Synthesis and physicochemical studies of model organogelators.

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Organogelators are small molecules self-assembling into fibrillar aggregates in organic solvents. These fibrils, in turn, assemble to form a solid network endowing the mixture with it viscoelastic properties.[1] Organogelators find many applications in cosmetics, drug release or coatings as rheomodifiers.

Many organogelators are known in the literature, with various functionalities, but the mechanisms of their self-assembly is still poorly known. Gelators self-associate into fibrils with a nucleation-growth mechanism. As we showed lately, this growth is more complex than described in the literature; it can follow different paths depending on concentration.[2] Moreover one still ignores which aggregation degree threshold triggers the formation of the fibrils. These fundamental questions must be resolved in order to improve the use of gelators and optimize them for applications.

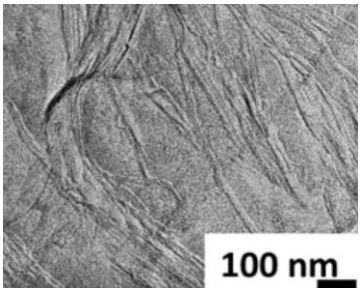

Fig. 1 freeze-fracture TEM of an organogel.

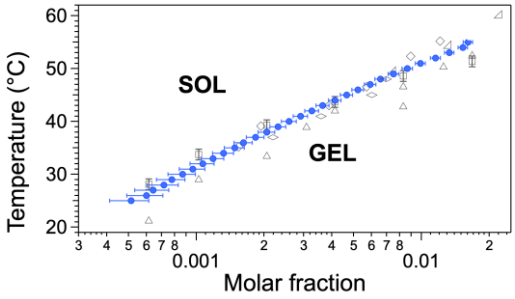

Fig 2. Phase diagram of an organogels mapped by VT-NMR.

We have proved that with variable temperature NMR, a single sample is sufficient to measure the soluble fraction of gelator a function of *T*, and hence to map out its phase diagram.[3] Simultaneously, one also measures the association rate of H-bonding functional groups such as alcohols or amides. From this rate, one can derive the size of the aggregates in solution. Therefore NMR provides good insights into the structure of the solution in equilibrium with the fibers. This Ph. D. project aims at exploiting those measurements to understand the first steps in formation of organogels. These measurements will be confirmed by experiments with other techniques: osmometry, DSC and FTIR.

The first part of the doctorate research will be devoted to the synthesis of model gelators. The shape and the size of the aggregates will be characterized by freeze-fracture electron microscopy and by small angle scattering techniques. The second part is the study of nature and the rate of the H-bonds. They will be identified and quantified at various *c* and *T* by NMR and FTIR. The size of the aggregates will be inferred from these studies. They will be confirmed by other techniques. The ultimate goal is to explain the first self-assembly in solution and the thermodynamics of their evolution into a tridimensional network of solid fibrils.

The ideal candidate must hold a master in chemistry and must be familiar with organic synthetic methods. He or she must be willing to learn several advanced techniques in physical chemistry on a multidisciplinary topic.

[1] R. G. Weiss, P. Terech, *Molecular Gels. Materials with Self-Assembled Fibrillar Network*, Springer, Dordrecht, The Netherlands, **2006**.
[2] E. Christ, C. Blanc, A. Al Ouahabi, D. Maurin, R. Le Parc, J.-L. Bantignies, J.-M. Guenet, D. Collin, P. J. Mésini, *Langmuir* **2016**, *32*, 4975–4982.
[3] E. Christ, D. Collin, J.-P. Lamps, P. J. Mésini, *Phys. Chem. Chem. Phys.* **2018**, *20*, 9644–9650.