CYCLODEPOLYMERIZATION OF BIODEGRADABLE POLYESTERS FOR THE SYNTHESIS OF MACROCYCLIC OLIGOMERS

D. Zannini[1,2], R. Utzeri[1], P. Stagnaro[1], L. Conzatti[1]

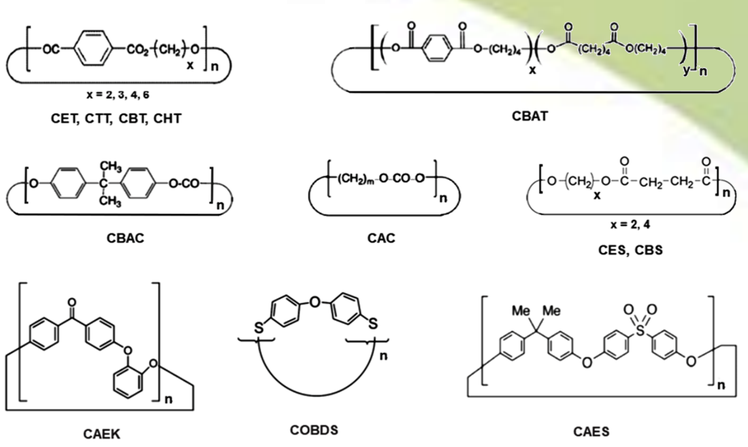
[1] Institute of Chemical Sciences and Technologies "Giulio Natta" SCITEC, National Research Council
via De Marini 16, 16149 Genova, Italy

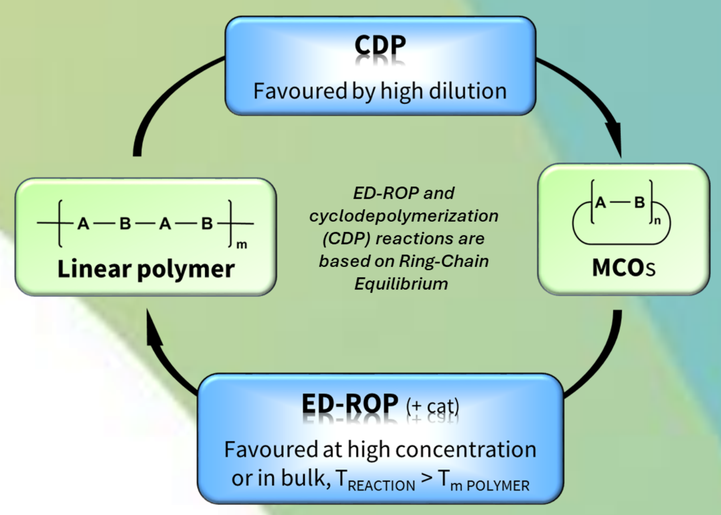
[2] Department of Chemical Sciences, Monte Sant'Angelo Campus, University of Naples "Federico II",
via Cinthia 4, 80126 Naples, Italy

e-mail: domenico.zannini@cnr.it

Introduction

Cyclodepolymerization (CDP) reaction can be considered an alternative for the chemical recycling of polyesters, polycarbonates and other polycondensates. Through CDP in dilute solution polycondensates are converted to the corresponding macrocyclic oligomers (MCOs) based on ring-chain equilibria (RCE), i.e., the equilibria existing between the linear polymer chains and corresponding families of MCOs. MCOs typically achieved by CDP are greater than ~14 ring atoms being thus practically strainless; as a consequence, their ring-opening polymerization (ROPs) are entropically-driven (ED-ROPs) [1].





ED-ROP and cyclodepolymerization (CDP) reactions are based on Ring-Chain Equilibrium

ED-ROP advantages

- No need for solvents
- No emission of volatiles
- Low temperature
- Little heat of polymerization
- Low viscosity of MCOs
- Good yields
- Short times
- High molecular weight product

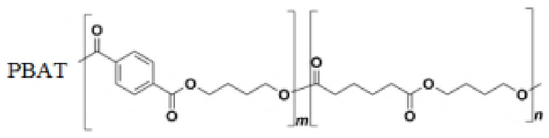
Environmentally-friendly features

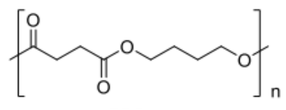
Potential applications:

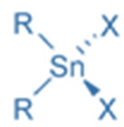
- *Compatibilization*
- *Micromoulding, pultrusion*
- *High-throughput (co)polymer synthesis*

Research objective

Study of the CDP reaction of biodegradable polyesters by using green solvents and catalysts alternative to those traditionally used

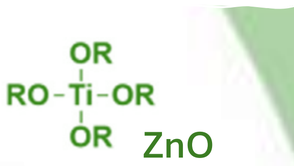




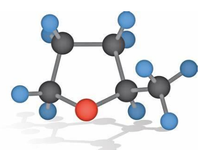


Catalysts based on Sn compounds

Traditional solvent ($CHCl_3$)



Non-toxic Ti- and Zn-based catalysts



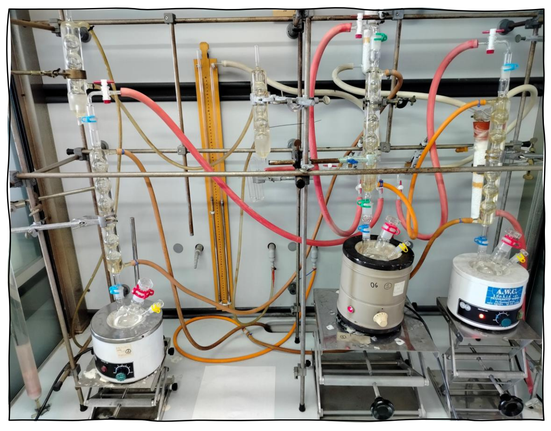
Green solvent (2-MeTHF)

Materials

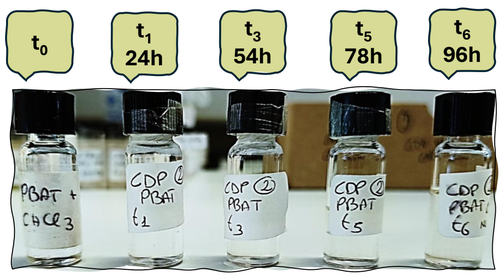
- **Biodegradable polyesters:** poly(butylene adipate terephthalate) (PBAT), poly(butylene succinate) (PBS)
- **Solvents:** $CHCl_3$, 2-methyltetrahydrofuran (2-MeTHF)
- **Transesterification catalysts**: *n*-dibutyltin(IV) oxide (*n*-Bu_2SnO), titanium(IV) 2-ethylhexyloxide ($Ti(OR)_4$) and zinc oxide (ZnO)

Methodology

- CDP reactions: high dilution (1% wt/vol), solvent reflux temperature, 3 mol% catalyst with respect to polymer [2]



- Withdrawals of the CDP reaction mixture every 24 h



- Thin layer chromatography (TLC) with CH_2Cl_2/acetone 94/6 vol/vol solvent mixture as eluent

Results

PBAT

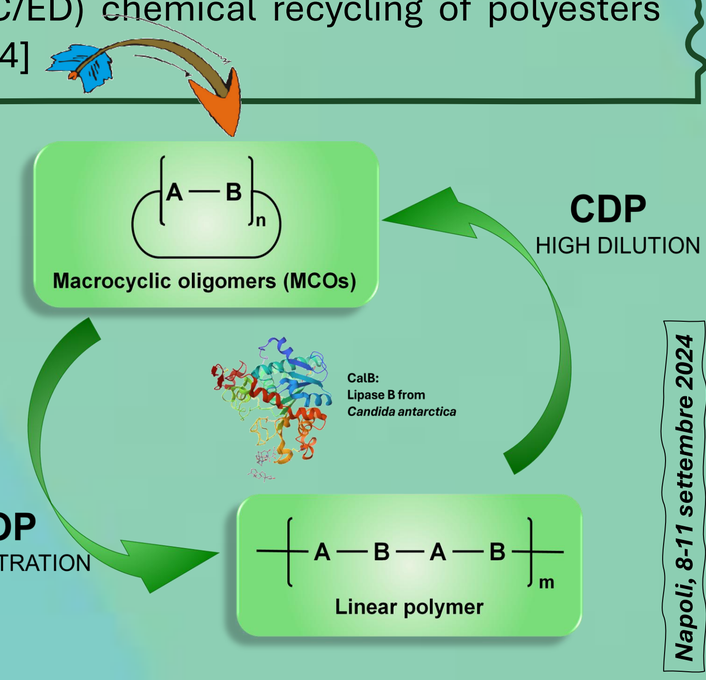
- *n*-Bu_2SnO is the most effective catalyst in both tested solvents [3]
- $Ti(OR)_4$ and ZnO catalysts are more efficient in 2-MeTHF than in $CHCl_3$

PBS

- In $CHCl_3$, *n*-Bu_2SnO resulted more efficient than non-toxic Zn- and Ti-based counterparts.
- Insoluble in 2-MeTHF

Conclusive remarks

- Widely used *n*-Bu_2SnO remains so far the most efficient catalyst in the explored conditions
- Non-toxic Zn- and Ti-based catalytic systems appear quite promising for CDP of PBAT performed in the green solvent 2-MeTHF, deserving further investigation
- The products obtained by CDP reactions will be characterized by molecular Gel Permeation Chromatography (GPC) analysis before subsequent ED-ROP tests
- Enzymatic cyclization/depolymerization (EC/ED) chemical recycling of polyesters will be investigated as well to obtain MCOs [4]



References

[1] P. Hodge, *Chem. Rev.*, vol.,114, pag.2278-2312 (2014).

[2] M. Alessi, L. Conzatti, P. Hodge, S. T. Scafati, P. Stagnaro, *Macromol. Mater. Eng.*, vol., 295, pag.374-380 (2010).

[3] L. Conzatti, E. Brunengo, R. Utzeri, M. Castellano, P. Hodge, P. Stagnaro, *Polymer*, vol., 146, pag.396-406 (2018).

[4] P. Stagnaro, E. Brunengo, and L. Conzatti, *Arkivoc*, part vi, pag.174-221 (2021).

Acknowledgments

- *MICS (Made in Italy-Circular and Sustainable) Extended Partnership, financed by the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)-Extended Partnership PE00000004-Spoke 3.*
- *The authors also thank Dr. Pierluigi Barbaro and Dr. Carmen Moreno-Marrodán at ICCOM-CNR (Florence) for providing us the ZnO catalyst.*

Finanziato dall'Unione europea NextGenerationEU
Ministero dell'Università e della Ricerca
Italiadomani PIANO NAZIONALE DI RIPRESA E RESILIENZA

Napoli, 8-11 settembre 2024