PhD position @ CP2M

Radical emulsion polymerization and dynamic covalent chemistry: formation of vitrimer films from polymer latexes

Polymérisation radicalaire en émulsion et chimie covalente dynamique :
formation de films de vitrimères à partir de latex polymères

The present project aims at designing new polymer latexes for the formation of crosslinked films with potential self-healing properties and/or recyclability owing to vitrimer-like properties.

- **Synthesis of surfactant-free latexes.** Polymer latexes, *i.e.* dispersion of polymer particles, are the key products of various applications. They are notably used as one of the primary components in the field of coatings, which require the processing of a liquid latex into a polymer film with specific properties such as adhesion, gloss, barrier to gas, wettability, corrosion and solvent resistances. The most widespread industrial process to form polymer latexes is radical emulsion polymerization, in which particle stability is ensured by low molar mass surfactants. However, when emulsion polymers undergo film formation, these hydrophilic species are prone to migration and segregation at film interfaces, which negatively impacts some properties. The design of surfactant-free latexes has therefore been a target for both academia and industry for more than 20 years. The use of macromolecular stabilizers strongly anchored to the particle surface at the end of the polymerization can lift some of these issues. Notably, the use of reactive hydrophilic macromolecules that can be involved in emulsion polymerization has received a great deal of attention. At CP2M we are taking advantage of the advances achieved in the synthesis of such macromolecules by controlled radical polymerization techniques, such as reversible addition-fragmentation chain transfert (RAFT),[i] to push this strategy forward and produce surfactant-free polymer latexes using macromolecular RAFT agents as reactive stabilizers (Figure 1).[ii]

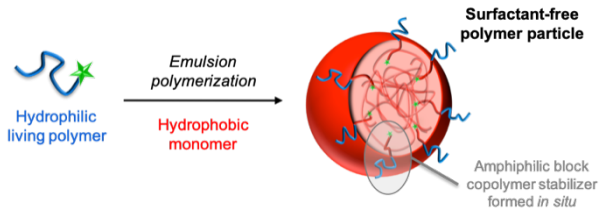

Figure 1: Use of hydrophilic and reactivable polymer chains for the synthesis of surfactant-free latexes

- **Crosslinked films and vitrimers**. Film properties can also be strongly enhanced by crosslinking, which can be induced during film-formation. Various strategies have been developed over the years, leading to films that are permanently crosslinked. However, introducing permanent yet dynamic crosslinks could significantly improve the properties of the films formed, as it is the case for vitrimers. Vitrimers are polymeric networks with exchangeable links such that their topology can rearrange without any loss of network integrity.[iii] These dynamic links provide strength akin to thermosets at operating temperature but allow for remolding at elevated temperature. The dynamic crosslinks are obtained by the reversible reaction between two adequatly chosen functional groups. Introducing such dynamic crosslinks in the films obtained from polymer latexes would allow preserving the desired chemical and mechanical properties of a crosslinked material, such as chemical, environmental stress cracking, creep and scratch resistances, but would also provide access to additional properties such as self-healing and recycling abilities as well as improved adhesion, all of which being of prime importance for coating applications. In addition, dynamic covalent chemistry can also be used to crosslink materials during their processing, thereby significantly simplifying their synthesis and processing.

• **The project.** The challenge of designing unique latex particles with vitrimer properties will be tackled at CP2M, expert in emulsion polymerization and macromolecular engineering. Different surfactant-free polymer latexes incorporating functional groups able to establish dynamic covalent bonds will be synthesized using RAFT and emulsion polymerization. These latexes will be then mixed with either another latex or free (macro)molecules containing the complementary functions needed to trigger the formation of exchangeable links. Adjusting the amount and location of each complementary function will allow us to tune the crosslinking density, and therefore the mechanical properties of the resulting films, as well as the dynamic of exchange. This project will thus enable us to demonstrate the applicability of vitrimer chemistry in radical emulsion polymerization, a typical high volume industrial process, to produce polymer films incorporating dynamic crosslinks with potential new properties.
The project will benefit from an on-going collaboration between CP2M and Renaud Nicolaÿ and Corinne Soulié-Ziakovic from the C3M laboratory at ESPCI (Paris), leader in the field of vitrimer chemistry. In the frame of this collaboration, we have identified specific functional groups and how to incorporate them into latex particles to induce both efficient film formation and good vitrimer properties. The ambition of this project is to build up on this knowledge to produce polymer films with vitrimer properties.

• **Candidate profile**. We are looking for a talented and motivated PhD student, with a background in polymer chemistry and/or polymer colloids. The PhD candidates should hold a MSc degree (or equivalent). They should demonstrate some practical experience or aptitude for polymer synthesis and characterization. They should possess a good command of written and spoken English.

• **Applications**. Please send your application file (including CV, letter of motivation and academic references) to:
Muriel Lansalot, PhD supervisor (HDR, muriel.lansalot@univ-lyon1.fr)
Franck D'Agosto, PhD co-supervisor (HDR, franck.dagosto@univ-lyon1.fr).

• **Host laboratory:**
Catalyse, Polymérisation, Procédés et Matériaux (CP2M) - UMR 5128 CNRS/CPE/UCBL, *Equipe Polymérisation, Catalyse et Matériaux (PCM)* - https://www.cp2m.org/ 43, Bd. du 11 Novembre 1918 – 69616 Villeurbanne Cedex

• References

[i] D'Agosto, F.; Rieger, J.; Lansalot, M. *Angew. Chem. Int. Ed.* **2020**, *59*, 8368-8392.
[ii] Lesage de la Haye, J.; Martin-Fabiani, I.; Schulz, M.; Keddie, J. L.; D'Agosto, F.; Lansalot, M. *Macromolecules* **2017**, *50*, 9315-9328.
[iii] Van Zee, N. J.; Nicolaÿ, R. *Prog. Polym. Sci.* **2020**, *104*, 101233.