

Bio-inspired catalytic platforms as a sustainable route to Polymers

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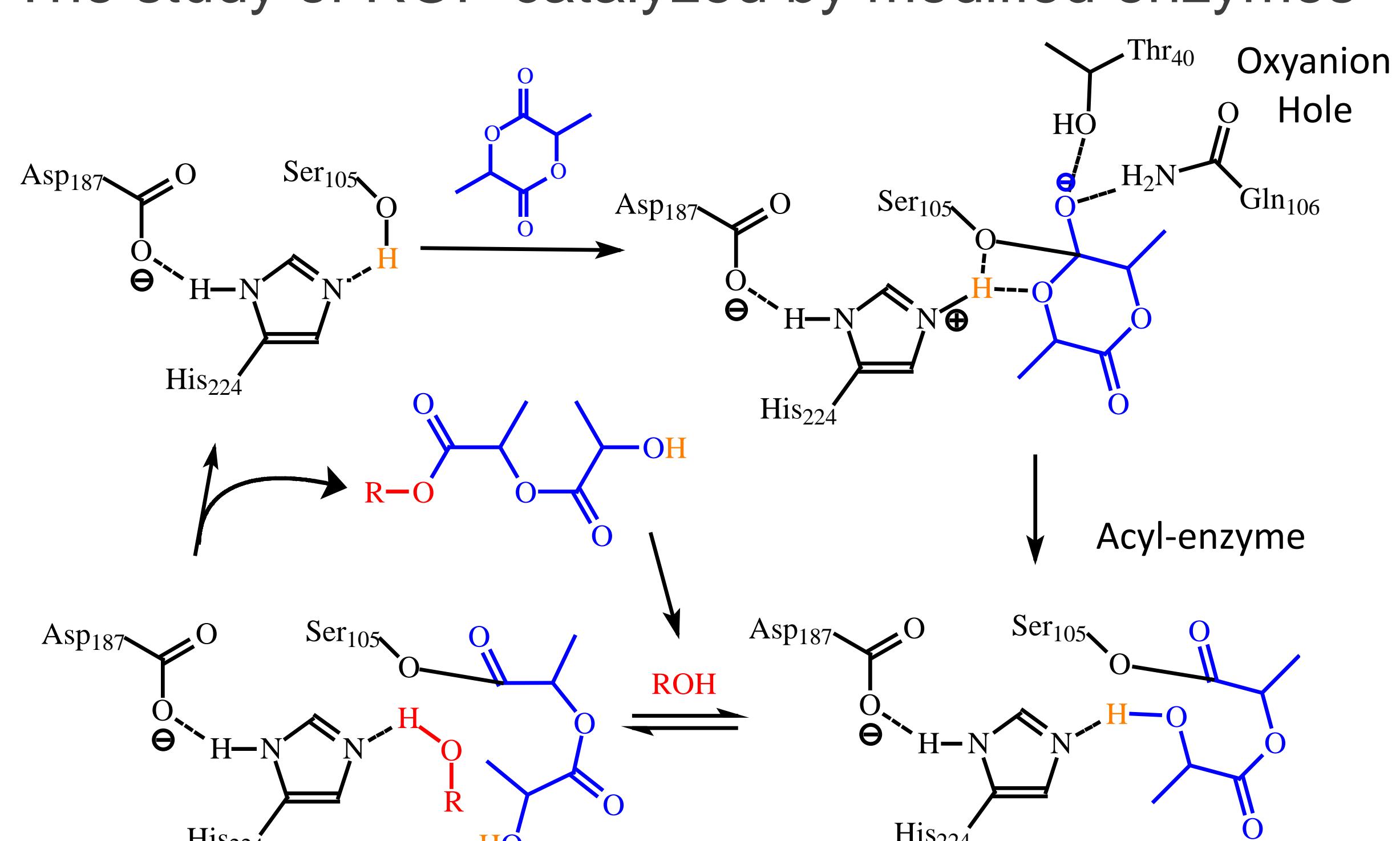
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Objectives of the project

Today, most of the polymers contain toxic metal residues (transition metals, Al., Cr., Sn., etc). Despite their low concentration, these latter are suspected to generate environmental and health problems, still not completely identified and quantified. Metal residues also limit the use of some polymers in important domains (biomaterials, pharmaceutical, electronics, food packaging).

Our main objectives were thus :

- The study of the Ring-Opening Polymerization (ROP) of lactide and lactones via metal-free catalyses
- The development of new bio-inspired synthetic routes thanks to organic catalytic platforms developping H-bonding interactions like lipases do (Scheme below)
- The study of ROP catalyzed by modified enzymes



ROP of lactide catalyzed by *Candida Antarctica Lipase B* (CALB)

Catalytic system ①

- Polymerization rate highly dependent on X-
- Living/controlled ROP of lactide in dichloromethane at RT or in bulk at 100° C
- Living/controlled ROP of lactones in bulk at 100° C
- Synthesis of block copolymers

Catalytic system ②

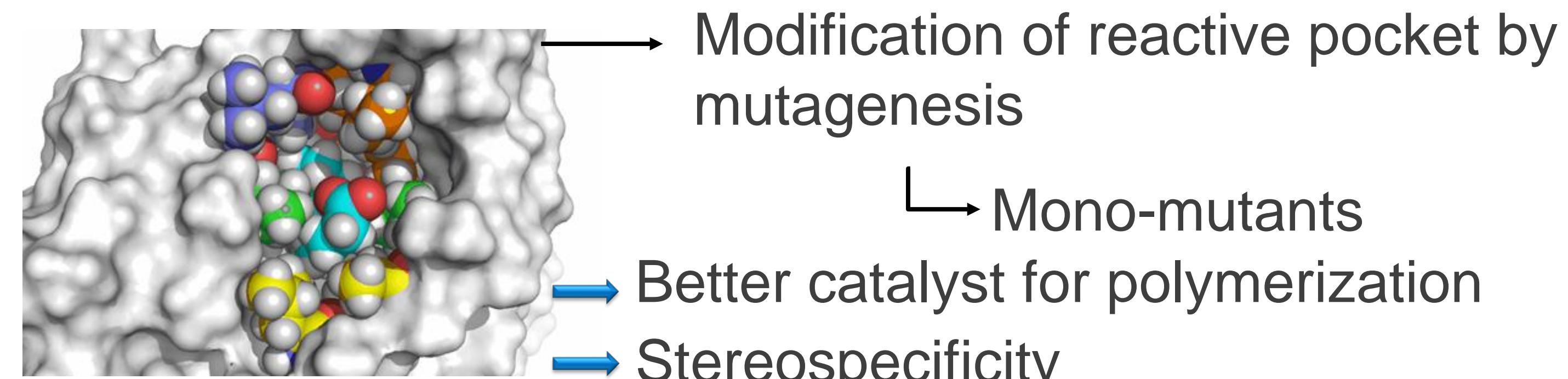
- Polymerization rate dependent on Y, R and tertiary amine
- Living/controlled ROP of lactide in CH₂Cl₂ at RT with high rate

Enzymatic polymerizations

Lipases = hydrolases BUT can perform polymerization of D-LA, lactones, carbonates, ... and polycondensation in non-aqueous media

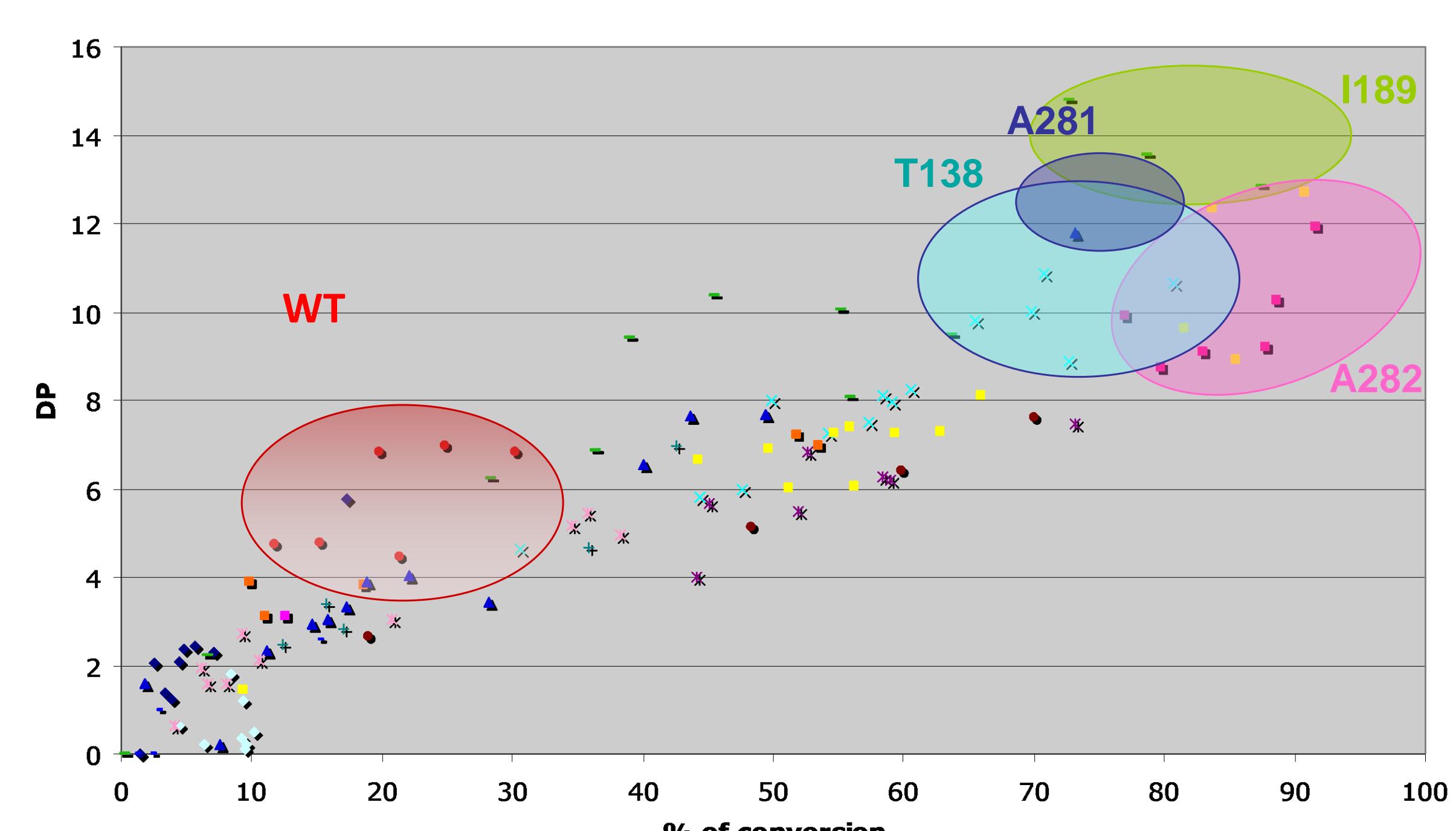
⊕ easily accessible robust (solvent, T)

⊖ high loading slow rate



- Improvement of polymerization rate
- Selectivity in hydrolysis reactions

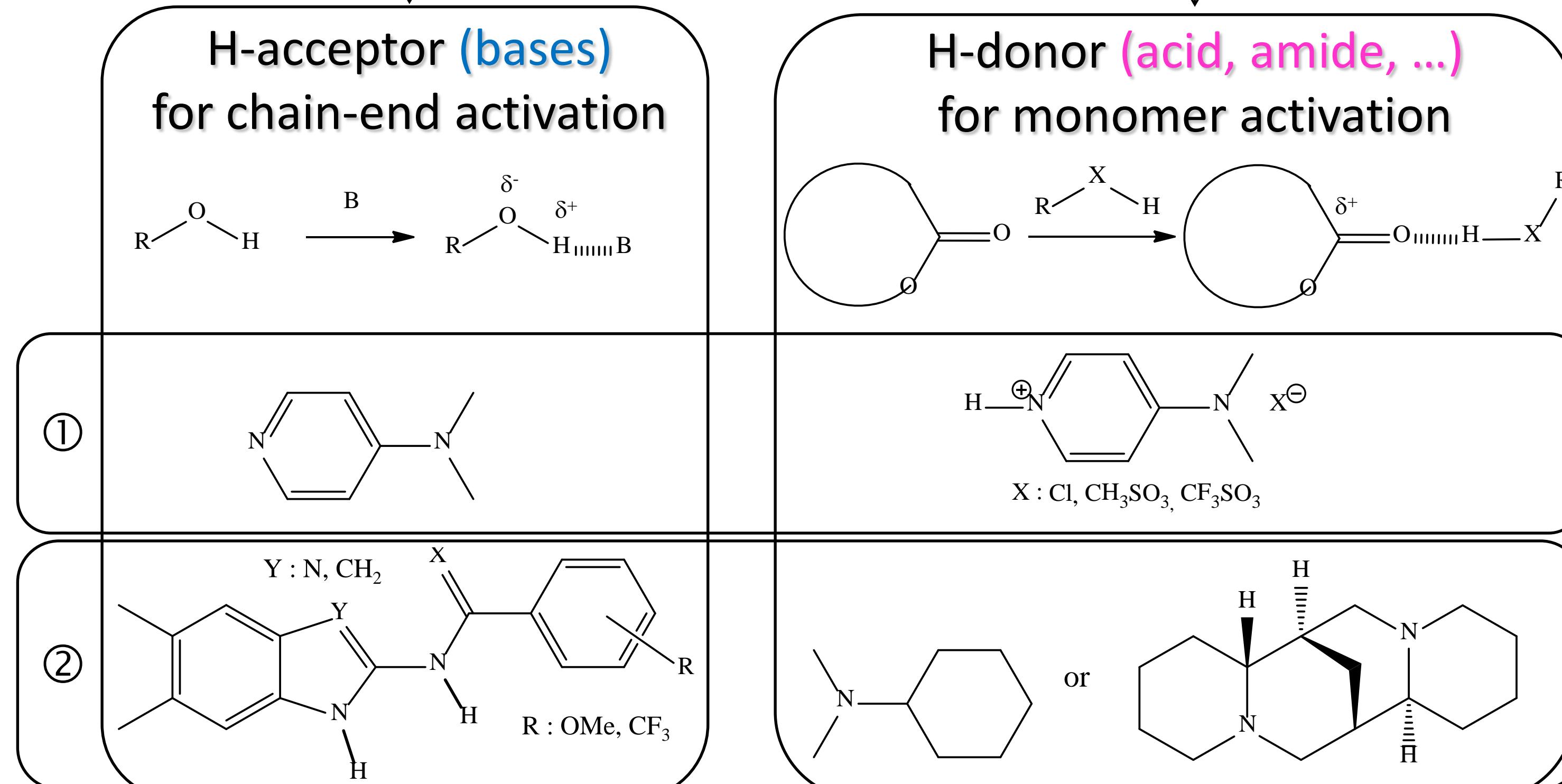
ε-CL, 15h, 60°C, toluène



J. Am. Chem. Soc., 131, 15088 (2009); *Chem. Eur. J.*, 16, 4196 (2010); *Macromolecules*, 43, 8874 (2010); *Appl. Environ. Microbiol.*, 76, 2684 (2010); *ACS Symp. Ser.*, 1063, 153 (2011); *Adv. Synth. Catal.*, 353, 1049 (2011)

Organo-catalyzed polymerizations

combine/associate



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