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Nanorod engineering by reinforcing hexagonally self-assembled PS–*b*–P4VP(DDP) with PPE

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Nanorods consisting of a polystyrene core and a poly(4-vinylpyridine) shell produced *via* the self-assembly route of comb-shaped supramolecules exhibit very poor mechanical properties. Adding a sufficient amount of poly(2,6-dimethyl-1,4-diphenyl oxide) 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.

Introduction

Self-assembling block copolymers are of great interest as building blocks for various nanotechnology applications.[1–5] Simple examples include nanoporous membranes[6,7] and nanorods.[8] 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.[9–11] Typically, the nanorods synthesised *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 polystyrene (PS) and poly-4-vinylpyridine (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. 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 polystyrene core and a poly(4-vinylpyridine) 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.[12]

The use of polymeric nanorods as templates for the production of polymer, metal, and hybrid nanotubes was discussed by Greiner and co-workers.[13] 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 our case, the P4VP corona makes the core–shell nanorods potentially very interesting as templates for *e.g.* transition metal oxide nanotubes.[14] 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.

Experimental

Polishing of alumina membranes

As substrates for the AFM measurements, 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.

Nanorod preparation

A diblock copolymer of polystyrene and poly(4-vinyl pyridine) (PS–*b*–P4VP) was used (M_n (PS) = 21 400, M_n (P4VP) = 20 700 and M_w/M_n = 1.13, Polymer Source, Inc.). To reinforce the nanorods, homopolymer poly(2,6-dimethyl-1,4-diphenyl oxide) (PPE) was used (M_w = 25 700 g mol^{-1}, M_w/M_n = 1.37), also acquired from Polymer Source, Inc. The polymers were

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Sample	Comb weight fraction
PS–b–P4VP(DDP)	0.772
PS–b–P4VP(DDP)/PPE$_{0.09}$	0.757
PS–b–P4VP(DDP)/PPE$_{0.17}$	0.743
PS–b–P4VP(DDP)/PPE$_{0.23}$	0.733
PS–b–P4VP(DDP)/PPE$_{0.28}$	0.726

used without further purification. 4-Dodecylphenol (DDP) 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 analysis 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 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 constant shear frequency of 1 Hz and strain amplitude of 50%. The samples were 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 $M = 12\,000$, 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.

AFM measurements

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.

SAXS measurements

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 $q = (4\pi/\lambda) \sin (\theta/2)$, where $\lambda = 0.1542$ nm and θ is the scattering angle. The measuring time for most samples was 1 h.

Results and discussion

The following cartoon (Fig. 1) illustrates the procedure to produce core–shell nanorods via the comb-shaped supramolecules route using suitable PS–b–P4VP diblock copolymers together with pentadecylphenol (PDP). Apart from the hexagonally ordered PS-cylinders, the P4VP(PDP) matrix is further self-assembled in a lamellar morphology below ca. 60 °C.[15] 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.

In the present study we focus on DDP but similar experiments have been performed using PDP. The PS–b–P4VP diblock copolymer used in our experiments has a molar mass of M_n (PS) = 21 400, M_n (P4VP) = 20 700 and $M_w/M_n = 1.13$. For bulk polystyrene, the molar mass between entanglements equals M_e (PS) = 19 100.[16] However, despite the fact that the PS-block has a slightly larger molar mass, due to specific
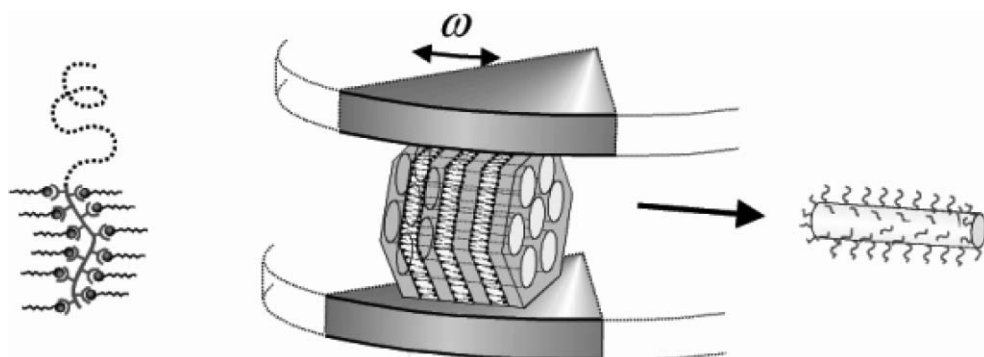

Fig. 1 Nanorod preparation from hexagonally self-assembled PS–b–P4VP(PDP).[9,12] The same principle applies in the case of DDP except that the lamellar morphology of the matrix is not present.
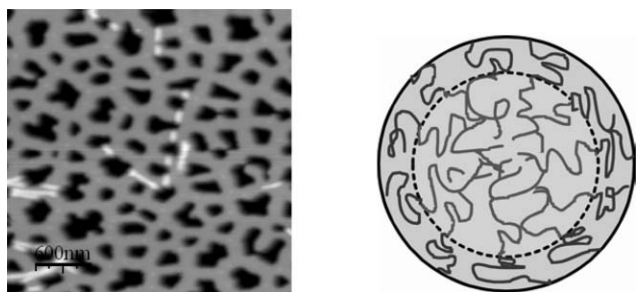
Fig. 2 AFM of PS–*b*–P4VP nanorods on a polished alumina ultrafiltration membrane. Cartoon presents PS–*b*–P4VP nanorod cross section with PS core and P4VP corona.

Fig. 4 AFM pictures of suspended PS/PPE–*b*–P4VP nanorods on a polished alumina ultrafiltration membrane. The rods are deflected about 40 nm in the middle of the pore probably due to the force exerted by the AFM tip. Cartoon illustrates the presence of additional homopolymer (PPE) in the core of the PS–*b*–P4VP nanorod.

orientation of the copolymer blocks away from the interface, no entanglements between the molecules should be expected. 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–*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–*b*–P4VP nanorods obtained after removing the DDP are estimated to have a diameter of $d = 23$ nm. A droplet of the PS–*b*–P4VP nanorods dispersed in ethanol was put on a nanoporous alumina membrane with Fig. 2 showing a characteristic AFM picture of the outcome. Invariably, those parts of the rods on top of the pores simply disappeared inside the pores.

Scanning electron microscopy confirmed the absence of rods bridging the pores. Hence, it is not due to the AFM tip breaking the nanorods, but rather the result of the capillary forces arising during the evaporation of the ethanol, illustrated in Fig. 3.[17]

In order to improve the mechanical properties, homopolymer poly(2,6-dimethyl-1,4-diphenyl oxide), PPE, with molar mass $M_w = 25\ 700$ g mol^{-1}, was added to the system. PPE is well known for its excellent thermodynamic miscibility with polystyrene.[18] 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,[16] 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
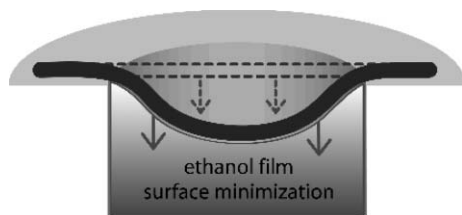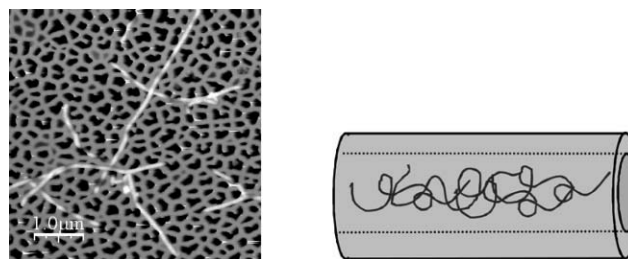
blocks will lead to a larger molar mass between entanglements compared to pure PPE. If we assume homogeneous mixing, an upperbound for the molar mass between entanglements can be simply estimated using $M_e(x) \cong M_e(x = 1.0)/x$, where x is the weight fraction PPE in the core.[16] Since a PPE with $M_w = 25.700$ g mol^{-1} was used, this relation implies that a weight fraction of $x \cong 0.17$ 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 confirmed by SAXS. For the highest amount of PPE used, the first order peaks were at $q^* = 0.192$ nm^{-1} and after removing the DDP, the rods are estimated to have a diameter of $d = 28$ nm, which is about 5 nm more than in the absence of PPE. AFM experiments (Fig. 4) 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.* Fig. 2), 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 ($M_n = 20\ 800$, $M_w/M_n = 1.07$) instead of PPE, nanorods with similar diameter were prepared, which, however, were too weak to span the pores.

In conclusion, we have demonstrated that the mechanical properties of core–shell nanorods, obtained *via* self-assembly of comb-shaped supramolecules, were initially quite poor. 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 ethanol suspension 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.

Acknowledgements

Fig. 3 Illustration of capillary forces working on the PS–*b*–P4VP nanorods during the evaporation of ethanol.

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