Amphiphilic molecules are everywhere, from the soap we use to wash our hands to the building blocks of our cells. The chemical structure of these molecules, composed of water-soluble and water-insoluble parts, confers on them the unique ability to spontaneously form supramolecular structures with well-defined shapes and sizes in aqueous systems. Amphiphilic block copolymers (BCPs) are a particular class of amphiphilic molecules composed of soluble and insoluble polymer chains. They are similar to natural amphiphiles, but their associative behaviour can be remarkably more complex. Despite their ubiquity, in fact, several fundamental aspects of BCP assembly are still unresolved. Understanding these aspects is of key importance to efficiently (and reliably) use BCPs in medicine and high-tech applications.

So far, most of the efforts dedicated to understanding the fundamental principles of BCP self-assembly have focused on the role of their chemical structure. This thesis approaches the problem from a different perspective, looking at BCP association "from the solvent’s point of view". The experimental and theoretical results demonstrate that the formation of BCP supramolecular structures in solution is richer and more complex than previously thought. This structural organization comprises of three different mechanisms: self-assembly, crystallization and phase separation. Solvency plays a key role in determining the dominant mechanism, and it can be tuned to create complex associative pathways where the different mechanisms operate simultaneously. This offers unprecedented opportunities to design materials with unique architectures and smart functions, such as capsules for the controlled delivery of anticancer drugs.

**Figure 1:** Schematic representation of possible pathways of a block copolymer dispersion. Red arrows represent associative-dissociative processes while grey arrows represent reorganizational processes. Rectangular blocks identify possible mixed states.

**Figure 2:** Schematic representation of a drug-loaded block copolymer micelle and theoretical prediction of the drug loading efficiency ($\Sigma G$) as a function of the drug solubility ($\phi_G$) at a fixed drug concentration ($\phi_G^*$). The condition $\Sigma G = 1$ indicates that all drug in solution is loaded inside the micelles.