Appel à projets 2024 – Institut de Sciences des Matériaux : Biobased Acids-homoCYSteine Thiolactone-based monomers for new generation of superabsorbent polymers (BACYST)

Part 1 – Scientific context of the project:

Superabsorbent polymeric materials (SAP) are hydrophilic crosslinked (co)polymer networks able to absorb extremely large amount of water.[1] Such type of hydrogels find wide industrial applications in disposable hygiene products but also in agriculture and environmental applications.[2] They are divided mainly in two classes depending on the type of resources and end-of-life: crosslinked polyacrylates/acrylamides and polysaccharide or polyester—based copolymers[3]. While the second class of SAPs is biobased and supposedly biodegradable, the first class –which is the most produced industrially- is petroleum-based and non-biodegradable. Yet, the depletion of oil resources is leading to an increase and unstability of the prices. This is one of the reason why it is necessary to find alternatives and renewable resources allowing to prepare SAPs with identical or superior properties compared to the existing ones. In parallel, the possibility to create these SAPs with a more eco-friendly approach and exploiting the green chemistry principles remain a major stake. Therefore the objectives of this project are dual.
In this project we aim to create a library of new 100%-biobased monomers starting from renewable *N*-acetyl homocysteine thiolactone (HTL)[4] combined with difunctional or trifunctional acids such as itaconic acid (IA)[5], fumaric acid (FA), malic acid (MA) and citric acid (CA) (**Figure 1**). While the aforementioned acids can be obtained by the fermentation of various (poly)saccharides such as sucrose, glucose, starch or molasse, HTL is derived from amino acids (methionine ou homocysteine). The original structures of these monomers will give us access to a large library of versatile building blocks for macromolecular engineering.

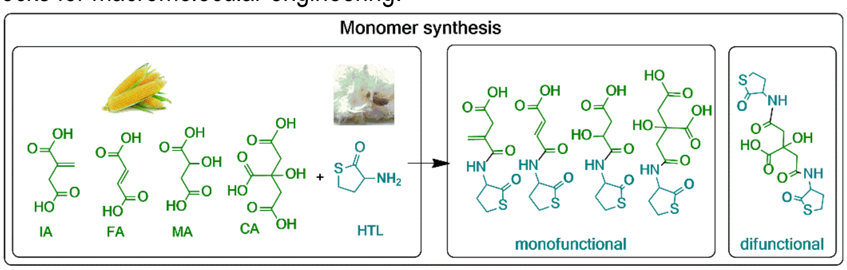

Figure 1 Library of biobased monomers derived from HTL and biobased di- and triacids

In a second step, innovative SAP will be prepared using the above building blocks either as reactants for one-pot double modification of polymers/polysaccharides (strategy I, **Figure2a**) or as monomers in various polymerization techniques including cascade polyaddition[6] (strategy II; **Figure 2a**) and free/controlled radical polymerization[7–10] followed by one-pot double post-polymerization modification (strategy III, **Figure 2a**). Interestingly, depending on the functionality of the monomer and on the chosen polymerization method, different architectures -presenting several free carboxylic acid groups- will be prepared (linear, brush and 3D-crosslinked polymer networks). The opening of the thiolactone moieties by nucleophilic primary amines will generate very reactive thiol groups, which can be used for additional functionalization or to obtain reversible disulfide bond hydrogels (**Figure 2a**). In addition, the SAP properties will be modulated by adjusting the chain molar masses and by playing with the nature of the primary amines (amino acids, branched or multi-functional compounds, biologically-active ingredients, **Figure 2b**)[11,12]. For instance, the use of an hyperbranched polyglycerol presenting an amine as anchor point (HPG-NH_2) should drastically increase the absorption properties. Additional properties, such as thermosensibility or recognition properties, could also be added in order to extend the field of applications. Eventually, the stability and, conversely, the biodegradability of the resulting structures will also vary according to the intended application. For instance, the modification of a chitosan backbone according to strategy I should enable the one-pot production of (bio)degradable networks. Interestingly, polyaddition polymers prepared according to strategy II should also be degradable thanks to the already reported intramolecular participation of neighboring carboxylic groups to the amide hydrolysis.[13,14] On the contrary, the alkyl chains prepared according to strategy III will be much more stable.

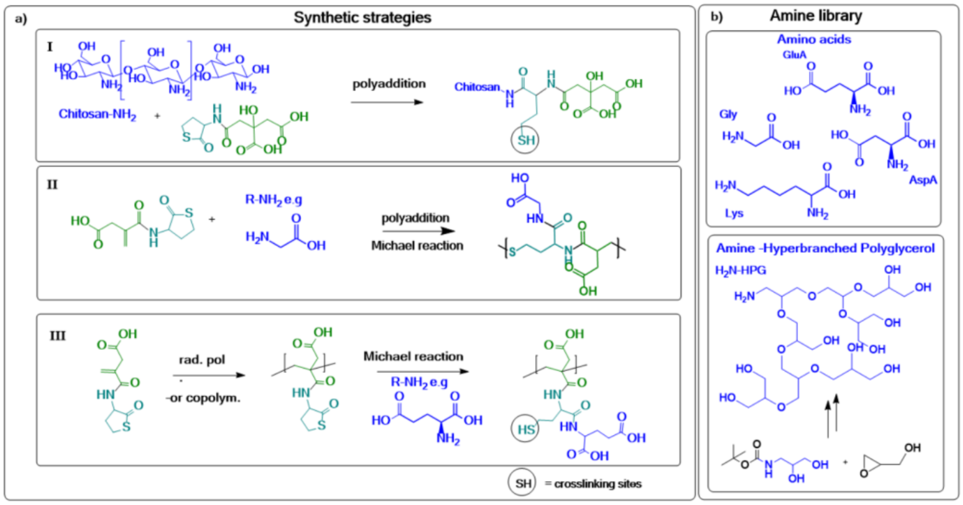

Figure 2 2a)Depiction of the envisioned strategies to achieve SAP formation 2b) Library of amines used in this project

Reducing the environmental impact of our structures is also a priority. Therefore, the syntheses will be carried out in green solvents or in the bulk.[15] It is also worth noting, that primary amine and thiolactone react spontaneously at room temperature. Gelation kinetics will be probed by rheological measurements. Influence of the pH on these kinetics will also be evaluated. Swelling properties in terms of kinetics and equilibrium will be investigated together with mechanical behavior of hydrogels in controlled environments (e.g : tensile tests in presence of water at various ionic strengths).[16]
To conclude, our project aims at the preparation of a large range of innovative SAP engineered in a sustainable fashion and using high-potential biobased compounds. Indeed, itaconic, fumaric, malic acids as well as glutamic and aspartic acid have been classified by the "US department of Energy" among the top twelve high added value chemical from biomass. The requested funding will enable to obtain enough results to establish industrial collaborations in the fast-growing and highly-competitive SAP market, which is projected to reach ca. 15 billion USD by 2030.

Risk management

Monomer syntheses by amidification reaction may seem straightforward. However, several secondary reactions can take place, such as the HTL homopolymerization (opening of the HTL ring by the amine lateral substituent of another HTL) and aza-Michael addition reaction in the case of itaconic acid functionalization. Preliminary studies have already been conducted in the ICPM group enabling the synthesis of monomers derived from IAn (itaconic anhydride) and HTL. These procedures still need to be optimized to improve the yields. Strategy I should deliver rapid results as thiolactone is commonly used as thiolation agent for chitosan.[4] Strategy II is more challenging but the first polyaddition reaction have been successfully carried out using the IA-HTL monomer in the presence of glycine/lysine leading to water-soluble oligomers. The radical polymerization of itaconic acid derivatives is notoriously challenging.[17] Preliminary trials of radical polymerization were performed in water or in a green solvent with the IA-HTL monomer, confirming the monomer ability to homo- and copolymerize.

Complementarity of the research team

The partners bring at each step complementary skills, necessary for the success of the project. **Members of the Parisian Institute of Molecular Chemistry (IPCM, Polymer chemistry team, Sorbonne Université – CNRS)** - The synthesis-related tasks will be supervised by **Fanny Coumes** (MdC) which will bring expertise in the field of radical polymerization and synthesis of bio-based macromolecules, and **Nicolas Illy** (MdC-HDR) which will bring expertise in the field of thiolactone chemistry for macromolecular engineering and polysaccharide functionalization. In addition, the IPCM-polymer team will provide scientific expertise at several levels in the field of polymer characterization. The project will benefit from the access to the IPCM facilities: NMR platform, mass spectrometry, DRX, SEC facilities. **Members of the "Sciences et Ingénierie de la Matière Molle" (SIMM, ESPCI Paris – Sorbonne Université – CNRS) –** The material characterization related tasks will be supervised by **Alba Marcellan (MdC-HDR, IUF member)** with her expertise in gel design and properties, as large strain mechanical response and swelling behaviour, and **Théo Merland (MdC)** who will bring his expertise for rheological measurements and scattering techniques (light, neutron). In addition, **Nadège Pantoustier (MdC)** will help in the polymer characterization using aqueous size exclusion chromatography techniques. SIMM team is internationally recognized in the field of hydrogel design and characterization. More recently, the team has begun research on the biodegradability of biosourced gels.

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Partie 2 - Plan de recherche avec calendrier prévisionnel (0,5 page)

Months → WPs↓	M3	M6	M9	M12	M15	M18	M21	M24	M27	M30	M33	M36
WP0												
Task 1.0												
WP1	**STRATEGY 1**											
Task 1.1												
Task 1.2												
WP2	**STRATEGY 2**											
Task 2.1												
Task 2.2												
WP3	**STRATEGY 3**											
Task 3.1												
Task 3.2												

■ = meetings, intermediate reports, ■ = final report. ■ = work done by the PhD at IPCM, ■ = work done by the PhD at SIMM, Task 1.0: monomer synthesis, throughout the project, Task 1.1 : polymer synthesis & characterization according to strategy 1, Task 1.2 kinetics of gelation, characterization of hydrogels ; Task 2.1 : polymer synthesis & characterization according to strategy 2, Task 2.2 kinetics of gelation, characterization of hydrogels, Task 3.1 : polymer synthesis & characterization according to strategy 3, Task 3.2 kinetics of gelation, characterization of hydrogels