

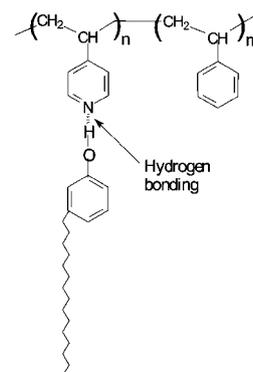
## “Hairy Tubes”: Mesoporous Materials Containing Hollow Self-Organized Cylinders with Polymer Brushes at the Walls\*\*

By Riikka Mäki-Ontto, Karin de Moel, Walter de Odorico, Janne Ruokolainen, Manfred Stamm, Gerrit ten Brinke, and Olli Ikkala\*

Self-organization leads to nanoscale polymeric structures based on competing interactions<sup>[1,2]</sup> and incorporation of several schemes of self-organization gives rise to hierarchical structures.<sup>[1,3-6]</sup> Previously we have introduced a concept where amphiphilic molecules are physically bonded selectively to one block of a block-copolymer to form specific *receptor-substrate supramolecules* (supramolecules are defined elsewhere<sup>[7,8]</sup>) and they self-organize to form structure-*within*-structures.<sup>[5,6,9]</sup> In this communication we show how the scheme allows the preparation of mesoporous materials. The starting material is the diblock copolymer polystyrene-*block*-poly(4-vinyl pyridine), PS-*block*-P4VP, with a stoichiometric amount of pentadecyl phenol, PDP, hydrogen bonded to the latter block. The block lengths have been selected to give a lamellar-*within*-cylindrical morphology, where the P4VP/PDP-blocks form cylinders within the rigid glassy PS-medium and where the P4VP/PDP-complexes, being of a *comb-like* architecture, self-organize as lamellae<sup>[10]</sup> within the cylinders. In addition to such a local order, we accomplish overall orientation by applying an oscillatory shear flow to align the cylinders. The orientation is verified using small-angle X-ray scattering (SAXS). Hollow cylinders with P4VP brushes on the interior walls are achieved in a straightforward way by dissolving the PDP molecules away from the cylinders, as shown by SAXS and FTIR. Such “hairy tubes” open possibilities for controllable mesoporous membranes as the conformation of the brushes depends on the solvent. In addition, P4VP further allows chemical modification to tailor the membranes.

Biochemical systems allow several examples of functional membranes, such as the cell walls with their transport proteins, and numerous biomimetic concepts have thus been pursued. Synthetic functional membranes have major technological applications, such as in purification. Potential concepts have been demonstrated based on mesoporous materials due to organic/inorganic assemblies,<sup>[11-13]</sup> cross-linked structures of amphiphiles containing crown ethers,<sup>[14,15]</sup> mesotubes based on degradable polymer fibers as templates,<sup>[16]</sup> polymerized tubes with polyacrylic acid brushes obtained by degradation process,<sup>[17,18]</sup> self-organization of rod-coil copolymers,<sup>[19]</sup> and nanoporous carbon membranes,<sup>[20]</sup> to mention a few.

In this communication we describe a simple method for constructing mesoporous materials, based on physically matching molecules as templates. Comb coil diblock copolymers form a specific architecture of self-organizing block copolymers,<sup>[2,21,22]</sup> in which a dense set of repulsive side chains is covalently connected to the backbone. Even carefully matched physical bonds suffice to bond the side chains to allow self-organization.<sup>[23,24]</sup> For example, in P4VP the pyridine groups are hydrogen-bonding acceptors that form sufficiently strong hydrogen bonds with stoichiometric amounts of alkyl phenols, such as PDP, to form lamellar order.<sup>[25]</sup> If such a receptor-substrate supramolecule is selected to be one block of a diblock copolymer, a comb coil supramolecule PS-*block*-P4VP(PDP)<sub>1.0</sub> is formed, capable of hierarchical self-organization<sup>[5,6,9]</sup> (Scheme 1).



Scheme 1.

In this work the block lengths are selected so that the weight fraction of the P4VP(PDP)<sub>1.0</sub> block is 0.25, as we aim at P4VP(PDP)<sub>1.0</sub> cylinders within a glassy PS-matrix. The advantage of using hydrogen-bonded supramolecule template PS-*block*-P4VP(PDP)<sub>1.0</sub>, instead of conventional block copolymer molecules, is that the cylinders can be emptied easily, as part of the template, that is, the oligomeric PDP “flows” easily out from the cylinders in a suitable solvent especially if the cylinders have been macroscopically oriented. In addition, the amount of hollow space within the cylinders can be tailored using different amounts of PDP.

We will first address the structure. Figure 1 shows the isotropic SAXS-intensity pattern of PS-*block*-P4VP(PDP)<sub>1.0</sub> at room temperature before shear orientation. A SAXS peak is observed at  $q_2^* = 0.165 \text{ \AA}^{-1}$ . It corresponds to the lamellar

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order of P4VP(PDP)<sub>1.0</sub> complex with a long period 38 Å. Note that in the corresponding homopolymer complex, the second order peak at 2q<sub>2</sub><sup>\*</sup> becomes faintly observable using synchrotron radiation,<sup>[26]</sup> indicating lamellar order. In addition, Figure 1 shows another peak at q<sub>1</sub><sup>\*</sup> = 0.03 Å<sup>-1</sup>, corresponding to a structure with an order of magnitude larger

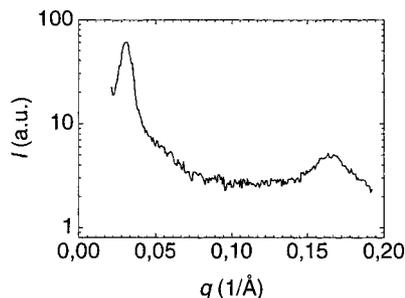


Fig. 1. SAXS intensity pattern of PS-*block*-P4VP(PDP)<sub>1.0</sub> at room temperature before annealing and orientation. Two characteristic peaks are observed. The peak at q<sub>1</sub><sup>\*</sup> = 0.03 Å<sup>-1</sup> corresponds to the formation of P4VP(PDP)<sub>1.0</sub> cylinders within the PS-medium (see Fig. 4). The peak at q<sub>2</sub><sup>\*</sup> = 0.165 Å<sup>-1</sup> corresponds to the lamellar order within the P4VP(PDP)<sub>1.0</sub> cylinders. From the previous studies the latter structure is known to have an order-disorder transition at about 65 °C [9,10].

length scale. The structure corresponding to the latter peak can be easily identified after annealing at 125 °C for 6 h, which renders in an oriented sample a six spot pattern at the magnitude of the scattering vector q<sub>1</sub><sup>\*</sup> = 0.03 Å<sup>-1</sup>, demonstrating hexagonal order (see Fig. 2a). Upon shear orientation at the same temperature using frequency 0.5 Hz and strain amplitude 20 %, the scattering pattern becomes even more pronounced. The presence of a hexagonal assembly of cylinders is illustrated in Figure 2a using SAXS in the tangential direction during cooling at 50 °C. Further decrease of temperature caused a less regular SAXS pattern (Fig. 2b) possibly due to deformation caused by the shrinking material and formation of the second structure due to P4VP(PDP)<sub>1.0</sub>. Figure 3 shows more comprehensive *ex-situ* SAXS patterns in the tangential, normal, and radial directions performed after the shearing was terminated. The smaller structure at q<sub>2</sub><sup>\*</sup> = 0.17 Å<sup>-1</sup> is not visible in the tangential direction but it is well-distinguishable in the other two directions, perpendicular to the large structure.

In conclusion, high orientation of the cylinders in the tangential direction is obtained by imposing shear flow.

The critical aspect to achieve membranes is whether the cylinders can be emptied from the additional templating agent PDP. The oriented samples were immersed for at least 12 h in methanol (which is a non-solvent for the glassy PS but a solvent for both P4VP and PDP), dried, and studied using SAXS and FTIR. As shown in Figure 3, the SAXS peaks that correspond to the self-organization of the cylinders within the glassy PS medium remained unchanged upon methanol treatment, whereas the peak corresponding to the lamellar self-organization of P4VP(PDP)<sub>1.0</sub> within the cylinder at q<sub>2</sub><sup>\*</sup> = 0.17 Å<sup>-1</sup> disappeared due to removal of PDP (Fig. 3b and Fig. 3c). So it seems to be possible to obtain nanometer-sized

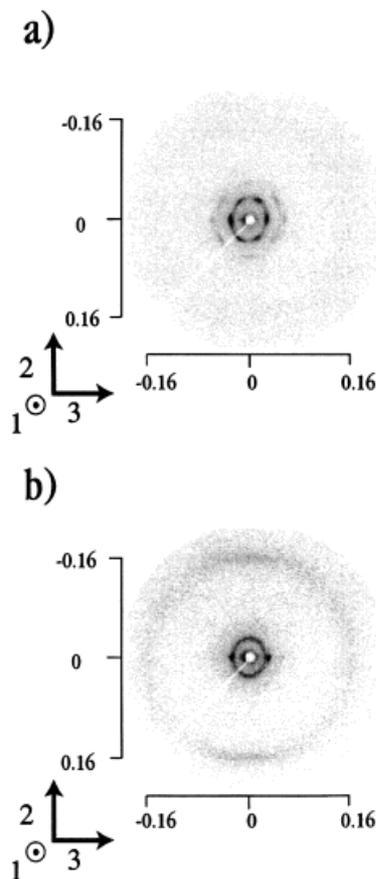


Fig. 2. In-situ SAXS patterns for PS-*block*-P4VP(PDP)<sub>1.0</sub> in the tangential direction after annealing and shear orientation at 125 °C. a) During cooling at about 50 °C, a well-defined hexagonal array of cylinders is shown with the magnitude of the scattering vector q<sub>1</sub><sup>\*</sup> = 0.03 Å<sup>-1</sup>. b) After reaching room temperature, a less perfect structure is obtained, possibly due to thermal shrinkage and formation of the smaller P4VP(PDP)<sub>1.0</sub> structure. Note that the smaller structure of P4VP(PDP)<sub>1.0</sub> is ideally not observable at the tangential beam orientation and the faint signal in (b) is only due to non-idealities. The coordinates used: 1, the shear direction; 2, the shear gradient direction; and 3, the vorticity direction. The scattering vectors are in units (1/Å).

almost empty cylindrical tubes in a macroscopic piece of polymer material (typically some mm<sup>3</sup>).

Next the effect of PDP removal on the SAXS peak at q<sub>1</sub><sup>\*</sup> ≈ 0.03 Å<sup>-1</sup> is studied in more detail. Firstly, methanol washing drastically increases the peak intensity (see Table 1). The densities of PS and P4VP(PDP)<sub>1.0</sub> are close to each other (Table 2).<sup>[9]</sup> These densities allow us to evaluate the average electron densities. The SAXS scattering intensity is directly proportional to mean square electron density fluctuation.

In the two-phase system

$$(\rho - \bar{\rho})^2 = (\rho_1 - \rho_2)^2 \omega_1 \omega_2 = (\Delta\rho)^2 \omega_1 \omega_2 \quad (1)$$

where  $\rho_1$  and  $\rho_2$  are the electron scattering densities of the materials 1 and 2, and  $\omega_1$  and  $\omega_2$  are the volume fractions of the materials with  $\omega_1 + \omega_2 = 1$ .<sup>[27]</sup> A simple indication for the increase of the SAXS intensity can now be given based on the difference in electron density between the matrix and the cylinder, that is assuming a two-phase system. Originally, the

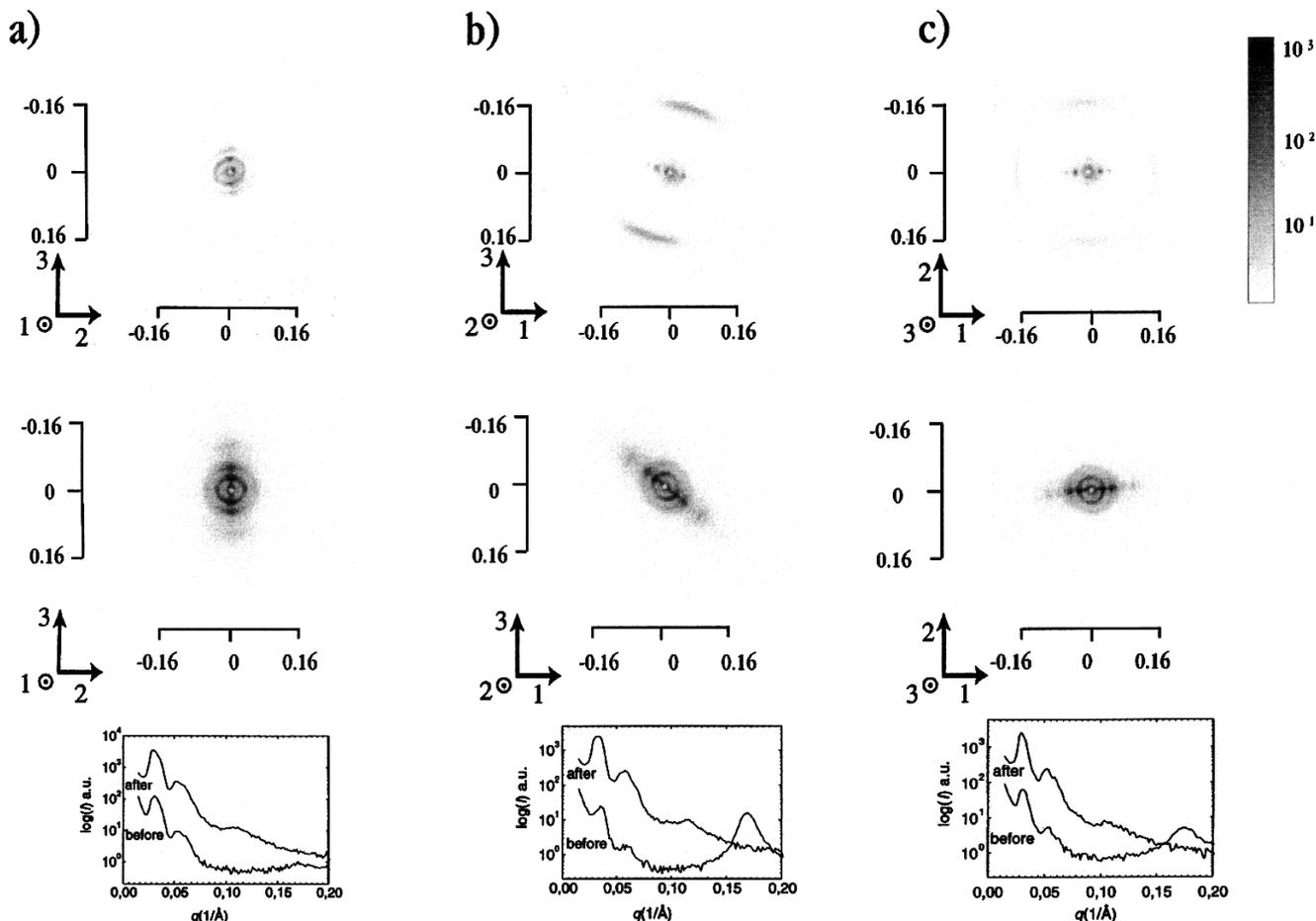


Fig. 3. SAXS intensity patterns for PS-*block*-P4VP(PDP)<sub>1.0</sub> in the a) tangential (1), b) normal (2), and c) radial (3) direction. The uppermost and middle figures depict the case before and after immersion in methanol, respectively, to remove PDP. In the bottom, the corresponding SAXS intensities are depicted. The peak at  $q_1^* = 0.03 \text{ \AA}^{-1}$  corresponds to self-organization of cylinders in PS whereas  $q_2^* = 0.17 \text{ \AA}^{-1}$  corresponds to lamellar order within the P4VP(PDP)<sub>1.0</sub> cylinders. The peaks corresponding to the large structure suggest that the cylinders are mainly along the shear direction (1) whereas the small structure is aligned perpendicular to the cylinders, that is the normals of the layers are in the 1-direction. The tilt in the middle figure of b) is not real but caused by misalignment of the sample in the SAXS beam. The coordinates used: 1, the shear direction; 2, the shear gradient direction; and 3, the vorticity direction. The scattering vectors are in units (1/Å).

Table 1. SAXS scattering intensities of the peak  $q_1^* = 0.03 \text{ \AA}^{-1}$  corresponding to the cylindrical organization of PS-*block*-P4VP(PDP)<sub>1.0</sub> within the PS-matrix before ( $I_{\text{before}}$ ) and after ( $I_{\text{after}}$ ) methanol washing. The intensity is determined to be the maximum of the peak.

		$I_{\text{before}}$	$I_{\text{after}}$	$I_{\text{after}}/I_{\text{before}}$
Experimental	Tangential	122	3437	28
	Normal	24	2500	104
	Radial	63	2583	41
Theoretical				329

Table 2. Density and electron scattering density.

	P4VP [c]	PS	P4VP(PDP) <sub>1.0</sub> [a]
Density (g/cm <sup>3</sup> )		1.047	0.98
Electron scattering density [b] (10 <sup>10</sup> cm <sup>-2</sup> ) $a\rho_e$	10.08	9.5	9.12

[a] The measured density of P4VP(PDP)<sub>1.0</sub> [9] and electron scattering density approximated based on it. [b]  $a$  is the classical electron radius  $2.8 \times 10^{-13} \text{ cm}$  and  $\rho_e$  is the mean electron density. [c] From ref. [29].

tubes are filled with P4VP(PDP)<sub>1.0</sub> and after methanol washing it is assumed that there is only P4VP and empty space, see

Figure 4. Using the electron scattering densities of Table 2, an estimate for the peak intensity differences was obtained. The theoretical value thus obtained is higher than the measured peak intensity ratio. The intensity ratio is, however, also in other cases of, for example, polymer blends and copolymers difficult to estimate, since it depends on the difference of relatively large numbers, which each have a considerable individual error. In the present case the concentrations of PDP and – in the empty template – of P4VP/PDP are not accurately known. Still, the strong increase in measured intensity is a clear indication that a substantial part of the PDP has been removed.

This is also demonstrated by FTIR spectroscopy, see Figure 5. FTIR spectra were measured for the washed diblock system and compared with those of the pure compounds. The spectrum corresponding to the methanol-washed complex resembles that of pure diblock PS-*block*-P4VP. In particular, the band at  $1008 \text{ cm}^{-1}$ , which is characteristic for hydrogen bonded pyridine, is no longer observed in the washed sample.<sup>[28]</sup> Also this shows that it is possible to remove almost all PDP from the material.

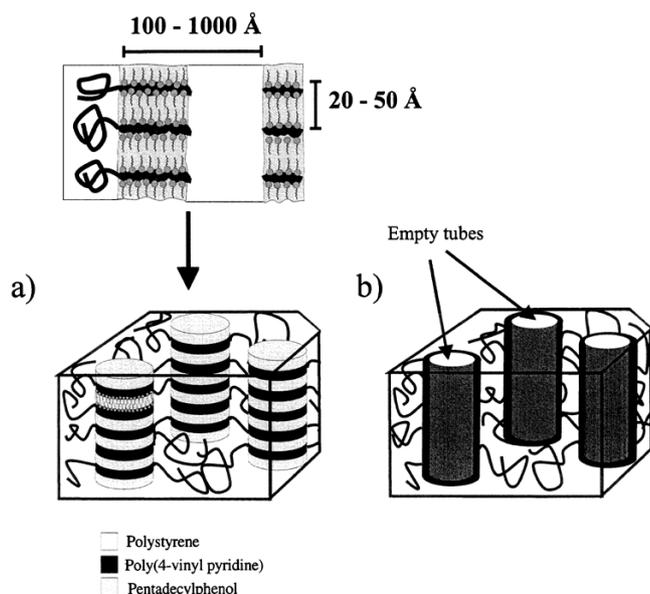


Fig. 4. Schematic picture of the procedure used to achieve empty nanoscale tubes with polymer brushes at the interior walls based on hydrogen bonded supramolecules. a) Lamellar-within-cylindrical structure observed before PDP removal. b) After the PDP removal the cylindrical self-organization remains due to the rigid glassy PS. Since the P4VP block can be expected to still cover the wall of the otherwise empty tubes, we call them “hairy tubes” in a matrix of PS. The lengths indicate typical dimensions obtainable when using different block copolymers and amphiphiles.

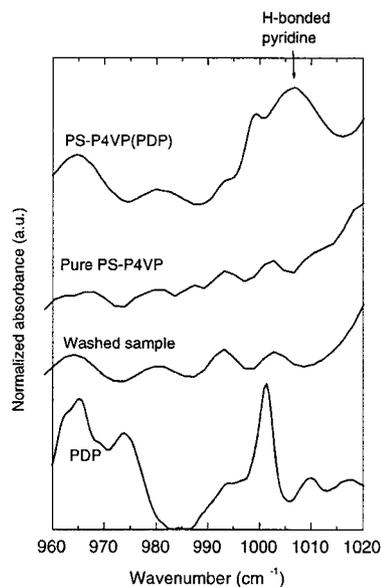


Fig. 5. FTIR for PDP, PS-*block*-P4VP, PS-*block*-P4VP(PDP)<sub>1,0</sub>, and methanol-washed PS-*block*-P4VP(PDP)<sub>1,0</sub>. In the last sample, there is no evidence of either hydrogen bonded pyridine (1008 cm<sup>-1</sup>) or 3-phenol (999 cm<sup>-1</sup>) [28]. The spectra of the methanol washed PS-*block*-P4VP(PDP)<sub>1,0</sub> resembles that of pure diblock PS-*block*-P4VP.

In conclusion, we have demonstrated a route for the preparation of self-organized hollow cylinders in a glassy rigid PS-medium. The cylinders are formed by self-organization of hydrogen-bonded supramolecules. Part of the supramolecular template, PDP, can be conveniently removed at the end after the structure has been formed, thus overcoming the need to

use degradation or corresponding methods to empty the tubes. The cylinders show relatively high macroscopic order due to annealing but the order can be improved by shear flow. The concept permits generalization and tailoring. Transport properties and tailoring of the tubes are the subject of our forthcoming studies.

## Experimental

**Materials:** PS-*block*-P4VP (Polymer Source Inc.) had  $M_w = 34\,000$  g/mol and 2900 g/mol, respectively, for the PS and P4VP blocks and  $M_w/M_n = 1.07$  for the complete polymer. 3-*n*-Pentadecyl phenol, PDP, (Aldrich, purity 98 %) was twice recrystallized with petrol ether and dried at 40 °C in vacuum for 4 days. The complexes PS-*block*-P4VP(PDP)<sub>1,0</sub> were prepared by dissolving both components, PS-*block*-P4VP and PDP, in analytical grade chloroform. Stoichiometric molar amounts of PDP was used, that is one alkylphenol for each repeat unit of the P4VP-block. The solvent was evaporated at 60 °C on a hot plate; thereafter the samples were vacuum dried at 60 °C for at least 12 h.

**Dynamic Rheological Orientation and In-Situ SAXS:** First the samples were heated to 120 °C in a cylindrical mold of 10 mm diameter. During the first 0.5 h no pressure was applied and the material was allowed to flow freely in to the mold. Subsequently, a pressure of 10 bar was exerted by a piston to press tablets of 1 mm thickness and 10 mm in diameter. The samples were immediately cooled to 50 °C with compressed air and removed from the press. The shear flow orientation was accomplished by a Bohlin CSM-50 stress-controlled rheometer in an oscillating mode using a parallel plate geometry. The sample was heated to 150 °C and then annealed at 125 °C for 6 h to obtain a homogeneous sample and a good contact to the plates. The shear was performed at 125 °C using the frequency 0.5 Hz and 20 % strain amplitude for 2.1 h.

Small-angle X-ray scattering was performed in-situ during the above shear orientation. The combined SAXS/dynamic rheometer consists of a Rigaku Rotaflex 18 kW rotating anode X-ray source with a graphite double monochromator at wavelength of  $\lambda = 1.54 \text{ \AA}$  (Cu K $\alpha$ ). Three pinholes collimate the beam over 1.5 m to a diameter of about 1 mm at the sample position. A Siemens multiwire type area detector was used. The sample-detector distance was 1.2 m, yielding an angular resolution of  $\Delta 2\theta = 0.07^\circ$  or  $\Delta q \approx 0.005 \text{ \AA}^{-1}$ . The scattering vector  $q$  is defined as  $q = 4\pi/\lambda \sin\theta$  with  $2\theta$  being the scattering angle. The measurements were corrected for non-uniformities in spatial distortion.

Having learned the feasible conditions to achieve orientation based on the combined dynamic rheological orientation and in-situ SAXS, samples were more straightforwardly prepared by first dynamic rheological orientation, followed by the structure determination by ex-situ SAXS in the following methods.

**Dynamic Rheological Orientation:** ARES (Rheometric Scientific Inc.) rheometer was used in oscillating mode with parallel plate geometry with gap of 1 mm. The sample was heated up to 150 °C and then annealed at 120 °C for 1 h. The shear was performed at 120 °C for 16 h using 0.1 Hz and 50 % strain amplitude.

**Ex-Situ SAXS:** The Bruker NanoSTAR equipment used consists of a Kristalloflex K760-8-3.0 kW X-ray generator with cross-coupled Göbel mirrors for Cu K $\alpha$  radiation resulting in a parallel beam of about 1 mm<sup>2</sup> at sample position. A Siemens multiwire type area detector was used. The sample-detector distance was 0.65 m.

**Preparation of Hollow Cylinders:** After the dynamic shear orientation, the SAXS intensity patterns were measured ex-situ in the tangential, normal, and radial directions near room temperature to verify the orientation. The sample was cut as to render path lengths through the sample approximately 1–2 mm in each direction. The cut pieces were immersed into analytical grade methanol at room temperature for at least 12 h to remove PDP within the cylinders. To verify that PDP has been removed, the SAXS intensity patterns were again measured at the tangential, normal, and radial directions and compared with the original measurements.

**FTIR Spectroscopy:** Infrared spectra were obtained using Nicolet 730 FTIR spectrometer. Samples were prepared by solvent casting from chloroform onto potassium bromide crystals.

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## Template Synthesis and Magnetic Behavior of an Array of Cobalt Nanowires Encapsulated in Polyaniline Nanotubes\*\*

By Huaqiang Cao, Zheng Xu,\* Hai Sang, Dong Sheng, and Chenyang Tie

Since the discovery by Yager and Schon in 1984 of a new type of microstructure, organic microtubules, in this material has aroused great interest among physicists, chemists, and ma-

terials scientists.<sup>[1]</sup> C. R. Martin et al. have been exploring a template synthesis method, which entails synthesizing the desired materials within the pores of a nanopore membrane. This method has been shown to be a versatile approach for preparing nanomaterials. Using this template synthesis method, nanotubules and nanofibrils composed of metals,<sup>[2]</sup> semiconductors,<sup>[3]</sup> polymers<sup>[4]</sup>, and various composites of these materials have been prepared. These materials often have useful optical,<sup>[5]</sup> electronic<sup>[6]</sup>, and magnetic<sup>[7]</sup> properties. For example, the distinctive anisotropic magnetic properties of an array of Ni and Co nanowires make this material a potential candidate for perpendicular magnetic recording. Also, the nanosize volume of this material reduces the turbulence current when a high-frequency field is applied, which is important for antenna materials in the high-frequency range. But the metal nanowires are very sensitive to air and moisture, which degrades the performance of the nanodevice. A polymer envelope would protect metal nanowires from oxidation and corrosion, giving good performance for a long time. In this communication we describe a new type of artificially nanostructured composite material with one-dimensional entities. Recently, we have used the template synthesis method to prepare nanotubules of polyaniline within the pores of an alumina template membrane (Fig. 1a). Using this array of polyaniline nanotubules with the alumina membrane support as a “second-order-template”, we have prepared cobalt nanowires within the nanotubules of polyaniline (Fig. 1b).

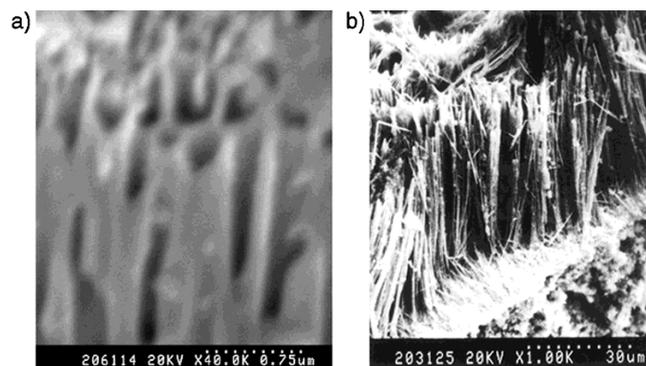


Fig. 1. Scanning electron micrographic images of a) polyaniline nanotubules and b) polyaniline nanotubules filled with cobalt nanowires obtained after dissolution of alumina.

The morphology of the array of cobalt nanowires encapsulated within polyaniline nanotubules (abbreviated as APC) inside the pores of the alumina template membrane has been studied by scanning electron microscopy (SEM). Figure 1b is an image of a cross section of a nanowire array after removing the top alumina layer with 6 N NaOH. In most cases, the length of the nanowires corresponds to the membrane thickness (about 60  $\mu\text{m}$ ) suggesting that the wires are mechanically stable under the sample preparation conditions.

The typical X-ray diffraction pattern of the sample (which was exposed to the air for two weeks before determination) is shown in Figure 2. The peaks can be regarded as due to cobalt and silver. The silver atom comes from the silver paste film,

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