PS-b-P4VP(PDP) comb-shaped supramolecules
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Nanorods consisting of a polystyrene (PS) core and a poly(4-vinylpyridine) (P4VP) shell produced via the self-assembly route of comb-shaped supramolecules exhibit very poor mechanical properties as a result of the absence of entanglements in the rods. Adding a sufficient amount of poly(2,6-dimethyl-1,4-diphenyl oxide) (PPE) introduces entanglements to the PS core resulting in nanorods with much better properties, which can be used as templates for e.g. transition metal oxide tubes.
2.1 Introduction

As has been amply demonstrated in the previous chapter, self-assembling block copolymers are of great interest as building blocks for various nanotechnology applications. Simple examples include nanoporous membranes and nanorods, which can be obtained by removing the minority resp. majority block of a cylindrically microphase separated block copolymer. If block copolymers are combined with supramolecular concepts to form e.g. comb-shaped supramolecules, additional possibilities arise and the procedures to form e.g. nanoporous membranes and nanorods are in some respects even simpler, as the additives used to create the supramolecules may be easily washed away (Figure 1.13). Typically, nanorods synthesized via the comb-shaped supramolecules route consist of diblock copolymers, with one block forming the core and the other forming the corona. The characteristic element of the supramolecular route, setting it apart from nanorods prepared via the traditional pure block copolymer approach, is the fact that for a given diameter of the rods, the corona may be considerably thinner than for pure block-copolymer systems. No longer does the core block have to be the minority block as becomes clear from the following example.

To prepare comb-shaped supramolecules, a block copolymer of PS and P4VP, PS-b-P4VP, is hydrogen bonded with alkylphenols with one alkylphenol molecule per pyridine group. The block lengths of the block copolymer are selected in such a way that the self-assembly gives rise to hexagonally ordered PS cylinders in a P4VP(alkylphenol) matrix. To arrive at this structure the volume fraction of the P4VP complex has to be of the order of 0.7-0.8 (see Figure 1.12). Since, for the alkylphenols used, e.g. dodecylphenol (DDP) or pentadecylphenol (PDP), the alkylphenol moiety corresponds to 70-75 w/w% of the complex, this can even be achieved if the P4VP block has a considerably lower molar mass than the PS block. From the hexagonally self-assembled structure it is possible to produce nanorods with a PS core and a P4VP corona by simply removing the alkylphenol molecules by dialysis with ethanol. The nanorods produced in this way generally have a length not exceeding 1 µm. Substantially longer nanorods, in the order of 10 µm or more, may be obtained if the cylindrical structure is first aligned by large amplitude oscillatory shear. The use of polymeric nanorods as templates for the production of polymer, metal, and hybrid nanotubes was discussed by Greiner and co-workers. They coined the phrase TUFT (tubes by fiber templates) for the concept of coating degradable template polymer fibers with the desired wall materials using various deposition techniques. Nanotubes are
subsequently obtained by removal of the core material. In this case, the P4VP corona makes the core-shell nanorods potentially very interesting as templates for e.g. transition metal oxide nanotubes. Such applications require the nanorods to possess sufficient mechanic properties to allow handling and manipulation. However, due to the specific orientation of the copolymer blocks away from the interface, the above procedure in general leads to a core-shell structure without entanglements between the molecules. Hence, very poor mechanical properties are expected. It is the objective of this study to show that this is indeed the case and to introduce a simple procedure to remedy this drawback.

2.2 Experimental section

2.2.1 Materials and sample preparation

Polishing of alumina membranes. As substrates for the measurements of the mechanical properties of the nanorods, alumina (aluminum oxide) ultrafiltration membranes (Whatman Anodisc, 200 nm pores) were used. Before use, the membranes were carefully polished for 70 min on a Kent polishing machine. The slowest rotation speed was used...
with a soft polishing pad (Kemet Int. Limited, MBL, 150 mm) and Buehler Masterpolish® 2 polishing medium as the polishing slurry. The membranes were attached to the wafer carrier with beeswax as the carrier film (Figure 2.1).

**Nanorod preparation.** A diblock copolymer of PS and P4VP, P105-S4VP with \( M_n(PS) = 21400 \text{ g mol}^{-1} \), \( M_n(P4VP) = 20700 \text{ g mol}^{-1} \) and \( M_w/M_n = 1.13 \), acquired from Polymer Source, Inc. was used. Homopolymer PS (\( M_n = 20800 \text{ g mol}^{-1} \), \( M_w/M_n = 1.07 \)) and homopolymer PPE (\( M_n = 25.700 \text{ g mol}^{-1} \), \( M_w/M_n = 1.37 \)) were also acquired from Polymer Source, Inc. The polymers were used without further purification. 4-Dodecylphenol was purchased from Aldrich as a mixture of isomers and was used as received.

To obtain the comb-shaped PS-\( b \)-P4VP(DDP) supramolecules, about 0.2 g of PS-\( b \)-P4VP was hydrogen bonded with a stoichiometric (with respect to the number of pyridine groups) amount of DDP. The samples were prepared by mixing PS-\( b \)-P4VP and the DDP in analytical grade chloroform, keeping the concentration below 2 wt% to ensure homogeneous complex formation. After stirring for 2 to 3 h, the solution was poured into a petri dish and the solvent was allowed to evaporate slowly overnight. After this, the sample was further dried in a vacuum oven at 40 °C for at least 48 h. For the reinforced polymers, different amounts of PPE were added to the mixture. All samples used are listed in Table 2.1, and on the basis of the comb weight fraction all fall within the cylindrical morphology range as further verified with SAXS. Subscripts denote the weight fraction of PPE in the PS domains of the self-assembled PS-\( b \)-P4VP(DDP) supramolecules.

Shearing was carried out with an AR 1000N rheometer (TA Instruments) in oscillatory mode with a cone–plate geometry (4° cone, 20 mm diameter). The oscillatory shear was performed with a constant shear frequency of 1 Hz and a strain amplitude of 50 %. The samples were

<table>
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<th>Table 2.1. Systems investigated.</th>
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<tr>
<td>Sample</td>
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<tr>
<td>P105(DDP)</td>
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<td>P105(DDP)/PPE(_{0.09})</td>
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<td>P105(DDP)/PPE(_{0.17})</td>
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<td>P105(DDP)/PPE(_{0.23})</td>
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<td>P105(DDP)/PPE(_{0.28})</td>
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<td>P105(DDP)/PS(_{0.28})</td>
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</table>
2.2 Experimental section

sheared for 2 h at 130 °C. After the alignment procedure part of the sample was placed in a dialysis tube of 29 mm diameter (SERVAPOR, cutoff M = 12000, Serva) filled with ethanol and dialyzed against ethanol for about 2 weeks. After 1 week, the solvent was replaced and after 2 weeks, the nanorod suspension in ethanol was recovered from the dialysis tube.

2.2.2 Instrumental methods

**Atomic Force Microscopy.** For the AFM measurements a small drop of a nanorod suspension was cast on a piece of polished ultrafiltration membrane and the ethanol was allowed to evaporate for several minutes before measuring. Tapping mode AFM measurements were carried out on a Digital Instruments MultiMode AFM equipped with a Nanoscope IIIa controller. Etched silicon cantilevers (Veeco, model TESP) were used.

**Small Angle X-ray Scattering.** SAXS measurements were carried out at room temperature using a NanoStar camera (Bruker and Anton Paar). A ceramic fine-focus X-ray tube, powered with a Kristallflex K760 generator at 35 kV and 40 mA, has been used in point focus mode. The primary X-ray flux is collimated using cross-coupled Göbel mirrors and a pinhole of 0.1 mm in diameter providing a Cu Kα radiation beam with a full width at half-maximum of about 0.2 mm at the sample position. The sample-detector distance was 1.04 m. The scattering intensity was registered by a Hi-Star position-sensitive area detector (Siemens AXS) in the q range of 0.1-2.0 nm⁻¹. The scattering vector q is defined as \( q = \left(\frac{4\pi}{\lambda}\right) \sin \left( \frac{\theta}{2} \right) \), where \( \lambda = 0.1542 \) nm and \( \theta \) is the scattering angle. The measuring time was 1 hour.

**Scanning Electron Microscopy.** SEM measurements were performed on a JEOL 6320F field emission scanning electron microscope operating at 3 kV (rods without PPE) or 1 kV (rods with PPE). Samples were coated with a ~2 nm layer of 80 % Pt and 20 % Pd under a rotating angle of 45 ° before measuring.

**Differential Scanning Calorimetry.** Temperature-modulated DSC was performed using a DSC 2920 (TA Instruments). Measurements were performed using a heating rate of 1 °C min⁻¹, an oscillation amplitude of 1 °C, and an oscillation period of 60 seconds. Samples were measured up-down-up and \( T_g \) values were taken from the reversing heat-flow data of the second heating.
2.3 Results and discussion

2.3.1 Alumina membranes

Whatman Anopore alumina membranes are produced via anodization of aluminum in certain acid electrolytes, e.g. phosphoric acid. Upon anodization, a porous oxide develops at the surface of the aluminum anode. This oxide has a uniform hexagonal array of pores, the size of which can be controlled by the anodizing voltage. The thickness of the film is determined by the current density and the anodizing time. However, there always exists a nonporous aluminum oxide barrier layer at the aluminum interface. In order to easily detach the porous film from this barrier layer, the barrier layer thickness is reduced in a few steps by lowering the anodizing voltage. The pores are then divided into smaller pores as the barrier layer becomes thinner, and finally the film detaches from the aluminum. This results in an asymmetric membrane structure: larger pores extending through the bulk of the thickness, with a very thin “skin” at the surface that was originally attached to the aluminum. This skin has a 20 nm poresize, and can subsequently be converted into larger poresizes by dissolving the fine pore layers and thinning the porewalls.15,16

![Figure 2.2. SEM picture of an unpolished alumina membrane with 200 nm pores.](image-url)
2.3 Results and discussion

A SEM image of this result for a membrane with 200 nm pores (acquired from Whatman) is shown in Figure 2.2. As can be seen, the surface of the membrane is very rough, and although the resulting pores have a uniform size, they are not well ordered.

In order to create a flat, porous surface for testing the properties of the nanorods, the 200 nm membranes were polished by a chemical mechanical polishing procedure, the result of which is shown in Figure 2.3. The polishing resulted in removal of the top layer of smaller pores, and what effectively is uncovered is the transition where smaller pores combine into bigger pores, explaining the non-uniform pore size. From the height profile however, the flat nature of the surface after polishing can easily be seen. Due to the pyramidal shape of the AFM tip it can not enter the pores completely, and the maximum depth in the height profile does not correspond to the true depth of the pores. Instead, the slope of the pore walls of ~30 ° closely reflects the tip angle of ~25 ° specified by the manufacturer.

2.3.2 Nanorod properties

Figure 2.4 illustrates the procedure to produce core-shell nanorods via the comb-shaped supramolecules route using suitable PS-\textit{b}-P4VP diblock copolymers together with PDP. Apart from the hexagonally ordered PS-cylinders, the P4VP(PDP) matrix is further self-assembled in a lamellar morphology below ca. 60 °C.\textsuperscript{17}

![Figure 2.3. Height AFM and profile of a polished alumina membrane.](image-url)
Chapter 2

The shear itself takes place at elevated temperatures (e.g. 120 °C) where the P4VP(PDP) matrix is still in a disordered state. In the case of dodecylphenol (DDP) the alkyl tail is too small to give rise to self-assembly of the P4VP(DDP) matrix even at temperatures as low as room temperature. This is reflected by the absence of an ODT endotherm in the DSC curve of DDP systems. Because of this absence of the ODT as well as the lack of any crystallization of the sidechains, the $T_g$'s in the system can easily be identified with DSC. DSC thermograms of these systems show one $T_g$ near 78 °C and a broad $T_g$ around room temperature. The $T_g$ at

![Figure 2.4](image1.png) Nanorod preparation from hexagonally self-assembled PS-b-P4VP(PDP). The same principle applies in the case of DDP except that the lamellar morphology of the matrix is not present.

![Figure 2.5](image2.png) Cartoon of PS-b-P4VP nanorod cross section with PS core and P4VP corona. Due to the orientation of the PS blocks away from the PS-P4VP interface and the low $M_e$ no entanglements are expected.
room temperature corresponds to P4VP, which is substantially lowered due to the presence of DDP. The fact that DDP was bought as a mixture of isomers may very well cause the broadness of the $T_g$. The $T_g$ at 78 °C corresponds to PS, which is also lowered from its normal value of ~100 °C due to the presence of a small amount of DDP in the PS domains, acting as a plasticizer (see Chapter 3). In systems with PDP, where the $T_g$'s can not be observed with DSC, these are situated under the ODT of $T_g$(PDP) (~60 °C) and the melting endotherm of PDP (~20 °C).

In the present chapter the focus lies on DDP but similar experiments have been performed using PDP. The PS-\textit{b}-P4VP diblock copolymer used in the experiments has a molar mass of $M_n$(PS) = 21400, $M_n$(P4VP) = 20700 and $M_w/M_n = 1.13$. For bulk polystyrene, the molar mass between entanglements equals $M_e$(PS) = 19100. However, despite the fact that the PS-block has a slightly larger molar mass, due to specific orientation of the copolymer blocks away from the interface, no entanglements between the molecules should be expected (Figure 2.5). This results in very poor mechanical properties as can be easily demonstrated in the following way.

First, the nanorods were prepared according to the procedure described above. SAXS of a sheared PS-\textit{b}-P4VP(DDP) sample taken with the X-ray beam parallel to the shear direction, demonstrated a good hexagonal alignment of self-assembled PS-cylinders. The first order peaks are at $q^* = 0.221$ nm$^{-1}$ and the PS-\textit{b}-P4VP nanorods obtained after removing the DDP are estimated to have a diameter of $d = 23$ nm. A droplet of the PS-\textit{b}-P4VP nanorods dispersed in ethanol was put on a nanoporous

![Figure 2.6](image.png)

*Figure 2.6. (a) AFM height image (\Delta z \sim 150$ nm) and (b) SEM of PS-\textit{b}-P4VP nanorods on a polished alumina ultrafiltration membrane.*
alumina membrane with Figure 2.6a showing a characteristic AFM picture of the outcome. Invariably, those parts of the rods on top of the pores simply disappeared inside the pores. As scanning electron microscopy (Figure 2.6 b) confirmed the absence of rods bridging the pores, the rods do not disappear due to the AFM tip breaking the nanorods, but the observed behavior is rather the result of the capillary forces arising during the evaporation of the ethanol, illustrated in Figure 2.7.19

2.3.3 Addition of PPE

In order to improve the mechanical properties, homopolymer PPE with molar mass $M_n = 25700$ g mol$^{-1}$, was added to the system. PPE is well known for its excellent thermodynamic miscibility with polystyrene.20 Therefore, when combined with PS-$b$-P4VP(DDP), PPE will segregate into the PS-cylinders even if its molar mass is larger than that of the PS-block. Since the molar mass between entanglements $M_e$ of pure PPE is only 4300,18 the PPE molecules, being diluted by the PS blocks, will form entanglements above a critical concentration.

To what extent the PPE mixes with the PS blocks protruding from the interface is not known yet. At any rate, the presence of the PS blocks will lead to a larger molar mass between entanglements compared to pure PPE. If homogeneous mixing is assumed, an upperbound for the molar mass between entanglements can be simply estimated using $M_e(x) \approx M_e(x = 1.0)/x$, where $x$ is the weight fraction PPE in the core.18 Since a PPE with $M_n = 25700$ g mol$^{-1}$ was used, this relation implies that a weight fraction of $x \approx 0.17$ is sufficient to introduce entanglements. Experiments using $x = 0.28, 0.23, 0.17$ and $0.09$ were performed to test this prediction. In all four cases, the presence of the hexagonally self-assembled morphology was

![Figure 2.7. Illustration of capillary forces working on the PS-b-P4VP nanorods during the evaporation of ethanol.](image)
confirmed by SAXS. For the highest amount of PPE used, the first order peaks were at $q^* = 0.192 \text{ nm}^{-1}$ and after removing the DDP, the rods are estimated to have a diameter of $d = 28 \text{ nm}$, which is about 5 nm more than in the absence of PPE.

AFM experiments (Figure 2.9) showed that the reinforcement effect of the added PPE indeed resulted in rods spanning the pores for the highest amount of PPE used, i.e. when the weight fraction of PPE was 0.28. For smaller amounts the rods essentially behaved as those without PPE (cf. Figure 2.6), being apparently still too weak to span pores of ca. 200 nm in size. The effect is not simply due to the larger diameter of the nanorods. Using homopolymer polystyrene of $M_n = 20800$ instead of PPE, nanorods
with an even larger diameter were prepared ($q^* = 0.169 \text{ nm}^{-1}, d = 32 \text{ nm}$), which, however, were too weak to span the pores. The larger rod diameter of rods with homopolymer PS as compared to the rods with the same weight fraction of PPE is a strong indication that PPE is quite uniformly distributed within the PS phase. The exact distribution of PPE within the PS phase will be dealt with in the next chapter.

### 2.4 Conclusion

In conclusion, it was demonstrated that the mechanical properties of core-shell nanorods, obtained via self-assembly of comb-shaped supramolecules, were initially quite poor due to the absence of entanglements in the PS core. To improve the properties, homopolymer PPE was added and nanorods with a PS/PPE-core and P4VP-corona were obtained that, for the highest amount of PPE used, withstood the capillary forces when a droplet of a nanorod suspension in ethanol was put on the alumina ultrafiltration membranes. This PPE-reinforcement may have important implications for the use of these kind of materials, e.g. as templates for oxidic nanotubes.²¹

### 2.5 References
