

## UNDERSTANDING OF CYCLODEPOLYMERIZATION KINETICS FOR THE PRODUCTION OF CYCLIC POLYETHYLENE FURANOATE OLIGOMERS

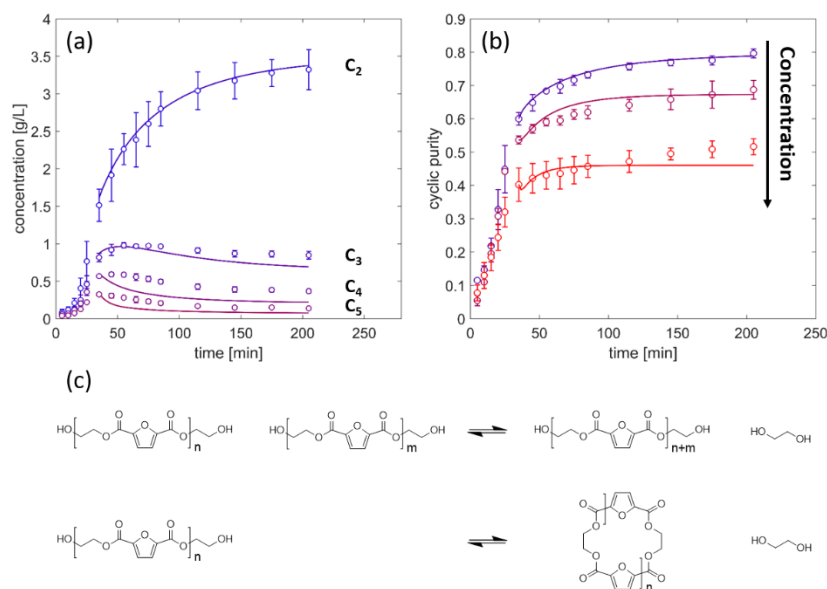
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In the last two decades intense research was focused on Polyethylene Furanoate (PEF) as a promising substitute for Polyethylene Terephthalate (PET). Comparisons of PEF and PET material properties revealed improved gas barrier properties, lower melting temperature, as well as higher tensile strength. Together with the reduced carbon foot-print, these properties make PEF an attractive alternative to PET.

Most PEF discussed in the literature is produced by polycondensation reactions (PC), a process, which is intrinsically slow due to diffusion limitations. In fact, it can take up to several days at high temperatures and high vacuum to produce high molecular weight PEF. The long exposure to high temperature is especially detrimental in the PEF case, since PEF is much more prone to thermal degradation than PET.



A possible alternative to PC is ring-opening-polymerization (ROP). The process is usually carried out in bulk and short reaction times are sufficient to reach high molecular weights, compared with PC. On the other hand, cyclic oligomers at sufficiently high purity are essential to achieve the same goal and the production of these cyclic oligomers is the major challenge in a ROP-based process for PEF manufacture.

In this work, cyclic oligomers of PEF were produced by cyclodepolymerization of preformed linear oligomers from the bio-based monomers furandicarboxylic acid and ethylene glycol. It was observed, that the cyclic yield was strongly influenced by the type of solvent used, where several aromatic and polar aprotic solvents were investigated. Focusing on two promising solvents, a full

**Figure 5** – (a) Evolution of individual cyclic oligomer concentrations during cyclodepolymerization. (b) Evolution of the cyclic purity over time. (c) Equilibrium reaction scheme.

characterization of the cyclization evolution could be carried out by HPLC analysis of the reacting liquid mixture (Fig. 1a). The reaction equilibrium, involving the competing second order chain elongation vs. first order backbiting for cycle formation (Fig. 1c), could be described by the classical model of Jacobson and Stockmayer, whose parameters could be evaluated at relevant operating conditions. The expected strong influence of reactant concentration on the equilibrium shift (Fig. 1b) could be well explained by the model. Such equilibrium model was then expanded to a kinetic model aimed to simulate the cyclisation kinetics. This model included propagation, end-biting, back-biting, and transesterification reactions. As shown in Fig. 1a,b, the resulting model captures well the evolution of individual cyclic and linear oligomers as well as the overall evolution of the cyclic yield. This model is expected to be a key tool in the development of a large scale, continuous process for the synthesis of cyclic oligomers as the most critical step towards the production of PEF by ROP.