Role of non-covalent interactions onto the metal catalyzed stereoselective ring-opening polymerization of functional β-lactones

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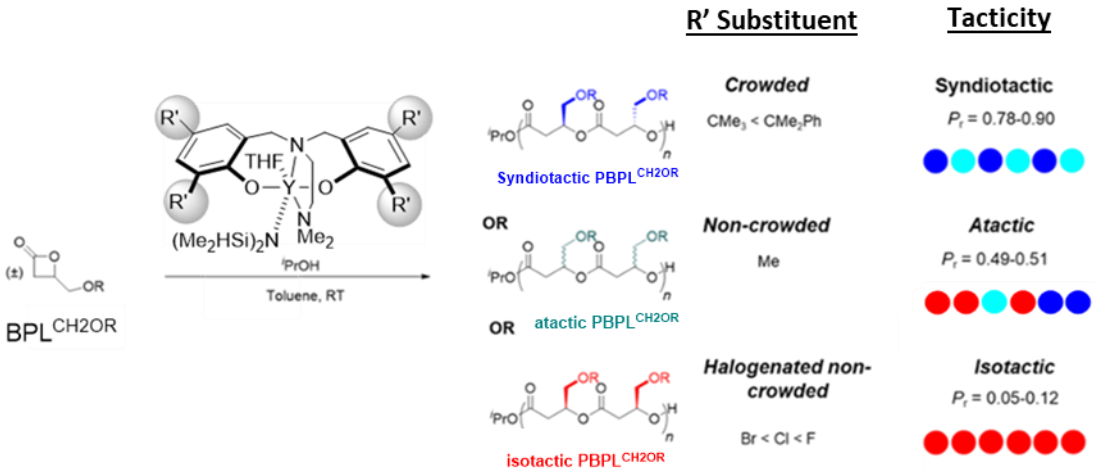
Poly(hydroxyalkanoate)s (PHAs) are a family of linear aliphatic biopolyesters that have in the recent years gained increasing interest in academia and industrial domains due to their eco-friendly character. PHAs, initially identified in the early twenties by M. Lemoigne as small granules of isotactic polyesters synthesized by bacteria, show a low thermal stability which limits their industrial use.[1,2] A convenient synthetic route to enhance the properties of PHAs is the ring-opening polymerization (ROP) of four-membered β-lactones using metal-catalyzed polymerizations.[3]

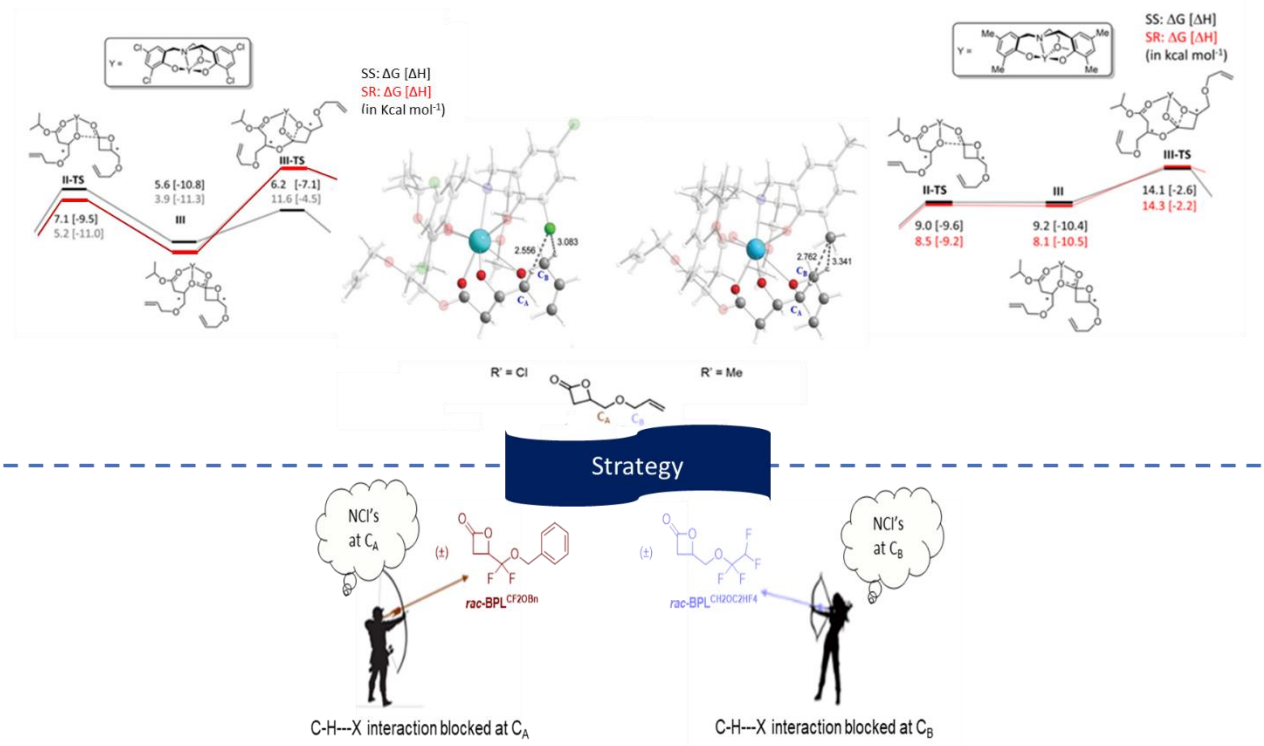
The achiral yttrium complexes with diamino-bis(phenolate) ligands $\{ONXO^{R'}\}_2^-$ (X = NMe_2), in the presence of an initiator (isopropanol), are regarded as a "privileged" class of catalysts due to their ability to efficiently promote the highly stereocontrolled ROP of 4-alkoxymethylene-β propiolactones (*rac*-BPL^{CH2OR}) into their corresponding poly(BPL^{CH2OR})s. Depending on the substituents flanked onto the yttrium ancillary (R' = Me, Cumyl, *t*Bu, halogen), the corresponding PHAs can exhibit different microstructures (Scheme 1).[4] Highly syndiotactic polymers are obtained when crowded substituted ligands are performing. However, the simple modification of *ortho*-substituents from crowded to dimethyl-substituted yttrium complex, gives atactic polyesters. Unexpectedly, the use of complexes bearing halogenated ligands induces the formation of highly isotactic PHAs.

Insights into the ROP mechanism by DFT calculations revealed the importance of "non-covalent" interactions (NCIs) between the methylene hydrogens in the ring-opened monomer of the growing chain and R' substituents on the yttrium ligand (Scheme 2).[5]



Scheme 1. Influence of R and R' substituents on the stereocontrolled ROP of *rac*-BPL^{CH2ORs} promoted by *in situ* generated Y{ONNO$^{R'}$}(OiPr) complexes.

The objective of my work is to further investigate the importance of such NCIs into the control of the PHAs' tacticity. To this end, unprecedented functional poly(BPL^{CH2OR})s have been successfully prepared from the similarly controlled ROP of *rac*-BPL^{CH2ORs} by yttrium complexes in the presence of isopropanol as co-initiator. We anticipate inhibiting NCIs upon replacing hydrogen atoms by fluorine atoms, thereby suppressing the monomer side-chain hydrogens/ ligand halogen interactions. Experimentally, this can be achieved by synthesizing BPL^{CH2ORs} bearing fluorine atoms on methylene C_A or C_B (Scheme 2). Our most recent advances in the understanding of the mechanism at play in the stereoselective ROP of fluorinated-BPL^{CH2ORs} will be presented.



Scheme 2. Structures of the transition state of rate determining step (III-TS) at the ring-opening step of *rac*-BPL^{CH2OAll} en-route toward isotactic (*SS*) (left) and atactic (right) PBPL^{CH2OAll} (top), showing NCIs between alkoxymethylene group in the ring-opened monomer and the ligand chloro (left) or methyl (right) substituents,[5] and the on-going strategy to investigate NCIs effect on the stereocontrolled ROP of fluorinated *rac*-BPL^{CH2OR}s (bottom).

1 B. Laycock, *et al.*, *Prog. Polym. Sci.*, **2013**, *38*, 536
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3 C. G. Jaffredo, *et al.*, *Chem. Eur. J.*, **2016**, *22*, 7629
4 *a*) R. Ligny, *et al.*, *Chem. Eur. J.*, **2019**, *25*, 6412 ; b) H. Li, *et al.*, *Chem. Eur. J.*, **2020**, *26*, 128 ; c) R. Shakaroun, *et al.*, *Polym. Chem.*, **2021**, *12*, 4022.
5 R. Ligny, *et al.*, *Chem. Commun.*, **2018**, *54*, 8024.