

pected, when the nanocrystal is isolated on a substrate a Coulomb blockade behavior is observed. With a monolayer both ohmic and Coulomb blockade contributions are observed, whereas with a fcc structure a well-defined ohmic behavior is seen.

Experimental

Silver nanosized particles were synthesized using reverse micelles, as described previously [19,20]: Colloidal silver particles were prepared by mixing two reverse-micellar solutions having the same water-content (i.e., the molar ratio $W = [\text{H}_2\text{O}]/[\text{AOT}] = 40$), where AOT is 2-ethylhexylsulfosuccinate. The first was made with 30 % Ag(AOT) and 70 % Na(AOT), and the second with hydrazine N_2H_4 as reducing agent with an overall concentration of 7×10^{-2} M and with 100 % Na(AOT). This gave an average particle diameter of 3.4 nm with 43 % size distribution. Dodecanethiol was added to the micellar solution ($1 \mu\text{L}/\text{cm}^3$). Selective reaction with the silver atoms at the interface of the particles occurred and the coated particles were then extracted from reverse micelles. The powder of coated nanocrystals thus obtained was then dispersed in hexane, giving an optically clear solution. The size distribution was still rather large (30 %), and to reduce it a size-selected precipitation process [20] was used. In this process two solvents, such as hexane and pyridine, are mixed. The first is a good solvent and the second a poor solvent for the alkyl chains. With this solvent mixture, the larger coated particles flocculated whereas the smaller ones remain in the solution, thus providing size selection. By repeating this process several times, a homogenous clear colloidal solution of dispersed 4.3 nm nanocrystals is obtained. The concentration of nanocrystals with final size distribution around 13 % was controlled.

Received: November 19, 1999

- [1] G. Shön, U. Simon, *Colloid Polym. Sci.* **1995**, 273, 202.
- [2] D. V. Averin, K. K. Likharev, in *Mesoscopic Phenomena in Solids* (Eds: B. L. Altshuler, P. A. Lee, R. A. Webb), North-Holland, New York **1991**, Ch. 6.
- [3] D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, P. L. McEuen, *Nature* **1997**, 389, 699.
- [4] C. Thirstrup, M. Sakurai, K. Stokbro, M. Aono, *Phys. Rev. Lett.* **1999**, 82, 1241.
- [5] R. Berndt, R. Gaisch, J. K. Gimzewski, B. Reihl, R. R. Schlittler, W. D. Schneider, M. Tschudy *Science* **1993**, 262, 1425.
- [6] R. Berndt, J. K. Gimzewski, *Phys. Rev. B* **1993**, 48, 4746.
- [7] M. M. J. Bischoff, M. C. M. van der Wielen, H. van Kempen, *Surf. Sci.* **1998**, 400, 127.
- [8] K. Ito S. Ohyama, Y. Uehara, S. Ushioda, *Surf. Sci.* **1995**, 324, 282.
- [9] P. Dumas, C. Strykh, I. V. Makarenko, F. S. Salvan, *Europhys. Lett.* **1997**, 40, 447.
- [10] A. E. Hanna, M. Tinkham, *Phys. Rev. B* **1991**, 44, 5919.
- [11] M. Amman, R. Wilkins, E. Ben-Jacob, P. D. Maker, R. C. Jaklevic, *Phys. Rev. B* **1991**, 43, 1146.
- [12] D. L. Klein, P. L. McEuen, J. E. Bowen Katari, R. Roth, A. P. Alivisatos, *Appl. Phys. Lett.* **1996**, 68, 2574.
- [13] R. P. Andres, T. Bein, M. Dorogi, S. Feng, J. I. Henderson, C. P. Ku-biak, W. Mahoney, R. G. Osifchin, *Science* **1996**, 272, 1325.
- [14] R. Wilkins, M. Amman, R. E. Soltis, E. Ben-Jacob, R. C. Jaklevic, *Phys. Rev. B* **1990**, 41, 8904.
- [15] M. Amman, S. B. Field, R. C. Jaklevic, *Phys. Rev. B* **1993**, 48, 12 104.
- [16] C. Petit, T. Cren, D. Roditchev, W. Sacks, J. Klein, M. P. Pileni, *Adv. Mater.* **2000**, 11, 1198.
- [17] U. Simon, *Adv. Mater.* **1998**, 10, 1487.
- [18] C. Petit, unpublished data.
- [19] C. Petit, P. Lixon, M. P. Pileni, *J. Phys. Chem.* **1993**, 97, 12974.
- [20] A. Taleb, C. Petit, M. P. Pileni, *Chem. Mater.* **1997**, 9, 950.
- [21] Au(111) films typically 100 nm thick are prepared on a mica substrate. The procedure uses argon-ion bombardment and annealing in ultra-high vacuum (UHV) with a base pressure in the low 10^{-10} mbar range.
- [22] A commercial UHV-STM (Omicron) is used. The STM tips were prepared electrochemically using Au wires (0.25 mm diameter) and cleaned after by argon-ion bombardment.
- [23] K. H. Park, M. Shin, J. S. Ha, W. S. Yun, Y. J. Ko, *Appl. Phys. Lett.* **1999**, 75, 139.
- [24] L. Motte, M. P. Pileni, *J. Phys. Chem.* **1998**, 102, 4104.

- [25] L. Motte, F. Billoudet, E. Lacaze, M. P. Pileni, *Adv. Mater.* **1996**, 8, 1018.
- [26] A. J. Rimbart, T. R. Ho, J. Clarke, *Phys. Rev. Lett.* **1995**, 74, 4714.
- [27] T. Ohgi, H. Y. Sheng, H. Nejo, *Appl. Surf. Sci.* **1998**, 130, 919.
- [28] A. Taleb, C. Petit, M. P. Pileni, *J. Phys. Chem.* **1998**, 102, 12974.
- [29] A. Taleb, V. Russier, A. Courty, M. P. Pileni, *Phys. Rev. B* **1999**, 59, 13350.

Polymer, Metal, and Hybrid Nano- and Mesotubes by Coating Degradable Polymer Template Fibers (TUFT Process)

By Michael Bognitzki, Haoqing Hou, Michael Ishaque, Thomas Frese, Michael Hellwig, Christoph Schwarte, Andreas Schaper, Joachim H. Wendorff, and Andreas Greiner*

The preparation and design of confinement structures on a submicrometer scale has received great attention because of their potential for new materials properties and applications in a broad range of areas such as electronics, medicine, sensor, and controlled release technology. A wide spectrum of materials with submicrometer dimensions have been processed, including inorganic materials (carbon, metals, ceramics, glass) and organic materials (biomolecules, polymers). The preparation of these objects using self-assembly and template techniques has been described in detail in several excellent reviews.^[1-5] In particular, tubular objects in the meso- and nanoscale range have attracted special attention over the past decade. The preparation methods reported in the literature include self-assembly of carbon or boron nitride,^[6-8] self-assembly of lipid surfactants,^[9-11] self-assembly of polypeptides,^[12] polymerization within pores of nanoporous matrices,^[13] and the use of biomembrane templates.^[14] Thin tubular polymer fibers were also obtained by the so-called Shin-gosen technology, which makes use of non-circular fiber cross-sections or special sewing technology.^[15] All of these techniques have their own merits as well as limitations.

Encouraged by our recent success in the preparation of degradable polymer fibers with diameters in the submicrometer range using the electrospinning technique, we have developed a straightforward and highly versatile template method for the production of polymer, metal, and hybrid nano- and mesotubes.^[16] The general concept is to take such extremely thin degradable template polymer fibers, and to coat them with the desired wall materials using various types of deposition techniques (Fig. 1). Tubes are sub-

* Prof. A. Greiner,^[+] Prof. J. H. Wendorff, Dr. M. Bognitzki, Dr. H. Hou,^[+] M. Ishaque, T. Frese, M. Hellwig, C. Schwarte, Dr. A. Schaper
Department of Chemistry & Materials Science Center
Institute of Physical Chemistry, Nuclear Chemistry, and
Macromolecular Chemistry, Philipps University Marburg
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)

[+] New address: FB Chemie und Pharmazie, Institut für Organische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany.

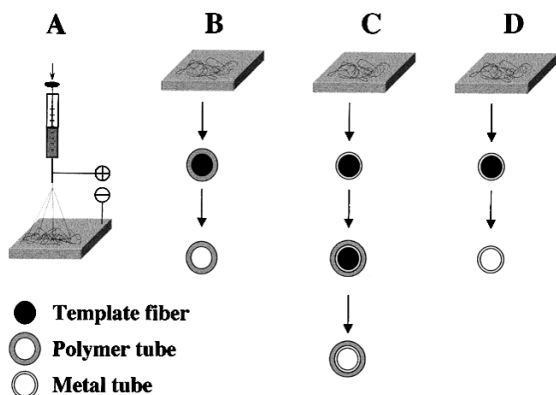


Fig. 1. A) Schematic diagram of the apparatus used for electrospinning. It consists of a syringe with a metal capillary (diameter 0.3 mm) and a pressure supply on the piston of the syringe. A high voltage field, typically in the range of 4 kV/cm, with the anode on the metal capillary, was applied to the polymer solution. Polymer fibers are formed as soon as a drop of the polymer solution has been formed at the tip of the capillary. These fibers are deposited on a glass substrate. B) Concept for the preparation of polymer tube. C) Concept for the preparation of polymer/metal hybrid tubes. D) Concept for the preparation of metal tubes.

sequently formed via selective removal of the core material, exploiting, for instance, the thermal degradation of the template fibers.

Poly(L-lactide) (PLA, Boehringer, Ingelheim) was selected as a suitable template candidate since it meets the requirements that the polymer should be processable to fibers with diameters in the submicrometer range, and that it should be stable during coating but should degrade under conditions that leave the wall material intact. The equilibrium melting temperature of PLA is 215 °C, which makes the template fiber thermomechanically stable.^[17] However, PLA is characterized by quantitative thermal degradability in the melt. Recently we overcame the limitations in the formation of PLA fibers of several tens of nanometers (diameter) by processing PLA in an electrical field and applying modified conditions. Fiber processing in an electrical field is known as electrospinning (also known as electrostatic spinning).^[18–20] The electrospinning process represents a highly efficient method to produce long and extremely fine polymer fibers by applying a divergent electric field to a polymer solution or melt. Fiber shape can be influenced by many parameters, such as the polymer, solvent, surface tension, solution viscosity, solution conductivity, glass transition of the polymer, and vaporization of the polymer, which have not yet been examined systematically.

PLA is soluble in solvents such as dichloromethane. PLA template fibers were thus obtained by electrospinning PLA/dichloromethane solutions in the set-up depicted in Figure 1A by using electric fields on the order of 4 kV/cm. Electrospinning of PLA/dichloromethane solutions resulted in PLA fibers with average fiber diameters (AFDs) of 1–3 μm. The fiber diameters of those samples used in our experiments ranged between 0.3 and 3.5 μm. The majority of the fiber diameters were about 1.0–1.5 μm. The conductivity of the solution and the surface tension of the

solution used for processing turned out to be an important processing parameter with respect to control of the diameter of the PLA template in terms of thinner fibers. A significant decrease in the AFD of PLA fibers processed from PLA/dichloromethane solutions was accomplished by adding small amounts of organosoluble ammonium salts, for example, triethyl benzyl ammonium chloride (TEBAC) (0.5–1.5 %), to the polymer solution.^[21] This caused an increase in conductivity in the PLA solution by four orders of magnitude up to 400 μS/cm and an increase in surface tension from about 25 mN/m to 40 mN/m. In fact, the AFD of the PLA fibers was reduced to 0.2 μm whereby fiber diameters ranged from 0.05 μm to about 0.7 μm. It is obvious that PLA is a promising candidate for the preparation of nano- and mesotubes via the template route because of the combination of degradability, its stability under coating conditions, and the control of fiber shape.

The coating of the template and thus the formation of the walls of the tubes was achieved by chemical vapor deposition (CVD) with poly(*p*-xylylene) (PPX) following the concept shown in Figure 1B. The walls could be prepared in this way without destruction of the template fibers. PPX deposition from the gas phase was accomplished, for instance, by vapor phase pyrolysis of the starting material [2.2]paracyclophane 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 (0.1 mbar). This mild coating technique results in conformal pinhole-free films of PPX (film thickness 50 nm to several micrometers) in quantitative yields.^[22] Structural analysis of the synthesis of PPX by CVD starting from [2.2]paracyclophane proved that PPX is pure. It can be obtained free of contamination by unreacted [2.2]paracyclophane or by rearranged [2.2]paracyclophane under standard reaction conditions.^[23] With respect to the template route, it is important that the melting point of PPX is 420 °C and that it shows high thermal stability for the preparation of tubes by coating heat-degradable template fibers. This makes PPX a perfect material to withstand thermal degradation conditions to which the PLA template fibers have to be subjected. Coating of the PLA template fibers with PPX by CVD yields PPX/PLA core-shell fibers. Subsequent annealing of these fibers above 250 °C under vacuum results in the degradation of the PLA core, which leads to PPX tubes. Characterization of the samples was performed by scanning electron microscopy (SEM) using a Cam Scan 4 at 20 kV accelerating voltage as well as by transmission electron microscopy (TEM) using a JEM 3010 operated at 300 kV. The tubes are organized in a layered assembly as shown by SEM (Fig. 2A) and they are connected by a PPX film, which results in a tubular network. This allows the preparation of macroscopic mats consisting of PPX tubes. The length of the tubes is >100 μm and the inner tube diameter was in the range of about 0.05–3.5 μm, depending on the diameter of the PLA template fibers obtained by elec-

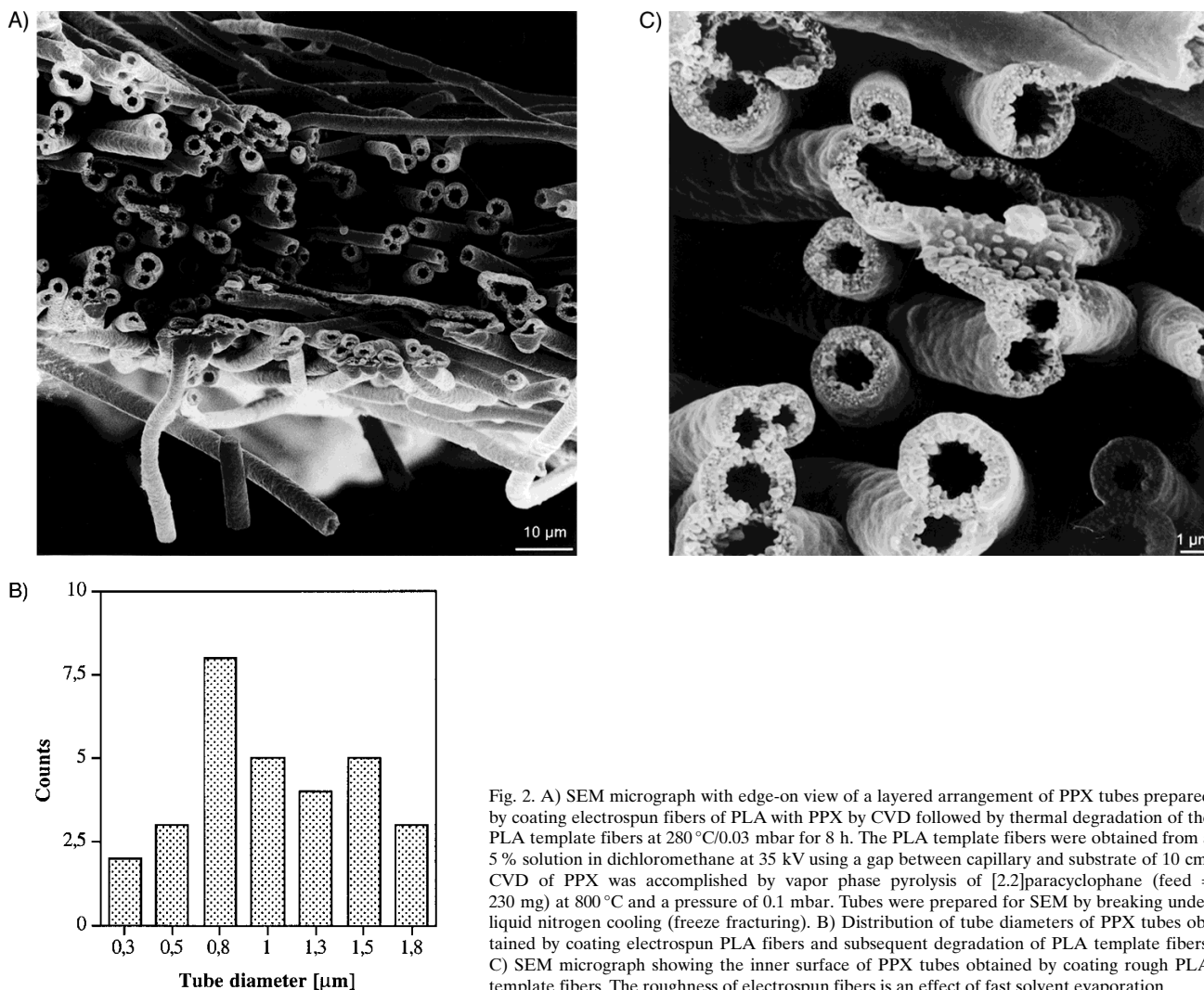


Fig. 2. A) SEM micrograph with edge-on view of a layered arrangement of PPX tubes prepared by coating electrospun fibers of PLA with PPX by CVD followed by thermal degradation of the PLA template fibers at 280 °C/0.03 mbar for 8 h. The PLA template fibers were obtained from a 5 % solution in dichloromethane at 35 kV using a gap between capillary and substrate of 10 cm. CVD of PPX was accomplished by vapor phase pyrolysis of [2.2]paracyclophane (feed = 230 mg) at 800 °C and a pressure of 0.1 mbar. Tubes were prepared for SEM by breaking under liquid nitrogen cooling (freeze fracturing). B) Distribution of tube diameters of PPX tubes obtained by coating electrospun PLA fibers and subsequent degradation of PLA template fibers. C) SEM micrograph showing the inner surface of PPX tubes obtained by coating rough PLA template fibers. The roughness of electrospun fibers is an effect of fast solvent evaporation.

trospinning. The evaluation of the tube diameter distribution of a representative sample is shown in Figure 2B.

The wall thickness of the tubes is in the range of about 0.1–1 μm depending on the feed of [2.2]paracyclophane. Using template fibers with a porous surface, one is able to fabricate tubes displaying a structured inner surface (Fig. 2C).^[24] This finding indicates again a conformal coating by PPX via the CVD route. Such highly structured surfaces are of great interest for applications related to large surface/volume ratios.

Meso- and nanotubes prepared by the template method were also obtained from polymer solutions by dip-coating PLA template fibers following the concept shown in Figure 1B. Polyimide (poly(*N,N*-(*p,p'*-oxydiphenylene)pyromellitic imide)) tubes were obtained, for instance, by dip coating PLA fibers into a solution of polyamic acid (poly(*N,N*-(*p,p'*-oxydiphenylene)pyromellitic acid)) followed by annealing at 150–285 °C.^[25] This results in the degradation of the PLA template fibers and in a conversion of polyamic acid to polyimide. The inner diameters of the fibers were in the range of 1–2 μm. The successful prepara-

tion of tubes involving dip-coating depends significantly on the coating parameters, particularly on the concentration of the polymer in solution. A systematic study with polyamic acid revealed an optimum concentration of polyamic acid centered at 2–4 wt.-% in the present case.

The preparation of meso- and nanotubes from a wide variety of materials offers quite different applications of these structures. The potential applications can be significantly extended by a proper functionalization of the polymer tubes. An example studied was the metallization of the inner part of polymer tubes following the concept shown in Figure 1C. PPX tubes with aluminum-functionalized inner surfaces were obtained by coating electrospun PLA fibers with aluminum by physical vapor deposition (PVD) and by subsequent coating with PPX via CVD. The hybrid PPX/aluminum tubes were developed by thermal degradation of the PLA template fibers. The resulting tubes show an aluminum layer on the inside of the PPX tube, shown by energy dispersive X-ray analysis (EDX), in the SEM (not shown here), and by TEM of cross-sectional samples after embedding the tubes in epoxy resin and then microtoming

(Fig. 3). Similarly, PPX tubes with gold-coated inner walls were obtained. Polymer/metal hybrid tubes with inner diameters ranging from 0.5–1.5 μm were observed.

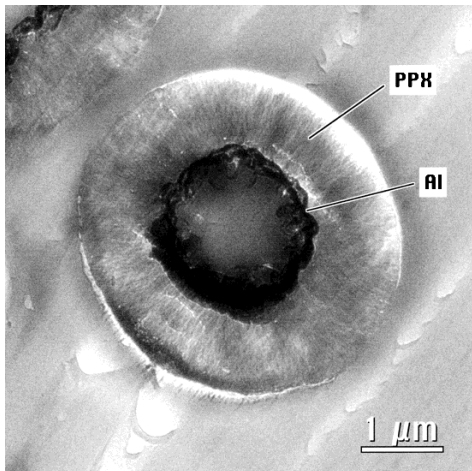


Fig. 3. TEM cross-sectional view of a PPX/aluminum composite tube prepared by coating PLA fibers with aluminum followed by PPX coating and subsequent thermally induced degradation of the template fibers. The uneven structure of the aluminum layer reproduces the rough structure of the PLA template fiber.

Finally, coating PLA template fibers solely with aluminum and subsequent thermal degradation of the PLA fibers following the concept shown in Figure 1D results in very stiff single-walled aluminum tubes. The inner diameters of these aluminum tubes were found to be in the range of 0.8 μm , as revealed by SEM (Fig. 4).



Fig. 4. SEM micrograph of aluminum tubes prepared by coating electrospun PLA fibers with aluminum, followed by thermally induced degradation of the template fibers.

The results presented here are based on a simple and efficient general route towards nano- and mesotubes using electrospun degradable polymer fiber templates. For this approach we coined the term TUFT process (tubes by fiber templates). This approach offers a great potential for the design of novel tubular devices—novel, in the sense of control of dimensions and shape and even with respect to the broad range of materials that can be manufactured. The

TUFT process will gain significance with improvement of the control of tube diameters, structuring, and functionalization of the tubes, which should be possible by adjusting the parameters for the preparation of template fibers by electrospinning, as mentioned above.

Received: October 27, 1999
Final version: January 10, 2000

- [1] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312.
- [2] G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612.
- [3] J. M. Schnur, *Science* **1993**, *262*, 166.
- [4] C. R. Martin, *Science* **1994**, *266*, 1961.
- [5] F. T. Edelmann, *Angew. Chem.* **1999** *111*, 1473; *Angew. Chem. Int. Ed.* **1999**, *38*, 1381.
- [6] S. Iijima, *Nature* **1991**, *354*, 56.
- [7] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zetel, *Science* **1995**, *269*, 966.
- [8] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, P. N. Provencio, *Science* **1998**, *282*, 1105.
- [9] P. Yager, P. E. Schoen, *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 381.
- [10] J. M. Schnur, R. Price, P. Schoen, P. Yager, J. M. Calvert, J. Georger, A. Singh, *Thin Solid Films* **1987**, *152*, 181.
- [11] S. L. Browning, J. Lodge, R. R. Price, J. Schelleng, P. E. Schoen, D. Zabetakis, *J. Appl. Phys.* **1998**, *84*, 6109.
- [12] M. Ghadiri, J. R. Granja, L. Buehler, *Nature* **1994**, *369*, 301.
- [13] C. R. Martin, *Acc. Chem. Res.* **1995**, *28*, 61.
- [14] E. Evans, H. Bowman, A. Leung, D. Needham, D. Tirrell, *Science* **1996**, *273*, 933.
- [15] T. Hongu, G. O. Phillips, *New Fibers*, Woodhead Publishing, Cambridge, UK **1997**, p. 164.
- [16] We have decided to use the two terms “nano” and “meso” in order to describe the dimensions of the hollow fibers in the range 50–2000 nm. This is clearly within but also beyond the size of nanoshaped objects, which were coined by Whitesides for objects up to 1–100 nm [1].
- [17] B. Kalb, A. J. Pennings, *Polymer* **1980**, *21*, 607. The sample from Boehringer Ingelheim used here showed a melting temperature of 186 °C (DSC, heating rate: 10 K/min)
- [18] P. K. Baumgarten, *J. Colloid Interface Sci.* **1971**, *36*, 71.
- [19] D. H. Reneker, I. Chun, *Nanotechnology* **1996**, *7*, 216.
- [20] R. Jaeger, H. Schönherr, G. J. Vansco, *Macromolecules* **1996**, *29*, 7634.
- [21] M. Bognitzki, T. Frese, A. K. Schaper, J. H. Wendorff, A. Greiner, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, in press.
- [22] W. F. Gorham, *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 3027.
- [23] C. Schmidt, V. Stümpflen, J. H. Wendorff, A. Hasenhiindl, W. Gronski, M. Ishaque, A. Greiner, *Acta Polym.* **1998**, *49*, 232.
- [24] Porous fibers by solution spinning of PLA have been reported before [17].
- [25] Polyamidic acid was prepared by polycondensation of *p,p'*-diaminodiphenylether (3 g, 13.7 mmol) and pyromellitic acid anhydride (2.75 g, 13.7 mmol) in 34 mL DMF at 0–5 °C for 12 h.

Ordered Colloidal Nanoalloys**

By Christopher J. Kiely,* John Fink, Jian Guo Zheng, Mathias Brust, Donald Bethell, and David J. Schiffrin

Since the realization that nanoscale metal and semiconductor particles exhibit unusual size-dependent properties

[*] Prof. C. J. Kiely, Dr. J. G. Zheng
Materials Science and Engineering, Department of Engineering
University of Liverpool
Liverpool, Merseyside, L69 3BX (UK)
J. Fink, Dr. M. Brust, Prof. D. Bethell
Prof. D. J. Schiffrin
Centre for Nanoscale Science, Department of Chemistry
University of Liverpool
Liverpool, Merseyside, L69 3BX (UK)

[**] JF has been supported by an EPSRC quota studentship and MB is the recipient of an EPSRC Advanced Research Fellowship.