A pseudo-polyrotaxane (pPR) is a pearl necklace-like supramolecule for which host macrocycles are threaded onto a guest polymer chain. A polyrotaxane (PR) is a stable pPR for which the polymer chain ends are capped with bulky groups to prevent the dethreading of the macrocycles.[1] Our group focuses on the synthesis of biocompatible pPRs and PRs from cyclodextrins (CDs), cyclic oligosaccharides with a truncated conic conformation. The peculiar repartition of the CD’s hydroxyl groups allows the building of pPRs and PRs with many kinds of polymer chains thanks to favourable hydrophobic interactions. From different examples, we will show that it is possible to control the local structure of pPRs and PRs such as the number of threaded CDs and their repartition along the polymer chain leading to specific mechanical and self-organization properties.

The first example deals with the elaboration of pPRs and PRs from α-CDs and poly(ethylene oxide) (PEO). The pPRs are obtained by quenching an α-CD/PEO mixture in water from 70 °C down to a lower temperature (typically in the range of 5 °C to 30 °C). The formation of pPRs induces a white physical gel due to phase separation. We established that pPRs are exclusively found in the precipitated phase although unthreaded α-CDs and unthreaded PEO chains are in the liquid phase. We demonstrated that, during their formation, pPRs self-organizes into nano-cylinders.[2] Furthermore, the control of the pPRs formation kinetics led us to the synthesis of PRs with a wide range of threaded α-CDs (from 3 to 227 α-CDs for a PEO chain of 20 kg.mol⁻¹).[3]

The second example deals with the mechanism of the pPRs formation from triblock copolymers of polyethylene oxide (PEO)-b-polypropylene oxide (PPO)-b-polyethylene oxide (PEO) (also known as pluronics®) and β-CDs. We found that favourable interactions between β-CD and PO units (instead of EO units) lead to the formation of pPRs which self-organize in the form of thin nano-platelets (see the Figure below).[4]

Finally, we will conclude on our last results concerning the elaboration of pPRs from α-CDs and star poly(ε-caprolactone). We will show that the star structure of these pPRs allows their solubilization while keeping their supramolecular structure during much more longer time than what it is observed with linear PRs. This property is exploited for the processing of these star-pPRs to elaborate nano-fibrous materials for biomedical applications.

Figure: a) Mechanism of the pPRs formation from an aqueous solution of pluronics and β-CDs showing the obtained structures at initial steady state at 70°C, at intermediary state just after mixing and thermal quenching at 40°C and the state after 8 hours ageing at 40°C. b) AFM image showing nano-platelets from F-68 pluronics / β-CD pPRs.