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Preparation and control of functional nano-objects: Spheres, rods and rings based on hybrid materials

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Abstract

This paper reports on a simple route to fabricate functional nano-objects via self-assembly of hybrid materials based on a diblock copolymer. In water–toluene mixtures, spheres, rod- and ring-like structures of metal loaded block copolymer micelles are fabricated. The binary solvent blends are modified to gain control over the formation of micellar morphologies. A mechanism leading to the formation of such aggregates is presented using a force balance approach. It is demonstrated that swelling of the micelle core due to the water content is the driving force that induces transitions of morphology. Based on various control experiments the effect of inorganic precursor and stoichiometric water contents on the micelle morphology is described.

Keywords: Block copolymer; Hybrid materials; Nano-objects

1. Introduction

Self-assembly of block copolymers in solution has been explored extensively during the past decade [1,2] and a wide variety of morphologies have been discovered [3,4]. Their architectures depend not only on the molecular parameters of the copolymer but also on factors such as solvent composition and the presence of additives, e.g. salts or surfactants. Controlling these parameters enables the fabrication of nano-capsules, like micelles and vesicles, which are of great importance in cosmetics and drug delivery [5–8]. The formation of such aggregates, particularly of block copolymers in solution, was investigated by Eisenberg and co-workers [9–11]. They found that the composition of solvent mixtures is a useful tool, which provides control over the morphology [12,13]. For instance, spherical and worm-like micelles, as well as vesicles, were prepared by tuning the properties of binary solvent blends. Some very recent reports demonstrate the fabrication of copolymer aggregates with even more complex morphologies including networks of worm-like aggregates as well as stacked- and cylindrical micelles having a structure-in-structure morphology [14–19]. The preparation of such morphologies requires a high degree of control and clearly demonstrates the potential of using block copolymers to generate self-assembled architectures. However, the full potential of self-assembled systems is achievable only if they can be loaded with various active agents or functional materials. As a result, a new hybrid material has been designed, which combines the copolymer's ability to self-assemble with the functionality of inorganic components. In such hybrid systems, the organic matrix dictates the assembly of inorganic nanoparticles, having special physical properties, e.g. fluorescence, conductance or magnetic properties that, however, cannot be achieved in the neat copolymer. Hence, this approach enables the fabrication of functional nanostructures via self-assembly of smart hybrid materials, with potential applications in optics, electronics and catalysis [20–22]. Moeller et al. have presented a concept to fabricate hexagonally ordered arrays of metallic nanoparticles in self-assembled thin films [23,24]. Their approach is based on the adsorption of metal loaded block copolymer micelles onto a solid substrate. Since

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the metallic nanoparticles are synthesized directly within the micelle core, their size and size distribution are controlled by self-assembly of the diblock copolymer.

The present work combines both approaches mentioned above to generate metallic nano-objects via self-assembly of hybrid materials based on a diblock copolymer. In dilute solution, the diblock copolymer forms aggregates, which can be loaded with an inorganic precursor. The size and morphology of these aggregates are strongly dependent on the solvent composition. Hence, their assembly can be tuned by using a blend of two different solvents and varying its composition. This concept is demonstrated by dissolving a polystyrene-*b*-poly(vinyl pyridine) copolymer in mixtures of water and toluene. Such copolymeric systems in water-in-oil emulsions have been investigated before [25–29]. However, the use of hybrid materials to generate functional nano-aggregates in solution has received very little attention to-date; the novelty of the present work resides in the formation of metallic nano-objects in water-in-oil emulsions.

Recently, Wiesner et al. also reported the preparation of interesting silica mesostructures of PI-*b*-PEO block copolymer hybrid materials via sol–gel processes [30–35]. A wide range of morphologies were obtained, which mainly represent the typical bulk microphases of diblock copolymers. It was demonstrated that film casting followed by re-dissolution and calcination can produce individual ceramic nano-objects [30–35]. In contrast to that, our approach does not rely on additional treatments to develop the nano-objects. The diblock copolymer, polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP), and the inorganic precursor are dissolved in a mixture of water and toluene. Metallic nano-objects in dilute solution are generated in situ using a simple "one-pot" reaction which includes micellization of diblock copolymers, their metallization and reduction. The morphologies obtained are quite similar to the bulk microphase including spherical and rod-like aggregates as well as vesicles; however, additionally we observed ring-shaped aggregates.

Previous reports mainly focused on the preparation of nano-objects of copolymers that contain at least one water soluble block [36–39]. For instance, Moffitt et al. presented a new approach to fabricate interesting morphologies in LB films on the water/air interface of PS–PEO block copolymers [40–43]. Depending on the spreading concentration they obtained spherical or cylindrical morphologies. He also demonstrated that these aggregates can be loaded with inorganic nanoparticles.

A totally different concept is described here, where water is a non-solvent for both blocks of the diblock copolymer (PS-*b*-P4VP). Nevertheless, water can trigger morphological changes in water-in-oil emulsions of PS-*b*-P4VP diblock copolymer based hybrid materials. As a result, a variety of morphologies are obtained including spherical-, rod- and ring-like micelles as well as vesicles. These nano-objects can be loaded with a variety of inorganic precursors to prepare several kinds of metallic nano-objects with novel characteristic properties.

2. Experimental section

The block copolymer, PS_{206}-*b*-$P4VP_{197}$, was purchased from Polymer Source Inc. and used as received. Metallic nano-objects were fabricated by dissolving a diblock copolymer (PS-*b*-P4VP) directly in mixtures of water and toluene. A gold precursor ($HAuCl_4$, Purum, Fluka) was added to the solution in stoichiometric amounts with respect to the number of pyridine units. Solutions of 0.5% copolymer in toluene were prepared, with a water content between 0.5 and 100 stoichiometric amounts with respect to the number of poly(vinyl pyridine) (P4VP) units. The water content is subsequently expressed as the ratio between the molarities of water and vinyl pyridine (n_{H_2O}/n_{4VP}). It is important to note that non-spherical morphologies (rods and rings) have been observed only if the solutions were stirred vigorously or under ultra-sonication at room temperature for 48 h. The gold recursor (Au^{3+}) was then reduced to metallic gold (Au^0) by adding 3-fold excess of borane–dimethylamine (98+%, ACROS) to the block copolymer solution. The mixture of nano-objects was separated by centrifugation (Eppendorf Centrifuge 5415c) at 6000 rpm for 3 min.

Native oxidized silicon wafers (<111>) were used as a substrate for all of the samples. The surface was cleaned using a piranha solution (H_2SO_4:H_2O_2:H_2O = 2:1:1) at 80 °C for 20 min. A second cleaning step in RCA-1 solution (H_2O_2:NH_4OH:H_2O = 4:1:1) was applied at 60 °C for another 20 min. After rinsing the surface with DI water, the substrates were blown dry with air. Subsequently, thin films were prepared by spin-casting block copolymer solutions (3000 rpm) on the silicon oxide substrates. The morphological characterization was performed by Tapping Mode™ scanning force microscopy in air using a Dimension IVa Nanoscope (Digital Instruments). We used standard silicon cantilevers with a resonance frequency of about 330 kHz, a spring constant of 45 N/m and a tip radius of less than 10 nm. The operating frequency was chosen to be on the repulsive side of the resonance frequency to increase scanning performance and stability.

For the TEM measurements, thin films were prepared on carbon coated copper grids (400 mesh/AGAR Scientific) by spin-coating the particular solution using a solid substrate support. The copper grid was then peeled off the substrate and analyzed in a TECNAI Biotwin (FEI Ltd.) transmission electron microscope at 100 keV. The instrument was operated at very low beam intensities to prevent electron damage of the polymer samples.

3. Results and discussion

Rather than generating microphase separated morphologies, this work describes the preparation of functional nano-objects via self-assembly of a hybrid diblock copolymer in dilute solutions. Organic–inorganic hybrid materials are designed by incorporating the metallic precursor selectively into one block of the diblock copolymer. Micelles of polystyrene-*block*-poly(4-vinyl pyridine) are used to synthesize Au-nanoparticles in situ with controlled size distribution (2–3 nm) [44,45]. These micelles are prepared in selective solvents, which dissolve only one block of the diblock copolymer (Fig. 1). The self-assembly is then driven by the repulsive interaction between the solvent and the insoluble block. For instance, toluene is a good solvent for polystyrene (PS), while poly(4-vinyl pyridine) (P4VP) is less soluble. Therefore, spherical micelles are

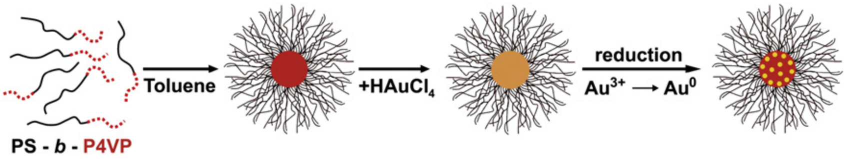

Fig. 1. Schematic representation of the preparation of PS-*b*-P[4VP(Au)] hybrid micelles. In toluene (selective solvent for the PS block) the copolymer self-assembles into spherical micelles. Their P4VP core can be loaded with inorganic precursors ($HAuCl_4$) that after reduction generate metallic nanoparticles.

formed, which consist of a solid P4VP core surrounded by a PS corona. The micelle core acts as a nano-reactor to generate the metallic nanoparticles (NPs), whose size distribution is directly determined by molecular parameters of the copolymer. Additionally, the polymer shell (PS) stabilizes the NPs and prevents aggregation.

In the particular case, auric acid ($HAuCl_4$), which serves as a gold precursor, is coordinated to the pyridine groups in the P4VP block. The affinity between pyridine and metal salt is based on strong acid–base interactions, whereas there is no attractive interaction with PS. This means, the metallic precursor coordinates to the P4VP block selectively. Hence, after reduction, elementary gold nanoparticles remain incorporated into the micelle core.

As shown in Fig. 2a, hexagonally ordered micelle arrays can be prepared via adsorption of micelles on solid substrates. Such metal loaded micelles have been used to fabricate ordered metallic nanoparticle arrays via thin-film self-assembly [24,46]. Thin films are prepared by spin-coating block copolymer/gold hybrids from solution on silicon oxide substrates. In dried films the micelle diameter is about 42 nm, as determined by AFM measurements.

Here we report on an attempt to change the solution conditions in water–toluene mixtures in such a way that the PS-*b*-P[4VP(Au)] hybrid material self-assembles into more complex morphologies than spherical micelles. A mixture of two different solvents (water and toluene) is used to dissolve the copolymer; their volume ratio determines the solution properties. Hence, to gain control over the morphology, solution properties such as polarity, selectivity and concentration, need to be adjusted. This can be done by changing the composition of the binary solvent blend by either using different solvents or changing their volume fraction.

In the present case, toluene is a good solvent for the PS block, while water is a non-solvent for the block copolymer. However, as shown in Fig. 2b, water can induce morphological transitions in the block copolymer solution. In binary solvent mixtures, spherical micelles, rod- and ring-like structures are observed. The copolymer was dissolved directly in water–toluene mixtures to obtain contents of 0.5% of copolymer; gold precursor was added in stoichiometric amounts with respect to the number of pyridine units (each pyridine unit forms a complex with the gold precursor, $4VP:HAuCl_4 = 1:1$). After stirring for 48 h, a milky suspension is obtained, indicating a typical water-in-toluene emulsion [29].

The swelling of the micelle core initiates the morphological transitions which are observed in water–toluene mixtures. According to previous reports, the morphology of block copolymer aggregates in solution is determined by a balance between three forces [47]. These are the degree of chain stretching of the core-forming block, the repulsive interaction among chains of the corona-forming block as well as the interfacial tension between the micelle core and the surrounding solvent. These interactions change when the block copolymer is dissolved in water–toluene mixtures rather than pure toluene; and the morphology changes as shown in Fig. 3. A force balance approach can be

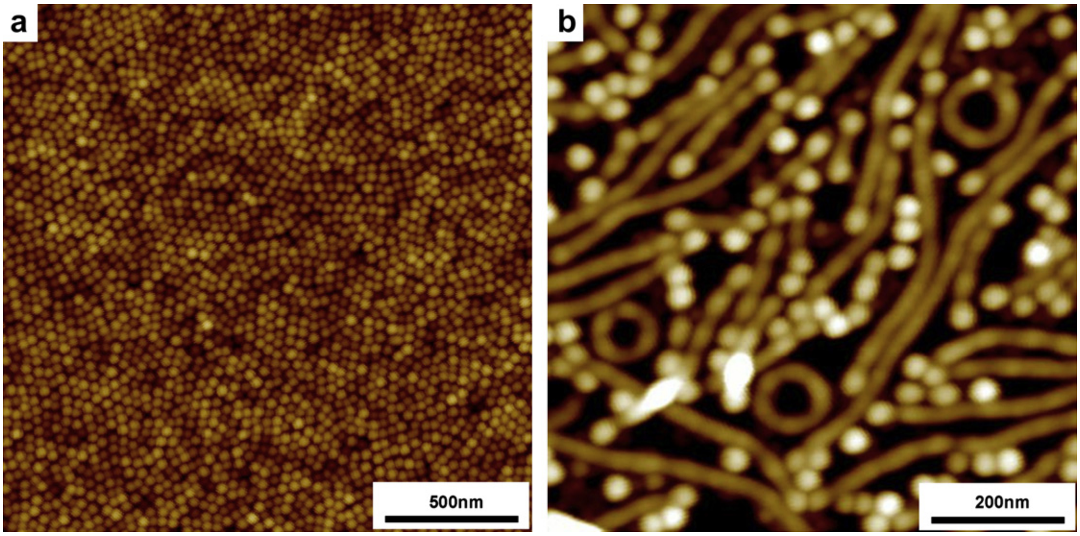

Fig. 2. Topographic AFM images showing the effect of water on the morphology of block copolymer based hybrid materials. (a) Hexagonally ordered thin films of micelles loaded with gold precursor, which are prepared in toluene. (b) If a water–toluene mixture is used to dissolve the copolymer hybrid material, spherical, rod- and ring-like morphologies are obtained.

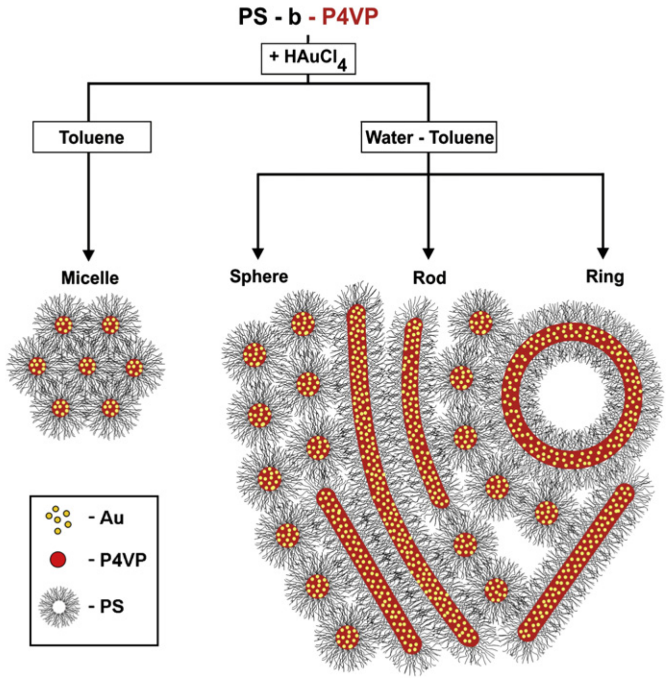

Fig. 3. Schematic illustration of nano-objects fabricated from block copolymer/gold hybrid materials. In toluene spherical micelles are obtained; these can be loaded with gold precursor. If the same system is prepared in water–toluene mixtures, a variety of morphologies are formed; these include spherical, rod- and ring-like micelles. The spherical morphologies in water–toluene differ from those in toluene because their core is swollen by water. If the degree of core swelling increases, the transition to rod- and ring-like micelles occurs.

used to describe the observed morphology transitions. First of all, water swells the P4VP block, which increases the degree of stretching of core-forming P4VP chains. Therefore, the micelle core becomes larger and the PS shell cannot effectively stabilize the swollen P4VP core against the surrounding medium. Additionally, the interfacial tension between the micelle core and the surrounding solvent increases, which leads to further destabilization of the micelle. The combination of both effects ultimately drives the morphological transitions. The repulsive interaction among corona-forming PS chains is not affected significantly. The reason is that the presence of water in the micelle core has no significant influence on the solubility behavior of the PS corona. In fact, the spherical morphologies, observed in water–toluene mixtures, are micelles with a swollen core; their diameter is 50 nm compared to 42 nm in pure toluene. If the swelling reaches a certain limit (according to $n_{\mathrm{H_2O}}/n_{\mathrm{4VP}} > 1$), the system reassembles into rod- and ring-like structures rather than only spherical morphologies to maintain the force equilibrium [29]. The diameter of the rod- and ring-like aggregates is slightly smaller ($\approx$45 nm) than those of the spherical micelles. Since PS and P4VP have very similar electron densities, TEM does not provide enough contrast to distinguish between both of these blocks. Usually staining agents are used to increase the contrast of one of the blocks. However, in the present case the contrast is also enhanced by presence of gold nanoparticles, which are selectively incorporated in the P4VP block. Thus, the TEM micrographs show only the P4VP region with incorporated Au-NPs, which appear as dark spots in the image. The diameter of the P4VP region ($\approx$28 nm) is significantly smaller than the diameter of the nano-objects obtained from AFM measurements.

Different control experiments were performed to evaluate the influence of water content, the presence of the gold precursor and the copolymer concentration on the micelle morphology. First, if no water is added to the solution under otherwise constant conditions, no rod- or ring-like micelles are found. In the absence of gold precursor only spherical micelles are formed even at very high water contents. The same spherical morphology is obtained, if the water is added to an existing micelle solution in toluene containing gold precursor. These experiments indicate that the formation of rod- and ring-like aggregates is controlled by the distribution of water during the self-assembly of precursor loaded diblock copolymer in water–toluene mixtures. Therefore, the quality of the mixing process is an important factor, which also determines the final morphology.

As confirmed experimentally, the observed rod- and ring-like morphologies cannot be prepared in the absence of a gold precursor. If only the neat PS-*b*-P4VP block copolymer is dissolved in water–toluene mixtures, spherical micelles are obtained, similar to those presented in Fig. 2a. The hydrogen bond between water and pyridine is not strong enough to drive the formation of rod- and ring-like nano-objects. The reason is that the gold precursor strongly enhances the interaction between pyridine and water by adding polarity to the P4VP block. As a result, the degree of swelling of the micelle core increases due to the contributions of water and gold precursor. Hence, the morphology transitions described here, are induced by the combined effect of water in the presence of the gold precursor.

Currently, a variety of aggregates are being observed including spheres, rod- and ring-like structures. These morphologies differ in the degree of core chain stretching and interfacial tension between micelle core and surrounding solvent. The amount of water, swelling the P4VP block, is the lowest in case of spherical micelles and increases for rod- and ring-like structures. As shown in Fig. 4a, the result is a mixture of various nano-objects loaded with a gold precursor. Subsequently, the gold precursor can be reduced to gold nanoparticles directly in solution without loosing structural integrity; thus metallic nano-objects are generated (see Fig. 4b). The addition of reduction agent (borane–dimethylamine) in 3-fold excess with respect to the number of metal ions ensures complete reduction, leading to the formation of gold nanoparticles; these are selectively incorporated into the P4VP block. Simultaneously, reduction decreases the effect of the ionic gold precursor with respect to the interaction between water and pyridine. However, after the reduction process, the water remains trapped within the micelles and still swelling the P4VP block. This means, the rod- and ring-like morphologies remain stable even after the reduction process. The internal structure of these nano-objects was analyzed by TEM measurements. There is a low contrast between PS and P4VP in TEM but due to their higher optical density, nanoparticles appear as dark spots in the image (Fig. 4c). Surprisingly, a narrow particle size distribution was observed with a mean

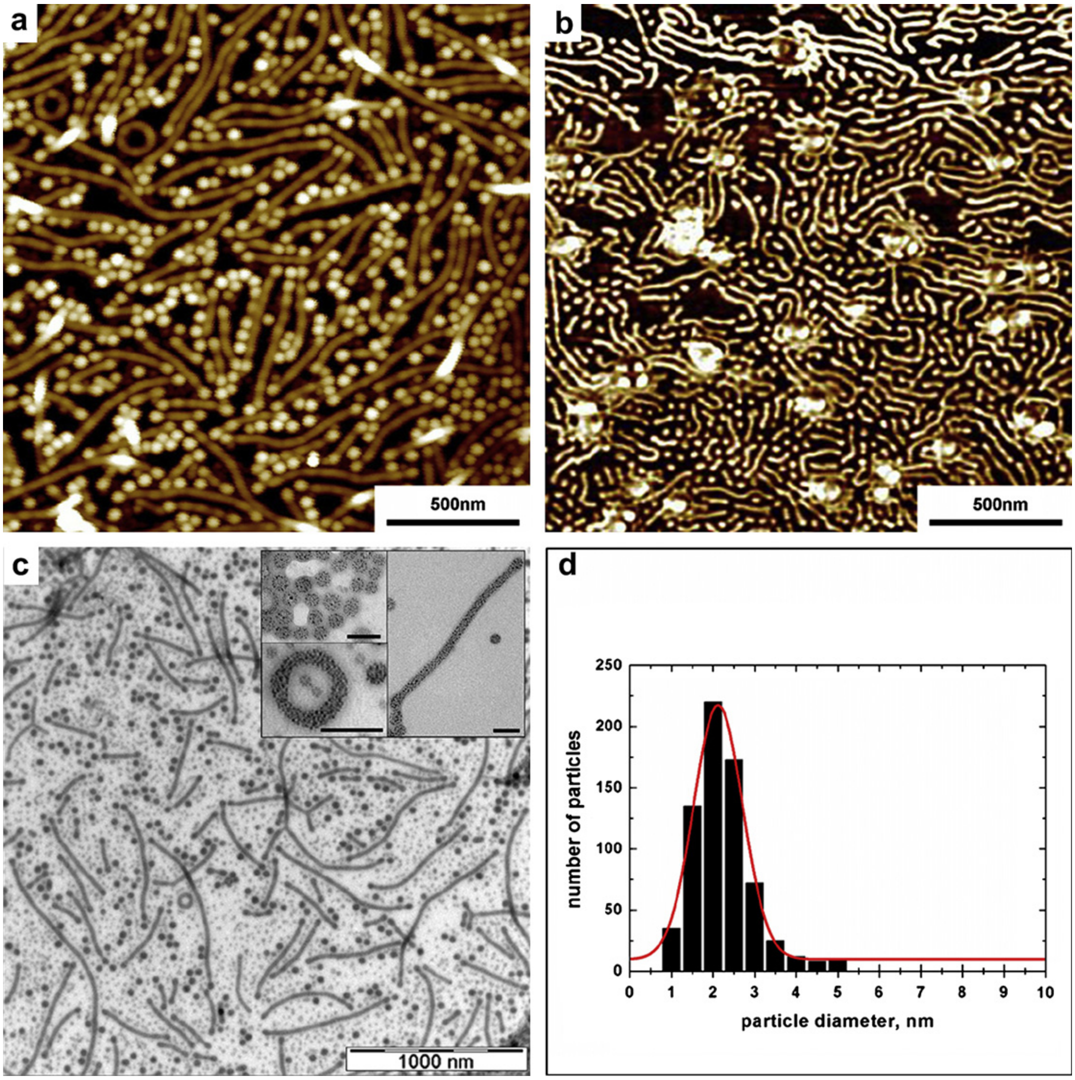

Fig. 4. (a) Topographic AFM image of self-assembled spherical, rod- and ring-like nano-objects of PS_{206}-*b*-$P4VP(HAuCl_4)_{197}$. (b) AFM phase image of PS_{206}-*b*-$P4VP(Au)_{197}$. The morphology is preserved when the reduction agent is added to the solution to form metallic nano-objects. (c) TEM micrograph of metallic nano-objects (gold nanoparticles appear as black spots). The inset shows individual morphologies including spheres, rods and rings; the scale bar is 150 nm. (d) Plot of the particle size distribution as determined directly from TEM measurements. A Gaussian fit results in a mean particle diameter of 2.3 nm and a standard deviation of 0.6 nm.

particle diameter of 2.3 nm and a standard deviation of 0.6 nm (see Fig. 4d).

A possible way of tuning the particle size is by changing the amount of precursor, which is coordinated to the pyridine block. Rather than using stoichiometric amounts of precursor, lower fractions could be applied to decrease the particle size. However, the gold precursor also proved to enhance the interaction between water and pyridine; therefore decreasing its concentration might also provide a possibility to control the morphology.

As reported before, the water content is the main determinant of the morphology of copolymeric systems in aqueous solvent blends [48]. The crucial parameter is the amount of water that effectively swells the P4VP block. This observation suggests that the morphology of PS-*b*-P[4VP($HAuCl_4$)] aggregates in solution can be influenced by adjusting the fraction of water in the micelle core.

In order to evaluate the influence of water in the present system and attempt to control the morphology, solutions with water contents between $n_{H_2O}/n_{4VP} = 0.5$ and 100 were prepared; the results are shown in Figs. 5 and 6.

At $n_{H_2O}/n_{4VP} = 0.5$ no rod- or ring-like aggregates have been found; thin films on native oxidized silicon show a disordered morphology containing mainly aggregates of spherical micelles. As the water content increases, rods and rings begin to form. The critical water content for the formation of cylindrical micelles in the present system is at $n_{H_2O}/n_{4VP} \approx 1$ as indicated in Fig. 5b.

At very low water contents between $0.5 < n_{H_2O}/n_{4VP} < 10$ there is a compelling influence on the morphology. In contrast to that, less significant differences were found between the samples at high water contents ($n_{H_2O}/n_{4VP} > 10$); all of them show comparable morphologies including spherical, rod- and ring-like structures. Though it is important to note that at $n_{H_2O}/n_{4VP} > 10$

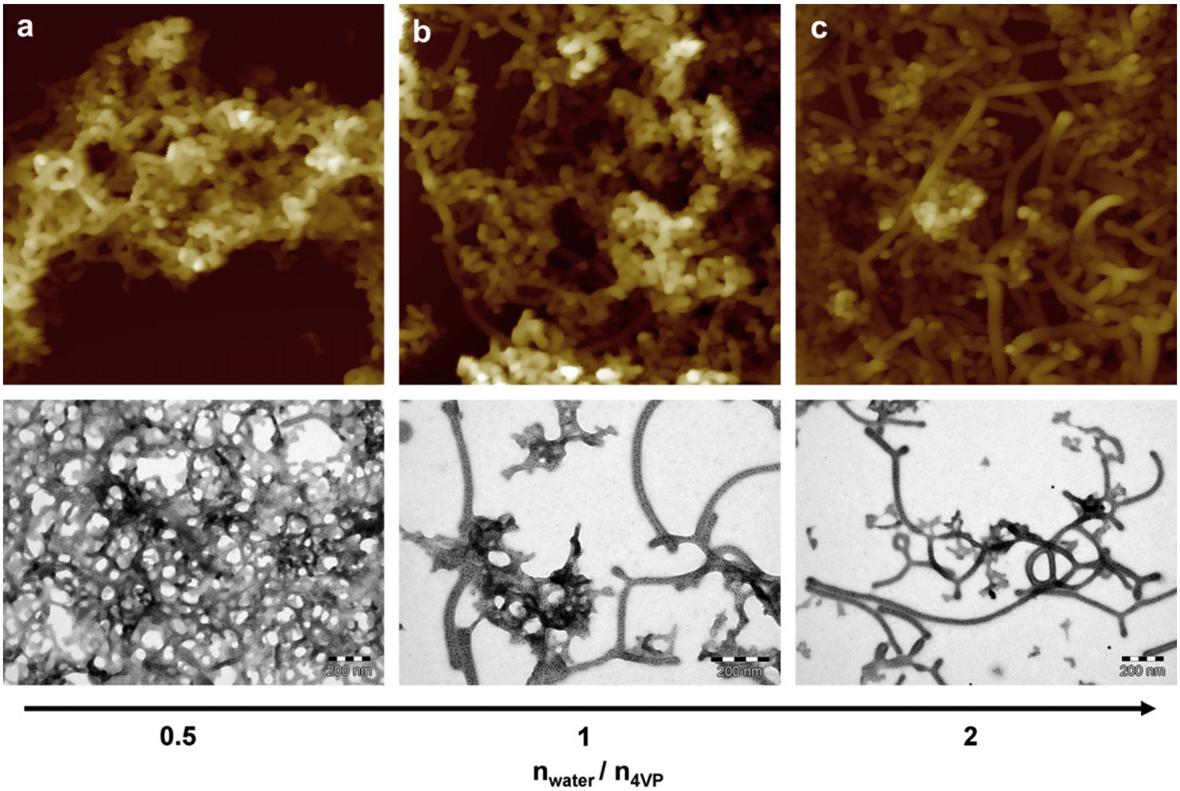

Fig. 5. Morphology of PS-*b*-P[4VP($HAuCl_4$)] aggregates in water–toluene mixtures at low water contents. The AFM images (top) (image size 2 μm, *z*-scale = 120 nm) are presented together with a corresponding TEM micrograph (bottom) of the same sample.

no spherical aggregates and a very large fraction of rod-like micelles was found (Fig. 6a–c). The dominant morphologies are rod-like micelles, which in some cases also form branched, Y-shaped aggregates and rigid networks. Such unusual structures are rarely reported so far and when modified with inorganic nanoparticles, interesting properties arise. Remarkably, as the water content increases further ($n_{H_2O}/n_{4VP} > 100$), a larger fraction of ring-like structures but also vesicles are generated.

These findings are largely in agreement with previous reports that demonstrated the influence of the water content on self-assembled block copolymer aggregates in binary solvent blends [49–51]. It was observed that the morphology of PS-*b*-PEO block copolymers can be shifted from spheres to rods and from rods to vesicles by increasing the water content. Considering the role of water in the present work, it is important to note that water is a non-solvent for the PS–P4VP diblock copolymer. Thus, this system (copolymer in water–toluene) is regarded as a suspension, rather than a solvent blend. Additionally, it was confirmed that the presence of auric acid, which serves as a gold precursor, plays an important role in the formation of rod- and ring-like aggregates.

It is assumed that, at a given polymer concentration, only a limited amount of water can be stabilized within the P4VP block. The reason is that water is swelling the P4VP block (micelle core) via hydrogen bonding; when all of the pyridine units are saturated, the residual water separates from the toluene-rich phase. Thus, primarily rod-like morphologies are obtained at high water contents. However, some spherical micelles are still present and increasing fractions of rings and vesicles are observed for ($n_{H_2O}/n_{4VP} > 100$). The occurrence of coexisting morphologies is a result of the locally inhomogeneous distribution of water within the copolymer-rich toluene phase. These inhomogeneities at low fractions of n_{H_2O}/n_{4VP} are the reason for multiple morphologies coexisting at the same time. At high excess of water ($n_{H_2O}/n_{4VP} > 50$), ensuring good mixing of all components, no spherical micelles are observed because the entire copolymer is sufficiently swollen with water. Since the formation of rod- and ring-like aggregates is dependent on the amount of water that is swelling the P4VP block, the kinetics- and quality of the mixing process play also an important role. The results show that under simple stirring (ineffective mixing) preferably spherical micelles are generated, while ultra-sonication (effective mixing) results in the formation of mainly rod- and ring-like structures as well as vesicles.

This observation shows that tuning the water content provides means to influence the morphology of the nano-objects. However, so far a full control over the morphology has not been achieved. The occurrence of several coexisting morphologies in the present system narrows the range of potential applications. In an attempt to obtain the fractions of single morphologies centrifugation was applied, in order to separate these coexisting spheres, rods and rings. First results show that spherical aggregates remain in solution, while the denser rods and rings can be collected from the bottom of the tube. Since the density of the nano-objects is very similar, the separation process is incomplete. However, samples with a majority of rod-like nano-objects with small fractions ($\approx 5\%$) of spherical micelles have been prepared successfully.

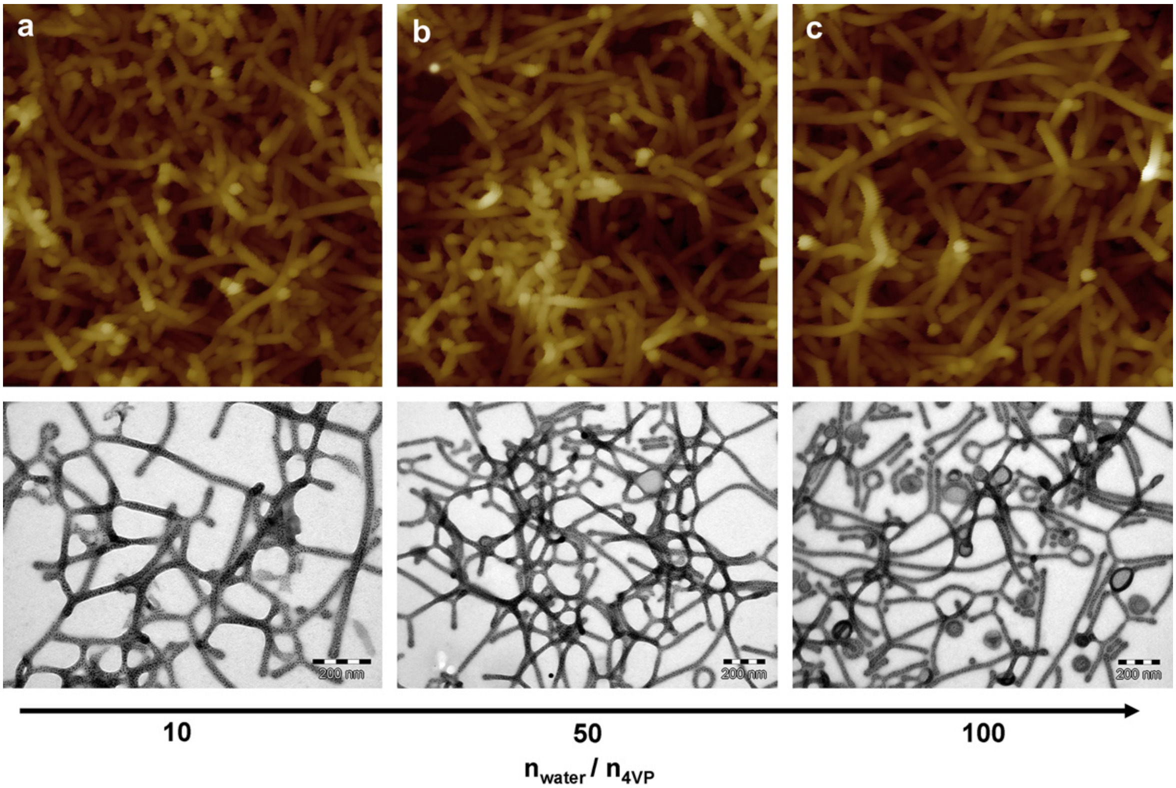

Fig. 6. Influence of high water contents on the morphology of PS-*b*-P[4VP($HAuCl_4$)] aggregates in water–toluene mixtures. A majority of rod-like nano-objects are observed if $n_{water}/n_{4VP} > 10$. The AFM images (top) (image size 2 μm) are presented together with a corresponding TEM micrograph (bottom) of the same sample.

The preparation of functional nano-objects via self-assembly of hybrid materials based on block copolymers is of great interest for pharmaceutical- and medical applications. Apart from gold, other metallic or semi-conducting nanoparticles can be incorporated into the block copolymer. For example, nano-objects loaded with direct semiconductors can be prepared and used, e.g. as fluorescent markers in biotechnology where as in storage media, magnetic materials are most favorable. Another option would be the application in drug delivery as functional multi-compartment structures that are able to carry several active agents.

4. Conclusions

In summary, the fabrication of functional nano-objects via self-assembly of hybrid materials was investigated. Diblock copolymer micelles have been used as nano-reactors to synthesize metallic nanoparticles; the confined environment provides excellent control over the particle size and size distribution. It was demonstrated that water can trigger morphological changes in solutions of diblock copolymer/gold hybrid materials. As a result metallic nano-objects were obtained, which include spherical, rod- and ring-like morphologies. Although such transitions have been reported before in solutions of neat block copolymers, extending this concept to hybrid materials is novel.

The possibility to incorporate metallic nanoparticles into self-assembled systems and controlling their morphology directly enables applications in drug delivery, cosmetics and biomedical research among many others. It was demonstrated that the morphology can be partially controlled by adjusting the water content stoichiometric with respect to the number of pyridine units. Additionally, centrifugation can provide external aid to separate mixtures of spheres, rods and ring-like structures to obtain large fractions of single morphologies. Future work will focus on the preparation of single nano-objects, their manipulation and orientation.

Acknowledgments

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