Chapter Six

“Hairy tubes”: Mesoporous materials containing hollow self-organized cylinders with polymer brushes at the walls


Abstract
In this chapter, a route to prepare “hairy tubes” is presented. Hydrogen-bonded supramolecules, based on PS-block-P4VP, self-organize into cylinders in a glassy rigid PS-matrix. Annealing the material and applying oscillatory shear flow increases the macroscopic order of the cylinders. Part of the supramolecular complex, i.e. PDP, can be conveniently washed out using methanol after the structure has been formed. Thus, empty tubes with P4VP “hairs” on the walls are obtained. This simple method allows tailoring the tubes and the transport properties, for example by tuning the block lengths or by chemical modification of the hairs.
6.1 Introduction

Self-organization leads to nanoscale polymeric structures based on competing interactions,\(^1,2\) and incorporation of several schemes of self-organization renders hierarchical structures.\(^1,3-6\) 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,\(^7,8\) and they self-organize to form structure-within-structures.\(^5,6,9\) Here, we demonstrate that the scheme allows the preparation of mesoporous materials. The starting material is diblock copolymer polystyrene-\emph{block}-poly(4-vinyl pyridine), PS-\emph{block}-P4VP, with a stoichiometric amount of pentadecyl phenol, PDP, hydrogen bonded to the latter block. The block lengths have been selected to render a lamellar-within-cylindrical morphology, where at room temperature 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\(^10\) 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 at 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 e.g. in purification. Potential concepts have been demonstrated based on mesoporous materials due to organic/inorganic assemblies,\(^11-13\) crosslinked structures of amphiphiles containing crown ethers,\(^14,15\) mesotubes based on degradable polymer fibers as templates,\(^16\) polymerized tubes with polyacrylic acid brushes obtained by degradation process,\(^17,18\) self-organization of rod-coil copolymers,\(^19\) nanoporous carbon membranes,\(^20\) to mention a few.

In this work, we introduce a facile method to construct mesoporous materials, based on physically matching molecules as templates. Comb coil diblock
copolymers form a specific architecture of self-organizing block copolymers\textsuperscript{2,21,22} where 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.\textsuperscript{23,24} 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 with a long period of 36 Å.\textsuperscript{25} If such receptor-substrate supramolecule is selected to be one block of a diblock copolymer, a comb coil supramolecule PS-\textit{block}-P4VP(PDP)\textsubscript{1.0} is formed, capable of hierarchical self-organization.\textsuperscript{5,6,9}

In this work the block lengths are selected so that the weight fraction of the P4VP(PDP)\textsubscript{1.0} block is 0.25, as we aim at P4VP(PDP)\textsubscript{1.0} cylinders within a glassy PS-matrix. The advantage of using hydrogen bonded supramolecule template PS-\textit{block}-P4VP(PDP)\textsubscript{1.0} instead of conventional block copolymer molecules is that the cylinders can be emptied easily, as part of the template, i.e. the oligomeric PDP, “flows” easily out from the cylinders 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.

6.2 Experimental section

6.2.1 Materials

PS-\textit{block}-P4VP (Polymer Source Inc.) had $M_w = 34,000$ g/mol and 2,900 g/mol, respectively, for the PS and P4VP blocks and $M_w/M_n = 1.07$ for the complete polymer. 3-\textit{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-\textit{block}-P4VP(PDP)\textsubscript{1.0} were prepared by dissolving both components, PS-\textit{block}-P4VP and PDP, in analysis grade chloroform. Stoichiometric molar amounts of PDP was used, i.e., one alkyl phenol 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 hrs.
6.2.2 Dynamic rheological orientation and SAXS

First the samples were heated to 120 °C in a cylindrical mold of 10 mm in diameter. During the first 0.5 hrs no pressure was applied and the material was allowed to freely flow to the mold. Subsequently, a piston exerted a pressure of 10 bars 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. Shear flow orientation was accomplished by a Bohlin CSM-50 stress-controlled rheometer in an oscillating mode using parallel plate geometry. The sample was heated to 150 °C and then annealed at 125 °C for 6 hrs to obtain a homogeneous sample and a good contact to the plates. The oscillation was performed at 125 °C using the frequency 0.5 Hz and 20 % strain amplitude for 2.1 hrs.

Small angle X-ray Scattering was performed in-situ during the above oscillatory 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 \( \lambda = 1.54 \text{ Å} \). Three pinholes collimate the beam over 1.5 m to a diameter of about 1 mm at the sample position. Siemens multiwire type area detector was used. The sample-detector distance was 1.2 m, yielding an angular resolution of \( \Delta \theta \approx 0.07^\circ \) or \( \Delta q \approx 0.005 \text{ Å}^{-1} \). The scattering vector \( q \) is defined as \( q = \frac{4\pi}{\lambda} \sin \theta \) with \( \theta \) 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. For this an ARES (Rheometric Scientific Inc.) rheometer was used in oscillating mode in parallel plate geometry. The gap was 1 mm. The sample was heated up to 150 °C and then annealed at 120 °C for 1 h. The oscillation was performed at 120 °C for 16 hrs using 0.1 Hz and 50% strain amplitude.

The Bruker NanoSTAR equipment used for the ex-situ SAXS consisted of a Kristalloflex K760-8- 3.0kW X-ray generator with cross-coupled Göbel mirrors for \( \text{Cu K}_\alpha \) radiation (\( \lambda = 1.54 \text{ Å} \)), resulting in a parallel beam of about 0.05mm\(^2\) at sample position. A Siemens multiwire type area detector was used. The sample-detector distance was 0.65 m. The SAXS intensity patterns were measured at room
temperature in tangential, normal and radial views, i.e., with the incident beam along the 1-, 2- and 3-direction respectively.

6.2.5 Preparation of hollow cylinders

After the 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 analysis-grade methanol at room temperature for at least 12 hrs 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 to the original measurements.

6.2.6 FTIR – spectroscopy

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

6.3 Results and discussion

We will first address the structure. Fig. 6.1 shows the isotropic SAXS-intensity pattern of PS-block-P4VP(PDP)$_{1.0}$ at room temperature before shear orientation. A SAXS peak is observed at $q_2^* = 0.165$ Å$^{-1}$. It corresponds to the lamellar order of P4VP(PDP)$_{1.0}$ complex with the long period 36 Å. Note that in the corresponding homopolymer complex, the second order peak at $2q_2^*$ becomes faintly observable using synchrotron radiation, indicating lamellar order. In addition, Fig. 6.1 shows another peak at $q_1^* = 0.03$ Å$^{-1}$, corresponding to a structure at an order of magnitude larger length scale. The structure corresponding to the latter peak can be easily identified after annealing at 125 °C for 6 hrs, which renders in an oriented sample a six spot pattern at the magnitude of the scattering vector $q_1^* = 0.03$ Å$^{-1}$, demonstrating a hexagonal order (see Fig. 6.2). Upon oscillation at the same
Figure 6.1. SAXS intensity pattern of PS-block-P4VP(PDP)$_{1.0}$ at room temperature before annealing and before orientation. Two characteristic peaks are observed. The peak at $q^*_{1} = 0.03 \text{ Å}^{-1}$ corresponds to the formation of P4VP(PDP)$_{1.0}$ cylinders within the PS-medium (see Fig. 6.5). The peak at $q^*_{2} = 0.165 \text{ Å}^{-1}$ corresponds to the lamellar order within the P4VP(PDP)$_{1.0}$ cylinders. From the previous studies the latter structure is known to have an order-disorder transition at ca. 65 °C.$^{9,10}$

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 Fig. 6.2a using SAXS in the tangential direction during cooling at 50 °C. Further decrease of temperature caused a less regular SAXS pattern (Fig. 6.2b) possibly due to deformation caused by the shrinking material and formation of the second structure due to P4VP(PDP)$_{1.0}$. Fig. 6.3 shows more comprehensive ex-situ SAXS patterns in the tangential, normal, and radial directions performed after the oscillation was terminated. The smaller structure at $q^*_{2} = 0.17 \text{ Å}^{-1}$ 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 oscillatory 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 hrs in methanol (which is a nonsolvent for the glassy PS, but a solvent for both P4VP and PDP), dried, and studied using SAXS and FTIR. As shown in Figs. 6.3 and 6.4, the SAXS peaks, which correspond to the self-organization of the cylinders within the glassy PS medium remained unchanged
Figure 6.2. In-situ SAXS patterns for PS-block-P4VP(PDP)$_{1,0}$ in the tangential direction after annealing and oscillatory shear orientation at 125 °C. a) During cooling at ca. 50 °C, a well defined hexagonal array of cylinders is shown with the magnitude of the scattering vector $q_1^* = 0.03$ Å$^{-1}$; b) After reaching room temperature, a less perfect structure is obtained, possibly due to thermal shrinkage and formation of the smaller P4VP(PDP)$_{1,0}$-structure. Note that the smaller structure of P4VP(PDP)$_{1,0}$ is ideally not observable at the tangential beam orientation and the faint signal in b) is only due to non-idealities.

upon methanol treatment, whereas the peak corresponding to the lamellar self-organization of P4VP(PDP)$_{1,0}$ within the cylinder at $q_2^* = 0.17$ Å$^{-1}$ disappeared due to removal of PDP. So it seems to be possible to obtain nanometer-sized almost empty cylindrical tubes in a macroscopic piece of polymer material (typically some mm$^3$).

Next the effect of PDP removal on the SAXS peak at $q_1^* = 0.03$ Å$^{-1}$ is studied in more detail. Firstly, methanol washing drastically increases the peak (see Table 6.1). The densities of PS and P4VP(PDP)$_{1,0}$ are close to each other (Table 6.2).$^9$ These densities allow us to evaluate the average electron densities. The SAXS scattering intensity is directly proportional to mean square electron density fluctuation. In a two phase system

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

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.$$^27$ A simple
Figure 6.3. SAXS intensity patterns for PS-block-P4VP(PDP)$_{1.0}$ in the a) tangential, b) normal, and c) radial directions before and after immersion in methanol to remove the PDP. The peak at $q_1^* = 0.03\,\text{Å}^{-1}$ corresponds to the self-organization of cylinders in the PS matrix, whereas $q_2^* = 0.17\,\text{Å}^{-1}$ corresponds to the lamellar order within the P4VP(PDP)$_{1.0}$ cylinders. The former suggests that the cylinders are mainly oriented along the shear direction ($i$), whereas the small structure is aligned perpendicular to the cylinders (lamellar normal in $I$-direction). The tilt in b) is caused by misalignment of the sample in the SAXS beam. Note the intensity increase after immersion in methanol.
Figure 6.4. Scattering intensity before and after immersion in methanol (radial direction). After washing out the PDP, the intensity has increased and the peak at \( q_2^* = 0.17 \text{ Å}^{-1} \), corresponding to the small length scale structure is absent.

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, i.e. assuming a two-phase system. Originally, the tubes are filled with P4VP(PDP)\(_{1.0}\) and after methanol washing, it is assumed that there is only P4VP and empty space, see Fig. 6.5. Using the electron scattering densities of Table 6.2, 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 e.g. 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.

Table 6.1: SAXS scattering intensities of the peak \( q_1^* = 0.03 \text{ Å}^{-1} \) corresponding to the cylindrical organization of PS-block-P4VP(PDP)\(_{1.0}\) 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.

<table>
<thead>
<tr>
<th></th>
<th>( I_{\text{before}} )</th>
<th>( I_{\text{after}} )</th>
<th>( I_{\text{after}}/I_{\text{before}} )</th>
</tr>
</thead>
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<tr>
<td><strong>Experimental:</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tangential</td>
<td>122</td>
<td>3437</td>
<td>28</td>
</tr>
<tr>
<td>Normal</td>
<td>24</td>
<td>2500</td>
<td>104</td>
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<tr>
<td>Radial</td>
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<td>2583</td>
<td>41</td>
</tr>
<tr>
<td><strong>Theoretical:</strong></td>
<td></td>
<td></td>
<td>329</td>
</tr>
</tbody>
</table>
Figure 6.5. Schematic picture of the procedure 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.

Table 6.2: (Electron) densities of PS, P4VP and P4VP(PDP)$_{1.0}$.

<table>
<thead>
<tr>
<th></th>
<th>P4VP$^1$</th>
<th>PS</th>
<th>P4VP(PDP)$_{1.0}$</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td></td>
<td>1.047</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>Electron scattering density ($10^{10}$ cm$^{-2}$) $a\rho_e^3$</td>
<td>10.08</td>
<td>9.5</td>
<td>9.12</td>
<td></td>
</tr>
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This is also demonstrated by FTIR spectroscopy, see Fig. 6.6. FTIR spectra were measured for the washed diblock system and compared to 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 cm$^{-1}$, which is characteristic for hydrogen-bonded pyridine, is no longer observed in the washed sample.$^{28}$ Also this shows that it is possible to remove almost all PDP from the material.

### 6.4 Conclusion

In this chapter, we demonstrated a route to prepare self-organized hollow cylinders in a glassy rigid PS-medium. The cylinders are formed due to self-organization of hydrogen-bonded supramolecules. Part of the supramolecular template, i.e. PDP, can be conveniently removed at the end, after the structure has been formed, thus

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1 from ref $^{29}$

2The measured density of P4VP(PDP)$_{1.0}$ $^{9}$ and electron scattering density approximated based on it.

3 Here $a$ is the classical electron radius $2.8 \times 10^{-13}$ cm and $\rho_e$ is the mean electron density.
overcoming the need to use degradation or corresponding methods to empty the tubes. The cylinders show relatively high macroscopic order due to annealing. The order can be improved by oscillatory shear flow, however. The concept allows generalization and tailoring. Transport properties and tailoring of the tubes are subject to our forthcoming studies.

6.5 References