Self-Organization of Water-Soluble Complexes of a Poly(2-vinylpyridinium)-*block*-poly(ethylene oxide) Diblock with Fluorinated Anionic Surfactants

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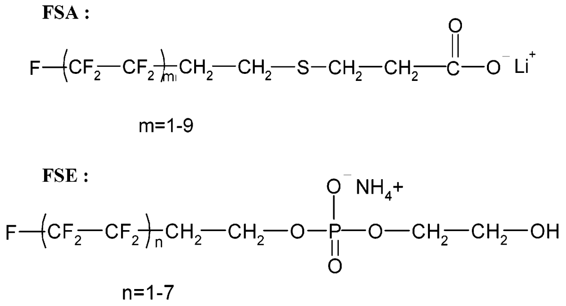
Nowadays, much attention is paid to strategies for polymers to self-organize into nanomaterials. The so-called “hairy-rod” or “comblike” polyelectrolyte−surfactant complexes are typical examples, which result from electrostatic interactions between a polyelectrolyte and oppositely charged ionic surfactants.[1] These objects are organized at a typical size of 1−6 nm, and their properties can be tuned by, e.g., the structure of the ionic surfactant. For example, partly fluorinated surfactants can impart low friction properties to the complexes.[2] Block copolymers are another class of polymeric materials able to self-organize, in bulk and in a selective solvent for one of the constitutive blocks. Moreover, they are at the origin of a wide variety of morphologies on a typical length scale of 10−200 nm.[3] Combination of block copolymers with surfactants in the bulk is a valuable tool to prepare hierarchical structures thus to associate within a single material driving forces to self-organization at two different length scales.[4] Moreover, water-soluble hierarchical systems can be prepared by mixing a double hydrophilic diblock copolymer[5] with a low molar mass surfactant known for specific interaction with one of the blocks of the copolymer. These complexes self-aggregate into micellar objects in water, with a core consisting of the polymer−surfactant complexes and a corona formed by the water-soluble uncomplexed blocks.[6−9] These types of micellar systems have potential as drug carriers[6] and in quite different fields, such as coatings, cosmetics, food, and enhanced oil recovery.[7]

This communication deals with the preparation and preliminary characterization of an aqueous hierachical system based on the complexation of a poly(2-vinylpyridinium)-*block*-poly(ethylene oxide) copolymer (P2VP-*b*-PEO) with partially fluorinated anionic surfactants (FSA and FSE). The $P2VP_{41}$-*b*-PEO_{204} copolymer was prepared by sequential living anionic polymerization of 2-vinylpyridine and ethylene oxide, as reported elsewhere.[10] The numbers in the subscripts are the average degree of polymerization for each block. The copolymer polydispersity is 1.05. The diblock copolymer was dissolved in water at pH = 3 (C = 1 g/L; 0.1 mol/L phosphate buffer), for the P2VP block to be protonated and water-soluble. The two blocks being solvated, no micelles nor aggregates were formed in water.[10] This solution was added with different amounts of an aqueous solution of a partially fluorinated anionic surfactant (C = 1 g/L, pH = 3, 0.1 mol/L phosphate buffer). Two surfactants were actually used, i.e., FSA and FSE (Scheme 1), purchased from E. I. du Pont de Nemours and used as received. They were selected because of solubility in water, partial negative charges at pH = 3 and a low surface energy component that could be attached to the polyelectrolyte by complexation.[11] At pH = 3, the P2VP blocks and the FSA (or FSE) molecules were oppositely charged and formed electrostatic complexes that were water soluble. These strong electrostatic interactions are believed to screen the weaker dipolar interactions between negatively charged FSA or FSE molecules and PEO blocks.

Scheme 1. Chemical Structures of the FSA and FSE Surfactants



The complexes were first analyzed by dynamic light scattering (DLS), 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. The intensity correlation function was measured, and its analysis by a cumulant expansion led to the average hydrodynamic diameter (D_h). Figure 1 shows the dependence of the normalized scattered intensity (I) and the average D_h on the stoichiometry of the $P2VP_{41}$-*b*-PEO_{204}/FSE complexes. From these data, it appears that the characteristic size of the aggregates formed by the $P2VP_{41}$-*b*-PEO_{204}/FSE complexes does not fall in the range known for starlike spherical micelles and that the smaller and more dense aggregates (higher I and lower D_h, in Figure 1) are formed when all the 2VP units of the P2VP block are complexed by FSE. The same type of dependence was also observed for the $P2VP_{41}$-*b*-PEO_{204}/FSA complexes and is reminiscent of complexes formed by cationic surfactants and a poly(sodium methacrylate)-*block*-poly(ethylene oxide) diblock.[8] Moreover, the position of the minimum in the curve shown in Figure 1 is strongly sensitive to pH, in direct relation with the ionization degree of both the interacting moieties. In this respect, a small increase in pH results in a decrease of the number of positively charged 2VP units, and the minimum in the curve (Figure 1) is in turn shifted to a lower x-axis value.[12] Whenever the pH is higher than 5, the P2VP block is almost completely deprotonated and no electrostatic complex with FSE is observed so far.[12]

The average D_h for the $P2VP_{41}$-*b*-PEO_{204}/FSE complexes does not change with dilution, which indicates that the structure of the aggregates is extensively “frozen” in. The electrostatic origin of the complexation

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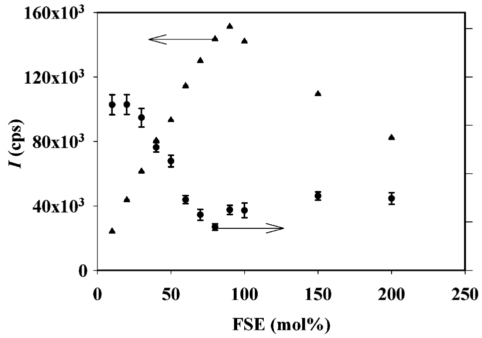

Figure 1. DLS data for P2VP$_{41}$-*b*-PEO$_{204}$/FSE complexes of different FSE contents (mol %) (left: normalized scattered intensity, *I*, in counts per second, cps; right: D_h in nm).

and aggregation was assessed by the addition of a salt (NaCl; 1 mol/L), which caused an important increase in D_h (from 210 to 700 nm) and a sharp decrease in *I* (from 1.5×10^5 to 2×10^4 cps). The screening of the electrostatic interactions that stabilize the P2VP$_{41}$-*b*-PEO$_{204}$/FSE(FSA) complexes, results in much looser aggregates of a large D_h and low *I*.

To get more information about their morphology, the P2VP$_{41}$-*b*-PEO$_{204}$/FSA(FSE) complexes were directly observed by transmission electron microscopy with a Philips CM 100 operating at a voltage of 100 kV. The images (Gatan 673 CCD camera) were transferred to a computer equipped with the Kontron KS 100 software. Samples were prepared by casting a drop of a diluted aqueous complex solution on a Formvar-coated copper TEM grid and stained by RuO$_4$ vapor. Figure 2 shows representative observations, i.e., micrometric vesicles which are uniformly distributed through the whole sample (Figure 2a), the same vesicles filled with small aggregates (Figure 2b) and "hairy" aggregates with a complex internal structure and a mean diameter of ca. 150 nm (Figure 2c). The small aggregates shown in Figure 2b look like a pearl-necklace and have a thickness of ca. 50 nm. The relative proportion of these three species is highly sensitive to the stoichiometry of the P2VP$_{41}$-*b*-PEO$_{204}$/FSA(FSE) complexes and to the pH.[12] There is no substantial difference between the complexes formed by the FSA and the FSE surfactants.

Vesicles were previously reported for poly(sodium methacrylate)-*block*-poly(ethylene oxide) diblocks mixed with cationic surfactants,[9] although they were much smaller (D_h ca. 90 nm) than the ones observed in this work. The spontaneous formation of vesicles was accounted for by the self-organization of the water-insoluble polyelectrolyte block/surfactant complexes into lamellae stabilized by the hydrophobic interaction of the surfactants tails. The water-soluble PEO block of the diblock maintains these complexes "soluble" in water. Finally, vesicles would be preferentially formed in order to avoid contact between water and the edges of the lamellae.

Vesicles and aggregates formed by the P2VP$_{41}$-*b*-PEO$_{204}$/FSA(FSE) complexes were deposited on a silicon wafer, dried and observed by atomic force microscopy (AFM). AFM was carried out with a Nanoscope IIIa microscope from Digital Instruments, operated with the tapping mode that provided height and phase cartography simultaneously. Height contrast images show that originally the surface is uniformly covered by the aggregates and vesicles, that flatten during the drying step. Although phase contrast is clearly seen (Figure 3), no lateral structure and no topographic feature are observed. The dark channels in Figure 3 are tentatively attributed to the P2VP/FSA electrostatic complexes and

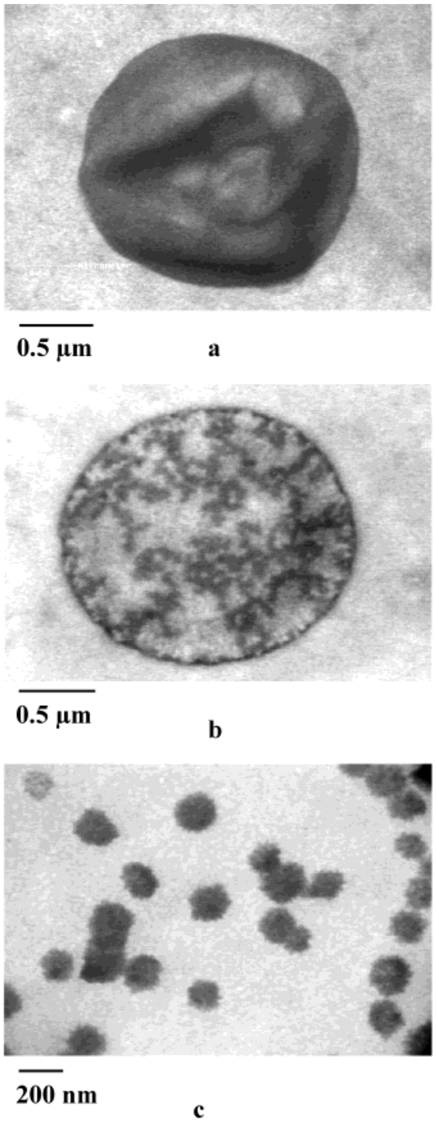

Figure 2. TEM pictures for the P2VP$_{41}$-*b*-PEO$_{204}$/FSE complex that contains 100 mol % FSE: (a) large vesicles; (b) large vesicles containing small aggregates; (c) "hairy" aggregates.

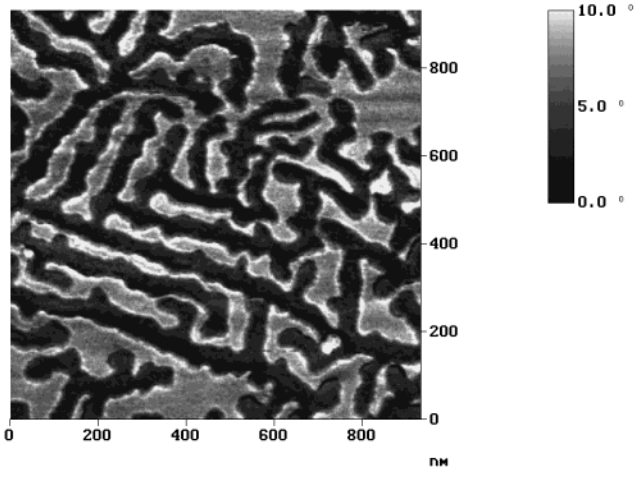

Figure 3. Phase contrast AFM picture for the P2VP$_{41}$-*b*-PEO$_{204}$/FSE complex (90 mol % FSA) dried on a silicon wafer.

the bright area to the PEO blocks. The thickness of these channels (ca. 45 nm) is essentially constant throughout the whole sample and consistent with the thickness of the hypothetical lamellae formed in the $P2VP_{41}$-*b*-PEO_{204}/FSA vesicles and with the thickness of the aggregates observed within the large vesicles (Figure 2b). Moreover, the phase contrast image of Figure 3 is time-dependent. Indeed, the relative area of the dark regions, thus of the $P2VP_{41}$-*b*-PEO_{204}/FSA complexes, increases with time, which indicates that the fluorinated component of low surface energy migrates to the air/solid interface. After two months, this migration is apparently complete, because no phase contrast is observed anymore. This surface reorganization was confirmed by measurement of the contact angle of water with time. Substitution of FSE for FSA does not change basically these observations.

According to this communication, water-soluble vesicles can be prepared by complexation of the $P2VP_{41}$-*b*-PEO_{204} diblock with fluorinated anionic surfactants (FSA, FSE). The vesicles are assumed to be stabilized by the water-soluble PEO block pointed out to the water phase. Whenever the complex is dried and exposed to air, the fluorinated segment migrates at the surface, which makes these water-soluble systems well suited to applications that require low friction and anti-adhesive properties.

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