Ring-opening polymerization for 100% renewables-based Polyethylene Furanoate (PEF) towards the "Green Bottle"

J. Rosenboom[1], P. Fleckenstein[1], G. Storti[1], M. Morbidelli[1]*

[1]ETH Zürich

Along the shift of our societies from fossil-fuel based economies towards more sustainable civilizations, polyethylene furanoate may replace one of the world's dominant fossil-based plastics, polyethylene terephthalate (PET). Recent efforts were invariably based on polycondensation followed by solid-state polycondensation, which is burdened with the necessary removal of condensation byproducts to reach high conversions and molecular weights, and thus typically requires reaction times in the order of days [1]. We present ring-opening polymerization (ROP) as a faster and living synthesis route to reach sufficiently high molecular weight PEF for commercial applications such as bottles, textiles, medical grafts, etc. [2].

Cyclic PEF monomers (cyOEF) can be derived from the 100% renewables-based building blocks 2,5-furandicarboxylic acid and ethylene glycol via depolymerization of short PEF oligomers in suitable solvents [3]. Within 4 hours, cyOEF are formed with a selectivity of >90% towards cyOEF. The remaining unconverted linear species and solvents can be recycled to maximize material use. Purification of cyOEF from residual linears via silica gel adsorption to yield >99% cycles is essential for ROP to deliver 1) high molecular weights, 2) reproducible reaction control and 3) colorless products.

Understanding of this raw material for ROP is essential to obtain PEF that is applicable to typical commercial applications of PET: The cyclic oligomers exhibit a distribution of ring sizes, showing melting points ranging from 270 °C to 370 °C and different reactivity. Successful full conversion of all cyclic species towards bottle-grade molecular weights (Mw = 60 kg/mol) was achieved well below their melting point using 230-280°C with tin-based catalysts. Lower temperatures are actually beneficial and allow for higher achievable molecular weights, due to the more limited impact of degradation, which was observed after reaching >95% conversion. The reaction is usually complete after less than 20 min, since there are no condensation by-products that have to be removed from the viscous melt. Combined with cyOEF synthesis time, it outperforms traditional polycondensation by about a factor of 10. Preliminary economics evaluation reveals that ROP can be cost-competitive with the established polycondensation process. The material properties of ROP-PEF essential for bottle manufacture were briefly analyzed: Higher glass transition temperature (85 °C vs. 73 °C), lower melting point (215 °C vs. 260°C) and a 5x higher oxygen diffusion barrier compared with PET confirm the expected advantageous properties of PEF.

While the scale-up to larger (kilogram) volumes and processing towards actual bottles is ongoing, the advantageous synthesis of PEF via ROP opens a new and promising pathway not only towards the highly anticipated "green bottle", but also enables advanced molecular architecture control of furan based polyesters through a "living" polymerization, e.g. for branching and block copolymers, which is infeasible with the current process based on polycondensation.

[1] L Sipos, E De Jong, MA Dam, JM Gruter, *ACS Symposium Series*, **2012**, 1105, P Smith(Ed.), 1-11
[2] J Rosenboom, J De Roo, G Storti,, M Morbidelli. *Macromol. Chem. Phys.*, **2017**, 218, 1600436.
[3] R R Burch, SR Lustig, M Spinu, *Macromolecules*, **2000**, 33, 5053-5064