Across the Board: Michael North

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**Abstract:** Abstract will be provided by the Editorial Office.

Ring-Opening Polymerisation

Ring-opening polymerisation (ROP) of strained lactones (Scheme 1) is a well-established methodology for the synthesis of polyesters.[1] The methodology has been extensively studied for the polymerisation of 4-, 6- and 7-membered ring lactones including: malonic acid derived -lactones **1**,[2] lactides **2**,[3] and -caprolactone **3**.[3,4] In contrast, 5-membered ring containing -lactones were found not to undergo ROP except under extremely harsh conditions. This was attributed to the low ring strain of -lactones (calculated to be just 33.6 kJ mol-1 for -butyrolactone **4**[5])which removes the driving force for ROP of these substrates. Thus, for example, lactone **4** underwent ROP only at 160 oC and 2 GPa pressure, whilst -angelica lactone **5**, which is more strained due to the two additional sp2 hybridised carbon atoms in the 5-membered ring, underwent ROP at 130 oC at atmospheric pressure.[6]



**Scheme 1.** Ring-opening polymerisation of lactones.

Mechanistically, ROP requires a hard nucleophile to react at the carbonyl of the lactone, liberating an alkoxide / alcohol which can then act as the nucleophile for the next ring-opening (Scheme 2). In the absence of a deliberately added nucleophile, adventitious water can act as the initiator, and, for example, -valerolactone **6** is known to polymerise on storage at room temperature.[5] However, many of the most effective initiators of ROP combine a hard nucleophile with a Lewis acid,[7] the latter acting to activate the carbonyl towards attack by the nucleophile. Thus, many of the most widely studied initiators are complexes of metal alkoxides.[8] ROP of -lactones can be an exception as cleavage of the alkyl-carbon to oxygen bond of the lactone by soft nucleophiles is also a facile process for these monomers.[9]



**Scheme 2.** General mechanism for ring-opening polymerisation of lactones.

The mechanism shown in Scheme 2 is a step-growth polymerisation in which each nucleophile initiates the growth of a single polymer chain and which under appropriate conditions can form a living polymerisation system. Compared to a conventional condensation polymerisation between a diacid, or a diester, and a diol (or of a hydroxyacid), this gives potential advantages including: control of molecular weight and molecular weight distribution, the ability to prepare block copolymers and the ability to control the polymer end groups.

The difficulty in polymerising -butyrolactone is unfortunate as it is readily prepared from succinic acid, one of the most important biomass derived chemicals.[10] Therefore, two papers from the Chen group constitute a major breakthrough in this area. In the first paper,[11] the use of lanthanide based initiators **7–11** (Scheme 3) for the ROP of lactone **4** was investigated. Initial studies carried out with initiator **7** at ambient temperature and pressure in various organic solvents resulted, as expected, in no polymer formation. However, the authors then carried out reactions at -40 oC in toluene and found that under these conditions, the polymer precipitates from the polymerisation mixture as it is formed. This provides an additional energetic driving force for the reaction and allowed the polyester to be obtained in 3% yield with Mn 12,100 and a polydispersity index (PDI) of 1.99. Initiators **8** and **9** gave similar results. The polymer formed under these conditions was found to be a mixture of linear and cyclic polymer, the latter resulting from facile backbiting which results in chain termination (Scheme 3).



**Scheme 3.** Use of initiators **7–11** to form linear and cyclic -butyrolactone

Addition of alcohols to the reaction mixture increased the polymer yield (to 67% with Ph2CHOH) and resulted in the formation of predominantly linear polymer. This was attributed to the in situ formation of metal alkoxides which are better initiators of ROP than metal amides and to a change in the carbonyl end group of the polymer to an ester which is less prone to backbiting cyclisation. On this basis, preformed yttrium alkoxide complexes **10** and **11** were investigated as ROP initiators and complex **11** was found to give up to a 90% yield of polyester in a reaction time of six hours.

In a subsequent paper,[12] the authors showed that the same methodology based on polymer precipitation at -40 oC could be used to allow the ROP of lactone **4** to occur under metal-free conditions if organic superbase **12** was used as the initiator either with or without an alcohol additive. In the absence of alcohol, 1 mol% of initiator **12** gave a 30% conversion of monomer **** to polyester with Mn 26,400 and PDI of 1.8 after 12 hours. When benzyl alcohol was added, the rate of reaction increased significantly, giving 70% conversion in 4 hours to a polymer with similar molecular weight and PDI.



**Scheme 4.** Polymerisation of -butyrolactone initiated by superbase **12**

In the presence of an alcohol, initiator **12** abstracts the alcohol proton, generating a more nucleophilic alcohol based ROP initiator (Scheme 4). However, in the absence of alcohol, superbase **12** forms the enolate of -butyrolactone which then acts as the nucleophile to start the ROP.

From a sustainable chemistry perspective, what the two papers from the Chen group illustrate is the importance of considering all the reaction parameters. Just developing a more highly active polymerisation initiator is not enough; the polymerisation of -butyrolactone **4** is thermodynamically, not kinetically, limited. However, by carrying out the reactions at -40 oC in an appropriate solvent the thermodynamic limitation could be overcome, though at such a low temperature highly active polymerisation initiators are needed. There remain a number of challenges for future work: the use of such low temperatures is very energy intensive so it would be desirable to find a (preferably non-petrochemically derived) solvent where the polymer precipitates at close to ambient temperature. In addition, the metal based initiators are based on endangered lanthanides and the superbase used in the metal-free system is expensive. Thus it would be desirable to develop ROP initiators with sufficient activity based on metals such as iron, aluminium or titanium. The fact that a range of initiators have already been shown to be compatible with the polymer precipitation methodology suggests that these issues will be solvable in future work.

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**Keywords:** ring-opening-polymerisation • lactone • polyester • lanthanide • superbase

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