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Morphology of Water-Soluble Interpolyelectrolyte Complexes Formed by Poly(2-vinylpyridinium)-*block*-poly(ethylene oxide) Diblocks and Poly(4-styrenesulfonate) Polyanions

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Supramolecular assembly formed by self-associating block copolymers in solution has raised vivid interest in the scientific literature.[1] In most cases, amphiphilic block copolymers are dissolved in a selective solvent of one constituent, and spherical micelles are formed that consist of a core formed by the insoluble blocks surrounded by a shell of the solvated blocks. In the recent years, other supramolecular organizations have been reported including rods, lamellae, vesicles, and tubules.[2] Most often, water is the selective solvent, although aqueous solutions are difficult to prepare, usually requiring the temporary use of an organic cosolvent to form well-defined, stable micelles.[3] Another strategy to form a micellar core in water consists of mixing oppositely charged chains, so that interpolyelectrolyte complexes (IPEC) are formed by mutual electrostatic interactions. A representative example may be found in the mixing of a water-soluble polyanion and a diblock copolymer containing two water-soluble blocks: one cationic and one neutral. A microphase separation results from the interpolyelectrolyte complexation, whose growth is arrested by the water-soluble nonionic block which remains in contact with the solvent and stabilizes the micellar aggregates. This strategy was recently worked out by several research groups to produce spherical micelles.[4] Vesicles have been however observed in mixtures of cationic surfactants and a poly(sodium methacrylate)-*block*-poly(ethylene oxide) diblock.[5]

This communication aims at reporting unusual supramolecular organization of poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (P2VP-*b*-PEO) diblocks complexed with sodium poly(4-styrenesulfonate) (PSS) homopolymers.

PSS homopolymers were purchased from Polyscience, with a polydispersity lower than 1.1. They will be designated by the acronym PSS(X), X being the $\bar{M}_n \times 10^{-3}$. The P2VP(4.3)-*b*-PEO(9.0) and P2VP(26.4)-*b*-PEO(5.9) diblock copolymers (the number in parentheses being $\bar{M}_n \times 10^{-3}$) were synthesized by sequential living anionic polymerization with a polydispersity lower than 1.15, as described elsewhere.[6] Being formed of two blocks water-soluble at low pH, these two diblocks exist as unimers in dilute acidic solution. The P2VP(4.3)-*b*-PEO(9.0) diblock shows however a pH-dependent micellization, in good agreement with previously reported observations.[6−8] Indeed, micelles are formed at pH higher than 5, the P2VP block being then essentially uncharged and thus hydrophobic. Moreover, aggregation has been also observed in P2VP homopolymers around a critical degree of neutralization, which depends of the tacticity of the P2VP chain.[9] In sharp contrast, the P2VP(26.4)-*b*-PEO(5.9) diblock precipitates out from the solution at pH ≥ 6, because the minor PEO block is too short to stabilize the micelles.

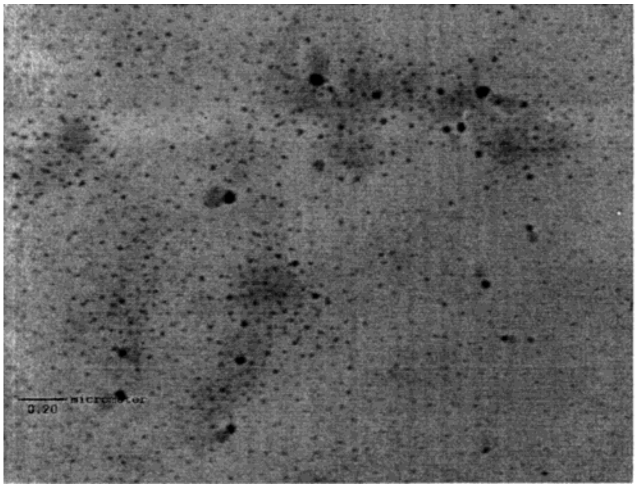

Figure 1. TEM picture of the spherical micelles formed in water by the P2VP(4.3)-*b*-PEO(9)/PSS(100.0) complex (scale: 1 cm = 300 nm).

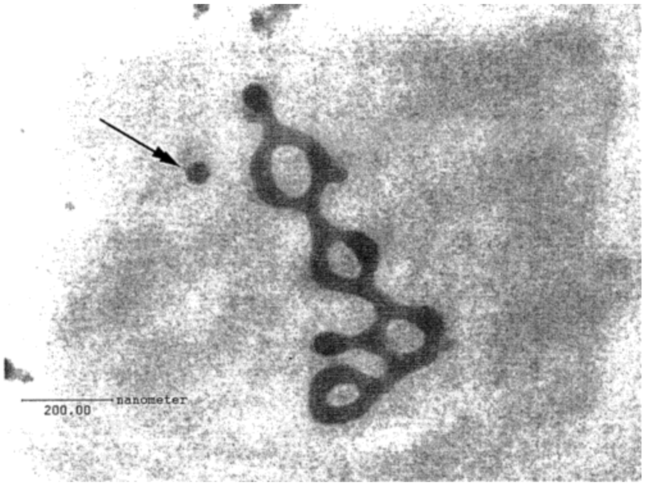

Figure 2. TEM picture of the aggregates formed in water by the P2VP(26.4)-*b*-PEO(5.9)/PSS(100.0) complex (scale: 1 cm = 165 nm).

Aqueous solutions of PEO-*b*-P2VP diblocks at pH = 3 have been mixed with aqueous solutions of PSS, such that the final polymer concentration is 1 g/L in all the cases, and the number of polyanionic and polycationic chains is the same. Since the PSS chains are usually longer than the P2VP blocks, these complexes contain an excess of sulfonate units. Bluish scattering solutions are observed for P2VP(4.3)-*b*-PEO(9)/PSS complexes. They form micellar systems which have been studied in detail elsewhere.[6] P2VP(26.4)-*b*-PEO(5.9)/PSS complexes form stable milky colloidal solutions at pH < 5,

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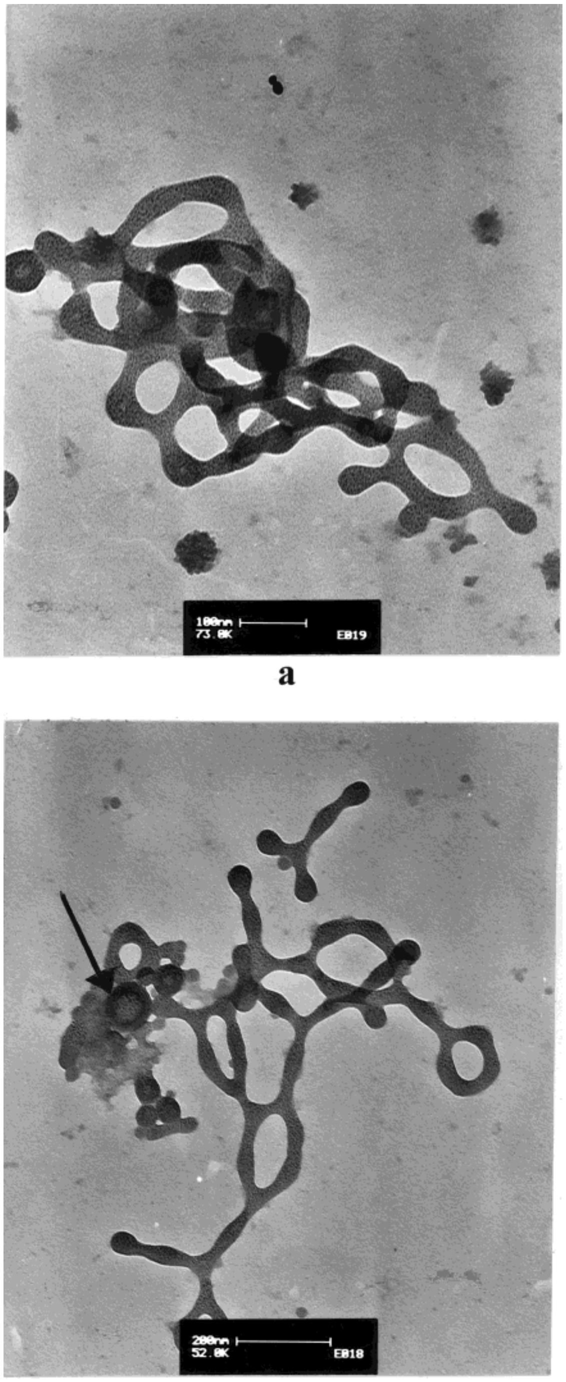

Figure 3. TEM picture of the complex aggregates formed in water by the P2VP(26.4)-*b*-PEO(5.9)/PSS(220.0) complex.

while the complexes are no longer soluble in water at higher pH.

The morphology of these IPEC has been analyzed by transmission electron microscopy (TEM). TEM observations were carried out with a Philips CM 100 operating at a voltage of 100 kV. TEM photomicrographs were directly recorded either with the CM 100 or with a Gatan 673 CCD camera. In the latter case, data were transferred to a computer equipped with the Kontron KS 100 software. Samples were prepared by dipping Formvar-coated copper TEM grid into the aqueous solution. $HAuCl_4$,which interacts selectively with the 2VP units, was added to the polymer solution in such a way that the n_{HAuCl4}/n_{2VP} ratio was equal to 0.1.

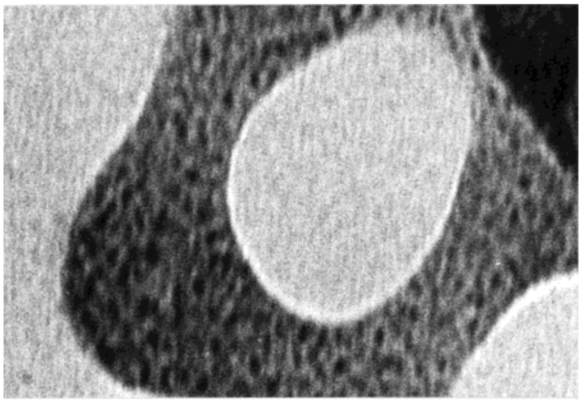

Figure 4. TEM picture of gold nanoparticles formed in the P2VP(26.4)-*b*-PEO(5.9)/PSS(220.0) complex (scale: 1 cm = 20 nm).

Formation of spherical micelles by the P2VP(4.3)-*b*-PEO(9)/PSS(100.0) complex at pH = 3 has been confirmed, as illustrated by the TEM picture of Figure 1. The micelles are observed as small black dots because the P2VP/PSS cores serve as nanoreactors for the reduction of the $AuCl_4^-$ anions into gold nanoparticles, promoted by electron irradiation.[10] Actually, the use of micellar cores to produce metal nanoparticles has generated much interest in the scientific literature.[11] Moreover, complexation of the P2VP block of P2VP-*b*-PEO diblocks with $AuCl_4^-$ has been recently used to produce gold nanoparticles.[8]

The morphology of the P2VP(26.4)-*b*-PEO(5.9)/PSS complexes has also been analyzed by TEM. Figure 2 shows the unusual morphology of the aggregates formed by the P2VP(26.4)-*b*-PEO(5.9)/PSS(100.0) complex. Rodlike micelles are systematically observed throughout the whole sample. They coexist with spherical micelles (see arrow in Figure 2), but they also arrange themselves into isolated and more or less extensively extended bucklelike structures. These supramolecular self-assemblies have never been reported before in the scientific literature for IPEC micelles, at least to our best knowledge. The same structures are also formed by the P2VP(26.4)-*b*-PEO(5.9)/PSS(220.0) complex, as shown in Figure 3. Vesicles (see arrow in Figure 3) are occasionally observed. Interestingly enough, formation of gold nanoparticles has been confirmed in the $AuCl_4^-$ loaded P2VP(26.4)-*b*-PEO(5.9)/PSS system. For instance, gold nanoparticles are uniformly dispersed in the bucklelike structure of Figure 3, as emphasized by Figure 4. It must be noted that the gold nanoparticles are exclusively observed inside the supramolecular assemblies, thus confirming that $NaAuCl_4$ microions are not released in solution.

Various morphologies formed by an amphiphilic diblock copolymer, including rodlike and bucklelike micelles, have been reported by Eisenberg et al. for the so-called “crew-cut” aggregates.[2] According to Eisenberg, the formation of different morphologies can be explained by considering the force balance of three factors: the stretching of the core-forming blocks, the surface tension between the micelle core and the solvent outside the core, and the intercorona−chain interactions. In the present study, the transition from the spherical morphology in the P2VP(4.3)-*b*-PEO(9.0)/PSS complexes to the rodlike one in P2VP(26.4)-*b*-PEO(5.9)/PSS complexes is likely controlled by the stretching of the P2VP/PSS IPEC. In this respect, the IPEC of larger size in the P2VP(26.4)-*b*-PEO(5.9)/PSS complexes results in an exceedingly high degree of radial stretching such that the spherical morphology is no longer stable. Since the stretching decreases when the shape changes from sphere to rod,[2] the P2VP(26.4)-*b*-PEO(5.9)/PSS complexes preferably form rodlike morphology.

Finally, these IPEC can disassemble when pH is increased while they are restored upon decreasing the pH.[6] The electrostatic interactions in IPEC can also be screened by the addition of a salt.[4d,6] The reversible formation of these water-soluble IPEC is an obvious advantage for practical applications. In this respect, it has been recently reported in the scientific literature that water-soluble IPEC has potential in biomedical applications, such as DNA vectors in gene therapy[4e] and enzyme entrapping agents.[4c]

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