Catalytic ring-opening polymerisation of renewable macrolactones to high molecular weight polyethylene-like polymers

Catalytic Ring-Opening Polymerisation of Renewable Macrolactones to High Molecular Weight Polyethylene-like Polymers.

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Catalytic ring-opening polymerisation (ROP) of cyclic esters is widely used for the synthesis of aliphatic polyesters. It is commonly agreed that the driving force behind the ROP of lactones is the release of ring-strain in the transition from the cyclic ester to the polyester chain or, in thermodynamic terms, by the negative change of enthalpy. Consequently, as the ring-strain decreases with increasing lactone size so does the reactivity in metal mediated ROP. It is therefore not surprising that only a few examples of metal-catalysed ROP of macrolactones like pentadecalactone can be found in the literature, which report only low molecular weights.[1,2] The best results were obtained using yttrium tris(isopropoxide) leading to high conversions and moderate molecular weights of up to M_n = 30 kg/mol.[3] Conversely, lipases like *Candida Antarctica* Lipase B show exceptionally high polymerisation rates for macrolactones.[4,5] The reactivity of lactones in this process is no longer determined by the ring-strain but the preference of the lipase for hydrophobic (fatty acid-like) substrates in the formation of the enzyme-activated monomer complex. It is thus commonly accepted that efficient polymerisation of macrolactones is only possible by enzymatic catalysis.

In this contribution we discuss the successful metal-catalysed ROP of various macrolactones (ring size 10-18) to unprecedentedly high molecular weight polyesters with polyethylene-like properties. For example, the bulk polymerisation of pentadecalactone at 90ºC afforded an *M_n of 120,000 g/mol within 10 minutes.* In solution, molecular weights close to *200,000 g/mol* were obtained. Moreover, the same catalyst system is also highly active in catalysing the ROP of small and medium size lactones. These results show that it is possible to polymerise macrolactones to high molecular weight polyethylene-like polymers using cheap and robust metal-based catalysts. Even the so-called medium-sized lactones (ring size: 9 – 12) can be polymerised with a reasonably good activity to high molecular weight products, which is truly exceptional. These results are unprecedented, they challenge the common theory of ring-tension driven ROP and they open doors to new (functional) polyolefin-like materials, which were not available before.

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