CATALYTIC RING-OPENING POLYMERISATION OF RENEWABLE MACROLACTONES TO HIGH MOLECULAR WEIGHT POLYETHYLENE-LIKE POLYMERS WITH TUNABLE FUNCTIONALITIES

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ABSTRACT

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.[1,2,3] 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. The drawback of enzymes is that they are expensive, allow little control over the polymerisation and cannot be used at high temperatures (melt polymerisation). It would therefore be highly desirable to be able to use catalysts to polymerise these renewable macrolactones to high molecular weight polymers with polyethylene-like properties.

In this contribution we discuss the successful metal-catalysed ROP of various macrolactones (ring size 11-17) 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. These results are unprecedented in the literature, they challenge the common theory of ring-tension driven metal-catalysed ROP. Since the catalyst is also capable of ring-opening small lactones or for example copolymerise epoxides + anhydrides and/or CO_2, the system opens doors to new, polyethylene-like materials with functionalities such as degradability, not available before.

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