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Control of the Morphology of Linear and Cyclic PS-*b*-PI Block Copolymer Micelles via PS Addition

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We have studied the effect of polystyrene (PS) homopolymer addition on the morphology of self-assembled block copolymer micelles made from linear or cyclic poly(styrene-*b*-isoprene), PS-*b*-PI, in a selective solvent for the PI block (heptane). Both copolymers have the same composition: the degree of polymerization is 290 for the PS block, and 110 for the PI block, and we focused on the influence of the addition of small amounts of PS homopolymer on the micellar morphology. For the copolymer concentrations considered, the linear copolymer self-organizes into spherical micelles while the cyclic copolymer forms cylindrical micelles. PS and PI chains constitute the core and the corona of these micelles, respectively, due to the different affinity of the blocks for heptane. Consequently, the PS homopolymer added is "solubilized" into the micellar core. Dynamic light scattering (DLS) data combined with atomic force microscopy (AFM) results show that the addition of PS homopolymer induces a drastic change in the micellar organization. Indeed, a morphological transition, from spheres to cylinders for the linear copolymer, and from cylinders to vesicles for the cyclic copolymer, is observed. These results highlight the fact that a small incorporation of PS homopolymer is clearly sufficient to modify the morphology (size and shape) of the micelles. This approach could be a key parameter for the design/control of micelles for specific applications in nanotechnology.

1. Introduction

One of the most interesting and useful properties of diblock copolymers is their ability to spontaneously self-assemble into nano-organized morphologies (micelles, vesicles, bilayers, etc...) when dissolved in a selective solvent for one of the two segments, as a result of the association of the insoluble blocks.¹ These well-organized nanostructures have received increasing attention in recent years^{2,3} due to their potential in technological^{4–7} and biomedical^{8,9} applications. For instance, block copolymers play a crucial role in nanofabrication processes^{10–12} and in drug delivery systems for neuroactive agents.^{13–15} In this context, the control of the micellar

morphology on the nanometer scale is of great importance to obtain the desired functions and properties.

Diblock copolymers consist of two chemically different polymer blocks connected together by a covalent junction. The aggregation of these copolymers, which results in micelle formation, is driven by the unfavorable interactions between the selective solvent and the insoluble blocks, which tend to aggregate to minimize their contact with the solvent. This process leads to micellar systems having a core-shell structure, with a corona constituted by the soluble blocks. A number of morphologies can be obtained for those aggregates, including spheres,^{16–18} cylinders,¹⁹ rods,^{4,20,21} worms,²⁰ lamellae,²² or vesicles.^{4,9,23–27} The formation of a specific morphology can be controlled by various factors,^{16,22–24,28,29} such as the temperature, the copolymer volume fraction and concentration, the solvent,

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the presence of additives, and the sample preparation procedure. Recently, we have studied³⁰ the impact of the cyclization of linear diblock copolymers on the micellar morphology, using poly(styrene-*b*-isoprene), PS-*b*-PI, copolymers as models. We have shown that the chain architecture is also a key parameter for controlling the organization into micelles formed in solution. Indeed, for the composition we considered, linear PS-*b*-PI copolymers always yield spherical micelles, a process which is not concentration-dependent, while cyclic PS-*b*-PI copolymers of the same composition aggregate into “sunflowerlike” micelles, which in turn assemble into giant wormlike micelles or vesicles depending on the copolymer concentration.

Molecular additives (organic molecules, salts, acids, alkali...) are known in the literature to modify the morphology of micelles formed by linear diblock copolymers.^{31–34} The effect of homopolymer as an additive to linear diblock copolymer micelles has also been investigated. Zhang and Eisenberg²⁹ found a modification of the self-assembled morphologies (rods and vesicles) with the addition of PS to PS-*b*-PAA rods and vesicles. For instance, in water, the morphology of PS₁₈₀-*b*-PAA₁₅ micelles changes from cylinders to spheres with the addition of 5% PS₃₈ homopolymer. A morphological transition from vesicles to spheres is also obtained upon the addition of 5% PS₃₈ to PS₂₀₀-*b*-PAA₈ diblock copolymers. In contrast, the addition of PS homopolymer to PS₅₀₀-*b*-PAA₅₈ and PS₁₁₄₀-*b*-PAA₁₆₅ spherical micelles does not modify the morphology in aqueous solution. Those changes correspond to a reverse effect of the chemical composition (relative PS and PAA weight fraction) as compared to micelles from the pure diblock copolymers. Indeed, in the case of those pure systems, a micelle morphology change, from sphere to cylinder (or rod), and then to vesicles, takes place upon increasing the PS block weight fraction, whereas an opposite morphology change is observed when the PS weight fraction is increased by addition of PS homopolymer, a situation quite fascinating. Attempts to understand those morphological changes are still under investigation.

In the same context, the effect of homopolymer addition on micelles made of cyclic copolymers is still unexplored. For that reason, this study was undertaken with the aim of determining how the addition of small amounts of PS homopolymer influences the aggregation of cyclic PS-*b*-PI diblock copolymers in the presence of heptane, a selective solvent for PI (the solubility parameter is 7.4, 8.1, 9.1 cal^{1/2}/cm^{3/2} for heptane, PI, and PS, respectively). As a reference case, we also investigate the influence of PS addition on the aggregation of the linear PS-*b*-PI copolymer having the same degree of polymerization: 290 and 110 for PS and PI, respectively. To detect and characterize micellar morphologies in solution and in the solid state, we use two efficient physical techniques, dynamic light scattering (DLS) and atomic force microscopy (AFM), respectively.

2. Experimental Section

2.1. Sample Preparation. An α -isopropylidene-1,1-dihydroxymethyl- ω -diethylacetal-heterodifunctional end functional linear diblock poly(styrene-*b*-isoprene) copolymer with DP_{PS block} = 290 (as determined by SEC analysis) and DP_{PI block} = 110

(estimated from the NMR isoprene/styrene signal integration and the DP_{PS block}), corresponding to a total molar mass of 37×10^3 g/mol, was first synthesized using living anionic polymerization.³⁰ The corresponding cyclic poly(styrene-*b*-isoprene) compound was obtained by direct end coupling of the α - and ω -ends of the linear poly(styrene-*b*-isoprene) copolymer. This method of synthesis, as has been already described,^{35–37} yields exactly the same DP for each block in the linear and cyclic copolymer systems, because the cyclic compound is made by closure of the linear diblock. The volume fraction of PS, Φ_{PS} , in both diblock copolymers is equal to 0.78. The polydispersity index for the two copolymers is less than 1.1. The polystyrene homopolymer used as additive has a molar mass M_n of 5000 and a polydispersity index of 1.05. The sample preparation is an extremely delicate step which may affect the micellar organization, in particular in the present case for which the PS homopolymer used as additive is insoluble in pure heptane at 20°C, the temperature of investigation. To “solubilize” in heptane with the PS-*b*-PI, the PS homopolymer (2 and 5 wt % with respect to the diblock copolymer) and the copolymer were premixed. The mixture was dispersed in heptane under stirring and continuously stirred for at least 3 days at 50 °C under inert atmosphere, yielding a homogeneous, slightly turbid, solution. All solvents were HPLC grade and were distilled and filtered through a 0.2 μ m PTFE membrane prior to use.

2.2. Dynamic Light Scattering. The dynamic light scattering measurements³⁸ were performed using an ALV laser goniometer, which consists of a 22 mW HeNe linear polarized laser with 632.8 nm wavelength and an ALV-5000/EPP Multiple Tau Digital Correlator with 125 ns initial sampling time. The samples were kept at exact and constant temperature of 25.0 °C throughout the experiments. The accessible scattering angle ranges from 15° to 155°. All samples were systematically studied at 90°, and some of them were also studied at different scattering angles. The solutions were put in ordinary glass cells, 10 mm in diameter. The minimum sample volume required for an experiment was 1 mL. The data acquisition was done with the ALV-Correlator Control Software, and the counting time varied for each sample from 5 to 15 min, depending on the sample, the concentration, and the required time to build up good correlation functions.

The autocorrelation functions of the scattered intensity were analyzed by means of the cumulant method to yield the effective diffusion coefficient as a function of the scattering angle. The mean apparent hydrodynamic radius R_h is calculated from the time of first- to third-order fitting according to the Stokes–Einstein eq 1.

$$R_h = \frac{kT}{6\pi\eta\Gamma} q^2 \quad (1)$$

Additionally, the constrained regularization method CONTIN³⁹ was used to obtain the distribution $A(t)$ of decay times. This method is now routinely used to analyze the dynamic light scattering (DLS) data for colloidal systems and allows the determination of the relaxation modes that characterize the dynamics of such systems.

2.3. AFM Measurements. AFM measurements were conducted in ambient atmosphere at room temperature using a Nanoscope IIIa microscope (Veeco, Santa Barbara, CA). The preparation of thin deposits of the copolymers was carried out by solvent casting at 20 °C, by depositing 15 μ L of a heptane solution on a freshly cleaved mica substrate (the concentration was varied from 3 to 0.3 mg/mL). Mica was chosen as the substrate because its surface is atomically flat over very large terraces; therefore, the topographic information collected on very thin polymer deposits is not perturbed by the substrate roughness. The thickness of the deposits is in the range of 10–100 nm, depending on the concentration of the copolymer solution. The

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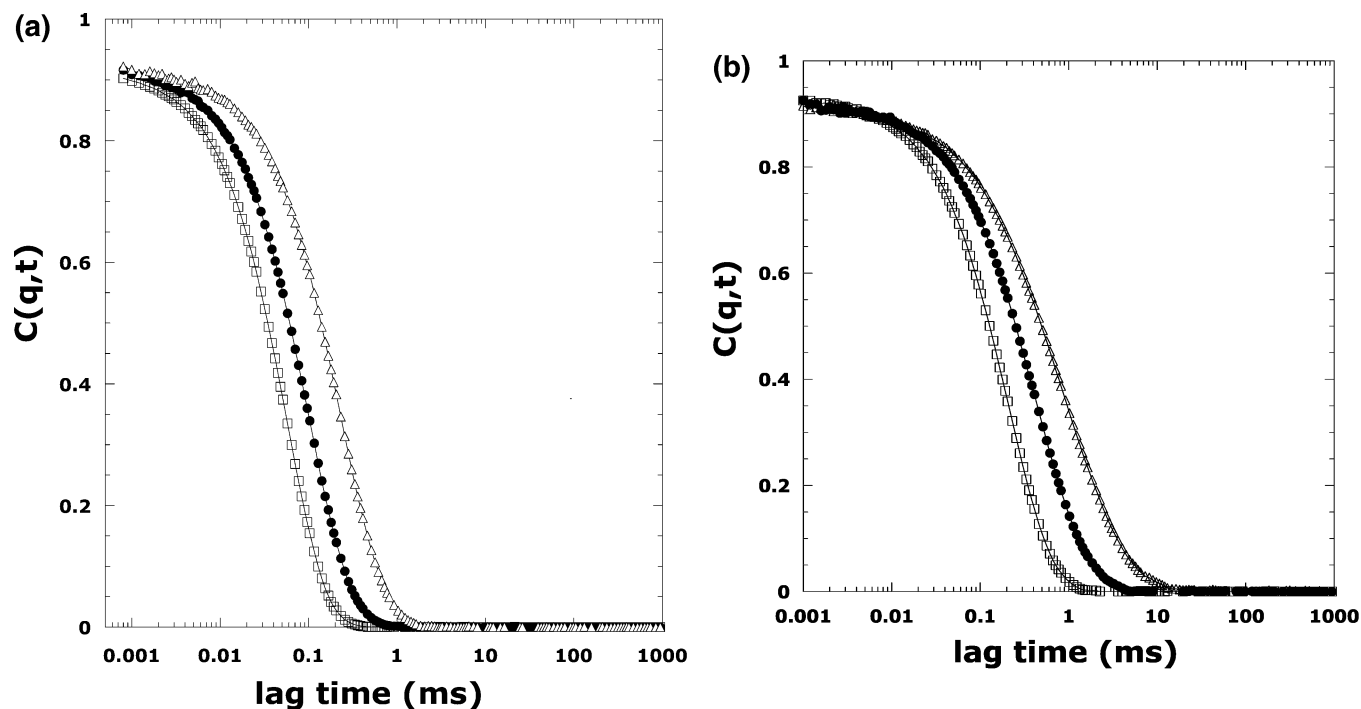


Figure 1. DLS autocorrelation functions on micelles formed from linear $\text{PS}_{290}\text{-PI}_{110}$ (a) and cyclic (b) block copolymers in heptane, with no PS added (\square), with 2% PS (\bullet), and with 5% PS (\triangle). The total polymer concentration was 3 mg/mL in all of the solutions.

samples were imaged after complete evaporation of heptane at 20 °C, using tapping mode (TM) AFM. TMAFM operation was chosen to minimize plastic deformations of the sample surface caused by the mechanical interactions between the surface and the AFM tip.

3. Results and Discussion

3.1. Dynamic Light Scattering. The DLS autocorrelation functions were measured at several concentrations for micelles made from linear or cyclic $\text{PS-}b\text{-PI}$ copolymer chains in heptane. Typical results are shown in Figure 1a and b. One observes that the autocorrelation functions for both systems are shifted to the right (increase in the relaxation times) upon addition of homopolymer. The interpretation of these curves leads to the following conclusions: the diffusion coefficient of the micelles is lower in the presence of PS, which can be correlated to an increase in the average micellar size.

It is well-known that the micelles made from pure linear $\text{PS-}b\text{-PI}$ copolymer in heptane are spherical and quite monodisperse in size.^{30,40} The CONTIN analysis (not shown here) of the curves exhibited in Figure 1a shows that not only the size of these micelles is increasing with the addition of PS but so does the dispersity in size; that is, the size distribution becomes broader. The average hydrodynamic radius of the micelles was extracted from the data in Figure 1 and is presented in Figure 2. The results show that the micelles from both copolymers (linear and cyclic) are increasing in size with the addition of PS homopolymer, clearly indicating that homopolymer PS chains are incorporated into the micelles.

It is interesting to note that the size for the micelles obtained in the mixture of the linear $\text{PS-}b\text{-PI}$ with 5% PS homopolymer is very close to the size observed for the micelles made from the pure cyclic $\text{PS-}b\text{-PI}$. The CONTIN analysis outputs (not shown here) for the DLS curves of these two solutions are also very similar. As we already know³⁰ that the micelles made from pure cyclic $\text{PS-}b\text{-PI}$

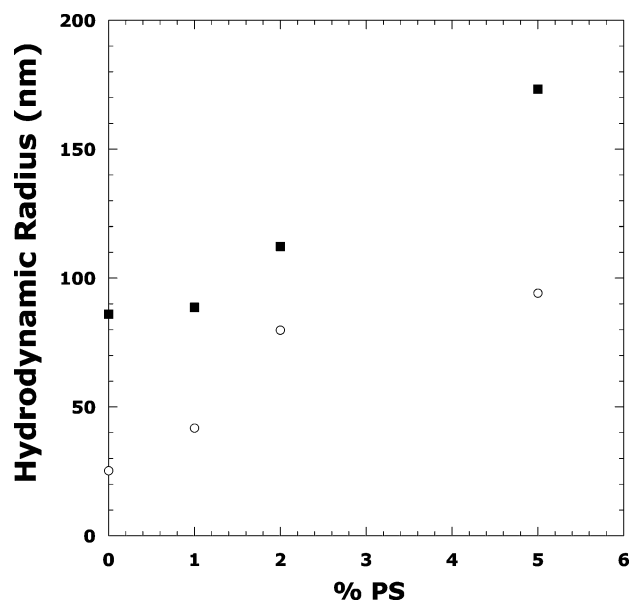


Figure 2. Hydrodynamic radius from second cumulant analysis of autocorrelation functions on micelles formed from cyclic (\blacksquare) and linear (\circ) $\text{PS}_{290}\text{-PI}_{110}$ block copolymers in heptane, as a function of the amount of PS homopolymer added. The total polymer concentration was 3 mg/mL in all of the solutions.

are wormlike objects at this concentration, these observations may be a hint that the micelles from the linear copolymer are driven into a sphere-to-worm transition due the incorporation of PS homopolymer.

The effect of homopolymer addition on the micelles made from the cyclic copolymer is even more drastic: the average hydrodynamic radius of the micelles with 5% PS added is about 180 nm. This value is, however, an average (first cumulant) because the DLS CONTIN results (not shown here) present a multimodal relaxation time.

3.2. AFM Results. To supplement the DLS results to understand and describe more precisely the evolution of the micellar morphology, AFM was used to characterize

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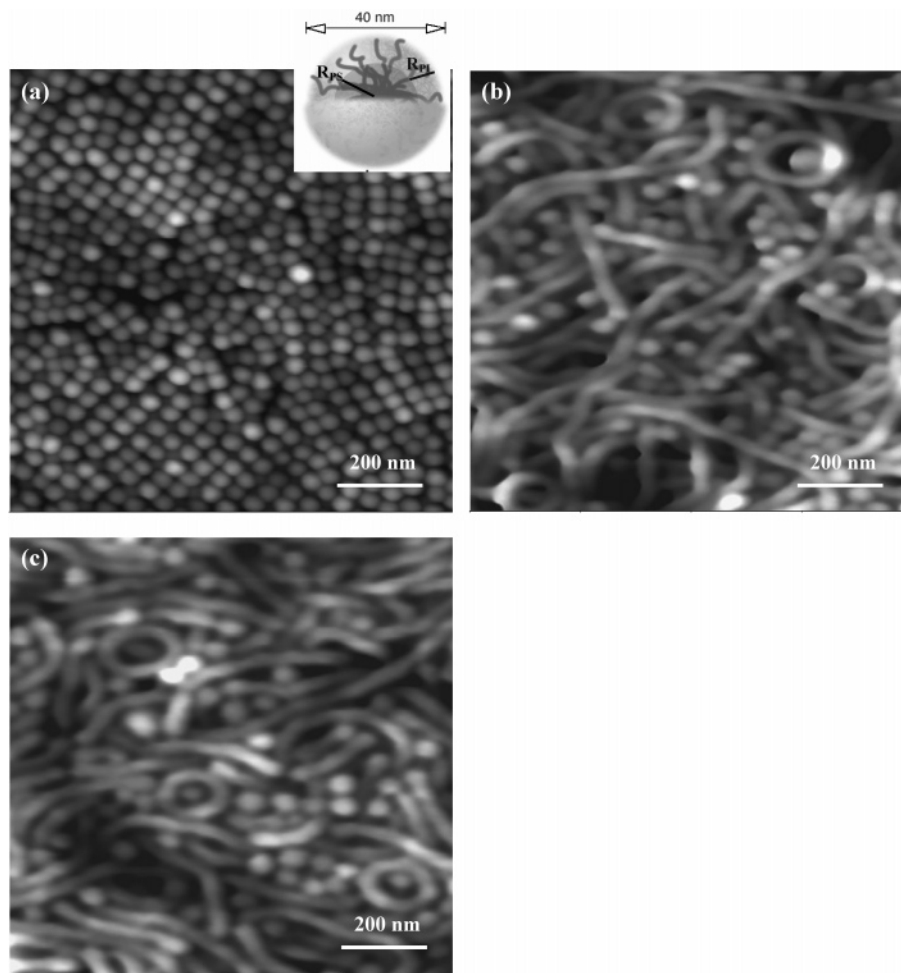


Figure 3. TMAFM topographic $1 \times 1 \mu\text{m}^2$ images of micelles of the linear $\text{PS}_{290}\text{-}b\text{-PI}_{110}$ block copolymer formed from 3 mg/mL solutions in heptane: (a) with no PS added in the solution; (b) with 2% PS; (c) with 5% PS.

thin deposits of linear or cyclic diblock copolymers containing increasing amounts of the PS homopolymer.

For the linear $\text{PS}_{290}\text{-}b\text{-PI}_{110}$ diblock copolymer, Figures 3 and 4 show topographic TMAFM images describing the effect of the addition of 2% and 5% PS to these systems, along with the pure copolymer system. As it has been shown recently³⁰ for the pure linear copolymer, the surface consists of a homogeneous deposit of spherical micelles (Figure 3a). These micelles have a very narrow size distribution; as determined from the power spectral density of the AFM images, their diameter is 40 ± 0.6 nm.

To see isolated micelles to better visualize their organization on the surface, the initial solution was rediluted 10 times in heptane and deposits were prepared from that diluted solution. As illustrated in Figure 4a, the dilution does not modify the “spontaneously formed” morphology, the dimensions of the formed micelles remaining constant. The formation and stability of the micelles in solution are thus clearly confirmed by these AFM observations. The PS segments constitute the core of the micelles because of their insolubility in heptane, while the PI segments form a thin corona. On the basis of the density values of PS and PI, the copolymer composition corresponds to a PS/PI volume ratio of 3.45:1. This leads to the following estimation of the micellar inner structure: the radius of the PS core, R_{PS} , is about 18.4 nm, while the thickness of the PI corona, R_{PI} , is about 1.6 nm. The aggregation number, N_{agg} , that is, the number of molecules per micelle, can be determined for the pure

linear copolymers because they yield spherical micelles with constant diameter, whatever the concentration. The aggregation number has been determined from both DLS and AFM data. By DLS, for a concentration of 2 mg/mL in heptane, a value of 847 was found,³⁰ while by AFM, this number is equal to 546 ± 24 . This difference is related to the fact that the diameter of the spherical micelles determined with DLS and AFM is different, due to the presence of the solvent in the corona in DLS measurements, which is not the case in AFM studies.

The PS homopolymer added is expected to be incorporated into the micellar core, which would lead to a swelling of the spherical micelles. In fact, we observe that the addition of a small amount of PS (2%) is apparently sufficient to deeply modify the micelle characteristics, from an exclusively spherical morphology (Figure 3a) to the coexistence of spheres and much longer, wormlike micelles (Figure 3b). The presence of PS thus strongly modifies the way linear $\text{PS}_{290}\text{-}b\text{-PI}_{110}$ copolymer molecules aggregate within naturally spherical micelles, leading to giant wormlike micelles.

To further understand the evolution of the morphology, the concentrated ($\text{PS-}b\text{-PI} + \text{PS } 2\%$) solution was also rediluted 10 times in heptane and deposits were prepared. The corresponding AFM data (Figure 4b) confirm that the morphology and the dimensions of the formed micelles are not modified by the dilution: we still observe the coexistence of spherical and cylindrical micelles. As the percentage of added PS increases from 2% to 5%, spheres and cylinders are still present (Figures 3c and 4c).

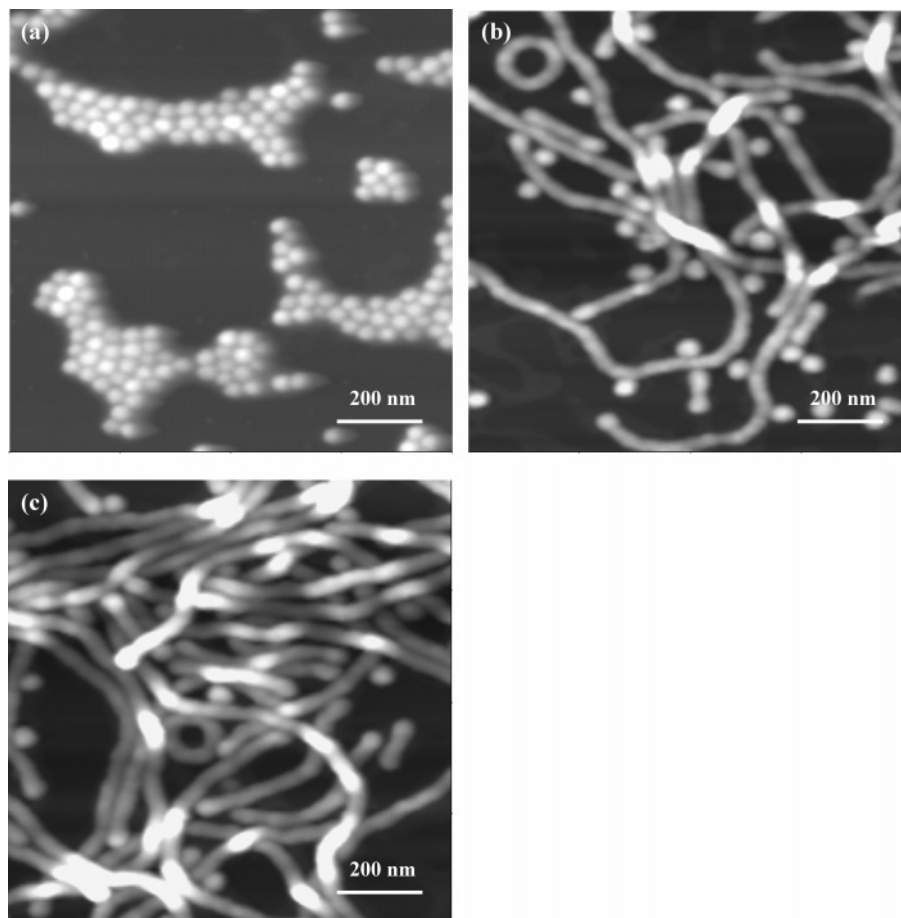


Figure 4. TMAFM topographic $1 \times 1 \mu\text{m}^2$ images of micelles of the linear $\text{PS}_{290}\text{-PI}_{110}$ block copolymer formed from 3 mg/mL solutions in heptane, then diluted 10 times: (a) with no PS added in the solution; (b) with 2% PS; (c) with 5% PS.

To our knowledge, the morphological transition from spheres to cylinders that we observe here when the nonsoluble homopolymer is added to spherical micelles has not been reported previously in the literature. Indeed, it is worth noting that the effect on the morphology of added PS is opposite of that observed by Eisenberg with $\text{PS-}b\text{-PAA}$ ²⁹ (i.e., change from cylinders to spheres), although in both systems the added homopolymer is expected to be incorporated in the PS core. It is not easy to understand this difference in behavior between the $\text{PS-}b\text{-PAA}$ system and the $\text{PS-}b\text{-PI}$ system studied here. Besides differences in the chemical composition and the solvent, it is noted that the micellization process is different. The $\text{PS-}b\text{-PAA}$ diblock copolymers were first dissolved in *N,N*-dimethylformamide (DMF), a common solvent for PS and PAA, and then water, a precipitant for PS, was added to induce the formation of micelles. DMF was finally removed from the micellar solutions by dialysis against distilled water. In our case, instead, the micelles are formed in a single step, from heptane, a bad solvent for PS. We believe that the low molar mass of the PS used here makes it slightly soluble in heptane, which allows for its diffusion into the micellar cores, where it is much better stabilized.

An interesting point regarding the linear $\text{PS-}b\text{-PI}$ + PS system is that the average diameters of both spheres and cylinders are equal: 40 ± 0.8 nm. These results suggest that wormlike micelles and spherical micelles are related to each other. We thus propose that wormlike micelles come from the unidirectional aggregation of primary spherical micelles because of the development of sphere-to-sphere PS interactions upon addition of increasing

amounts of PS homopolymer. This suggests that, upon PS addition, the core volume of $\text{PS-}b\text{-PI}$ spheres cannot easily grow to accommodate the PS homopolymer while maintaining stable spherical micelles. Therefore, it becomes obvious as a corollary that the addition of PS would result in an increase in the core density. This could be the reason for the destabilization of the spherical micelles to the benefit of cylindrical ones, for which an expansion along the axis would allow optimization of the core density, thus efficiently stabilizing the cylindrical micelles.

The AFM analysis also shows that the morphology observed is not homogeneous because spherical micelles are still present on the surface: the presence of remaining spheres most probably corresponds to micelles of the pure linear copolymer that did not incorporate PS; their shape and diameter are therefore unchanged.

In the majority of the cases reported in the literature, the transition from spherical micelles to cylindrical micelles is induced by reducing the weight fraction of the soluble block, for example, PAA in the case of $\text{PS-}b\text{-PAA}$ diblock copolymers in water^{29,41} or PEO in the case of poly(ethyleneoxide-*b*-butadiene), $\text{PEO-}b\text{-PB}$, diblock copolymers^{42,25} in aqueous solutions. Similarly, for poly(styrene-*b*-2-cinnamoyl ethyl methacrylate), $\text{PS-}b\text{-PCEMA}$ in cyclopentane, a selectively bad solvent for PCEMA, Ding et al.⁴³ observed a transition from spherical micelles to the coexistence of spherical and cylindrical micelles by a

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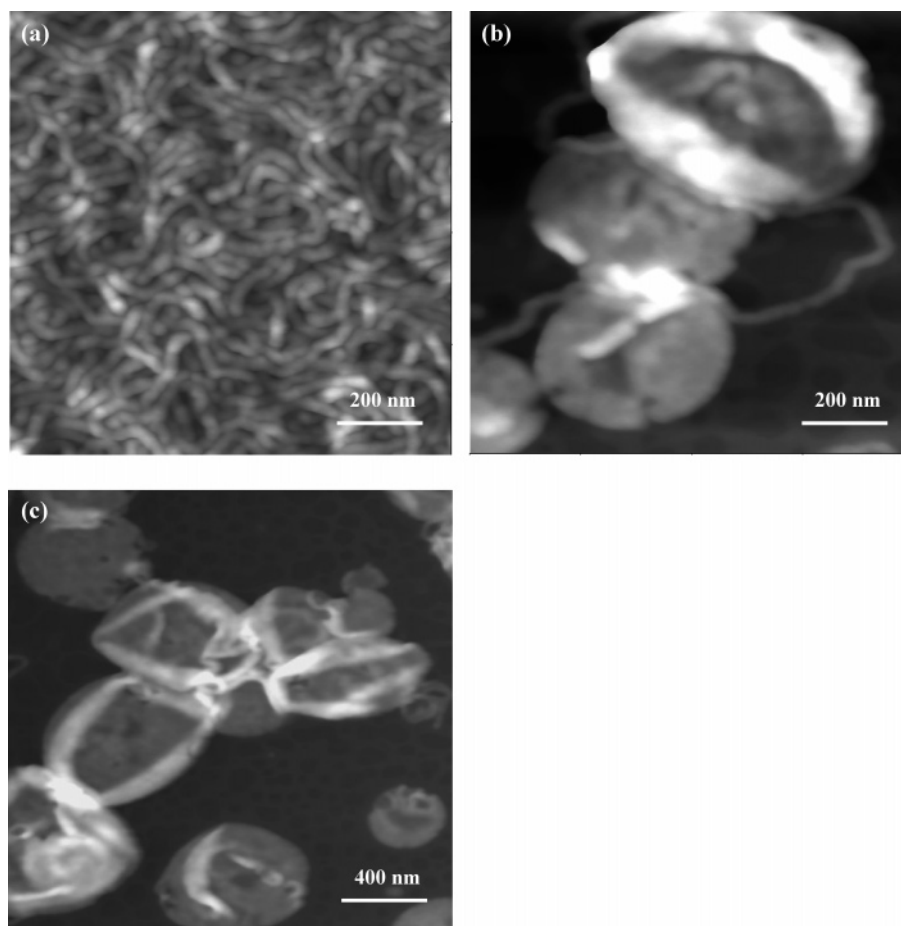


Figure 5. TMAFM topographic $1 \times 1 \mu\text{m}^2$ images of micelles of the cyclic $\text{PS}_{290}\text{-PI}_{110}$ block copolymer formed from 3 mg/mL solutions in heptane: (a) with no PS added in the solution; (b) with 2% PS; (c) with 5% PS. Images b and c were obtained after the initial 3 mg/mL solution in heptane was diluted 10 times. The size of image c is $2 \times 2 \mu\text{m}^2$.

decrease in the length of the soluble block relative to that of the PCEMA. Our results are consistent with those observations; that is, the increase of the insoluble PS fraction by addition of PS homopolymer, which induces a change from spheres to cylinders, is equivalent to reducing the fraction of the soluble component.

For the cyclic $\text{PS}_{290}\text{-}b\text{-PI}_{110}$ diblock copolymer, the addition of PS homopolymer has a very different impact on the micellar morphology, as illustrated in the AFM images shown in Figure 5a–c: they correspond to the addition of 2% and 5% PS in heptane solution, along with the pure copolymer system. We present here images of deposits obtained from the solutions diluted 10 times in heptane, to visualize directly and more clearly the influence of PS on the micellar organization. Let us recall that the dilution does not modify the shape and size of the micelles formed in solution. The morphology of the solid deposits obtained from the concentrated solutions is identical to that observed for the samples from the diluted solutions; it is simply more difficult to exploit the AFM data because of the larger quantity of material present on the surface.

In the absence of PS homopolymer, cyclic copolymer molecules self-assemble into elementary micelles that we have called “sunflowerlike” micelles.^{30,44} These organized systems, which have a disk shape, are made up of a dense core formed by the PS block chains surrounded by a corona composed of the PI block chains. When the copolymer

concentration is in the range of 3 mg/mL and over, the “sunflowerlike” micelles aggregate in one direction, generating wormlike micelles, as observed in Figure 5a. The diameter of those cylindrical micelles is 30 ± 0.5 nm. Considering that the PS/PI volume ratio is the same as that of the linear copolymer (because the two compounds have the same composition), one can estimate that the radius of the PS core is about 13.2 nm and the thickness of the PI corona is about 1.8 nm (i.e., a value very close to that of the corona in spherical micelles of the linear copolymer).

As shown in Figure 5, the addition of 2% PS provokes a drastic change in both the shape and the size of micelles. The very large objects found on the surface most probably are the remnants of large vesicles present in solution, which have collapsed upon solvent evaporation. Therefore, the addition of PS homopolymer to cyclic copolymer molecules strongly perturbs the aggregation mechanism in heptane: this apparently leads to a morphological transition from cylindrical micelles to vesicles. This situation is somewhat similar to the well-known behavior of block copolymers in the bulk solid state:^{45–47} in a cylindrical morphology, the increase in the relative amount of the component forming the cylinders eventually leads to the formation of a structure with alternating lamellae. In other words, a morphological transition from one-dimensional to two-dimensional objects takes place. We

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observe the same type of process here: the cylindrical PS core of the wormlike micelles cannot accommodate the added PS homopolymer. As a result, the system tends to form 2-D PS objects. Flat PS lamellae would obviously not be stable in heptane. Instead, the PS domains are "coated" on both sides with a PI layer and they form closed objects, that is, vesicles, in which the PS forming the core of the membrane is not in contact with the solvent. It is also important to note that the AFM data are consistent with the DLS experiments, which show a dramatic increase of the R_h value upon PS addition.

Note that Figure 5b also shows a few cylindrical objects probably corresponding to micelles that have not incorporated PS homopolymer. When 5% PS homopolymer is added to the cyclic copolymer, only collapsed vesicles are observed (Figure 5c), which is consistent with the incorporation of a larger amount of homopolymer.

To our knowledge, such a modification of the morphology, from cylindrical micelles to vesicles, upon addition of the insoluble homopolymer has never been reported for cyclic block copolymers. Instead, such a rod-to-vesicle transition can be induced for instance by varying the block copolymer composition and by increasing the insoluble block fraction: such a situation is exemplified for PS-*b*-PAA²⁹ diblock copolymers (although a reverse effect is noticed when homopolymer PS is added to PS-*b*-PAA vesicles). Won et al.²⁵ and Jain and Bates⁴⁸ have reported a similar transition from cylinders to vesicles for PB-*b*-PEO diblock copolymers in water with the decrease of the weight fraction of the PEO block. This behavior is explained by the authors as follows: to accommodate the increased asymmetry between hydrophilic and hydrophobic volumes per chain, interfacial curvature increases with increasing the insoluble fraction, while respecting the constraints imposed by the connectivity between the two blocks and the incompressibility of the core domain. This morphological transition from rod to vesicle can also be induced by other factors. For example, for PS-*b*-PAA diblock copolymers in dioxane/water mixtures, this change in the micelle shape and dimensions is provoked by an increase of the water content.⁴⁹ Therefore, the morphological change observed here upon increasing the insoluble polymer fraction by adding PS homopolymer can be considered to be in line with that quite general behavior.

4. Conclusions

The present results show that the addition of small amounts of the insoluble homopolymer to PS-*b*-PI micelles, made either from linear or from cyclic copolymer chains, has a dramatic influence on their size and shape. The DLS data clearly point to increases of average micellar size (up to 100%) that are inconsistent with a simple volume expansion due to PS incorporation. Indeed, morphological transitions take place, as confirmed by the AFM results. For the linear copolymer, the added PS turns spherical micelles into cylindrical aggregates of about the same diameter. The wormlike micelles initially formed by the cyclic block copolymer are turned into much larger objects, most probably vesicles. Using those two block copolymers and some PS additive, one can thus control the shape of the micelles, from spheres to cylinders and to vesicles. This behavior is in agreement with most observations concerning the effect on the morphology of an increase of the weight fraction of the insoluble polymer component.

The fact that the addition of small amounts of PS has such a drastic effect on the micellar morphology suggests that the copolymer composition studied here is close to a phase transition in the phase diagram of the system. Investigations of similar copolymers with different PS/PI volume ratio, and the influence of PS addition, are in progress.

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