MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Proposition de stage 2016-2017
Internship Proposal 2016-2017

Spécialité(s) / *Specialty(ies) :*
☐Chimie Analytique, Physique, et Théorique */ Analytical, Physical and Theoretical Chemistry* :
☐Chimie Moléculaire / *Molecular Chemistry* :
☑ Matériaux / *Materials:*
☐Ingénierie Chimique / *Chemical Engineering:*

Laboratoire d'accueil / *Host Institution*
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Responsable équipe / Team leader : Costantino Creton
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Responsable du stage (encadrant) / *Direct Supervisor :* Dominique Hourdet
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Période de stage / *Internship period* * : Janvier à Juin 2016
Gratification / *Salary : ~ 554 € (according to French legal dispositions)*

Hydrogels with thermo-responsive mechanical properties

Scientific project

By covalently crosslinking water-soluble polymers, it is possible to get soft elastic materials with defined shape (nano-, micro- or macroscopic) that display very interesting swelling and sieving properties. They are actually involved in many applications as superabsorbants, electrophoresis, contact lenses, drug delivery and scaffolds for tissue engineering. However an important issue with hydrogels is that these elastic materials are generally very brittle as they do not have many intrinsic mechanisms to retard fracture propagation.

Recent works on hydrogels have shown that their mechanical properties could be drastically reinforced by introducing weak interactions in the covalent network. This is typically the case when hydrophobic interactions are introduced inside a hydrophilic 3D structure[1,2] or when the polymer matrix specifically interacts with inorganic particles[3-5]. Whereas these secondary interactions cannot be finely triggered within these hybrid hydrogels, we have recently designed original networks where the physical interactions can be easily switched "on/off" by tuning the temperature[6,7].

Initially based on a graft copolymer strategy, combining a water-soluble polymer with a polymer exhibiting by a Lower Critical Solution Temperature in aqueous media (LCST), these new hydrogels have shown a dramatic enhancement of their mechanical properties upon heating which are correlated with the micro-phase separation induced by the collapse of the thermoresponsive polymer; the water-soluble macromolecular counterpart allowing to keep the volume integrity of the gel during the phase transition (see **Figure 1**).

This strategy, which was successfully extended to other architectures like interpenetrated networks (IPN), is really exciting as it paves the way to new ideas for developing soft materials with stimuli-responsive toughness playing with the chemical nature of macromolecules and/or their architectures.

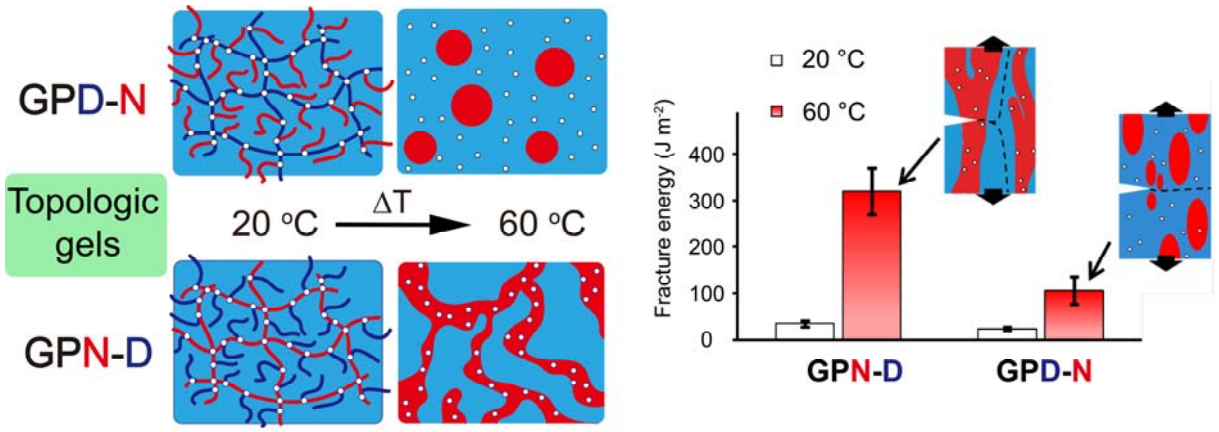

Figure 1. Thermo-toughening of hydrogels under isochoric conditions[7]: the collapse of **red polymer chains** can be triggered by temperature, while **water-soluble blue chains** prevent drastic volume change.

The project of this master internship, that will come to support the PhD work of Cécile Mussault, will be devoted to the synthesis and characterization of new hydrogels designed with grafted and/or semi-interpenetrated architectures based on different thermo-responsive precursors.

This work will be divided into 3 main parts:

1) the synthesis of hydrophilic and thermo-responsive polymer (or macromonomer) precursors and their copolymerization with antagonistic monomers in order to design grafted or semi-IPN networks,

2) the characterization of the thermodynamic behaviour of prepared hydrogels by swelling experiments, differential scanning calorimetry and/or UV spectroscopy,

3) the analysis of the mechanical properties under low (dynamic rheology) and large deformations (tensile test). These experiments will be carried out at various temperatures in order to quantitatively analyze the variation and the reversibility of the mechanical reinforcement induced by the micro-phase separation process.

Required background

Master student at the Master 2 level (or equivalent) with academic knowledge in polymer chemistry and physical chemistry.

References

1. G. Miquelard-Garnier, S. Demoures, C. Creton, D Hourdet, Macromolecules 39, 8128 (2006).
2. M. A. Haque, T. Kurokawa, G. Kamita, J. P. Gong, Macromolecules 44, 4997 (2011).
3. K. Haraguchi, T. Takehisa, Adv. Mat. 14, 1120 (2002)
4. L. Petit, L. Bouteiller, A. Brûlet, F. Lafuma, D. Hourdet, Langmuir 23, 147 (2007).
5. S. Rose, A. Dizeux, T. Narita, D. Hourdet, A. Marcellan, Macromolecules 46, 4095 (2013)
6. H. Guo, N. Sanson, D. Hourdet, A. Marcellan, Advanced Materials 28, 5857–5864 (2016)
7. H. Guo, C. Mussault, A. Brûlet, A. Marcellan, D. Hourdet, N. Sanson, Macromolecules 49, 4295-4306 (2016)