

Morphology of core-shell-corona aqueous micelles: II. Addition of core-forming homopolymer

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Abstract

The poly(styrene)-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) triblock copolymer PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀, where the subscripts refer to the number average degrees of polymerization, forms spherical micelles in water, that consist of a PS core, a pH-responsive P2VP shell and a PEO corona. This triblock has been added with homo-PS before micellization in order to increase the volume fraction of the core-forming block. The length of the added homo-PS has been varied with respect to the length of the PS core-forming block: much shorter, much longer and approximately the same. The structure of the micelles has been investigated by transmission electron microscopy, static and dynamic light scattering. Homo-PS phase separates whenever its length is larger than the one of the PS core-forming chains; otherwise this phenomenon occurs beyond a critical concentration that depends on molecular weight. The addition of homo-PS has no influence on the morphology of the micelles and on the characteristic size of both the PS core and the P2VP shell, although the hydrodynamic diameter of the micelles is decreased. Substitution of styrene for homopolystyrene results in transition from a spherical to a dominant rod-like morphology.

Keywords: Block copolymers; Micelles; Morphology

1. Introduction

Formation of aqueous micelles as a result of the self-organization of block copolymers in water is an area of intense research [1] which stems from a large range of potential applications, such as detergency, surface coating, waste-water treatment, oil recovery, drug-release and nanotechnology [2]. In the latter application, the core of block copolymer micelles with well-defined shape and size can act as a nanoreactor for the synthesis of metallic nanoparticles [3].

Although amphiphilic diblock copolymers are usually used to produce aqueous micelles, ABC triblock copolymers have the advantage to form more complex nanostructures [4-5]. In this respect, well-defined core-shell-corona (CSC) micelles have been prepared from poly(styrene)-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) triblock copolymers [6-9]. These micelles consist of a PS core, a pH-responsive shell and a PEO corona. Very similar systems, referred to as 'onion' micelles, have been previously prepared by co-precipitation of two diblock copolymers, both of them containing a P2VP block [10-12]. However, these systems are generally less defined than the ones obtained from low polydispersity ABC triblock copolymers and behave differently as a function of pH. Due to the ability of P2VP to coordinate metal salts, gold nanoparticles have been prepared from spherical CSC micelles [6]. Effort is now devoted to the synthesis of CSC micelles of various morphologies, i.e. rods, lamellae and vesicles, that could be used as templates for inorganic nanoparticles with various shapes and sizes [8].

The morphology of amphiphilic block copolymers micelles has been shown to depend mainly on the interplay of three parameters, i.e. stretching of the core-forming block, core-corona interfacial energy, and mutual repulsion of the coronal blocks (due to steric crowding and electrostatic repulsion in case of charged coronal chains) [13]. Whenever amphiphilic ABC triblock copolymers form CSC micelles, the entropy of both the core-forming and the shell-forming chains has to be considered, together with the core-shell and shell-corona interfacial energies. One of the direct ways to modulate size and morphology of PS-*b*-P2VP-*b*-PEO aqueous micelles consists in changing the entropy of the core-forming PS chains. In this respect, it is well-known that an increase in the volume fraction of the core-forming block of spherical micelles results in an entropy penalty [14] and beyond a critical volume fraction, a morphological sphere-to-rod transition is observed [14]. In this contribution, homo-PS chains of various molecular weights have been added to a PS-*b*-P2VP-*b*-PEO copolymer, with the purpose to change the volume fraction of the PS core-forming blocks.

2. Experimental part

2.1. Materials

PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ triblock and PS₇₀, PS₁₇₀ and PS₅₉₀ homopolystyrene (the numbers in subscript being the number average degrees of polymerization) were synthesized by living anionic polymerization, as reported elsewhere [7]. The first PS block was analyzed by SEC (calibrated with PS standards): $M_n=20,000$ g/mol. The intermediate PS-*b*-P2VP copolymer was analyzed by SEC (PDI=1.07) and by ¹H NMR. Its composition was determined on the basis of 2VP protons at 6.2 ppm and the aromatic protons of styrene and 2VP in the 6.2–7.2 ppm range. M_n (P2VP)=14,000 g/mol based on the diblock composition and M_n PS. Finally, the PS-*b*-P2VP-*b*-PEO triblock was analyzed by SEC (PDI=1.10) and by ¹H NMR (α protons of the EO units at 3.6–3.7 ppm). M_n (PEO) was found to be 26,000 g/mol. Fig. 1 shows the SEC traces for the first block (PS), the intermediate diblock (PS-*b*-P2VP) and the final triblock.

The polydispersity of all the samples was lower than 1.2. Styrene was purchased from Aldrich and passed through a silica column before use.

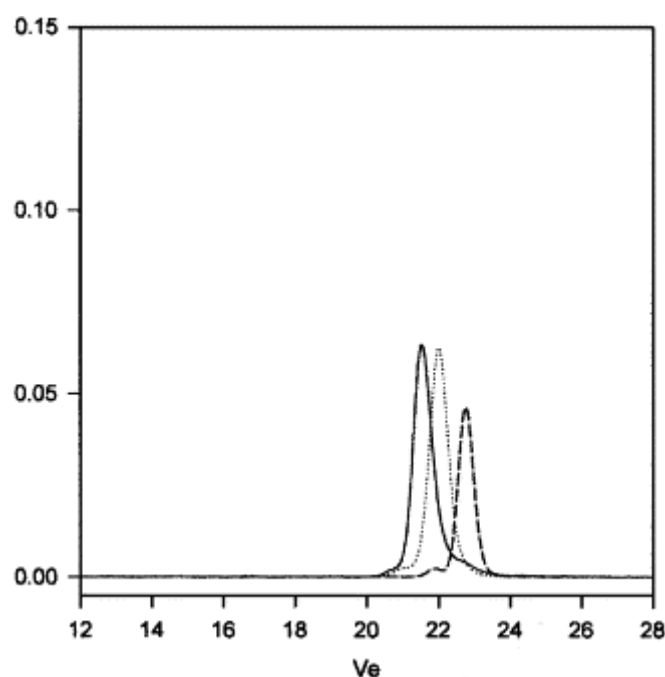


Fig. 1. Size exclusion chromatography. (---): First PS block, $M_n=20,000$, PDI=1.03; (- · -): diblock PS(20,000)-*b*-P2VP(14,000), PDI=1.05; (—): triblock PS(20,000)-*b*-P2VP(14,000)-*b*-PEO(26,000), PDI=1.10.

2.2. Preparation of the micelles

2 wt% solutions were prepared by dissolving mixtures of homo-PS and PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ of various compositions in 0.9 g of *N,N*-dimethylformamide (DMF). The content of homo-PS will be referred to as the wt% with respect to the total (copolymer+homoPS) amount. Afterwards, 0.1 ml of water was dropwise added in order to trigger micellization. Two milliliters of water were then added to freeze the micelles, and DMF was removed by dialysis against regularly replaced deionized water. In another experiment, 0.02 g of PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ was dissolved into 0.9 g of a 70/30 wt/wt DMF/styrene mixture instead of pure DMF. 0.5 g water was then added dropwise to the solution under vigorous stirring, which was maintained for 24 h. Then, the micelles were frozen in by adding 1 g of water. The organic solvent was removed by dialysis against water and, in some cases, against ethanol.

2.3. Transmission electron microscopy (TEM)

TEM images were recorded with a Philips CM100 microscope equipped with a Gatan 673 CCD camera, and transferred to a computer equipped with the Kontron KS100 system. Samples were prepared by dipping a

Formvar-coated copper grid into a dilute micellar solution (0.05 wt% polymer) and contrasted with RuO₄ vapor. Some samples were also stained by a phosphotungstic aqueous solution. In this case, a drop of 0.1 wt% phosphotungstic acid aqueous solution was deposited onto the surface of the sample-loaded grid. Three minutes later, excess solution was removed using filter paper, and the sample was washed with water and dried in air. The core+shell diameter (D_{CS}) of the micelles was averaged over at least 50 objects.

2.4. Light scattering (LS)

LS was performed with a 'Brookhaven Instruments Corp.' BI-200 apparatus equipped with a BI-2030 digital correlator and an 'Ion Laser Technology' argon laser at a wavelength of 488 nm. Static light scattering (SLS) experiments were carried out in order to determine the average molecular weight, M_w , of the micelles (Zimm-plot analysis). For dynamic light scattering (DLS) experiments, the experimental intensity correlation function was measured and analyzed as described elsewhere [15]. Each sample was measured at least 10 times in order to check the reproducibility. The average hydrodynamic diameter (D_h) was accordingly calculated. The pH-dependence of micellar size was analyzed by DLS, at pH 2 and 7, respectively. The micellar solution was added with the amount of HCl (0.01 M) required to set pH at 2 and by NaOH (0.01 M) until reaching neutrality, respectively.

3. Results and discussion

The addition of a homopolymer (A) to a block copolymer (AB) has been extensively studied in the bulk [1]. The phase behavior of these binary blends is primarily governed by the degree of polymerization of the homopolymer chain (N_A) compared to the copolymer (N_{AB}). Three distinct regimes have been identified. Whenever $N_A < N_{AB}$, the homopolymer A tends to be selectively solubilized in the A domains of the AB block copolymer, which results in the swelling of these domains and an increased interfacial area. A transition in the phase morphology may be accordingly observed. This regime has been designated as the 'wet-brush' regime. In the specific case where $N_A \approx N_{AB}$, the added A chains are soluble in the A microdomains. They are, however, preferentially localized in the core of these microdomains, the interfacial area of which does not change significantly. This regime is known as the 'dry-brush' regime. If $N_A > N_{AB}$, the A chains are insoluble into the A microdomains, and a macrophase separation occurs. These three regimes have been experimentally and theoretically studied for many years, as reviewed in Ref. [1].

In this work, the three regimes have been considered for the formation of aqueous micelles from homo-PS/PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ blends. Solutions of these blends in DMF have been added with water in order to trigger micellization. Upon DMF removal by dialysis, 'frozen' micelles are collected in pure water and analysed by TEM and DLS. The experimental observations depend on the average degree of polymerization of homo-PS (N_{PS}). Whenever N_{PS} is higher than the average degree of polymerization of the PS block of the PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ triblock (N_{PST}), an unstable milky solution (followed by precipitation) is formed upon water addition. In contrast, the addition of water to a DMF solution of the neat triblock results in an optically clear and stable solution of spherical micelles, that consist of a PS core, a P2VP shell and a PEO corona [6-7]. Precipitation is observed whenever water is added to a 0.05 wt% solution of PS₅₉₀ in DMF. Therefore, PS₅₉₀ also precipitates from the PS₅₉₀/triblock solution in DMF, which indicates that it is not blended within the PS core of the micelles, as it is the case in the bulk [1].

Fig. 2 illustrates the stable micelles which are formed by the PS₁₇₀ (less than 8 wt%)/PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ blends, in the typical $N_{PS} \approx N_{PST}$ case. The PS core and the P2VP shell of these micelles have been stained by RuO₄ before being observed by TEM. It appears that the addition of a certain amount of homo-PS does not change the micellar morphology and spherical micelles are systematically observed. Indeed, the original core-shell-corona morphology of the neat PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ triblock [6-7] persists, as confirmed by the selective staining of the P2VP shell by phosphotungstic acid (Fig. 3). P2VP is observed to wrap around the PS core, whereas the concomitant staining of the PS and P2VP blocks by RuO₄ results in completely dark nanodomains (Fig. 2), the outer part of which must be a corona of water-soluble PEO blocks.

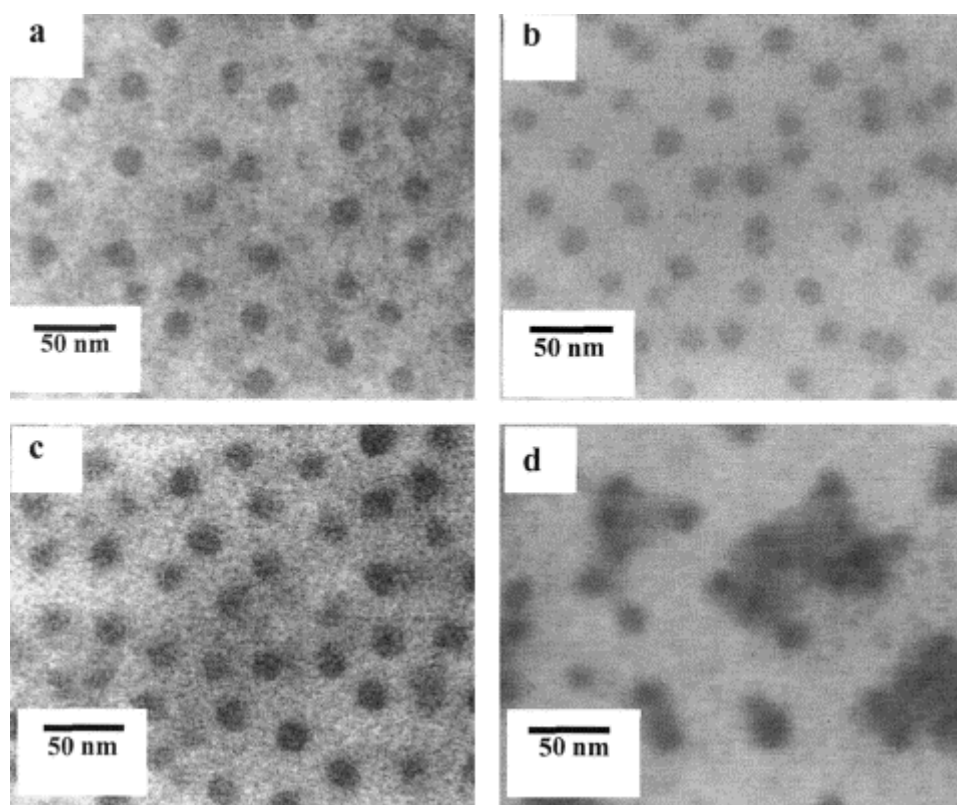


Fig. 2. TEM pictures of PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} aqueous micelles containing 0 wt% (a), 4 wt% (b), 5 wt% (c), and 8 wt% (d) of PS_{170} , stained by RuO_4 .

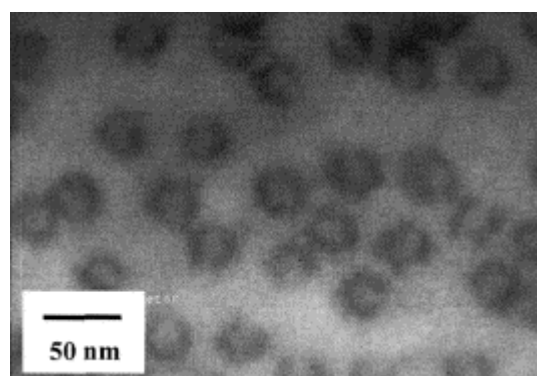


Fig. 3. TEM pictures of PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} aqueous micelles containing 5 wt% PS_{170} , stained by phosphotungstic acid.

Whenever the content of PS_{170} exceeds 8 wt% with respect to triblock, thus 26.5 wt% with respect to (PS_{170} +PS block) mixture, the homo-PS starts to precipitate as illustrated by Fig. 2(d) (i.e., coexistence of spherical micelles with ill-defined homo-PS domains). Thus, beyond a critical content of homo-PS (C_{sat}), the excess cannot accommodate further in the PS core of the micelles and PS phase-separates in water. C_{sat} of homo PS_{170} is approximately 8 wt% in the PS_{170}/PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} blend. Observation of C_{sat} is in agreement with previous results reported for crew-cut aggregates prepared in water from blends of PS_{410} homo-PS and PS_{410} - b - PAA_{20} polystyrene-*block*-poly(acrylic acid) diblock copolymer. C_{sat} is then in the 10–20 wt% range [16]. At low PS_{410} content, this homopolymer is dissolved in the core of the crew-cut aggregates. However, beyond a critical content, much larger aggregates accommodate the major part of homo-PS and show an internal structure of reverse diblock copolymer micelles. In this investigation, no specific structure is observed for the large homo-PS particles that phase-separate. Some triblock copolymer chains might, however, be adsorbed at the surface of the homo-PS particles.

The characteristic size of the core+shell constitutive part of the micelles (stained by RuO_4) has been measured from the TEM pictures, as a function of the PS_{170} content. Fig. 4 (open circles) shows that the core+shell diameter (D_{CS}) is essentially constant (26 ± 2 nm), whatever the blend composition. These data have been confirmed by the selective staining of the P2VP shell by phosphotungstic acid. This constancy of the shape and size (D_{CS}) of the micelles upon PS_{170} addition, strongly suggests that PS_{200} - b - P2VP_{140} - b - PEO_{590} chains are substituted by PS_{170} ones, with formation of a larger number of micelles that accordingly contain less stabilizing PEO blocks. This mechanism is indirectly confirmed by a loss in the stability of the micelles. Indeed, although the micelles formed by the neat triblock copolymer in water are stable for more than 6 months, the micelles of the PS_{170} /triblock mixture starts to coalesce 48 h after preparation. This can be accounted for by a less effective steric stabilization of the PS_{170} /triblock micelles, because, at constant PS block aggregation number, there are less PEO blocks in the corona compared to the neat triblock micelles. The original micelles then aggregate into large clusters that precipitate.

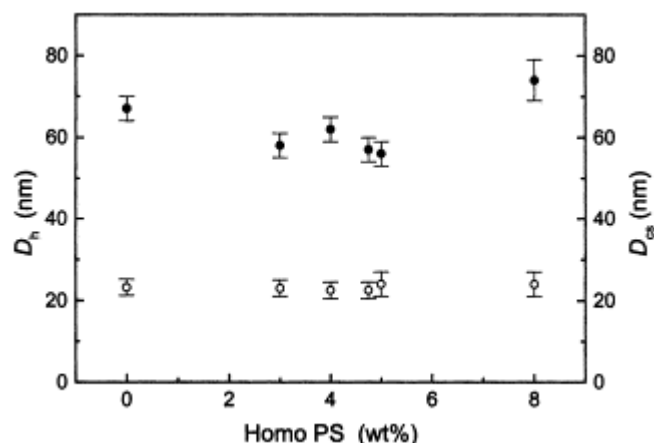


Fig. 4. Hydrodynamic diameter, D_h (solid circles, from DLS), and (core+shell) diameter, D_{CS} (open circles, from TEM), vs. the wt% of added PS_{170} .

Another interesting experimental observation can be found in DLS experiments. The hydrodynamic diameter (D_h) of the micelles initially decreases upon addition of PS_{170} (left part of Fig. 4), in contrast to the constancy of D_{CS} . This modification is consistent with the substitution of PS_{170} chains for PS_{200} - b - P2VP_{140} - b - PEO_{590} ones, because the water-soluble PEO blocks experience less steric repulsion in the corona and can adopt a less stretched conformation. This situation is schematized in Fig. 5, that compares micelles containing the PS_{200} - b - P2VP_{140} - b - PEO_{590} triblock, with (right) or without (left) PS_{170} . When C_{sat} is reached, D_h increases (Fig. 4) in agreement with the formation of large PS_{170} particles.

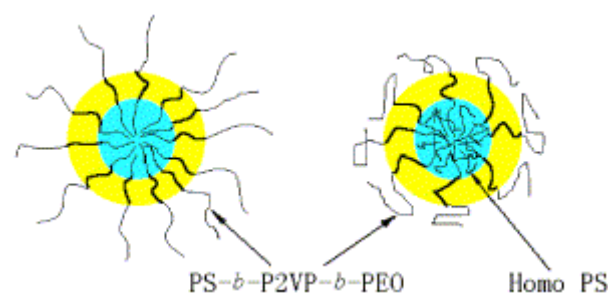


Fig. 5. Schemes for the CSC micelles of neat triblock copolymer (left) and a mixture of triblock copolymer and homopolymer chains (right).

In order to give credit to this explanation, static light scattering experiments have been performed in order to measure the weight average molecular weight of the PS_{200} - b - P2VP_{140} - b - PEO_{590} triblock micelles, with and without PS_{170} . The angular dependence of the SLS data (extrapolated to zero concentration) is shown in Fig. 6. The apparent M_w has been determined from the intercept of the straight line with the Y-axis and found to be $(7.12 \pm 0.12) \times 10^6$ for the neat triblock micelles and $(6.92 \pm 0.09) \times 10^6$ for the triblock micelles containing 4.5 wt% of PS_{170} . These values agree with a mean aggregation number of approximately 120 chains for both types of

micelles, which is in line with the assumption that homo-PS chains are substituted for $PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ triblocks in the micellar core.

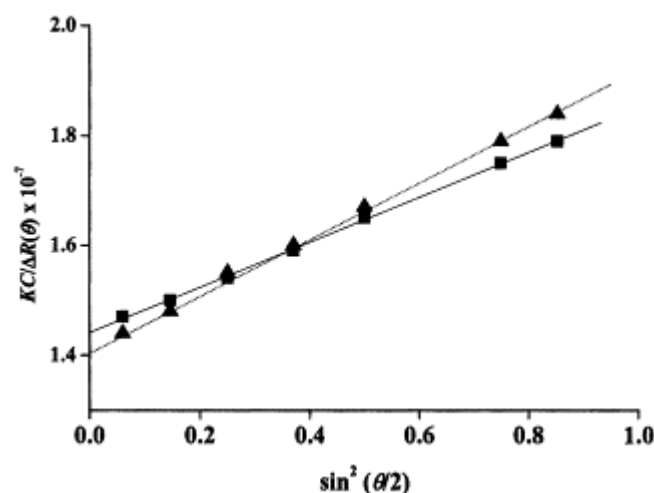


Fig. 6. Angular dependence of the SLS data extrapolated to zero concentration for $PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ micelles (triangles) and $PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ micelles containing 4.5 wt% of PS_{170} (squares).

The response of the $PS_{170}/PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ micelles to pH changes has been also investigated. A previous investigation reported on the reversible response to pH of the P2VP shell of $PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ micelles. At $pH > 5$, the P2VP shell is hydrophobic and collapses on the PS core, whereas it is positively charged, water-soluble and highly stretched at $pH < 5$ [6-7]. Webber et al. also studied the influence of pH on the micellization of P2VP-*b*-PEO diblocks. Titration light scattering data showed that both P2VP and PEO are soluble in water at pH lower than 5 and that P2VP turns insoluble with formation of micelles at higher pH [17].

Because pK_a of P2VP depends on the ionization degree, five is not the actual pK_a , but rather a critical pH at which micellization occurs [18]. In this work, the effect of pH change on the micellar size has been studied by DLS, as shown in Fig. 7 for $PS_{170}/PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ micelles. Upon addition of acid, an important increase in D_h is noted. Neutralization of the protonated P2VP shell, however, restores the initial diameter. The process can be repeated several times without alteration of D_h of the neutral micelles. In contrast, D_h of the protonated micelles decreases as the number of cycles is increased. The original data are, however, restored whenever the salt formed at each neutralization step is eliminated by dialysis, consistent with the electrostatic screening of the protonated P2VP chains by NaCl [6].

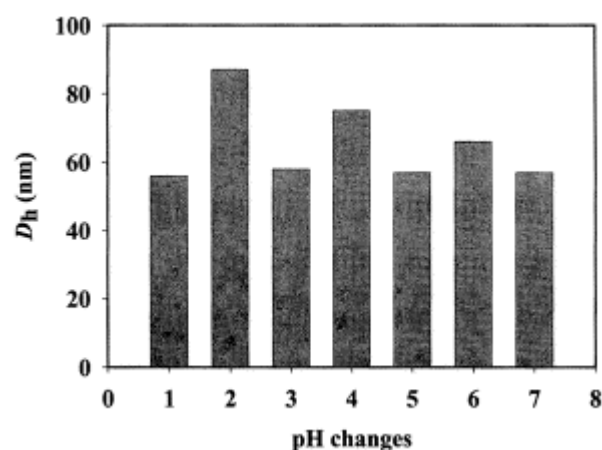


Fig. 7. Effect of pH variation on D_h of the micelles formed by the PS_{170} (4.5 wt%)/ $PS_{200}\text{-}b\text{-}P2VP_{140}\text{-}b\text{-}PEO_{590}$ blend (1: original 'neutral' sample; 2, 4, and 6: addition of HCl 0.01 mol/l; 3, 5 and 7: addition of NaOH 0.01 mol/l).

The PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} triblock has been blended with PS_{70} , in order to investigate the third $N_{PS} < N_{PST}$ regime. This system is quite similar to the PS_{170}/PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} one. C_{sat} is increased by approximately a factor of two, i.e. $C_{sat}=18$ or 59.5 wt% with respect to the $(PS_{70}+PS)$ block mixtures. Below C_{sat} , D_{CS} is constant (25 ± 2 nm, Fig. 8(a)) and close to the value reported for the PS_{170}/PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} system. This observation suggests again that the added homo-PS does not merely swell the PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} micelles. Above C_{sat} , large PS_{70} particles are formed in addition to micelles (Fig. 8(b)). It must be noted that the samples have been contrasted with phosphotungstic acid in Fig. 8, in order to selectively stain the P2VP shell. The large PS_{70} particles are observed by TEM as black spheres, more likely because triblock copolymer chains are adsorbed at their surface, the P2VP block of which immobilizes phosphotungstic acid molecules. Details about the contrasting methods of PS - b - $P2VP$ - b - PEO micelles can be found elsewhere [7]. The major difference between the micelles that contain PS_{70} and PS_{170} , respectively, is C_{sat} . Indeed, the C_{sat} ratio for the two homo PS ($18/8=2.25$) is very close to the reverse ratio of their molecular weights ($17,000/7000=2.43$), which suggests that C_{sat} is inversely proportional to the molecular weight of the blended homo PS.

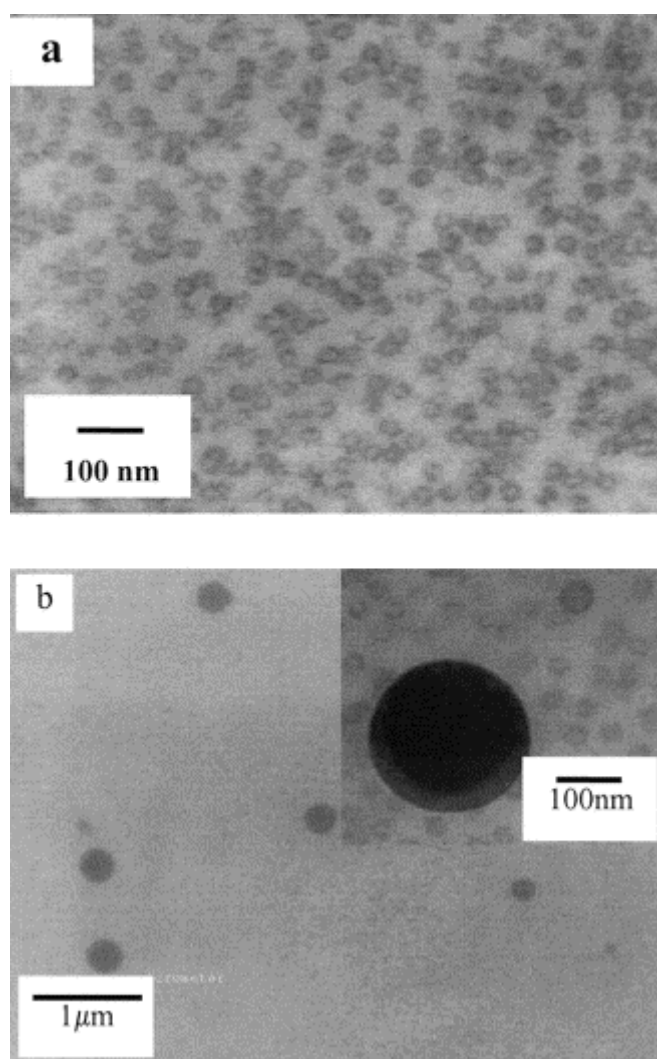


Fig. 8. TEM pictures of PS_{200} - b - $P2VP_{140}$ - b - PEO_{590} aqueous micelles containing 18 wt% (a) and 50 wt% (b) of PS_{70} , stained by phosphotungstic acid.

Zhang and Eisenberg observed a morphological transition from spherical micelles to a mixture of rod-like micelles and vesicles as the PS_{410} fraction in the PS_{410}/PS_{410} - b - PAA_{20} blend was increased from 10 to 20 wt%, at total polymer concentration constant [16]. Whenever the PS_{410} content exceeded 30 wt%, spherical micelles coexisted with hollow spaces containing larger structures [16]. In the present work, no transition from spherical to rod-like or vesicular morphology is observed. Spherical micelles persist until the solubility limit of homo-PS in the micellar core (C_{sat}) is reached. At higher content, spherical micelles coexist with large homo-PS particles. A difference in the composition of the two copolymers might account for this apparent discrepancy. In a recent

paper, we have shown that the addition of a selective solvent (toluene) for the PS core of the PS-*b*-P2VP-*b*-PEO micelles could trigger a sphere-to-rod transition [8]. It is quite surprising that no morphological transition is observed upon addition of homo-PS to the PS-*b*-P2VP-*b*-PEO micelles below C_{sat} . In order to address this question, styrene has been substituted for homo-PS in the micellization process of the PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ triblock copolymer. The triblock was initially dissolved in a 30/70 wt/wt styrene/DMF mixture, to which water was added to trigger micellization. The mixture was then thoroughly dialyzed against pure water. The morphology of the micelles prepared in the presence of styrene is shown in Fig. 9. Clearly, rod-like micelles coexist with spherical micelles. Moreover, the rod-like micelles have spherical extremities, which strongly suggests that the rod-like micelles result from the merging of spherical ones. Styrene is therefore able to increase the volume fraction of the PS core and to trigger a transition towards a rod-like morphology. It must be noted that the effect of styrene on the micellar morphology is the same as observed whenever benzene or toluene is added to the micelle forming medium [8]. At low styrene content (less than 4 wt%), only spherical micelles are observed, in agreement with the previous report on the toluene and benzene swollen micelles [8]. The addition of water to the copolymer solution in a styrene/DMF mixture results in a milky emulsion-like system. However, a macrophase separation occurs during dialysis against water. The lower layer is an opalescent solution of cylindrical micelles, as observed by TEM. The upper layer contains styrene, which disappears during dialysis. As a rule, all the observations agree with the (quasi) complete elimination of any organic solvent by dialysis. For instance, dialysis was repeated against ethanol, such that the PEO and P2VP blocks are soluble and the PS core is directly exposed to solution. The micellar structure and size are exactly the same as observed in case of dialysis against water (Fig. 9 and Fig. 10). Similarly, no change in shape and size is observed during TEM observation in ultra-high vacuum [8], which also indicates that no solvent is left in the core of the micelles.

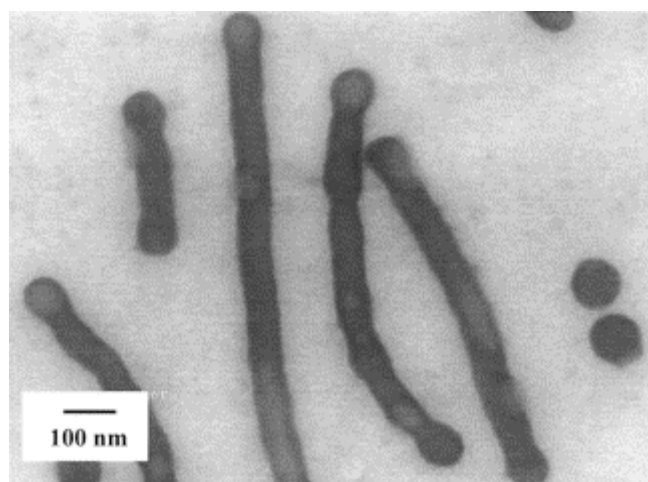


Fig. 9. TEM picture of rod-like PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ aqueous micelles prepared in the presence of styrene, dialyzed against water and stained by RuO₄.

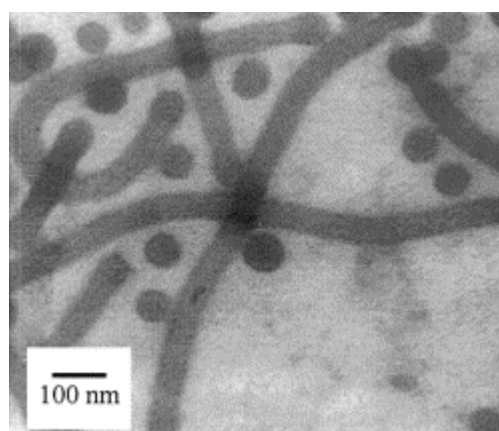


Fig. 10. TEM pictures of rod-like micelles of PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ stained by RuO₄ and formed from a DMF-styrene mixture, dialyzed against ethanol for 3 days and finally against water for 2 days.

The difference in morphology for micelles prepared in the presence of homo-PS and styrene, respectively, can be accounted for by entropy changes during micellization. The entropy of mixing is much lower for the homo-PS/PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ pair than for the styrene/PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ one. Therefore, when a microphase separation is triggered by the incremental addition of water, the PS-rich phase, which separates and nucleates PS micellar cores, can accommodate a much larger amount of styrene than preformed homo-PS, which may account for a transition from spheres to rods. Moreover, Eisenberg et al. reported that when micellization occurs in the presence of a good solvent for the core-forming blocks, these chains are stretched in the core [19]. In this work, styrene has a solubility parameter (19.0 (MPa)^{1/2}) close to PS (16.6–20.2 (MPa)^{1/2}), and thus interacts favorably with the PS blocks which are accordingly stretched. A transition from spheres to cylinders then occurs, that suppresses the extra free energy for the stretching of chains confined in spheres.

4. Conclusions

Spherical core-shell-corona micelles have been prepared from blends of homo-PS and the PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ triblock copolymer. The average degree of polymerization of homo-PS (N_{PS}) has been varied from smaller, to nearly equal and to higher than the one for the PS block of the triblock (N_{PST}). Whenever $N_{PS} > N_{PST}$, homo-PS is immiscible with the PS core of the micelles and precipitates from solution. For $N_{PS} \approx N_{PST}$ and $N_{PS} < N_{PST}$, homo-PS is dissolved within the PS core of the micelles until a critical content is reached. Above this content, micelles coexist with homo-PS macrodomains. Both the morphology and the core+shell size of the PS₁₇₀/PS₂₀₀-*b*-P2VP₁₄₀-*b*-PEO₅₉₀ micelles are independent of the addition of homo-PS, which suggests that the PS blocks in the micellar core are substituted by homo-PS chains. As a result, the number of micelles is increased and the number of stabilizing PEO chains per micelle is decreased. However, there is a homo-PS content beyond which the system is unstable and homo-PS particles coexist with micelles. Rod-like micelles are formed when styrene is substituted for homo PS before micellization. This transition from spheres-to-rods is consistent with an increase in the entropy of mixing when the core-PS chains coexist with styrene rather than with homo-PS.

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References

- [1] Hamley IW. The physics of block copolymers. Oxford: Oxford, University Press; 1998. pp. 332-54.
- [2] Förster S, Antonietti M. *Adv Mater* 1998; 3:195.
- [3] See for example: (a) Qi L, Cölfen H, Antonietti M. *Nano Lett* 2001;1: 61. (b) Spatz JP, Sheiko S, Möller M. *Macromolecules* 1996; 29:3220. (c) Bronstein LM, Sidorov SN, Valetsky PM, Hartmann J, Cölfen H, Antonietti M. *Langmuir* 1999;15:6256.
- [4] Goldacker T, Abetz V, Stadler R, Erukhimovich I, Leibler L. *Nature* 1999;398:137.
- [5] Stupp SI, LeBonheur V, Walker K, Li LS, Huggins KE, Keser M, Amstutz A. *Science* 1997;276:384.
- [6] Gohy JF, Willet N, Varshney S, Zhang JX, Jérôme R. *Angew Chem Int Ed* 2001;40:3214.
- [7] Gohy JF, Willet N, Varshney S, Zhang JX, Jérôme R. *e-Polymers* 2002;35.
- [8] Lei L, Gohy JF, Willet N, Varshney SK, Zhang JX, Jérôme R. *Macromolecules* 2004;37:1089.
- [9] Stepanek M, Humpolickova J, Prochazka K, Hof M, Tuzar Z, Spirkova M, Wolff T. *Collect Czech Chem Commun* 2003; 68:121.
- [10] Prochazka K, Martin TJ, Webber SE, Munk P. *Macromolecules* 1996; 29:6526.
- [11] Talingting MR, Munk P, Webber SE, Tuzar Z. *Macromolecules* 1999; 32:1593.
- [12] Plestil J, Kriz J, Tuzar Z, Prochazka K, Melnichenko YB, Wignall GD, Talingting MR, Munk P, Webber SE. *Macromol Chem Phys* 2001;202:553.
- [13] Zhang L, Eisenberg A. *Macromolecules* 1999;32:2239.
- [14] Zhang L, Eisenberg A. *Science* 1995;268:1728.
- [15] Gohy JF, Varshney SK, Antoun S, Jérôme R. *Macromolecules* 2000; 33:9298.
- [16] Zhang L, Eisenberg A. *J Polym Sci: Part B* 1999;37:1469.
- [17] Martin TJ, Prochazka K, Munk P, Webber SE. *Macromolecules* 1996; 29:6071.
- [18] Kirsh YE, Komarova OP, Lukovkin GM. *Eur Polym J* 1973; 9:1405.
- [19] Yu Y, Zhang L, Eisenberg A. *Macromolecules* 1998; 31:1144.