

POLYGREEN

Non-isocyanate organo-catalyzed synthetic routes to polyurethanes from bio-sourced synthons

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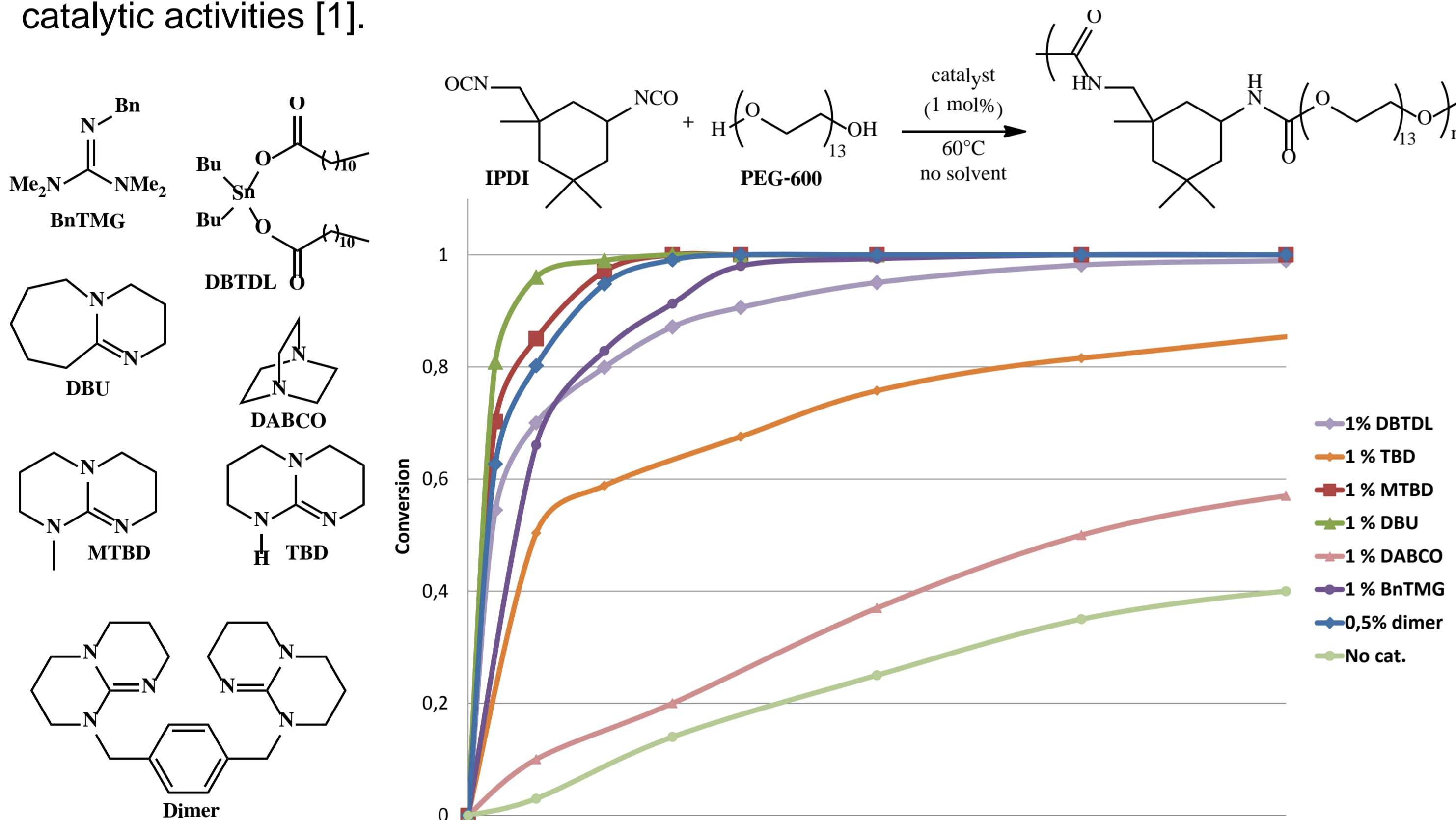
Four partners are involved in this project :

- H. Cramail and E. Cloutet from the *Laboratoire de Chimie de Polymères Organiques (LCPO, Pessac)*,
- C. Alfos and B. Gadenne from the *Institut Technique d'Etude et de Recherche sur les corps Gras (ITERG, Pessac)*,
- Y. Landais, F. Robert ("Synthesis" group) and T. Tassaing ("Spectroscopy" group) from the *Institut des Sciences Moléculaires (ISM, Talence)*.

This project aims to tackle the synthesis of "supergreen" polyurethanes from renewable **bio-sourced polyols**, **without isocyanates** and in the **absence of metal-based catalysts**. Preparation of these materials will be based on the use of CO₂, abundant starting material and valuable surrogate of toxic and corrosive phosgene, on vegetable fatty oils for the monomers synthesis and on small organic molecules as organometallic surrogates. Polymerizations are performed without the use of solvent, *i.e.* in bulk or in CO₂ medium in order to obtain easily processable polyurethane materials.

Organocatalyst design

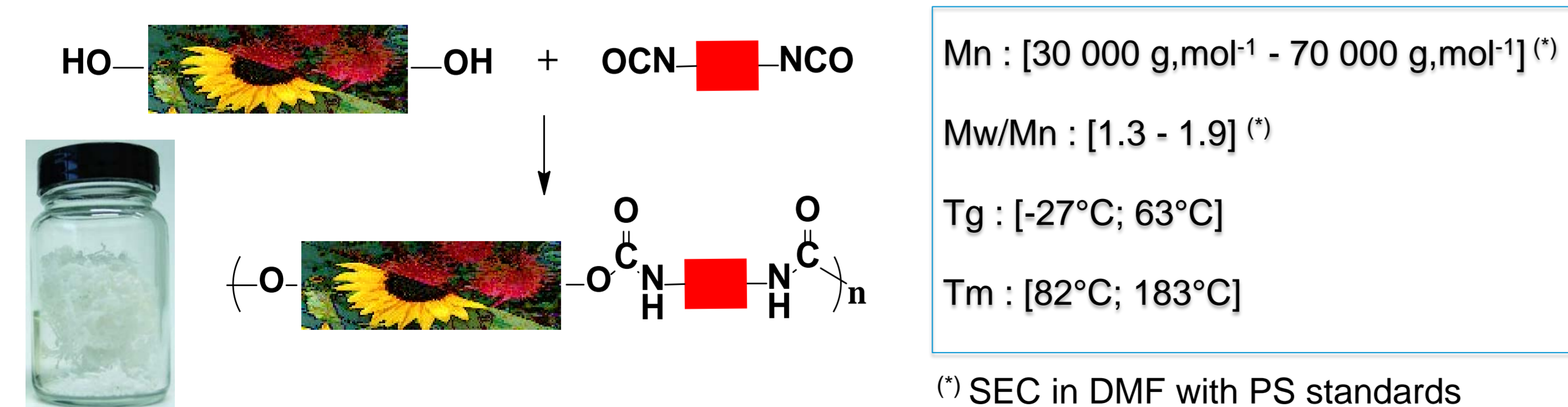
The synthesis of polyurethanes is most generally catalyzed by organometallic species, including tin and titanium reagents. Such catalysts should be replaced as they are known to have a high persistence in the environment, leading to bioaccumulation and toxic effects in the food chain. Replacement of such organometallic catalysts with environmentally more acceptable organocatalysts for polymerization reactions is attracting considerable interest. A screening of organocatalysts was therefore carried out, from which bicyclic guanidines emerged as the most efficient. Kinetic and mechanistic studies were performed to rationalize their reactivity. Rational design and synthesis of analogs finally led to a range of novel organocatalysts exhibiting attractive catalytic activities [1].



Bicyclic pentaalkyl guanidines were shown to be effective non metal-based catalysts for the formation of the urethane linkage. We synthesized novel bicyclic guanidines that display unprecedented catalytic activities for the synthesis of polyurethanes. Mechanistic and kinetic studies are still in progress to understand their mode of action.

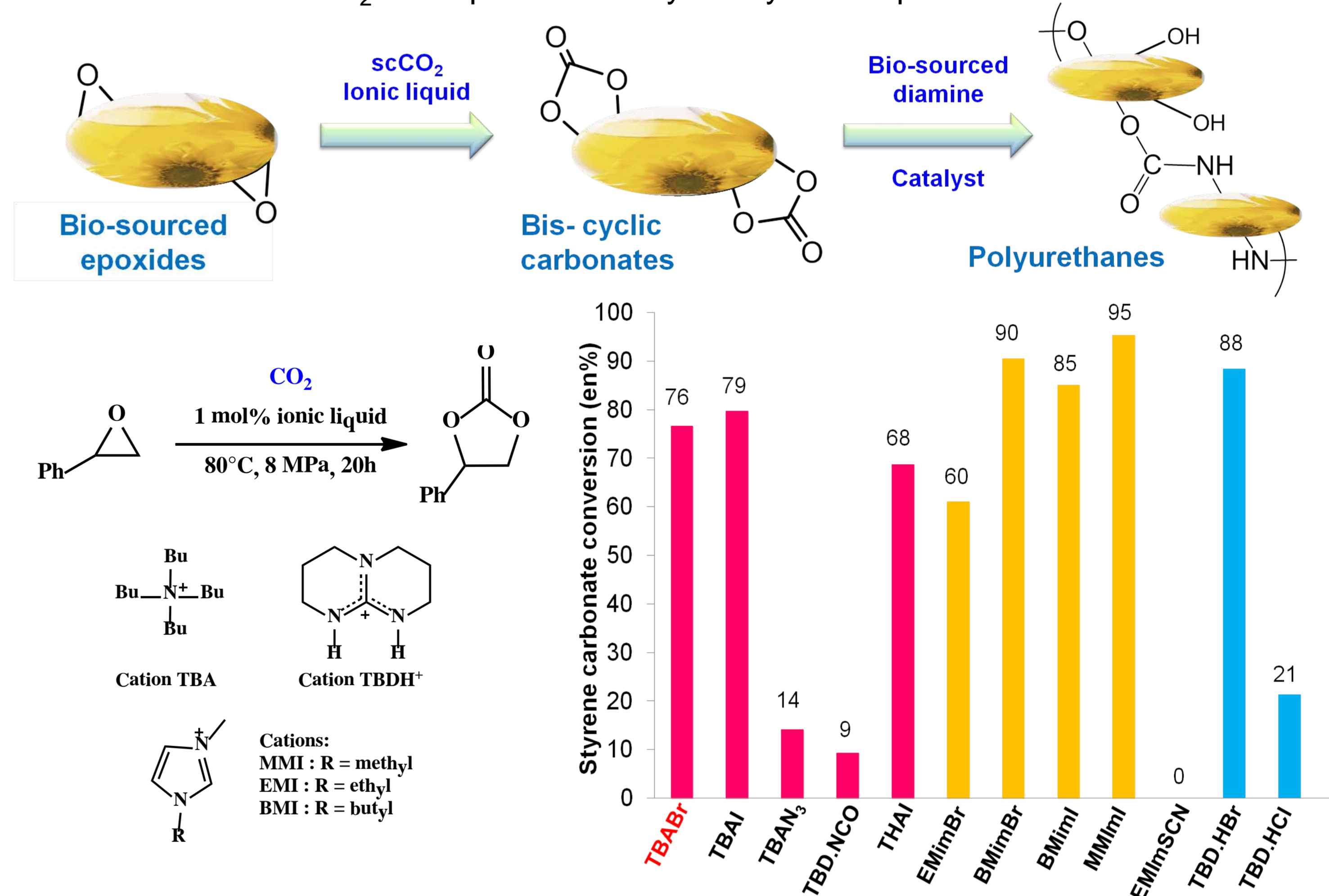
Polyurethanes from bio-sourced polyols

A series of bio-based diols containing ester, ester-amide and amide linkages were synthesized from methyl undecenoate (derived from ricin oil) and methyl oleate (derived from sunflower oil). These polymerization grade monomers were polymerized to obtain a plethora of thermoplastic polyurethanes (TPUs) with tuned thermo-mechanical properties. As expected, the PUs displayed amorphous to semi-crystalline features with respect to the nature of the diols and diisocyanates [2].



Synthesis of cyclic carbonates from epoxides and CO₂

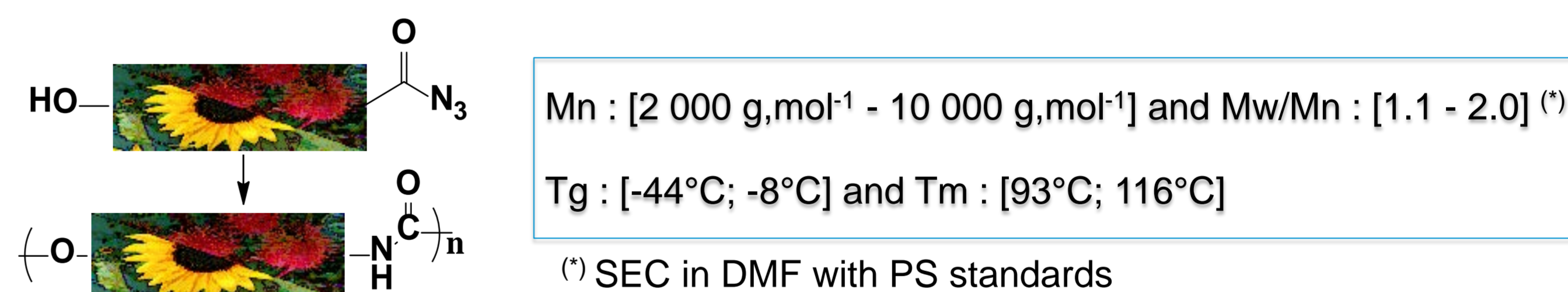
To avoid the use of toxic isocyanates, we finally propose to use bis-carbonate precursors accessible through the ring-opening of bis-epoxides in supercritical CO₂, an excellent alternative to various toxic solvents. After a previous study on the phase behavior of several epoxides / supercritical CO₂ binary systems [3,4], we focused on the chemical fixation of CO₂ with epoxides catalyzed by ionic liquids.



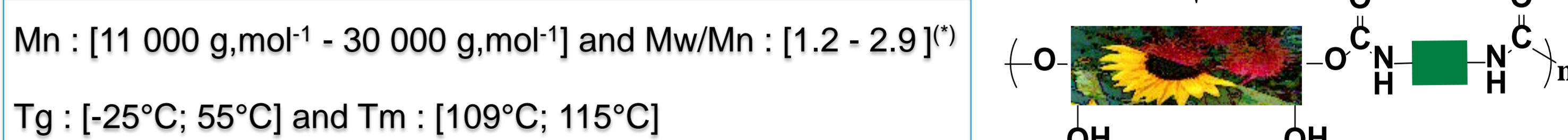
High yields of cyclic carbonate were obtained using scCO₂ both as a solvent and reagent at 80°C and 8 MPa. Two catalysts (TBD.HBr and MMIImI) have shown better efficiency than the standard TBABr. We have now to investigate these catalysts with vegetable based epoxidized oils.

Bio-based polyurethanes from non-isocyanate routes

AB-type self-condensable monomers containing hydroxyl-acyl azide functionality were synthesized from methyl oleate and methyl undecenoate. A series of polyurethanes was prepared using an AB-type self-polycondensation reaction of hydroxyl-acyl azide moiety [5].



Linear polyurethanes were also synthesized by bulk polyaddition of diamines with vegetable-based bis-carbonates produced from fatty acid methyl esters.



References:

- 1) J. Alsarraf, Y. Ait Ammar, F. Robert, E. Cloutet, H. Cramail, Y. Landais *Macromolecules* **2012**, *45*, 2249-2256.
- 2) L. Maisonneuve, T. Lebarbé, N. Nguyen, E. Cloutet, B. Gadenne, C. Alfos, H. Cramail *Polymer Chemistry* **2012**, *3*, 2583-2595.
- 3) S. Foltran, L. Maisonneuve, E. Cloutet, B. Gadenne, C. Alfos, T. Tassaing, H. Cramail *Polymer Chemistry* **2012**, *3*, 525.
- 4) S. Foltran, E. Cloutet, H. Cramail, T. Tassaing *The Journal of Supercritical Fluids* **2012**, *63*, 52.
- 5) A. S. More, B. Gadenne, C. Alfos, H. Cramail *Polymer Chemistry* **2012**, *3*, 1594-1605.

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