Non-Ionic Diborane Catalysts for the Preparation of Defined Oligo- and Polyethers[1]

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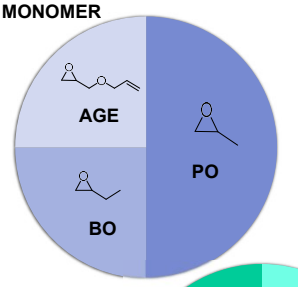
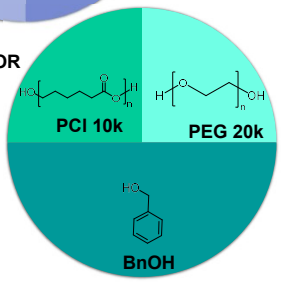
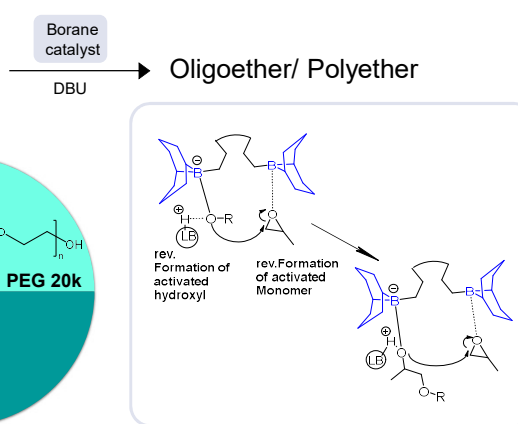
Borane catalysis has proven to be an effective technology for epoxide polymerization. We have investigated the ability of 13 different diborane catalysts with non-ionic backbones to facilitate oligomerization and polymerization of propylene oxide (PO), 1-butylene oxide (BO) and allyl glycidyl ether (AGE). From a structural point of view, particular attention has been paid to catalysts with different linker lengths and linker flexibilities. It is noteworthy that this screening could be carried out both under typical polymerization conditions and under conditions relevant to large-scale production, characterized by the presence of alcohol chain transfer agents (CTAs) in excess. We reason that the pre-organization of borane groups, as observed for biphenyl derivatives, provides a straightforward route to the development of high performance catalysts and the quantitative conversion of the epoxide monomers studied. Furthermore, diborane-catalyzed oligomerization can be sustained by repeated addition of monomer batches (14 steps) for up to six weeks, resulting in complete conversion and the production of well-defined oligoethers [1].

MONOMER

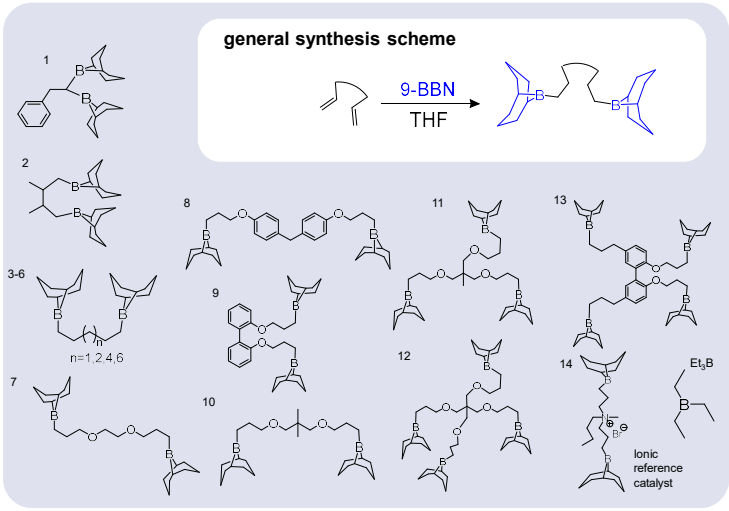


INITIATOR





BORANE CATALYSTS



OLIGOMERIZATION

BnOH

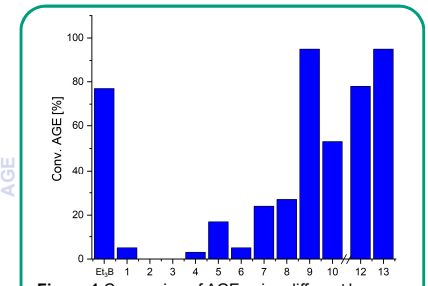


Figure 1:Conversion of AGE using different borane catalysts, DBU/1-14/BnOH/AGE = 1:2:100:100, 24 h, RT.

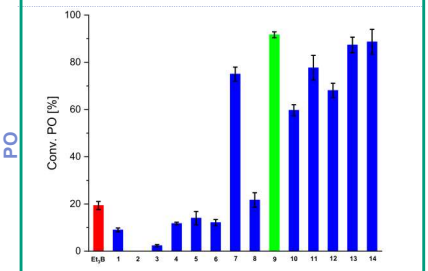


Figure 2:Conversion of PO using different borane catalysts, DBU/1-14/BnOH/PO = 1:2:100:100, 2 h, 50°C.

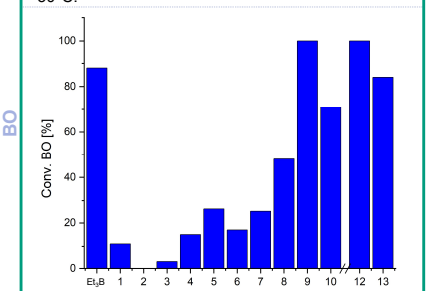
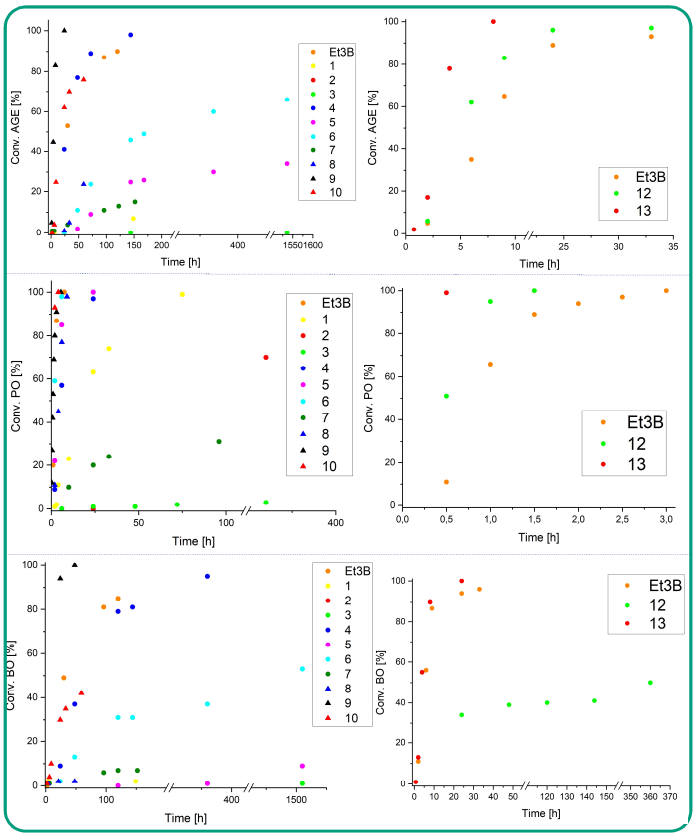


Figure 3:Conversion of BO using different borane catalysts, DBU/1-14/BnOH/BO = 1:2:100:100, 24 h, 50°C.

POLYMERIZATION

BnOH



PEG 20k

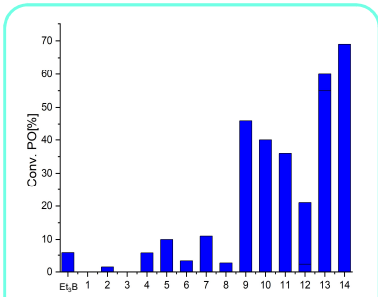


Figure 4:Conversion of PO using different borane catalysts on PEG20k Macroinitiator, 3000eq PO, 2 h, 80 °C.

PCl 10k

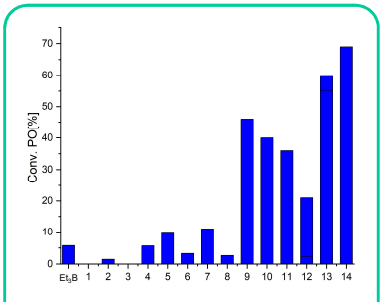


Figure 5:Conversion of PO using different borane catalysts on PCl 10k Macroinitiator, 3000 eq PO, 2 h, 80 °C.

CONCLUSIONS

Oligomerization: Especially oxygenated linkers with reduced conformational freedom seem preferable, highlighting a biphenyl-derivative (Borane 9) as the most promising structure. With this compound, it is possible to keep oligomerizations alive for more than 50 days, whereby additional monomer dosing can be conducted at will, entailing well-defined oligoethers and quantitative monomer consumption

Polymerization: Borane 9 is also very effective in the polymerization of PO, BO and AGE, delivering well-defined polymer products.

[1] Haug, I., Eberhardt, M., Krappe, U. & Naumann, S. A Systematic Study of Nonionic Di- and Multiborane Catalysts for the Oligomerization and Polymerization of Epoxides. *Chemistry – A European Journal* e202401268 (2024) doi:10.1002/CHEM.202401268.