Dynamic combinatorial mesophases: selection of supramolecular self-assemblies through pH-modulation

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We recently introduced the concept and developed the first examples of amphiphilic dynamic block copolymers (“Dynablocks”) in which hydrophobic and hydrophilic blocks are reversibly linked together [1]. When several Dynablocks compete from a set of constituents, it is possible to tune their molecular associations by pH modulations, which results in structuring variations of the supramolecular self-assemblies (Fig. 1). The molecular dynamic of the studied systems is provided by the reversible imine covalent bond between an aldehyde and amines having variable lengths of polyethylene glycol (PEG) units and reactivities.

![Fig. 1: General principle of the Dynablock approach](image)

We have demonstrated that Dynablocks libraries can be characterized by scattering techniques (neutron, X-ray and light scattering) at various length scales. It allowed in particular evidencing the ability of the Dynablocks to respond to pH modulation by reshuffling at the molecular level leading to a modification of the concentration of each Dynablocks in competition and to a structural reorganization at the supramolecular one (Fig. 2).

![Fig. 2: (a) Evolution of the Dynablock concentration as a function of pH. (b) SANS profiles at different pH with the best fits. (c) Schematic representation of the supramolecular exchange between Dynablocks.](image)

These supramolecular objects present several aspects to achieve a precise control over self-assembled structures and their reversible recombination confers to them the possibility to finely tune their structures by external triggers, which is interesting for drug discovery applications or bio-inspired materials.