SELF-ASSEMBLY OF PEPTIDE-BASED DIBLOCK RODCOIL COPOLYMERS : FROM MICELLES AND VESICLES TO NANOCAPSULES

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The self-assembly of block copolymers is used to create functional materials with nanoscopic dimensions, structural complexity, and/or hierarchy without any additional process required. The so-called "supramolecular" structures that can be obtained and their properties are essentially controlled at the molecular level by the right choice of the block copolymer (in our case block length ratio, chemical composition, entropic constraints, specific interactions…).

Recently, we synthesized a series of diblock copolymers consisting of a rod-like polypeptide-block and a flexible polymer block [1]. These rod-coil type block copolymers are of potential interest as building blocks for the development of novel self-assembled materials [2]. The rod-coil transition undergone by the peptide-block, due to a change in the secondary structure, can provide the molecular basis for stimuli-responsive materials; i.e. the supramolecular organization and properties of these materials can indeed be manipulated by specific variations of temperature, pH or ionic-strength. Even if these amphiphilic rod-coil molecules have been intensively studied in bulk [1,2], we focused in this work on the solution properties of polybutadiene-*b*-poly(γ-L-glutamic acid) PB-*b*-PGA diblocks. A series of compounds have been synthesized in order to vary rod-like block volume ratio (Figure 1).

The aggregation behavior of these block copolymers have been investigated by means of fluorescence spectroscopy, dynamic (DLS) and static (SLS) light scattering, transmission electron microscopy and small angle neutron scattering (SANS). The diblock copolymers were found to form well-defined spherical micelles and vesicles in water, depending on the ratio of the hydrophilic peptide block to the hydrophobic polybutadiene one. By combining all these experimental techniques, we have been able to fully characterize the essential features of this system, in term of size, shape and their modifications as a function of stimuli applied (temperature, pH, ionic strength…) Figure 2 represents two characteristic examples of SANS data obtained from block copolymer micelles (Figure 2a) and vesicles (Figure 2b).

A series of experiments was then carried out to demonstrate that the size of these micelles and vesicles can be reversibly manipulated as a function of both pH and ionic strength [3] For instance, the hydrodynamic radii R_H of the vesicles measured by DLS were found to vary from 100nm to 150nm depending on the pH of the aqueous solutions (Figure 3a). Even at high NaCl concentrations, where all the charges are effectively screened, pH-induced changes in the polypeptide secondary structure can be used to reversibly vary the dimensions of aggregates (see figure 3). Compared to other polyelectrolyte-based block copolymers, this PB_{40}-*b*-PGA_{100} copolymer exhibits an unique feature, which is the capability of its polypeptide block to fold into a compact and well-defined secondary structure as confirmed by circular dichroïsm measurements. Furthermore, by using the 1,2-vinyl double bonds present in the polybutadiene block, we demonstrate that the morphology of such a system can be covalently fixed and a transient supramolecular self-organized aggregate transformed into a permanent "shape-persistent stimuli-responsive" nanoparticle [4].

Finally, these nanoparticles, nanocapsules or polymersomes may be suitable for a number of applications including the encapsulation and/or the release of hydrophilic as well as hydrophobic active species, sensors for nano-devices, and other applications in cosmetics, paints or lubricants...

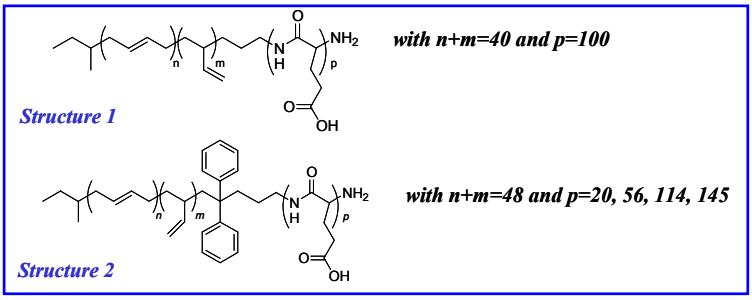

Figure 1. Schematic representation of the peptide-based diblocks under study.

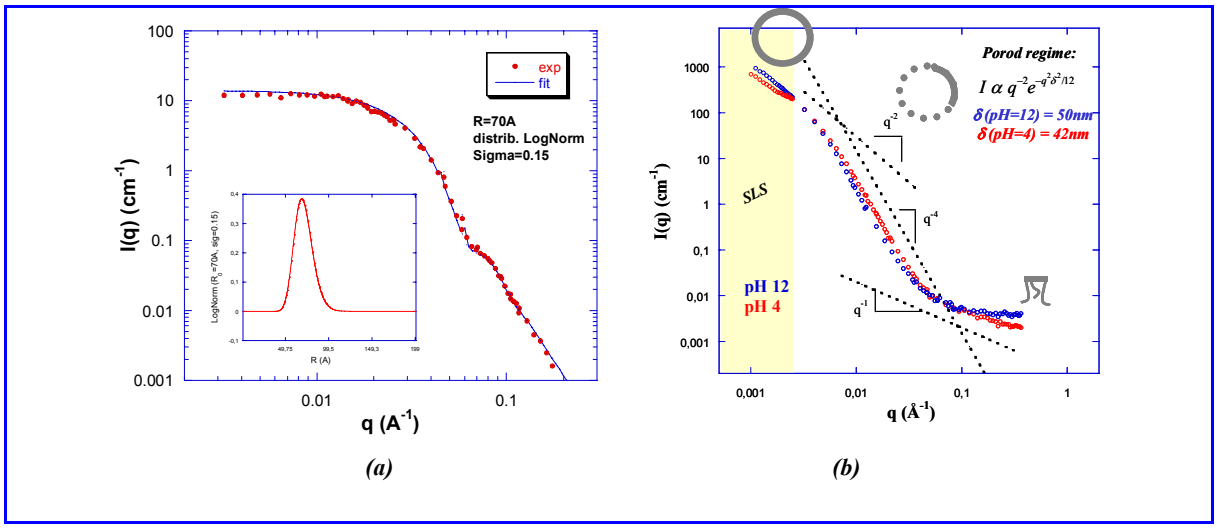

Figure 2. SANS intensity I(q) as a function of q for (a) micelles formed by the PB_{48}-b-PGA_{114} in water at pH=12. The blue full line curve is the form factor of a sphere of an average radius of 70Å with a LogNormal distribution with a sigma=0.15 (represented in the inset) [5], (b) vesicles of PB_{40}-b-PGA_{100} in water at pH=4 and 12. Static light scattering intensities are added in the low-q range to the SANS data.

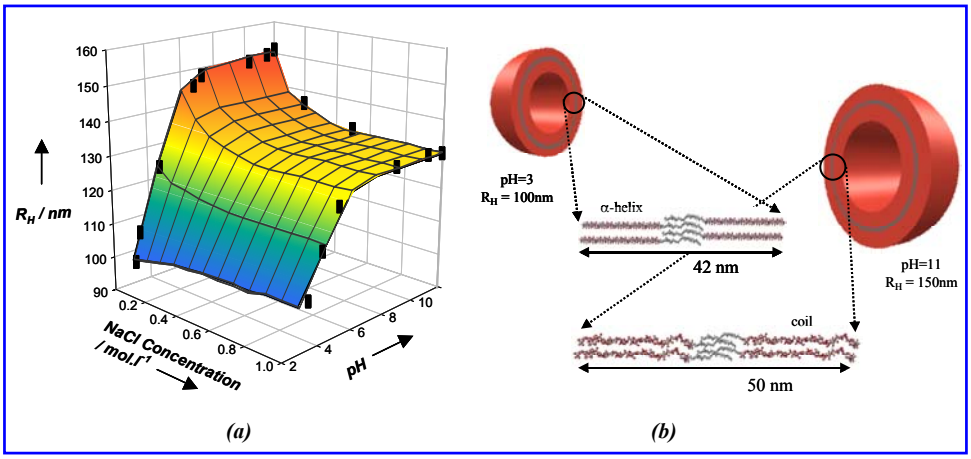

Figure 3. (a) Hydrodynamic radius R_H as a function of NaCl concentration and pH. (b) Schematic representation of the peptosome and its change in size as function of pH due to a coil to α-helix secondary structure transition in the peptide part.

References

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[5] Modelisation done with the help and in collaboration with J. Oberdisse (LLB).