

Functional Polycarbonates via CO₂-Epoxide(s) Co-/Ter-polymerization

Nishant Chaudhary¹,

A. Stephen K. Hashmi², Jean-François Carpentier¹, Sophie M. Guillaume¹

a) Institut des Sciences Chimiques de Rennes ISCR, CNRS-Université de Rennes, France

b) Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Keywords: Organoborane catalyst, ring-opening copolymerization (ROCOP), post-polymerization modification

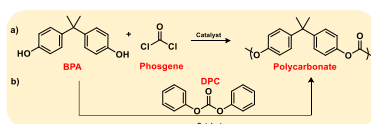
Introduction: CO₂ utilization has garnered significant attention over the past few decades towards a sustainable world. Developing CO₂-based polymers is a versatile approach for its valorization into valuable goods. Aliphatic polycarbonates, a class of polymer prepared from ring-opening copolymerization of CO₂ and epoxides important in substituting the conventional petrochemical-based polymers. This polymer class offers a wide range of benefits in terms of their applications, recyclability, biodegradability, and reduction in reliance on fossil fuels.

In this study, we explored metal-free and metal-based catalytic systems towards ROCOP of CO₂ with benzyl glycidyl ether (BnGE) towards the synthesis of co- and ter-polycarbonates with benzyloxy-functionalized backbone which were further explored in post-polymerization strategies.



Polycarbonate synthesis : overview

Conventional Approach

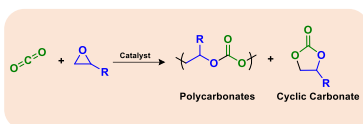


Relying on petrochemical-derived raw materials

Use of hazardous chemicals (BPA, phosgene)

Toxic chlorinated byproduct

Greener Approach

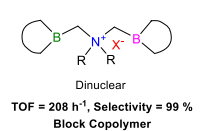
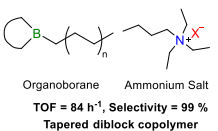
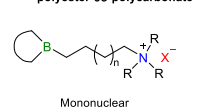
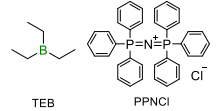
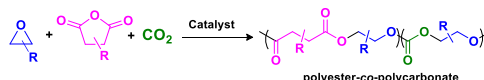


CO₂ : a natural feedstock

Reduction of reliance on fossil fuels

Biodegradable & Sustainable polycarbonates

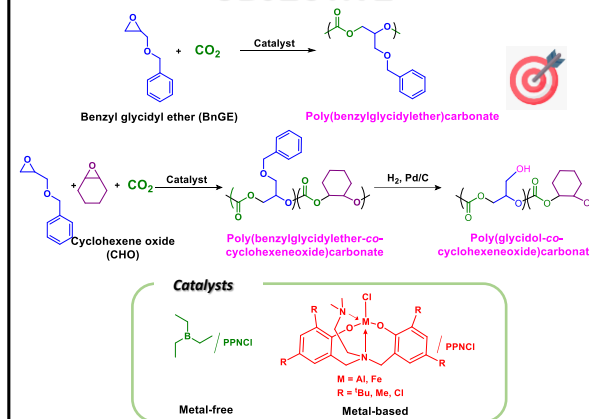
Terpolymerization : SOTA^{1,2}



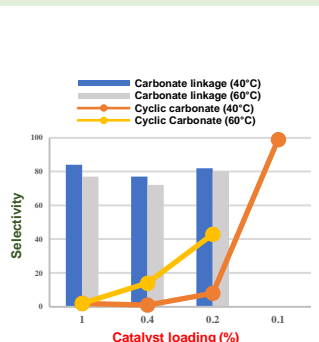
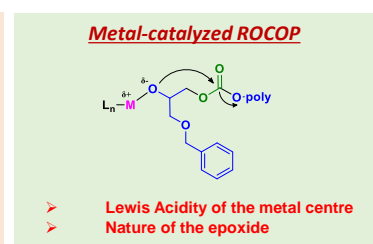
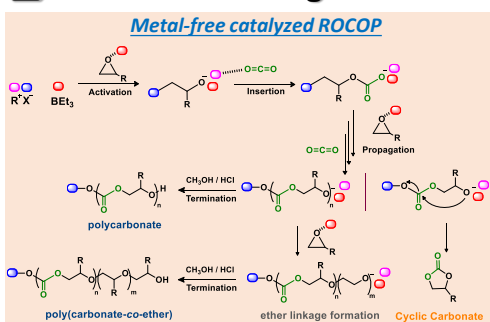
Binary Catalyst

Bifunctional Catalyst

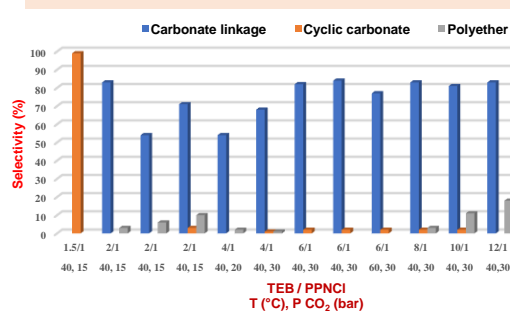
OBJECTIVE



Mechanistic insights

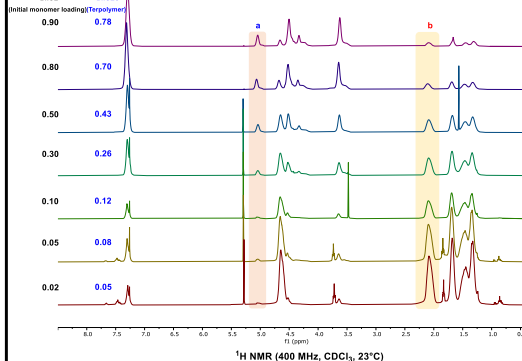
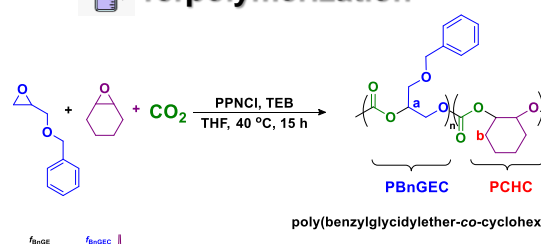


Impact of catalyst loading on the selectivity



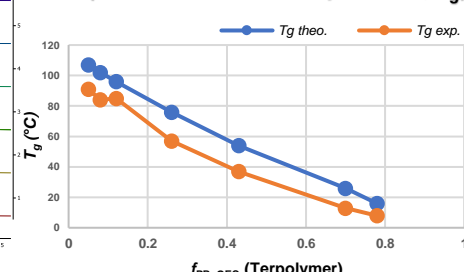
Comparison of TEB/PPNCI equivalents on the selectivity

Terpolymerization

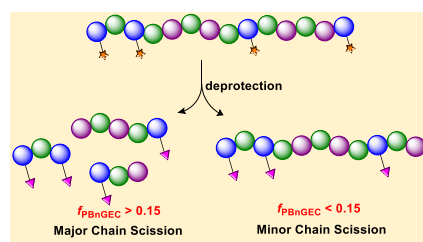
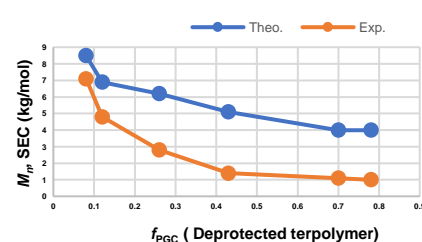
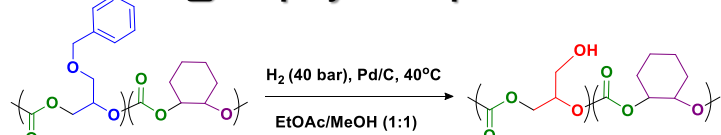


$f_{\text{BnGEC}}(\text{terpolymer}) = 1$

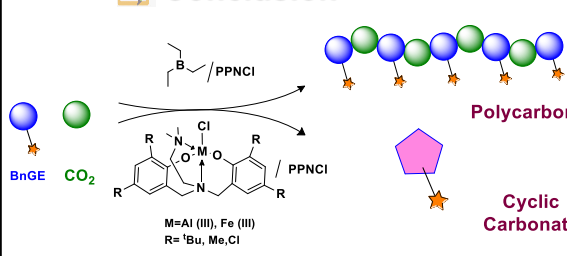
Thermal behavior
(Glass transition temperature, T_g)



Terpolymer deprotection

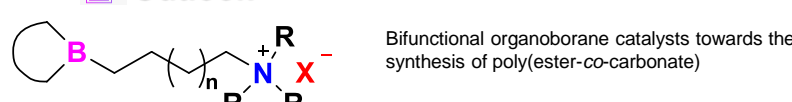


Conclusion



- ✓ TEB/PPNCI, an effective catalytic system for polycarbonate synthesis
- ✓ Metal catalyst selectively produced cyclic carbonate
- ✓ Dilution effect alters selectivity at higher monomer loadings
- ✓ Deprotection of terpolymers with higher benzyloxy contents leads to chain scission resulting in low molar mass

Outlook



References

- G.-W. Yang, R. Xie, Y.-Y. Zhang, C.-K. Xu and G.-P. Wu, *Chem. Rev.*, **2024**, 124, 12305–12380.
- D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, *J. Am. Chem. Soc.*, **2016**, 138, 11117–11120.

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