A PROCESS FOR THE PRODUCTION OF BOTTLE GRADE POLYETHYLENE FURANOATE BY RING-OPENING POLYMERIZATION

Peter Fleckenstein, Institute for Chemical and Bioengineering, ETH Zürich, Zürich
peter.fleckenstein.rosenboom@chem.ethz.ch
Jan-Georg Rosenboom, Institute for Chemical and Bioengineering, ETH Zürich, Zürich
Giuseppe Storti, Institute for Chemical and Bioengineering, ETH Zürich, Zürich
Massimo Morbidelli, Institute for Chemical and Bioengineering, ETH Zürich, Zürich

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In the quest towards more sustainable societies, polyethylene furanoate (PEF) represents a promising renewable resource-based bioplastic as replacement for fossil-based polyethylene terephthalate (PET) with even improved material properties. However, the synthesis of PEF through conventional polycondensation remains a challenge, since the typical reaction times of several days lead to degradation and undesired discoloration of the product. In this work we discuss the synthesis of cyclic oligomers of PEF (cyOEF) and their rapid ring-opening polymerization (ROP) to PEF, which opens a faster synthetic route for PEF to deliver sufficient molecular weight in a more controlled and living fashion.

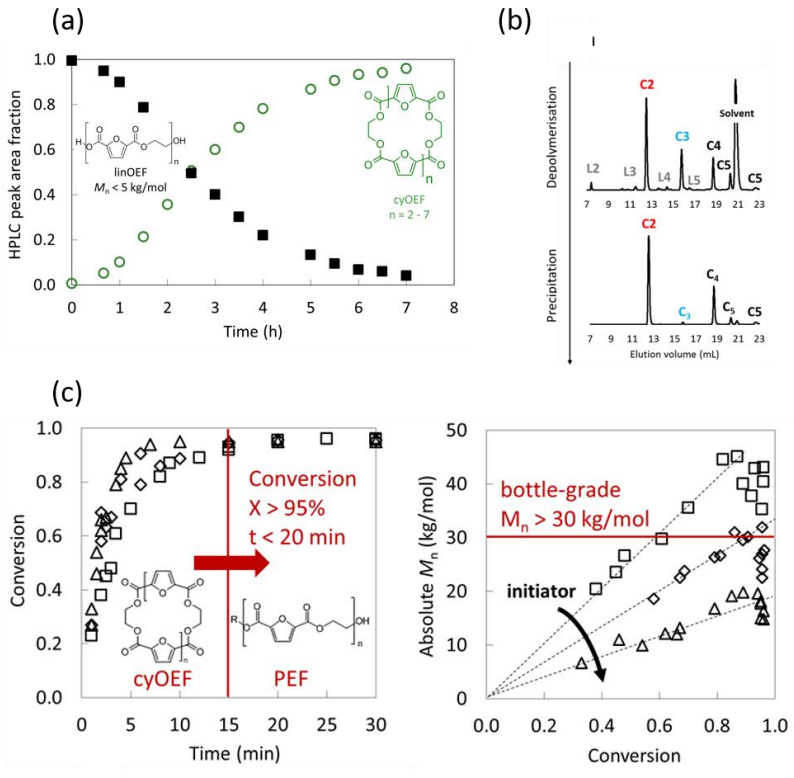

Figure 8 – (a) Evolution of the cyclic purity during cyclodepolymerization. (b) Cyclic oligomer distribution in HPLC during reaction (top) and after purification (bottom). (c) Conversion of cyOEF to high MW PEF.

Cyclic oligomers were derived from the bio-based monomers furandicarboxylic acid (FDCA) and ethylene glycol (EG), where depolymerization in high boiling solvents followed by selective precipitation yielded >95% cyOEF. The understanding of reaction equilibrium, kinetics and purification of such cyclisation reactions could facilitate the development of an efficient process for their production.

It was observed that the melting point of the obtained cyclic oligomer mixture lies around 370 °C, which is well above the degradation temperature of PEF (~329 °C). An otherwise impossible homogeneous melt polymerization at much milder conditions is achieved by plasticization: By initiation of ROP in the presence of a high boiling, yet removable, and inert liquid plasticizer, cyOEF could be converted to PEF within minutes, thereby avoiding degradation and discoloration. Tuning of the catalyst type and content then enables the synthesis of bottle-grade PEF (M_n > 30 kg/mol, conversions > 95%, color-free products, superior material properties compared with PET). Finally the understanding of the reaction and degradation kinetics of the ROP lead to the development of a kinetic model, which, together with the model for cyclisation, can aid the development of techno-economically efficient processes from FDCA to PEF.