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Mechanistic Insights into the Fe(II)-Catalyzed ROP of Challenging Aliphatic Lactones: A DFT Study

Mechanistic Insights into the Fe(II)-Catalyzed ROP of Challenging Aliphatic Lactones: A DFT Study

The growing concern over plastic pollution and microplastic contamination has intensified efforts to identify sustainable alternatives to fossil-derived polymers. In this context, aliphatic polyesters from cyclic esters (lactones) have emerged as promising candidates, particularly when designed for biodegradability or chemical recycling to monomer (CRM) [1]. While efficient polymerization strategies exist for strained monomers like lactide and ε-caprolactone, δ-substituted δ-lactones remain poorly explored due to their low ring strain and substitution at the δ-position, which limit reactivity. Nevertheless, these monomers are naturally occurring, commercially available, and widely used in the flavor and fragrance industries, making them attractive for sustainable materials research. Recently, new highly active three-coordinate pyridylamido Fe(II) complexes (Fig1a) have been reported for the ring-opening polymerization (ROP) of lactide and ε-caprolactone[2,3]. In this study, we extend their application to the ROP of more challenging monomers, such as δ-hexalactone, δ-nonalactone, δ-undecalactone, and ε-decalactone (in Fig1b the investigated monomers). A comprehensive Density Functional Theory (DFT) investigation was performed to explore the polymerization mechanisms promoted by the iron catalyst. The study evaluates various mechanistic pathways (Fig1c), including the role of the alcohol as an initiator and the potential formation of dimeric catalytic species. Differences in monomer reactivity are rationalized based on the side-chain length and steric effects. These insights contribute to understanding structure–reactivity relationships in iron-based ROP catalysis and support the design of next-generation recyclable polyesters.

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