Mesoporous Block Copolymer Nanorods by Swelling-Induced Morphology Reconstruction

Yong Wang,* Ulrich Gösele, and Martin Steinhart*

Max Planck Institute of Microstructure Physics, Weinberg 2, D-6120 Halle, Germany

Received July 27, 2008; Revised Manuscript Received August 20, 2008

ABSTRACT

Engineering the topography of thin block copolymer (BCP) films by surface reconstruction associated with selective swelling of one of the blocks has been investigated intensively. Here we show that swelling-induced structural transitions in nanorods consisting of amphiphilic BCPs involve pronounced reshaping of the nonswollen glassy domains in the course of the transition from the equilibrium morphology of the molten BCP in cylindrical confinement to that of the BCP dissolved in the swelling agent. The reconstruction process can be quenched to retain intermediate nonequilibrium morphologies. The collapse of the swollen chains upon drying yields polymeric nanorods exhibiting complex nanoscopic architectures characterized by a variety of mesopore structures and surface topographies, including channels along the nanorods, bunches of partially interconnected strands, and strings of spheres. The complex BCP nanorods thus obtained can be used as soft templates for the rational arrangement of metal nanoparticles.

Block copolymers (BCPs) are versatile molecular soft templates for the rational design of architectures with periods from below 10 nm up to the 100 nm range because of their ability to form self-assembled ordered arrays of nanoscopic domains, the nature of which depends on the composition of the BCP. Whereas BCPs in thin-film configurations have been studied intensively, much lesser efforts have been directed to the exploration of BCPs as soft templates for the generation of nanorods with mesoscopic fine structures. A well-established approach to the preparation of one-dimensional nanostructures involves the infiltration of target materials or precursors thereof into shape-defining hard templates containing arrays of aligned cylindrical nanopores, such as self-ordered anodic aluminum oxide (AAO). Synthetic routes to mesoporous nanorods based on sol/gel chemistry exploit amphiphilic BCPs as structure-directing soft templates, but the range of thus accessible mesoporous scaffolds formed by condensation of corresponding precursors is limited to inorganic oxides such as silica and amorphous carbon. However, nanorods with engineered mesoporous fine structures consisting of polymeric instead of inorganic scaffolds are highly interesting components for functional membranes, filters, bioinspired adhesive structures, sensor arrays, drug delivery systems and nanocomposites. It appears to be straightforward to exploit not only the intrinsic ability of BCPs to self-assemble but to employ them also as the scaffold material. Whereas direct infiltration of liquid BCPs into AAO yields solid nanorods exhibiting a mesoscopic morphology that originates from microphase separation in cylindrical confinement, the generation of mesopores in BCP nanorods requires the removal of sacrificial blocks. Hence, BCPs containing selectively degradable components must be used to this end, which is a serious limitation of this approach. The access to polymer nanorods having rationally designed mesoporous structures or surface topographies has thus remained a challenge.

Here we show that selective swelling of one component in BCP nanorods is, on the one hand, a surprisingly simple strategy to generate cylindrical channels parallel to their long axes. On the other hand, it is also a generic approach to the rational manipulation of the mesoscopic fine structure of BCP nanorods via morphology reconstruction. Surface reconstruction in thin BCP films induced by exposure to solvents or solvent vapors selectively swelling one component, whereas the other component remains in the glassy state, is a well-known phenomenon. If the glassy component frustrates the swelling component, the volume increase of the latter can only be accommodated by its segregation to the film surface. In the case of systems characterized by moderate swelling ratios (volume of the swollen polymer divided by the volume of the native polymer), BCP films containing spheres or cylinders of the swellable block in a glassy matrix are thus converted into porous films.

Specific interactions between the swellable block and the swelling agent may result in dramatically increased swelling ratios, as it is the case if polystyrene-block-poly(vinyl...
pyridine) (PS-b-PxVP; x = 2, 4) is exposed to acidic solutions. Because of the presence of a free electron pair at the nitrogen, the neutral pyridyl groups of the PxVP repeat units are then converted to cationic pyridinium groups. Thus, electrostatic repulsion dominates over conformational entropy so that the PxVP blocks seek to adopt a stretched conformation and to increase the spacing between them. PxVP microgels were reported to show a sharp increase in volume by up to 2 orders of magnitude in acidic solutions.26,27 Chai et al. reported that in plane-oriented cylindrical P2VP domains in PS-b-P2VP films pierce through the PS overlayer to form mushroomlike structures on the surface of the films.22,24 Correspondingly, poly(acrylic acid) blocks in amphiphilic BCPs such as polystyrene-b-poly(acrylic acid) show similar behavior in basic solutions.17,18

Upon exposure of BCP nanorods to swelling agents selectively interacting with one of the components, the volume taken up by the swellable domains should significantly increase. Hence, subsequent drying accompanied by the collapse of the swollen blocks while the mesoscopic morphology is fixed by the glassy component will yield mesoporous nanorods. Chen et al.28 coated the pore walls of AAO with a mesoscopic layer of cylinder-forming polystyrene-block-poly(ethylene oxide) (PS-b-PEO) by infiltration of diluted solutions of this BCP into the pores. The walls of the PS-b-PEO nanotubes thus produced exhibited PEO cylinders perpendicular to their surfaces. After the release of the PS-b-PEO nanotubes, the PEO cylinders could be converted into nanopores by swelling with water/methanol mixtures. However, the system used by Chen et al. is characterized by only moderate swelling ratios, and the mesoscopic morphology motifs accessible in a tubular geometry are essentially the same than in conventional thin-film configurations. In the case of solid BCP nanorods, the absence of rigid BCP/substrate interfaces and of the confinement imposed by the thickness of the BCP films (typically a few tens of nm) results in morphology reconstruction processes qualitatively different from those in thin-film configurations, as discussed below.

To explore the potential of swelling-induced morphology reconstruction associated with swelling ratios ranging from moderate to high, we selected cylinder-forming PS-b-P2VP (M\(_n\) (PS) = 50 000 g/mol; M\(_n\) (P2VP) = 16 500 g/mol; M\(_{n}\)/M\(_{n}\)(PS-b-P2VP) = 1.09; Polymer Source Inc., Canada) as a model system. PS-b-P2VP nanorods were prepared by heating the BCP on top of AAO with a mean pore diameter of 180 nm and a pore depth of 100 nm at a temperature of 230 °C for 24 h while applying a load of approximately 0.7 kg/cm\(^2\) to accelerate infiltration.29 Residual PS-b-P2VP was scraped off from the surface of the AAO with sharp blades prior to the etching of the AAO with 40 wt % aqueous KOH solution for 20 min at room temperature. Subsequently, three washing steps involving centrifugation, removal of the supernatant solution and redispersion, another washing step with 40 wt % aqueous KOH solution, and three washing steps with deionized water as described above, were performed. At this stage, the liberated native PS-b-P2VP nanorods appeared to be essentially featureless when imaged by transmission electron microscopy (TEM).30 as expected given the similar mass density of the PS and P2VP domains, and only occasionally disordered mesopore structures were found (not shown). However, selective staining of the P2VP domains with iodine30,31 unveils the internal fine structure of the PS-b-P2VP nanorods. Since the pore diameters of self-ordered AAO scatter to a certain degree around the mean pore diameter, the diameters of the PS-b-P2VP nanorods also vary to some extent. For example, stained PS-b-P2VP nanorods with a diameter of 170 nm imaged by TEM exhibit four dark lines parallel to their long axes that represent cylindrical P2VP domains, and stained PS-b-P2VP nanorods with a diameter of about 210 nm, such as that displayed in Figure 1, show five dark lines. The section across a PS-b-P2VP nanorod seen in the inset of Figure 1 contains a dark circular rim of P2VP initially segregated to the AAO pore walls that surrounds cylindrical P2VP domains with a center-to-center distance of about 40 nm and nonhexagonal coordination. Therefore, the minor component P2VP preferentially segregates to the pore walls of the AAO hard template while forming cylinders parallel to the long axes of the PS-b-P2VP nanorods away from the external interface. This picture is perfectly consistent with the results previously obtained by Xiang et al. with asymmetric polystyrene-block-poly(butadiene) infiltrated into AAO with a mean pore diameter of about 200 nm.3

Ethanol is a polar but nonacidic solvent that selectively swells the cylindrical P2VP domains. The pyridyl groups are not ionized and can interact with the solvent molecules only via hydrogen bonds. Therefore, the attainable swelling ratio is not large enough to break up the cylindrical microdomain structure imposed by the molecular architecture of the native BCP. However, the collapse of the swollen P2VP blocks upon drying leads to the formation of cylindrical channels with a diameter of the order of 15 nm oriented along the BCP nanorods. Both PS-b-P2VP nanorods exposed to ethanol at 60 °C for 10 min and PS-b-P2VP nanorods kept in ethanol for 6 months at room temperature showed

Figure 1. TEM top-view image of an as-released nanorod consisting of cylinder-forming PS-b-P2VP after staining the P2VP with iodine. The dark lines parallel to the nanorod axis represent cylindrical P2VP domains. Inset: TEM image of an ultrathin slice containing a section across a PS-b-P2VP nanorod. The P2VP domains stained with iodine are darker than the background.
this interesting architecture, which should have great potential for a broad range of applications. In the TEM images of released PS-b-P2VP nanorods displayed in Figure 2a,b, the channels can easily be identified as bright lines because at their positions the mass thickness along the pathway of the incident electrons is reduced. The channels are present over the entire length of the PS-b-P2VP nanorods, though some structural defects are apparent. Notably, staining results in contrast inversion, and instead of bright channels dark lines are seen, as in case of the PS-b-P2VP nanorod kept in ethanol for 10 min at 60 °C shown in Figure 2c. This finding confirms that the walls of the channels that remain after a swelling/collapsing cycle consist of P2VP. Apparently, after 10 min swelling in ethanol at 60 °C the P2VP blocks are segregated to the outer surface of the PS-b-P2VP nanorods to significantly higher extent than directly after their release from the AAO hard templates, as is obvious from a comparison of Figure 1 and Figure 2c. The inset of Figure 2c shows a detail of a stained PS-b-P2VP nanorod. A sharp, dark contour line indicative of an outermost P2VP layer is clearly discernible and significantly more pronounced than in case of the as-released PS-b-P2VP nanorods (cf. Figure 1).

Under conditions where the neutral pyridyl groups of the P2VP blocks are converted into cationic pyridinium groups, the structure seen in Figure 1 represents only the first stage of a swelling process that eventually leads to a complete reconstruction of the mesoscopic structure of the BCP nanorods. We added 0.8 mL of 0.01 M aqueous HCl solutions to 0.2 mL of ethanolic suspensions of the PS-b-P2VP nanorods and heated the mixtures to either 80 or 95 °C for different periods of time ranging from 10 min to three days. After 10 min heating at 80 °C, stage 1 morphologies characterized by cylindrical channels along the nanorods are exclusively found, which were still present after 2 h (Figure 3a, b). Noticeably, the apparent diameter of the channels amounts to about 50 nm and is unambiguously larger than that of the PS-b-P2VP nanorods swollen with ethanol (cf. Figure 2a,b). After 15 h, the PS-b-P2VP nanorods show a significantly different mesoscopic architecture characterized by isolated but partially interconnected strands with a diameter of about 50 nm separated by voids having approximately the same size. Samples heated to 95 °C, a temperature close to but below the glass transition temperature of PS (about 100 °C), exclusively showed the strand structure indicative of the second stage of the reconstruction process already after 10 min (Figure 3c,d). Topological confinement and concave curvature of cylindrical channels impede swelling so that only massive reshaping of the glassy PS matrix of stage 1 allows accommodating the drastically increased volume of the P2VP domains. Thus, the P2VP pierces through the glassy PS matrix, and eventu-

Figure 2. TEM images of released nanorods consisting of cylinder-forming PS-b-P2VP after exposure to ethanol at 60 °C for 10 min. (a) Large-field view and (b) detail of unstained PS-b-P2VP nanorods containing nanochannels parallel to their long axes. (c) PS-b-P2VP nanorod after staining P2VP with iodine. The walls of the nanochannels seen in panels a and b consisting of P2VP appear as dark lines. Inset: detail of a stained PS-b-P2VP nanorod clearly showing an outermost P2VP layer appearing as a dark contour line separating nanorod and background.
ally an inversion of the morphology occurs, resulting in the formation of a scaffold of partially interconnected PS strands surrounded by a PVP corona.

After heating to 80 °C for three days or to 95 °C for 15 h, the third stage of the morphology reconstruction process is reached. Stage 3 involves the transformation of the strands into strings of spherical particles, in which a PS core is surrounded by a P2VP corona. After drying the samples, strings of spheres with a diameter of about 80 nm are obtained (Figure 3e,f). Analogous to the breakup of liquid threads into drops known as Rayleigh-Plateau instability, the conversion of stage 2-morphologies into stage 3-morphologies reduces the interfacial area between the PS and P2VP domains as well as the free surface area. Moreover, the transition from the convex two-dimensional curvature of the PS/P2VP interface in stage 2 to the convex three-dimensional curvature in spherical stage 3-entities enables better accommodation of the stress associated with electrostatic repulsion between the cationic repeat units of the P2VP chains fixated at the glassy PS cores. This is because of

---

Figure 3. TEM images of nanorods consisting of cylinder-forming PS-b-P2VP at different stages of morphology reconstruction after exposure to acidic environment. (a) Large-field view and (b) detail of nanorods with stage 1 morphology (cylindrical channels in solid matrix) obtained by heating them to 80 °C for 2 h while suspended in a 1:4 ethanol/0.01 M HCl(aq) mixture; (c) large-field view and (d) detail of nanorods with stage 2 morphology (interconnected strands) obtained by heating them to 95 °C for 10 min while suspended in a 1:4 ethanol/0.01 M HCl(aq) mixture; (e) and (f) nanorods with stage 3 morphology (strings of spheres) obtained by heating them to 95 °C for 15 h while suspended in a 1:4 ethanol/0.01 M HCl(aq) mixture.
geometric reasons: larger spacing between the chains is possible in the directions of the convex curvature of the PS cores. A thread-to-sphere transition therefore allows larger separations between the chains not only in one but in two dimensions.

We assume that the initial morphology of the nonswollen PS-b-P2VP nanorods characterized by P2VP cylinders parallel to their long axes (Figure 1) corresponds to the equilibrium structure of the PS-b-P2VP melt confined to a cylindrical nanopore with a non-neutral wall and a diameter exceeding the period of the BCP multiple times. In turn, heating a 0.5 wt % solution of as-received PS-b-P2VP in acetic acid to 110 °C for 12 h leads to the formation micelles with a PS core surrounded by a swollen P2VP corona. After drying, the collapsed micelles have a diameter of about 65 nm, and the P2VP shells surrounding the PS cores can be visualized by staining with iodine (Figure 4). Since the PS is soft at 110 °C so that kinetic trapping of nonequilibrium morphologies can be ruled out, it is reasonable to assume that micelles indeed represent the equilibrium state in acidic solutions. Thus, swelling-induced morphology reconstructions can be regarded as transitions from equilibrium morphologies of molten amphiphilic BCPs in cylindrical confinement to equilibrium morphologies of the corresponding BCPs dissolved in selective swelling agents. The kinetics of swelling-induced morphology reconstruction can be controlled by swelling time, swelling temperature, and the nature of the swelling agent. Notably, morphology reconstruction in PS-b-P2VP nanorods also occurs at temperatures far below the glass transition temperature of PS. For example, stage 2 morphologies are obtained in acetic acid at 60 °C after only 10 min exposure time. We speculate that the rate at which the pyridyl moieties of the P2VP blocks are converted into pyridinium cations rather than the segmental mobility of the PS blocks in the glassy cores determines how fast the morphology of the PS-b-P2VP nanorods is transformed.

Chai et al. demonstrated that P2VP domains in PS-b-P2VP films can be loaded with tetrachloroauroate AuCl₄⁻, and that subsequent plasma treatment yielded continuous Au nanowires, the position and size of which were determined by the morphology of the BCP. Tentative experiments revealed that selective swelling can be exploited to load the P2VP domains of the PS-b-P2VP nanorods with gold even under gentle neutral conditions where the cylindrical morphology of the native BCP is conserved. To this end, the PS-b-P2VP nanorods were incubated with a solution of 2 mg/mL HAuCl₄ in a 1:1 H₂O/ethanol mixture for 1 h at room temperature. Subsequently, the nanofibers were suspended in a solution of 5 wt % NaBH₄ in a 1:1 H₂O/ethanol mixture for 1–2 h at room temperature to reduce the gold. As can be seen in Figure 5, the Au nanoparticles thus obtained do not form continuous wirelike structures. However, it is noteworthy that they reside in the volume defined by the swollen P2VP domains. This is remarkable because, in contrast to thin film configurations, no rigid interface limits the growth of the Au nanoparticles which commonly show a strong tendency toward the formation of large crystallites.

Figure 4. Micelles consisting of PS-b-P2VP forming cylinders in the bulk, which were obtained from a 0.5 wt % solution of the BCP in acetic acid after heating to 110 °C for 12 h. The collapsed P2VP coronas were stained with iodine and appear darker than the PS cores.

Figure 5. TEM images of PS-b-P2VP nanorods loaded with gold nanoparticles located in the volume defined by the P2VP domains. (a) Large-field view; (b) detail.
In summary, swelling-induced morphology reconstruction in nanorods consisting of amphiphilic BCPs differs from surface reconstruction processes in thin film configurations and involves the conversion of equilibrium morphologies of molten BCPs in cylindrical confinement to equilibrium morphologies of the corresponding BCPs dissolved in selective swelling agents. The rate at which morphology reconstruction takes place depends on swelling temperature, exposure time, and the nature of the swelling agent. Non-equilibrium morphologies can be retained by quenching the morphology reconstruction process at intermediate stages. Swelling-induced morphology reconstruction is highly complementary to the preparation of tubular and spherical nanoobjects by self-assembly of amphiphilic BCPs in solution \(^{30-38}\) and should also be applicable to electrosprun BCP nanofibers. \(^{39,40}\) The collapse of the swollen chains upon drying leads to the formation of complex nanoscopic architectures characterized by a variety of mesopore structures and surface topographies. In the example discussed above, cylindrical channels were obtained by swelling cylindrical P2VP domains in a glassy PS matrix. Further swelling accompanied by morphology inversion resulted in BCP nanorods consisting of bunches of partially interconnect ed strands that were eventually converted to strings of spheres. The approach reported here may pave the way for the rational design of mesoporous polymeric nanorods either aligned in arrays or in the form of powders, which can in turn be used as templates in further functionalization steps. The pronounced and selective affinity of inorganic precursors for functional target materials to the swellable blocks enables the rational arrangement of inorganic nanoobjects on a mesoscopic scale in complex nanorod architectures. Moreover, one-dimensional nanostructures accessible via swelling-induced morphology reconstruction exhibiting pH-responsive behavior, which was previously reported for polyelectrolyte-modified porous membranes \(^{12,21,41}\) and fabrics of electrosprun fibers, \(^{40}\) could be promising components for smart devices ranging from sensors to filters to bioinspired adhesive structures to drug delivery systems.

Acknowledgment. Y.W. thanks the Alexander von Humboldt Foundation for a fellowship. Technical support by S. Kallaus, K. Sklarek, and R. Möhner, as well as funding by the German Research Foundation (Priority Program “Nanowires and Nanotubes”, STE 1127/6), are gratefully acknowledged.

References

(21) Cong, Y.; Zhang, Z.; Fu, J.; Li, J.; Han, Y. Polymer 2005, 46, 5377.
(30) TEM investigations were carried out with a JEOL 1010 microscope operated at 100 keV. Either suspensions of released PS-b-P2VP nanorods were directly dropped onto copper grids coated with a holey carbon film or ultrathin slices containing sections across PS-b-P2VP nanorods were probed. The ultrathin slices were prepared by depositing PS-PS-P2VP nanorods into conical molds and embedding them in epoxy resin (Durcupan ACM). After curving at 60 °C for 48 h, the specimens were mounted on an ultramicrotome equipped with a diamond knife. Slices with a thickness of 100 nm or less, as determined from their interference colors, were transferred onto copper grids coated with holey carbon films. Some of the samples thus prepared were stained with iodine in a sealed container heated to 60 °C for 30 min. The sublimated iodine selectively enriched in the PS2VP domains.

NLS022687