

## Offer for a research thesis position (C2P2)

### Dépolymérisation mécano-catalytique de polymères: vers des molécules plateformes fonctionnelles valorisables

### Mechano-catalytic depolymerization of polymers: towards valorizable functional platform molecules

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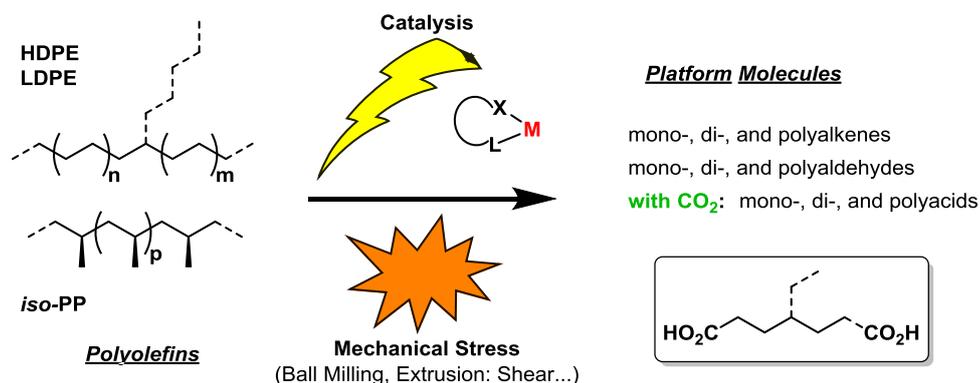
**Supervisors:** Jean Raynaud et Vincent Monteil

**General context:** Polymers are omnipresent in modern life, in personal care products, clothes, vehicles, and food packaging to name a few. A dizzying variety of polymers are used for those applications, with various physico-chemical properties and chemical structures which makes their recycling/elimination at the end of their life cycle a major problem to tackle. The challenge is important both from an environmental and societal point of view at a time where the demand in polymer products is becoming stronger and more varied while the legislative regulations on their production, use and disposal become more stringent. If some of them can be relatively easily recycled, such as polyethylene terephthalate (PET) or depolymerized, such as synthetic polymers carrying a heteroatom in the polymer chain (*e.g.* polycarbonates, polyamides in some cases), this is not the case of polyolefins (*e.g.* polyethylene and polypropylene) whose chemical and thermal inertness constitute a major obstacle in terms of chemical recycling and recovery, especially in the food packaging sector. Reprocessing would be a potential solution, but when attempting to re-extrude polyolefins, many uncontrolled radical degradative processes take place and damage erratically the polymer chains.

Among the different methods currently available for the management of plastic wastes, the chemical valorization of end-life polymer products has emerged as a promising alternative and is expected to develop in the coming years in addition to energy recovery and recycling of materials.<sup>1</sup> Indeed, it is in principle the ideal way of recycling since it consists in chemically decomposing macromolecules in order to obtain molecules of lower molecular weights that could be reused as feedstock in a more sustainable circular economy loop. However, current chemical methods, notably in the case of polyolefin wastes treatment, required high temperatures (> 600 °C) in order to push the polymer deconstruction towards the formation of low molecular weight products (pyrolysis or thermal cracking). In some cases, catalysts such as silica, silica-alumina or even zeolite type can also be used to achieve higher selectivity than a purely thermal process and to lower the temperature by a few hundred degrees (catalytic hydrocracking). Nevertheless, the products obtained are mixtures of hydrocarbons which are difficult to valorize and the production of petrochemical cuts from polyolefin waste does not seem economically viable.

#### Description of the research project:

This thesis proposal aims to develop a disruptive approach towards the depolymerization of polymers into higher-added value functional molecules by combining mechanochemistry and catalysis (Scheme 1). Mechanochemistry is a non-thermal technology which has been known for a long time to activate strong covalent bonds by external mechanical forces. Recently, mechanocatalysis has emerged as a promising concept to break-down polymer chains and been successfully applied to the deconstruction of biopolymers such as cellulose or lignin.<sup>2</sup> In contrast to conventional mechanical treatment, mechanocatalysis is based on a synergistic effect between the action of a catalyst and mechanical forces. Mechanical forces provide energy to the catalyst through pressure and frictional heating allowing reactions to take place without the need of external heat and under solvent-free conditions.



**Scheme 1.** Strategy envisioned for the mechano-catalytic depolymerization of polymers.

### Thesis program:

- Different families of polymers having various chemical structures and properties will be considered. Polymers having activable functional groups within their backbone (*e.g.* polyesters and polyacrylates with ester moieties, polyamides and polyacrylamides with amide moieties...) will be first evaluated as a proof of concept but our ultimate and more ambitious goal seeks the depolymerization of polyolefins (varying branching-density polyethylenes and *isotactic* polypropylene) into highly functional molecules.
- Functionality/polarity will be introduced *via* catalysis (principally heterogeneous catalysis) using two prominent and well documented organic transformations: i) the direct carboxylation of C-H bonds by **CO<sub>2</sub>** to yield mono, di or polyacids; ii) the oxidative deshydrogenation to create in one single operation multiple unsaturations and/or aldehydes.

We expect by merging mechanochemistry and catalysis to contribute to the overall trend for clean, and effective chemical recovery of polymer wastes.

This research project is clearly multidisciplinary involving various field of science: materials and polymer science, organometallic chemistry and catalysis and we have within the C2P2 laboratory the unique opportunity to gather all the competences needed *via* the strong expertise of its two teams in heterogeneous catalysis and polymer chemistry. In addition, the research director pioneered different studies regarding the catalytic cleavage of the C-H and C-C bonds of alkanes by Surface Organometallic Chemistry and discovered, as a follow-up, the catalytic hydrogenolysis of polyethylene and polypropylene to diesels or lower alkanes using a zirconium hydride supported on silica-alumina.

**Profile of the candidate:** Master degree or engineer having good knowledge in polymer chemistry and catalysis.

<sup>1</sup> S. M. Al-Salem, P. Lettieri, J. Baeyens, *Progress in Energy and Combustion Science*, 36, (2010) 103-129.

<sup>2</sup> F. Jérôme, G. Chatel, K. De Oliveira Vigier, *Green Chemistry*, 18 (2016) 3903-3913.