LORD OF THE RENEWABLE RINGS - HOW TO MASTER CYCLIC OLIGOMERS FOR THE SYNTHESIS OF POLYETHYLENE FURANOATE (PEF)

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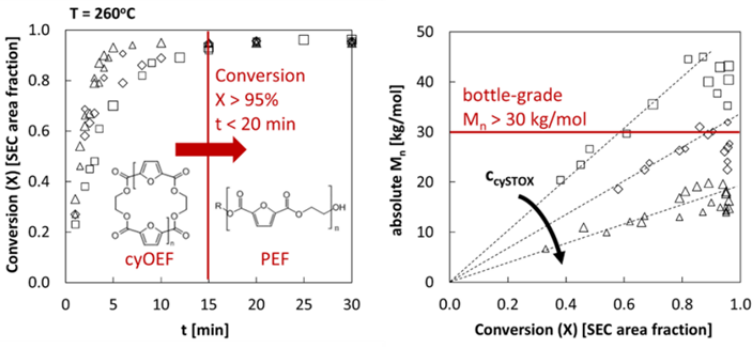
Towards a more sustainable future, Polyethylene furanoate (PEF) has gained attention as a promising candidate to replace the petrol-based polyethylene terephthalate (PET) with a renewable resource-based bioplastic [1]. However, conventional synthesis via diffusion-limited solid-state polycondensation remains a challenge, since PEF appears less stable than PET to the high required processing temperatures (~200°C) and the reaction times of several days, which results in degradation and undesired discolouration of the product [2]. This study reveals the successful rapid synthesis of bottle-grade PEF via condensation-free ring-opening polymerisation (ROP) from cyclic PEF oligomers within minutes, by which degradation and discolouration can be avoided [3,4].

We find that the mixture of cyclic oligomers of PEF is made of different ring-sizes, where the surprisingly dominant dimer is leading to melting points of the mixture up to 370°C, which is well above the degradation temperature of PEF (~300°C). The innovation of this work is to enable homogeneous melt polymerisation at much milder conditions by applying tetraethylene glycol dimethyl ether as inert plasticiser, which allows to overcome any diffusion limitations and thus facilitates homogeneous distribution of effective initiators inside the mixture of purified cycles. With optimised reaction conditions, sufficiently high molecular weights (M_n > 30-45 kg/mol, where bottle-grade is 30 kg/mol), conversions (X > 95%) and colour-free products were achieved within less than 30 min at 260-280°C using ROP. Similar to polycondensation-derived PEF, favourable thermal properties (T_g = 85°C, T_M = 215°C) and an improved gas diffusion barrier (5x higher for an M_n = 25 kg/mol solution cast polymer film) compared with PET complement the synthesis of PEF via ROP as an excellent candidate for the method of choice towards the “green bottle”.



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