

Lord of the Renewable Rings - How to master cyclic Oligomers for the rapid Synthesis of Polyethylene Furanoate (PEF)

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Polyethylene furanoate (PEF) represents a promising renewable resource-based bioplastic as replacement for fossil-based polyethylene terephthalate (PET) with improved material properties^{1,2}. However, the synthesis of PEF through conventional polycondensation remains challenging, since the diffusion-limited, and thus time-intensive reaction leads to degradation and undesired discolouration of the product.

As an alternative process, Ring-Opening Polymerization (ROP) can offer a much more controlled and rapid synthesis route to bottle-grade PEF from cyclic PEF oligomers within minutes, thereby avoiding degradation and discoloration. Cyclic oligomers, which can be produced at high purities (>95%) by distillation-assisted depolymerization of short PEF oligomers in a high boiling solvent, do not feature end groups that form products that have to be removed during polymerization, which is why the latter can be extremely fast³. However, the melting point of such mixture of cyclic oligomers lies around 370 °C, well above the degradation temperature of PEF (~329 °C). This challenge can be overcome, exploiting the self-plasticizing effect of the forming polymer itself (which melts around 220 °C) by initiation in the presence of a high boiling, yet removable, and inert liquid plasticiser. This concept yields polymer grades required for bottle applications ($M_n > 30 \text{ kg mol}^{-1}$), which are even superior to PET (6x higher gas diffusion barrier, 50% improved strength)⁴. These promising results, together with the application of kinetic computer models and alternative more bio-compatible catalysts, pave the way for the efficient production of sustainable polymers.

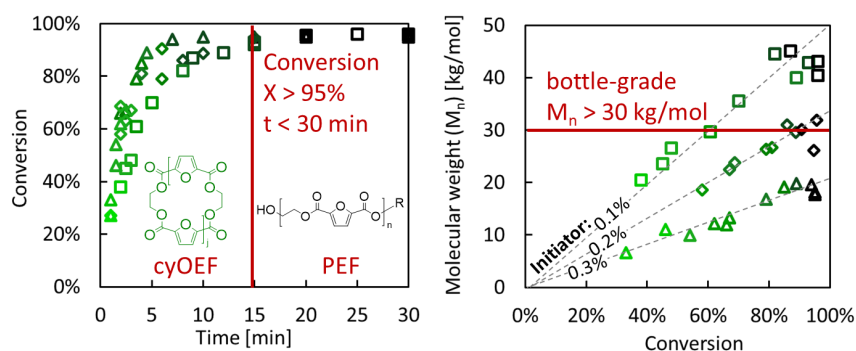


Figure 1. Conversion and number-average molecular weight of tetraglyme-plasticized Ring-Opening Polymerization (ROP) of cyclic oligomers to PEF using 0.1% (squares), 0.2% (diamonds) and 0.3% (triangles) of cyclic stannoxane initiator with 33% tetraglyme (per weight cyOEF) at 260°C.

[1] Zhu, Y., Romain, C. & Williams, C. K. *Nature* **2016**, 540, 354–364. [2] Eerhart, A. J. J. E., Faaij, A. P. C. & Patel, M. K. *Energy Environ. Sci.* **2012**, 5, 6407–6422 [3] Fleckenstein, P., Rosenboom, J.-G., Storti, G. & Morbidelli, M. *Macromol. React. Eng.* **2018**, 12, 1800018 (2018). [4] Rosenboom, J.-G., Hohl, D. K., Fleckenstein, P., Storti, G. & Morbidelli, M. *Nat. Commun.* **2018**, 9.