Poly(*p*-xylylene) Nanotubes by Coating and Removal of Ultrathin Polymer Template Fibers

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Nanotubes can be made from a variety of materials including carbon, ceramics, metals, and polymers, which were discussed in several reviews.[1−3] Methods for the preparation of nanotubes are based on self-assembly or template techniques. For example, carbon,[4] polypeptide,[5] and polyaniline[6] nanotubes were prepared by self-assembly, whereas conductive polymers (for an overview see ref 3), poly(*p*-xylylene), and composite tubes[7] were prepared by template methods. Naturally, inner diameters of nanotubes prepared by template methods depend on the dimensions of the templates. In the case of poly(*p*-xylylene) and of composite tubes prepared by the so-called TUFT process (TUFT = tubes by fiber templates) only tubes with inner diameters of several hundred nanometers were possible depending on available fiber templates. These fiber templates were obtained by electrospinning, which represents a versatile method for the preparation of thin polymer fibers (for a recent review see refs 8 and 9). Up to now we were only able to prepare cylindrically shaped template fibers with diameters down to 100 nm.

Nylon 4/6, poly(tetramethylene adipamide) (PA, Aldrich), and poly(L-lactide) (PLA, Boehringer, Ingelheim) were selected as suitable template fibers since they meet the requirements that the polymers should be processable to fibers with diameters in the submicrometer range and that they should be stable during coating but should be soluble under selected conditions or pyrolizable without destruction of the coating layer (the walls of the tube). Electrospinning of PLA from dichloromethane solution results in fibers with diameters between 300 and 1800 nm, and electrospinning of PLA from dichloromethane solution in the presence of organo-soluble ammonium salts results in PLA fibers with average fiber diameter of 200 nm.[7] Electrospinning of PA from formic acid results in fibers with diameters of 100 nm without any additives. However, the controlled preparation of cylindrically shaped polymer and composite tubes with inner diameters <100 nm is still a challenge. This challenge might be of particular interest for research on materials confinement effects,[10−12] which become more effective as dimensions become smaller.

In this communication we present an approach to polymer and composite tubes with inner diameters as low as a few nanometers. It is known that the fiber diameters can be decreased in electrospinning by using lower polymer concentrations in solution. The disadvantage is that this sometimes gives rise to the formation of beaded fibers.[13] We tried to suppress the tendency toward bead formation by using specific additives giving rise to an increase of the conductivity of the solutions, whereas viscosity and surface tension were only changed gradually by these additives. Using this approach, cylindrically shaped PA fibers a few tens of nanometers in diameter were obtained by electrospinning of low concentration solutions (8 wt %) of PA/formic acid in the presence of pyridine (2 wt % related to PA).[14] PLA fibers with even lower diameters were obtained by electrospinning of PLA (1.5 wt %)/dichloromethane in the presence of palladium(II) diacetate (0.75 wt %). Characterization of the fibers was performed by scanning electron microscopy (SEM) using a Hitachi S-4100 at 1 kV accelerating voltage as well as by transmission electron microscopy (TEM) using a JEM 3010 operated at 300 kV. TEM of PA fibers shows fiber diameters centered at 50 nm (Figure 1A). SEM of gold-coated PLA fibers shows only fibers with diameters above 10 nm, while TEM of uncoated PLA fibers reveals fiber diameters as low as 5 nm (Figure 1C). This illustrates the contribution of gold coating to the fiber diameter observed in the SEM (Figure 1B). It should be stated here that average inner fiber diameter is, however, in the range of about 10 nm.

Polymer coating of these ultrathin template fibers and thus the formation of the walls of the tubes were achieved by chemical vapor deposition (CVD) with poly(*p*-xylylene) (PPX, trade name: Parylene N).[15] The walls were prepared in this way without destruction of the PLA template fibers. The PPX deposition by CVD was performed by vapor phase pyrolysis of the starting material [2.2]paracyclophane (dimer) and subsequent CVD of the monomer, 1,4-quinodimethane, the pyrolysis product. Spontaneous polymerization of 1,4-quinodimethane occurs as soon as it is deposited on a solid substrate surface at temperatures below 30 °C (pressure in apparatus = 0.1 mbar). This mild coating technique results in high-quality conformal pinhole-free films of PPX (film thickness 50 nm to several micrometers) in quantitative yields. It is important in the context of the template process that the melting point of PPX is 420 °C and that it shows a very good thermal stability as well as solvent resistance. This makes PPX a perfect material to withstand thermal degradation conditions (0.1 mbar, 280 °C, 6 h) to which the PLA template fibers have to be subjected for removal or to withstand solvent extraction conditions for PLA or PA. Solvent extraction of the PLA/PPX (extraction by chloroform for 12 h) and PA/PPX (extraction by formic acid for 24 h) core−shell fibers resulted in the formation of PPX tubes. Quantitative removal of PLA and PA template fibers was monitored by FT-IR spectroscopy. Tubes should be obtained as result of the removal of the template fibers, which is directly imaged by TEM without staining or cutting of the samples. The inner diameters of the tubular structures represent the diameter of the PA and PLA template fibers. Tubes with inner diameters ranging from 5 to 50 nm and outer diameters of 50−250 nm were prepared (Figure 2A−C). The outer diameter of the tubes is governed by the thickness of the PPX wall, which in turn is controlled by the CVD conditions (in particular by the amount of dimer; compare parts B and C of Figure 2) whereas the inner diameter is controlled by the size of the electrospun template fibers.

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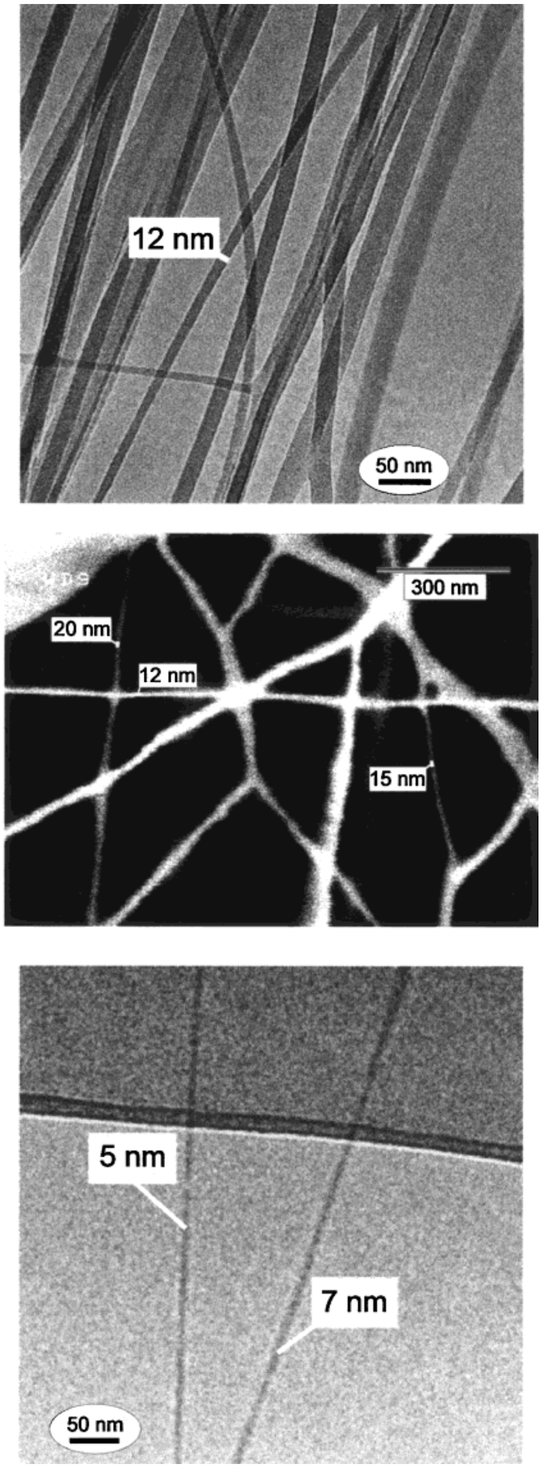

Figure 1. TEM of electrospun PA template fibers (A, top); SEM (B, middle) and TEM (C, bottom) micrograph of electrospun PLA template fibers.

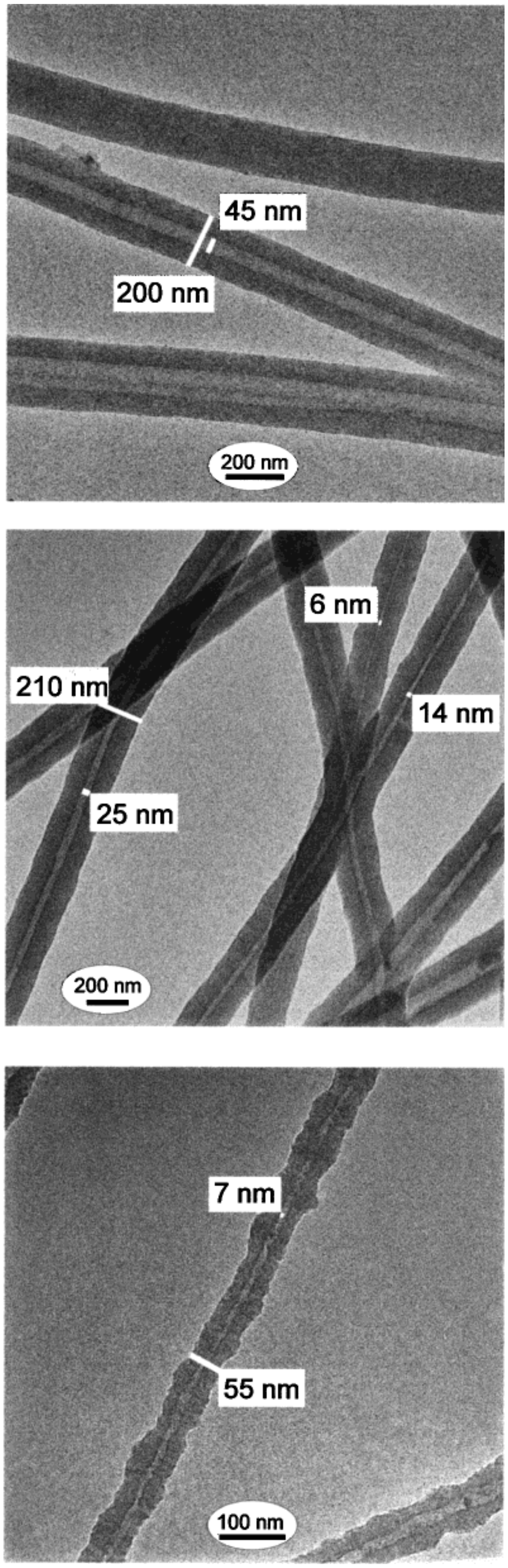

Figure 2. TEM of PPX nanotubes, obtained by coating of PA template fibers with 35 mg of dimer, after extraction with formic acid (A, top), from PLA template fibers obtained by coating with 37 mg of dimer (B, middle) and by coating with 22 mg of dimer after extraction with chloroform (C, bottom).

Palladium(II) diacetate was chosen as a conductivity modifier for a specific reason. Annealing of the PLA/PPX core shell fibers at 280 °C for 6 h resulted in PPX/Pd hybrid tubes. TEM of unstained samples of PPX/Pd hybrid tubes clearly shows thin wirelike structures of Pd (Figure 3). FT-IR spectroscopy proved that PLA was removed by pyrolysis. Palladium(II) diacetate was converted to Pd upon annealing, which was also confirmed by the color change of the sample, by FT-IR spectroscopy, by energy-dispersive X-ray analysis (EDX), and by wide-angle X-ray diffraction (WAXS) (Figure 4). WAXS proved for PPX the β-phase by the prominent at $2\theta = 20.12°$ reflection (compare ref 16) and metallic Pd by the signals at $2\theta = 40.26$ (111), 46.52 (222), 68.18 (220), and 82.06° (311) (compare JPDS database). The crystallite size of the metallic Pd crystals was found to be 4 nm based on WAXS line shape analysis. Another proof of the presence of Pd and its crystalline nature is

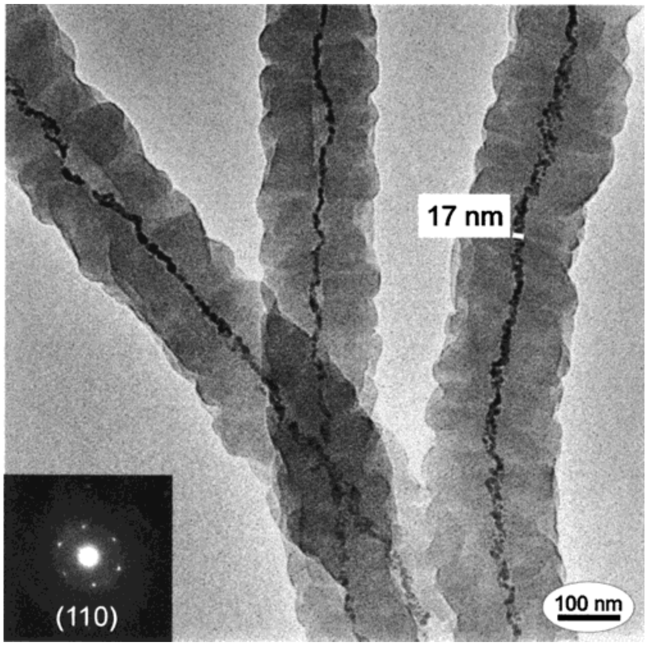

Figure 3. TEM of PPX/Pd TUFT hybrid nanotubes obtained after pyrolysis of PLA template fibers. Inset displays the electron diffraction pattern of Pd crystallites using a nanobeam.

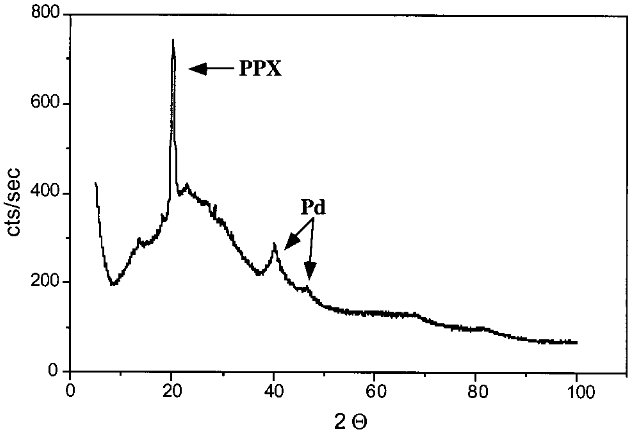

Figure 4. WAXS analysis of PPX/Pd TUFT hybrid nanotubes obtained after pyrolysis of PLA template fibers.

provided by electron diffraction studies using the nanobeam diffraction (NBD) mode with the beam converged to a 2 nm probe diameter using TEM. The inset in Figure 3 shows such a diffraction pattern corresponding to a single Pd particle inside one of the tubes. It displays the diffraction spots of the fcc structure of Pd along the [110] zone axis.

The results presented here are based on an efficient general route toward nanotubes of different materials using electrospun removable polymer template fibers (TUFT process). This approach offers a great potential for the design of tubular devices, novel in the sense of control of dimensions and shape. Tubes with inner diameters <10 nm and outer diameters of several tens of nanometers can be prepared in significant quantities, which opens perspectives for investigation of confinement effects and for materials with novel combination of properties. A challenge for future research will be the preparation of oriented nanoshaped polymer tubes.

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