böhlinger Ingelheim ($M_n = 150\,000$ g/mol, $M_w/M_n = 2$), PC (Typ 2800) from Bayer. Polyvinylcarbazole was purchased from Aldrich ($M_w = 1\,100\,000$ g/mol, specification by the manufacturer). All polymers were used without further purification. Dichloromethane was distilled before using. The electrospinning set-up used here has been described previously [6,7]. The polymer solution, stored within a reservoir, was pumped through a metal capillary connected with a voltage supply using a peristaltic pump. The circular orifice of the capillary had a diameter of 500 μm . A circular-shaped counter electrode with a diameter of 18 cm was located below the reservoir, so that a vertical arrangement of the electrodes resulted. Fibers were collected on selected substrates, e.g., glass slides, placed on top of the counter electrode. The distance between the tip of the capillary and the counter electrode was typically of the order of 20 cm, the applied voltages were in the range from 35 kV to 45 kV.

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Self-Organized Oligosilanes; a New Class of Organic Hole-Transport Materials

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Molecular and polymeric solids with high carrier mobilities are considered as key components in various photonic and electronic applications such as xerography, electroluminescence, and even molecular devices. In any of these, ease of processing and capability of molecular design are crucial factors, and new materials possessing such advantages should be extensively sought for technological uses.

Here we propose oligosilanes as a novel class of organic hole-transport materials. Oligosilanes are linear organo-silicon compounds containing repeated Si-Si bonds in their main chains with various kinds of aliphatic and aromatic substituents. σ -Conjugated electrons delocalized along their main chains^[1] give rise to a variety of electronic properties such as ultraviolet (UV) absorption,^[2] luminescence,^[3] photoconductivity,^[4] etc. Previous structural analyses established that, when vapor-deposited, permethyloligosilanes $(\text{CH}_3\text{--}[\text{Si}(\text{CH}_3)_2]_n\text{--})$

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