

Synthesis of building-blocks with controlled functionalities based on lignin for the synthesis of biopolycondensat by reactive extrusion

Synthèse de synthons basés sur les lignines avec un contrôle des fonctionnalités pour la synthèse de biopolycondensats par extrusion réactive

Level: PhD

Profile of the candidate: Candidate should hold a Master of Chemistry degree with at least 5 months internship in a research academic or industrial laboratory. Following skills are associated to this project: Catalysis, Polymer and Biomass Chemistry; so, good to basic knowledge in these areas is essential. Additionally, for conducting the project, handling of pressurized stainless steel reactors, and chromatographic and spectroscopic analyses (GC-FID, HPLC, SEC, NMR, IR, UV-Vis) will be used. Initial experience in these aspects will be appreciated. Speaking basic French is required.

Team(s): PhD work will be partly carried out in the CDFA team at IRCELYON, and for the part focusing on polymerisations studies, at IMP-Lyon.

Contact(s):

Dr. L. DJAKOVITCH, DR CNRS, HDR; laurent.djakovitch@ircelyon.univ-lyon1.fr

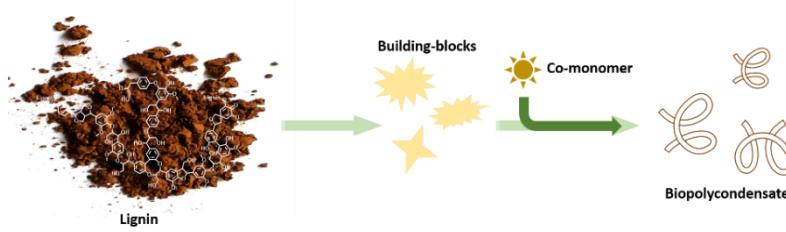
Dr. V. BOUNOR-LEGARÉ, DR CNRS, HDR ; veronique.bounor-legare@univ-lyon1.fr

Keyword(s): Biopolycondensates, Lignin, Polymer, Catalysis, Reactive extrusion

Scientific context: The project aims at developing the use of lignin from paper industries (Kraft or Soda process) or from biorefineries (Organosolv) for the synthesis of polymers, particularly polycondensates by reactive extrusion. Actually, lignin the only biopolymer resulting from random polycondensation of three aromatic precursors (i.e. monolignols) leading to complex polyaromatic structures encountered in plants, and mainly woods. It is a co-product of paper industry available in relatively high amounts (despite its use as energy source for the paper industry process), and

contrary to cellulose and hemicellulose little valorized. Therefore to improve the economical balance of paper industries and other biorefineries, upgrading lignin to higher

value added products is necessary. Thus, upgrading lignin to building-blocks usable to



produce new biopolycondensate appears here as an interesting alternative to other currently evaluated valorizations (i.e. to fuels, chemicals...).

Missions: To reach the objective of this project, we propose to study functional modifications of various lignins to introduce in controlled way, in nature and in density, functionalities matching the targeted polymerization chemistries and the constraints of the reactive extrusion process. These modifications could be achieved by: 1- selective partial catalytic depolymerisation of the initial biopolymer keeping the poliaromatic structure; 2- chemical modifications, via a catalytic route (e.g. cross-coupling, telomerisation, functional group interconversion (FGI)...), of the original lignin functionalities controlling their nature (hydroxyl, carbonyl, carboxyl, amine, alkyldienyl...) and their number (from 2 to x / monomeric block). A part of the work will focus on studying the various catalytic transformations made on lignin that will require the use of different complementary analytical techniques (FTIR, NMR, SEC...). This step is mandatory to design well-defined "monomeric" building blocks. Their thermal stability that is a strong limitation to use them in mass polymerization will be deeply evaluated. Once synthesized and characterized, depending on introduced functionalities, these building blocks will be evaluated for the synthesis of polymer in mass, and more particularly polycondensates. The main challenge of the study is to develop a class of biosourced building blocks from lignin usable under the conditions applied in reactive extrusion process that are high temperature, short reaction times and viscosity evolution as a function of the reaction progress. The polymerization will be followed by classical methods like NMR, SEC and viscosity. The control of the

stoichiometry is a major key to reach polycondensates with high molar mass and ultimately final properties similar to those of more classic polycondensates.



Reference:

- 1- Sebhat, W.; El-Roz, A.; Crepet, A.; Ladavière, C.; Perez, D. D. S.; Mangematin, S.; Almada, C. C.; Vilcocq, L.; Djakovitch, L.; Fongarland, P., Comparative study of solvolysis of technical lignins in flow reactor, *Biomass Conv. Bioref.*, **2019**,
- 2- Zahreddine, W.; Karamé, I.; Pinel, C.; Djakovitch, L.; Rataboul, F., First study on telomerization of chitosan and guar hemicellulose with butadiene: Influence of reaction parameters on the substitution degree of the biopolymers, *Molecular Catalysis*, **2019**, ASAP on-line.
- 3- Kuznetsov, B. N.; Chesnokov, N. V.; Sudakova, I. G.; Garyntseva, N. V.; Kuznetsova, S. A.; Malyar, Y. N.; Yakovlev, V. A.; Djakovitch, L., Green catalytic processing of native and organosolv lignins, *Catal. Today* **2018**, 309, 18-30.
- 4- Cayuela J, Da Cruz-Boisson F; Michel A; Cassagnau P; Bounor-Legare V, Synthesis of bisphenol-A polycarbonate-poly(epsilon-caprolactone) copolymers by reactive extrusion through in situ epsilon-caprolactone polymerization, *Polymer*, **2016**, 104;156-169.
- 5- Chabert M, Bounor-legaré V, Mignard N, Cassagnau P, Chamignon C, Boisson F, Formation of new alkyl functionalized poly(ethylene terephthalate) oligomers through exchange reactions with titanium alkoxides in melt conditions, *Polymer Degradation and Stability*, **2014**, 102;122-131.

Application: Please send CV, motivation letter, copy of M1 and M2 grades, one or two recommendation letters including contact information **until May 20th, 2020**.