RECYCLABLE POLYMERS WITH LINEAR AND CYCLIC STRUCTURES SYNTHESIZED BY RING-OPENING POLYMERIZATION OF γ-BUTYROLACTONE

Reported by Junrou Huang April 20, 2021

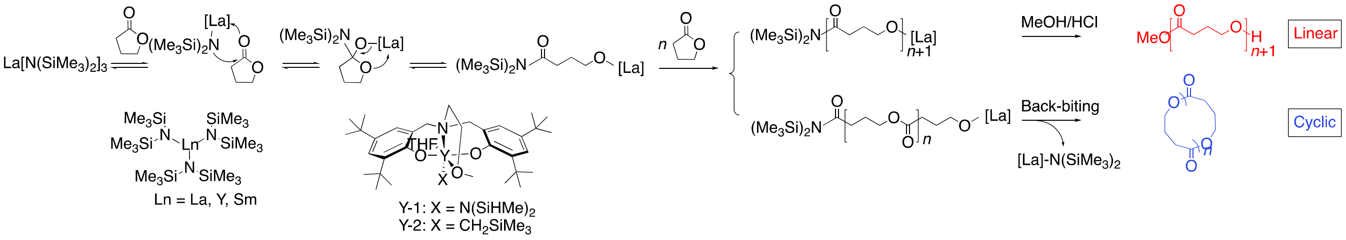
INTRODUCTION

Ring opening polymerization of lactones or lactides is a direct way to make bio-degradable and biocompatible polyesters. Among the polyesters, chemical synthesis methods for poly(4-hydroxybutyrate), or P4HB, are mostly absent, which limits its application. One possible and straightforward method of synthesizing P4HB is the ring opening polymerization of γ-butyrolactone. However, γ-butyrolactone is commonly considered non-polymerizable by ring opening polymerization owing to low strain of the ring.[1] Although some examples of ring opening polymerization of γ-butyrolactone are known, these reaction conditions are harsh (high temperature, ultrahigh pressure) and only produce oligomers with low molecular weights. Recently, the ring opening polymerization of γ-butyrolactone has been addressed using catalysts. Notably, the ring opening polymerization can selectively yield linear or cyclic polymers, which diversifies the structures of polymers and potential applications. Lastly, because of the low ceiling temperature, recycling of polymer to monomer could be achieved by shifting the equilibrium from polymerization to depolymerization.[2]

METAL CATALYZED RING-OPENING POLYMERIZATION OF γ-BUTYROLACTONE

In 2016, Chen and co-workers reported the first ring opening polymerization of γ-butyrolactone using catalysts.[3] In this work, the authors successfully identified the initiation and propagation mechanism of polymerization by proposing a coordination-insertion step. On the basis of their insights, they further investigated the termination mechanism and illustrated the importance of alcoholysis versus back-biting in this step (Scheme 1). The selective formation of linear and cyclic polymer could be tuned by adjusting the bulk of the alcohol initiator and the ratio of monomer/metal/alcohol initiators. Finally, the authors compared the thermal properties and recyclability of cyclic and linear polymer.

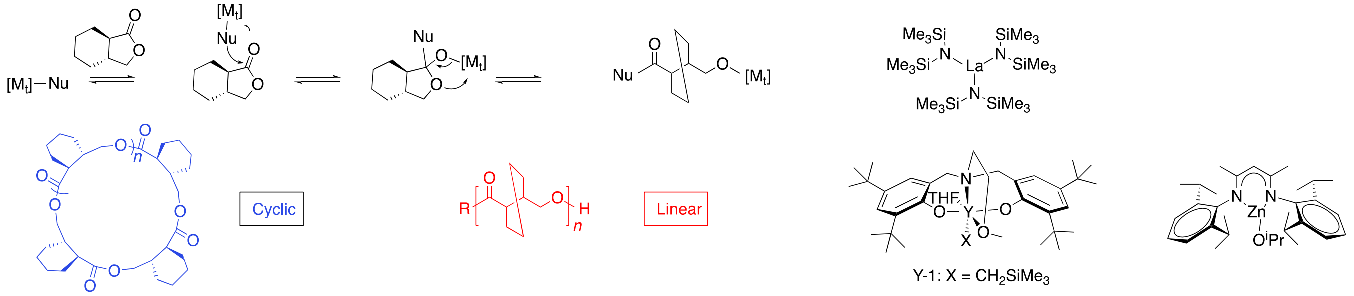
Scheme 1. Mechanism for Metal Catalyzed Polymerization of γ-Butyrolactone.



METAL CATALYZED RING-OPENING POLYMERIZATION OF *TRANS*-CYCLOHEXYL-FUSED γ-BUTYROLACTONE

Inspired by the promising synthetic approaches and recyclability of poly(γ-butyrolactone), Chen and coworkers further investigated the polymerization and depolymerization of its derivatives, trans-cyclohexyl-fused γ-butyrolactone. Compared with γ-butyrolactone, the 3,4-*trans*-cyclohexyl-fused γ-butyrolactone exhibits a higher thermodynamic preference for polymerization owing to the enhanced strain from substituents at the α, β position (Scheme 2).[4] Notably, the cis isomer cannot polymerize, stressing the importance of the twisted conformation in facilitating polymerization.

Scheme 2. Mechanism for Initiation in Polymerization of 3,4-*trans*-Cyclohexyl-fused γ-Butyrolactone



These authors also investigated the polymerization of 4,5-*trans*-cyclohexyl-fused γ-butyrolactone, which has substituents at the β,γ-position,[5] and proposed a living coordination polymerization mechanism. The two cyclohexyl-fused γ-butyrolactone derivatives have similar recyclability, but the molecular interaction between enantiomeric isotactic polymers is different.

METAL-FREE RING-OPENING POLYMERIZATION OF γ-BUTYROLACTONE

Chen and co-worker also explored the possibility of using small molecule as catalysts for the polymerization of γ-butyrolactone.[6] They discovered that the superbase P4-phosphazene base could readily deprotonate the γ-butyrolactone and generate highly reactive enolate anions, and therefore initiate the polymerization.

REFERENCES

(1) Odian, G . Principles of Polymerization 3rd ed.; Wiley-Interscience, 1991. (2) Coates, G. W.; Getzler, Y. D. Y. L. *Nat. Rev. Mater.* **2020**, 5 (7), 501–516. (3) Hong, M.; Chen, E. Y. X. *Nat. Chem.* **2016**, *8* (1), 42–49. (4) Zhu, J. B.; Watson, E. M.; Tang, J.; Chen, E. Y. X. *Science.* **2018**, *360* (6387), 398–403. (5) Zhu, J. B.; Chen, E. Y. X. *Angew. Chem. Int. Ed.* **2018**, *57* (38), 12558–12562. (6) Hong, M.; Chen, E. Y. X. *Angew. Chem., Int. Ed.* **2016**, *55* (13), 4188–4193.