Synthesis and polymerizations of new biobased macrobisphenols derived from ferulic acid

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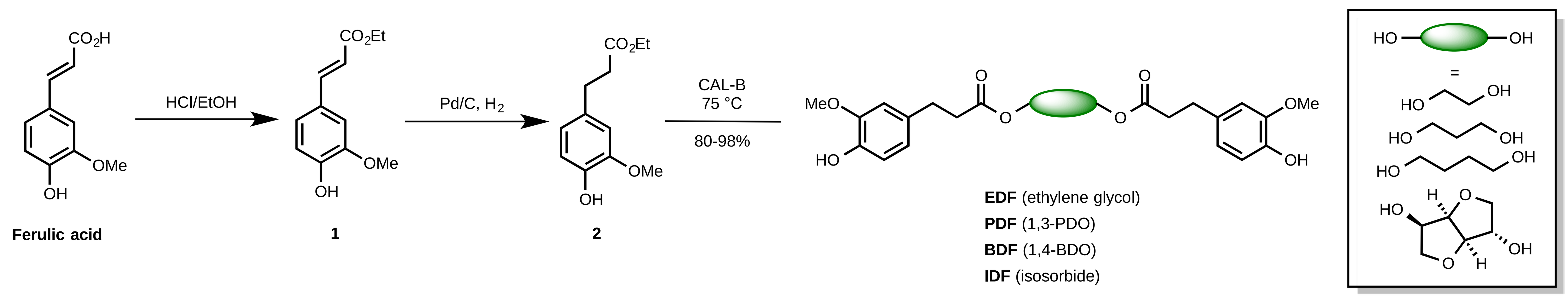
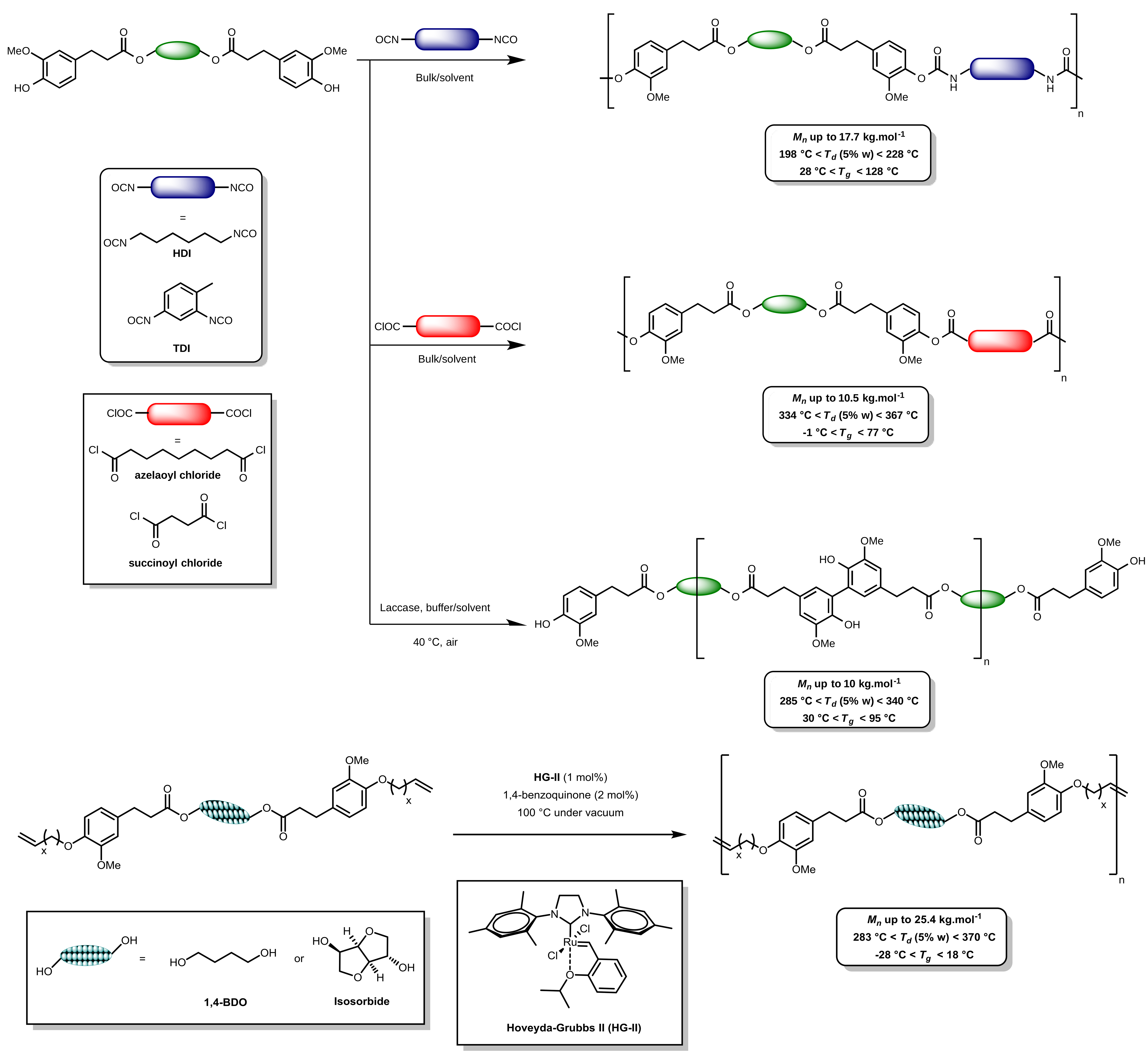
According to REACH, the use of Bisphenol A is being restricted due to its potential toxicity. In this context, we dedicated ourselves to (1) the lipase-catalyzed synthesis of a new class of macrobisphenols as potential biobased substitutes of BPA from ferulic acid and biobased polyols,[1] and (2) their use as macromonomers for the preparation of polyesters[2], poly(ester-urethane)s[3] , polyphenolic oligomers[4] and poly(ester-alkenamer)s[5].

Candida antarctica lipase B-mediated chemo-enzymatic synthesis of ferulic acid-based macrobisphenols[1]



- Solvent-free enzymatic reaction performed under vacuum (or in hexanes under reflux with Dean-Stark apparatus)
- No need of protection/deprotection sequence for the phenol moiety (enzyme selectivity)
- Immobilized resin reusable up to 6 times
- Applicable to all *p*-hydroxycinnamic acids
- Optimal conversion in *ca.* 5 hours for primary alcohols (*ca.* 48 hours for isosorbide)

Polymerizations of macrobisphenols: an access to renewable aliphatic-aromatic polyesters,[2] poly(ester-urethane)s[3], polyphenolic oligomers[4] and poly(ester-alkenamer)s[5]



Polyesters and poly(ester-urethane)s

- Renewable aliphatic-aromatic polymers
- Metal-free polymerizations
- Highly-thermostable polymers
- Tunable glass transition temperature (T_g) by playing with macrobisphenol structure and co-monomer chain length or nature (aliphatic or aromatic)

Polyphenolic oligomers

- Enzymatic polymerization
- Exclusive 5-5 biaryl bonding pattern (verified by 2D NMR and MALDI-TOF)
- Free phenols regularly distributed along the linear chain
- Hyperconjugated bisphenols
- Antiradical/antioxidant activities[6]
- Plasticizing activity under investigation

Poly(ester-alkenamer)s

- Renewable aliphatic-aromatic polymers
- Solvent free polymerizations
- Highly-thermostable polymers
- Tunable glass transition temperature (T_g) by playing with macrobisphenol structure and chain length

A new class of biobased macrobisphenols was successfully obtained from renewable starting materials through lipase-mediated biocatalysis in solvent-free conditions. Polymers resulting from the co- or homopolymerization of these macrobisphenols exhibit high thermal stability and tunable glass transition temperatures. In conclusion, these results demonstrate that ferulic acid-based macrobisphenols are promising green and safer alternatives to Bisphenol A in polymer synthesis but also, along with their corresponding phenolic oligomers, potent biobased antiradical additives.

References

(1) F. Pion, A. Reano, P.-H. Ducrot, F. Allais *RSC Adv.* **2013**, *3*, 8988. (2) F. Pion, P.-H. Ducrot, F. Allais *Macromol. Chem. Phys.* **2014**, *5*, 431. (3) M. Z. Oulame, F. Pion, P.-H. Ducrot, F. Allais *submitted*. (4) (a) Allais et al. Patent pending, (b) A. F. Reano, F. Pion, P.-H. Ducrot, F. Allais *in preparation*. (5) I. Barbara, A. L. Flourat, F. Allais *Eur. Polym. J.* **2015**, *62*, 236-243. (6) A. F. Reano, J. Chérubin, Q. Wang, T. Clément, M.-N. Maillard, P.-H. Ducrot, S. Domenek, F. Allais *in preparation*.