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Dependence of the structure of core–shell–corona micelles on the composition of water/toluene mixtures

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Abstract

The poly(styrene)-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) triblock copolymer, PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590}, where the subscripts refer to the average degrees of polymerisation of the constitutive blocks, has been dissolved in water/toluene mixtures with a large range of composition, i.e. in (i) toluene added with a small amount of water, (ii) water-in-toluene emulsion forming mixtures, (iii) toluene-in-water emulsion forming mixtures, and (iv) water added with a small amount of toluene. These solutions have been cast on a carbon-coated copper grid, and the morphology of the dried copolymer deposition has been observed by transmission electron microscopy. Rod-like aggregates with a core–shell–corona micellar structure are formed in cases (i) and (iv). Nevertheless, PEO is the core and PS is the corona in case (i), whereas the reverse situation prevails in case (iv). When an emulsion is the precursor of the dried copolymer aggregates, either onion-like structures (case ii) or vesicles mixed with more complex aggregates are formed (case iii). These structures are thought to reflect the self-organization of the PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} copolymer at the water/toluene interface of the water-in-toluene and toluene-in-water emulsions, respectively.

Keywords: Triblock copolymers; Micelles; Morphological transition

1. Introduction

Micelles with tailored shape and size are receiving a rapidly growing attention as templates for the production of well-defined nanoobjects.

Eisenberg and coworkers have pioneered the control of micellar morphologies, which basically depends on three key parameters, i.e. (i) stretching of the core-forming chains, (ii) core–corona interfacial energy and (iii) repulsion between the coronal chains. These parameters have a direct impact on the Gibbs free energy of the micelles, as exemplified by the morphological transitions displayed by the so-called crew-cut micelles formed by highly asymmetric block copolymers that contain a major insoluble core-forming block [1]. Indeed, Eisenberg and coauthors were able to trigger these morphological transitions not only by changing the copolymer composition [2] but also by adding salts [3] or non-selective cosolvents [4]. Although diblock copolymers are the most popular promoters of micelles, ABC triblock copolymers deserve interest because of the higher complexity of the generated nanostructures [5,6]. A typical example may be found in formation of spherical core–shell–corona (CSC) micelles by poly(styrene)-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) triblock copolymers in water [7,8]. These micelles consist of a PS core, a pH-responsive shell and a PEO corona. Although the range of the structural characteristic features of these micelles can be increased by changing the length and composition of the PS-*b*-P2VP-*b*-PEO copolymers, a more direct strategy can rely on the use of cosolvents, as assessed by a sphere-to-rod morphological transition triggered by the addition of a small amount of toluene to water [9]. This transition is the answer of the micelles to the selective swelling of the core-forming PS chains by toluene. Indeed, an increase in the volume fraction of the core-forming blocks of spherical micelles results in an entropy penalty, such that a morphological sphere-to-rod

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transition is observed beyond a critical volume fraction [1,2]. Until now, the rod-like micelles have been collected and studied in water after dialysis of toluene [9]. This study aims at preparing PS-*b*-P2VP-*b*-PEO micelles in water/toluene mixtures of various toluene contents and at investigating the impact of the swelling of the PS core on the micellar morphology.

2. Experimental part

2.1. Micelles preparation

The PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} triblock copolymer (the numbers in subscript being the average degree of polymerisation of each block) was synthesized by living anionic polymerization with a polydispersity index of 1.1, as reported elsewhere [7]. It was dissolved in (i) toluene containing a small amount of water, (ii) water-in-toluene emulsion forming mixtures, (iii) toluene-in-water emulsion forming mixtures and (iv) water containing a small amount of toluene, respectively. In case (i), 0.01 g of PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} was dissolved into 10 ml of dried toluene ($C=1$ g/L). Then, various amounts of water were dropwise added under vigorous stirring that was maintained for 48 h. When the water content exceeded 0.10 vol%, a milky solution was formed as a typical water-in-toluene emulsion (case ii). At water content higher than 60 vol%, the inverse emulsion was observed (case iii). Micelles ($C=1$ g/L) in case (iv) were prepared as reported elsewhere [7]. Reverse micelles formed in toluene-rich mixture (less than 0.1 vol% water) were cross-linked by reaction of the P2VP chains with 1,4-diiodobutane, molar ratio = 1/2) under stirring at room temperature for 72 h. The cross-linked micelles were insoluble in THF at room temperature (milky solution) in contrast to the uncross-linked material that formed a clear solution under the same conditions.

2.2. 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 casting a drop of the micellar solution onto a carbon-coated TEM grid and contrasted with RuO_4 vapor. Samples were also stained by a phosphotungstic acid 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, the solution excess was removed with a filter paper, and the sample was washed with water and dried in air. The standard deviation for the characteristic sizes measured by TEM was 3 nm for all the pictures.

3. Results and discussion

A previous paper has shown that the addition of a selective solvent for the PS block of the PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} copolymer was able to trigger a morphological sphere-to-rod transition in the micelles formed in water [9]. Fig. 1 is a typical TEM picture of the accordingly formed rod-like micelles. The PS core is easily discriminated from the P2VP shell by the proper use of selective staining agents. Indeed, RuO_4 selectively stains both the PS core and the P2VP shell, whereas phosphotungstic acid is a selective staining agent for the P2VP shell. As a result, the characteristic diameter of the PS core plus the P2VP shell, D_{CS}, the diameter of the PS core, D_C, and the thickness of the P2VP shell, H_S, can be directly determined from the TEM pictures of the dried micelles. All these data are reported in Table 1. The thickness of the corona, H_{Co}, was also determined from a TEM picture, whose the background was negatively stained and the PS and P2VP phases were contrasted by RuO_4 [9]. These rod-like micelles can be observed in water/toluene mixture containing less than 0.1 vol% of toluene (case iv).

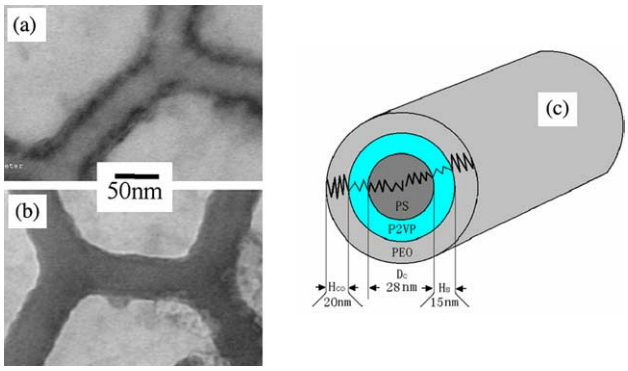

Fig. 1. Rod-like aggregates of PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} formed in water-rich toluene/water mixtures and stained by phosphotungstic acid (a, selective for P2VP) or RuO_4 vapor (b, selective for both PS and P2VP). A scheme of these structures is shown in (c).

Whenever the PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} copolymer is dissolved in pure toluene, no micellization occurs as assessed by the solution analysis by dynamic light scattering. Consistently, no micelle is observed when the solution is cast on a carbon-coated TEM grid, rather a film is formed with a typical lamellar morphology. Nevertheless micellization occurs as soon as ~0.03 vol% of water is added to a 1 g/L copolymer solution in toluene. Actually, this critical amount of water is very close to the limit of solubility of water in toluene at room temperature [10], which might indicate that micellization is driven by the formation of water microphases and the migration of the triblock copolymer towards the toluene/water interface in order to minimize the interfacial tension. It must, however, be noted that the copolymer solution in toluene remains optically clear until the water content in toluene is ~ 0.10 vol%. Interestingly enough, this water content is increased up to 0.15 vol% when the copolymer concentration in water is two times higher (2 g/L). These observations give credit to the hypothesis that the primary role of water is to solvate the PEO blocks by hydrogen-bonding interactions. A rough calculation indicates that there is approximately one water molecule per PEO unit when the 1 g/L solution of PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} copolymer is added with 0.03 vol% water. No water microphase would thus