SORBONNE UNIVERSITÉ

AAP China Scholarship Council - CSC 2023

PROJET DE RECHERCHE DOCTORALE (PRD)

Titre du PRD : Thiolactones, a powerful tool to design sustainable polymers

DIRECTION de THESE

Porteuse ou porteur du projet (***doit être titulaire de l'HDR***) :

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Ecole doctorale de rattachement : ED397 - Physique et Chimie des Matériaux

Nombre de doctorants actuellement encadrés : 5

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Ecole doctorale de rattachement : ED397 - Physique et Chimie des Matériaux

Nombre de doctorants actuellement encadrés : 2 (chacun à 50%)

CO-TUTELLE INTERNATIONALE envisagée : ☐ OUI ☒ NON

DESCRIPTIF du PRD :

*Ce texte sera affiché en ligne à destination des candidates et candidats chinois : il ne doit pas excéder **2 pages** doit être rédigé en **ANGLAIS***

The global plastics production was 367 million metric tons in 2020.[1] Due to the damages caused by this abundance on the environment and to the inevitable depletion of oil resources, the future of the polymer industry relies on the development of sustainable polymers.[2] A key challenge is the issue of sourcing and replacing petro-resources with bio-resources for the manufacture of polymer materials.[3] In addition, plastic materials end of life is also a crucial issue.[2] Two different situations have to be considered. In the first case if it is possible to collect the waste, plastics are recovered energetically, recycled mechanically or landfilled. In many countries, energy recovery is the main outlet for waste. Nevertheless, this process generates atmospheric pollution and the production of so-called ultimate waste. The physical (mechanical) recycling of polymers is strongly promoted by public authorities. However, it suffers from several disadvantages such as the inevitable loss of quality of the recycled materials due to the degradation of the polymer chains and to the contamination by accumulated additives.[4] Landfill damages the ecosystems and is a loss of economically-valuable materials.[5] A growing number of studies are interested in the development of chemically recyclable plastics that would allow us to move towards a virtuous circular economy.[4] Two main strategies have been developed: repurposing and depolymerization processes. Repurposing consists of breaking down polymer chains by adjusting the pH or in the presence of a chemical reagent in order to convert them into new "building blocks" that can be used to synthesize new virgin materials with high added value.[6] The depolymerization processes put forward a cycle of polymerization-depolymerization allowing to regenerate the original pure monomer and thus to re-synthesize a virgin polymer having its native properties, e.g. the polymerization-depolymerization cycle of poly(lactic acid) - lactic acid.[6] In the second case if polymers end up in the environment, e.g. polymers found in cosmetics and detergents, or microplastics issued from paints, coating, tires and washing of textiles.[7] For example, polyethylene oxide (PEO) is produced in millions of tons, and is a major component of the cosmetics, detergents and pharmaceutical industries due to its excellent solubility in aqueous media. For these applications, no waste collect is possible, and the polymers end up in wastewater and in waterways. The issue of their accumulation in the environment has therefore become crucial and the use of biodegradable polymers is a priority. Studies demonstrate the bacterial biodegradability of low molecular weight PEO in aqueous media and the crucial role of hydroxyl end-groups in the degradation process.[8] The degradation of PEO with higher Mn is more difficult and challenging.

Recently, our group has developed the alternating copolymerization of epoxides with thiolactones using various organo-catalysts.[9] This polymerization technique has subsequently been used to prepare biobased alternating structures.[10] The generated poly(ester-alt-thioether) are attractive functional materials due to the presence of both degradable ester groups and oxidizable thioether groups in each repeating unit of the main backbone.

This PhD project has the objective to use the reactivity of thiolactones with epoxides to synthesize sustainable polymers addressing polymer end of life issues. The project is divided into 2 main parts. The first part will demonstrate the possibility of chemically recycling poly(ester-alt-thioether)s issued from the copolymerization of γ-thiolactones and epoxides. For this purpose, the polymer methanolysis will be performed to prepare a dimeric α-methyl ester, ω-hydroxy compound. After characterization, its polycondensation will be performed to regenerate the original alternating polymer structures; the efficiency of various catalysts will be evaluated. The properties of the recycled polymer will be compared with the ones of the original polymer. The number of efficient recycling cycles will also be evaluated. The second part will be devoted to the introduction of welldistributed cleavable ester groups into polyether backbones to reduce their environmental impact and to accelerate their degradation rate. Due to the reactivity of thiolactones towards alcoholates, the introduction of the cleavable units will be done by slow and controlled addition of the thiolactone. The method will be applied to the synthesis of degradable analogues of commercial surfactants, present in cosmetics and detergents. The surface active properties of these molecules will be characterized. Moreover, degradation studies will be conducted in basic medium to determine the influence of the integration frequency of the thiolactone units on the degradation rate of the compounds. In conclusion, the main challenge will be to develop high performance sustainable polymers, either easy to recycle or innocuous to the environment materials. The thesis will take place at the Laboratoire de Chimie des Polymères in the Institut Parisien de Chimie Moléculaire at Sorbonne University. The laboratory is well-recognized in the field of polymer chemistry and is equipped with all the required material for the synthesis (Schenk lines, glove box) and for the characterization of macromolecules (SEC, NMR, MALDI-ToF, mechanical and thermal characterization, Dynamic Light Scattering, rheometry). N. Illy and P. Guégan have a strong expertise in polymer synthesis, especially anionic ring-opening polymerization. They have established collaborations with physico-chemists at S.U, University of Technology of Compiegne and ESPCI.

References

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