SMART NANOMATERIALS BASED ON METALLO-SUPRAMOLECULAR BLOCK COPOLYMERS: FROM MICELLAR GELS TO FUNCTIONALIZED NANOPOROUS THIN FILMS

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ABSTRACT

In recent years, supramolecular polymer chemistry applying the principles of supramolecular chemistry to the synthesis and self-organization of macromolecules, has gained increasing interest. Metallo-supramolecular block copolymers based on metal-ligand interactions offer several advantages compared to their covalent counterparts [1-2]. The reversibility of the supramolecular bond enables the design of smart switchable materials with tailor-made properties. In this presentation, we focus on two different types of smart materials derived from metallo-supramolecular block copolymers, namely micellar gels and nanoporous thin films.

Smart micellar gels have been obtained from the hierarchal self-assembly of a PS-*b*-PtBA diblock copolymer end-functionalized with a terpyridine ligand. The first level of self-organization consists in the formation of micelles in a selective solvent of the PtBA blocks. The accordingly obtained micelles thus consist of a PS core and PtBA coronal chains with terpyridine ligands at their extremity. The second level is obtained by the addition of various metal ions (Ni^{2+}, Fe^{2+} and Zn^{2+}) to the micelles to induce either the formation of flower like micelles in the diluted regime [3] or supramolecular gels in the concentrated one [4]. The obtained supramolecular gels exhibited an exciting stimuli responsive behavior as evidenced by rheology and SANS.

In the second part an amphiphilic metallo-supramolecular block copolymers containing either *bis*-terpyridine cobalt(III) or nickel(II) complexes is presented [5]. The accordingly synthesized PS_{240}-[Co^{III}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230} metallo-supramolecular block copolymers have the advantage to offer a supramolecular junction stable enough to maintain the integrity of the block copolymer structure but that can be easily opened upon application of an adequate chemical stimulus. This is firstly demonstrated on spherical micelles leading thus to micellar core precipitation after the release of the coronal chains. The opening of the complex is further investigated on thin films with cylindrical morphology perpendicular to the surface of the substrate. Preliminary results evidence the formation of nanoporous thin films containing free terpyridine ligands inside the pore walls.

References:

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