

# DFT INSIGHTS ON HOMOPOLYMERIZATION OF CYCLIC ESTERS PROMOTED BY Fe(II) PYRIDYLAMIDO CATALYSTS

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## Introduction

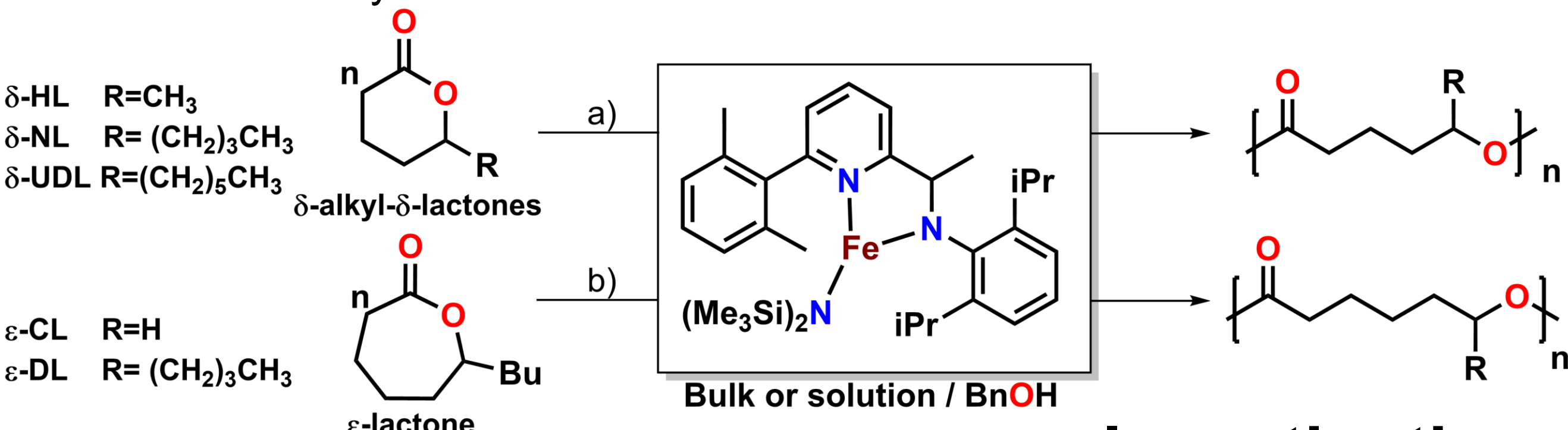
Can we design high-performance, chemically recyclable polymers from natural lactones?

### • Context & Motivation

The **growing concern over plastic waste and microplastic pollution** has driven the search for sustainable alternatives to fossil-derived polymers. A key challenge is to designing materials that combine high performance with true degradability or chemical recyclability<sup>1</sup>, aligning with circular economy goals.

### • Research Focus

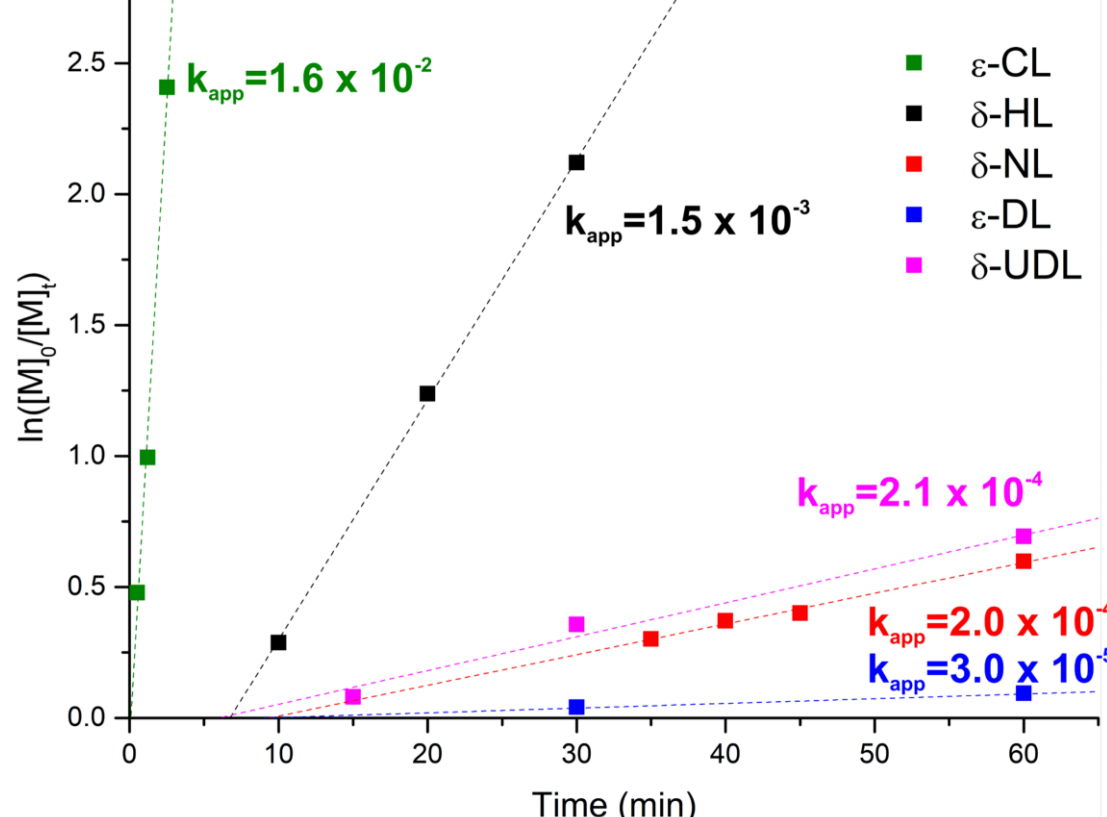
**Natural lactones** are promising monomers for the development of **biodegradable and chemically recyclable polymers**, being readily available and used in the fragrance and flavor industries. Their polymerization, however, remains challenging due to their low ring strain and limited reactivity<sup>2</sup>.



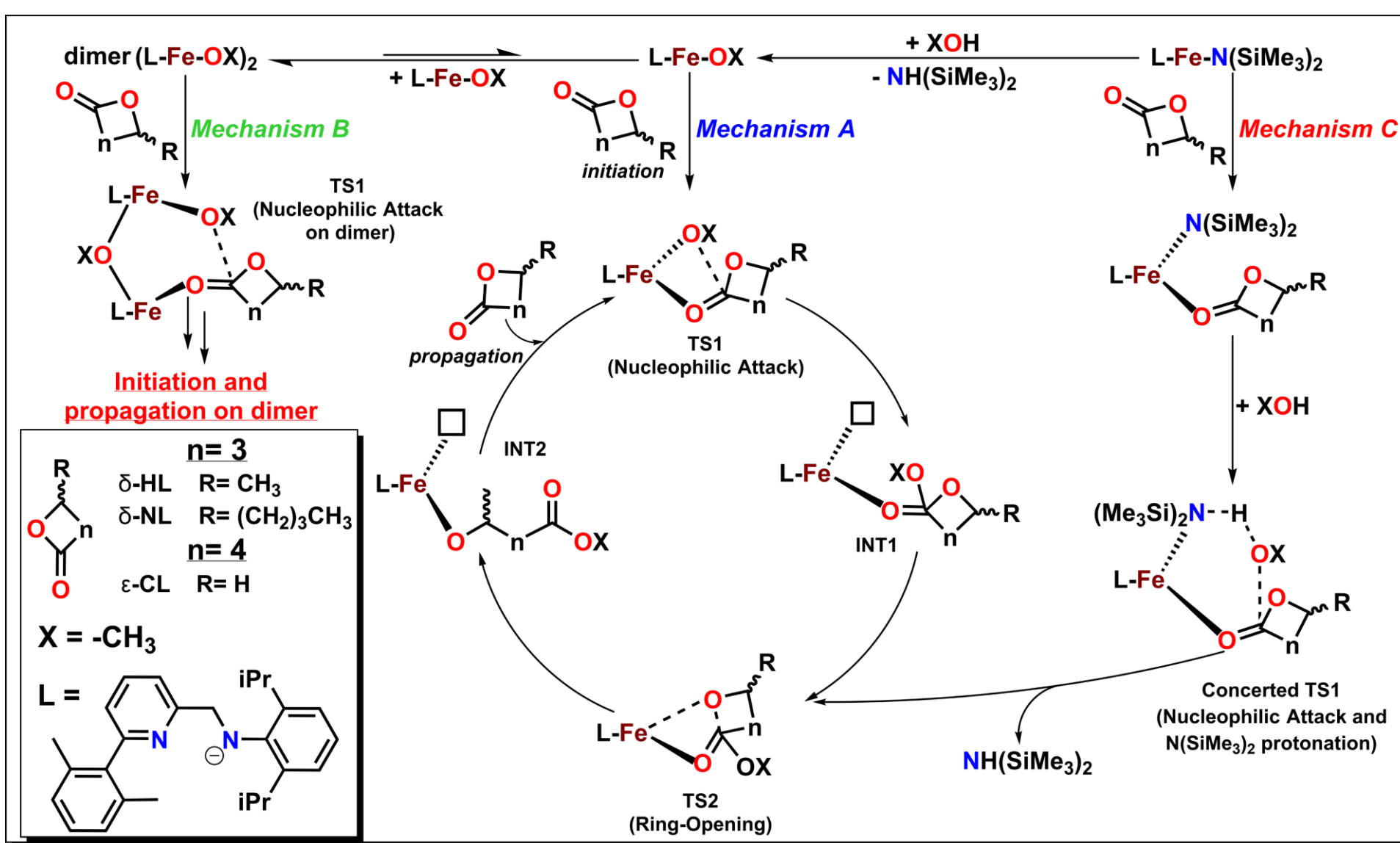
### • Our Approach

We investigate three-coordinate pyridylamido Fe(II) complex<sup>3</sup> as catalysts for the ring-opening polymerization of low-reactivity lactones. DFT calculations and experimental data suggest alternative mechanisms<sup>4</sup> involving initiator effects and catalyst aggregation to explain reactivity trends across different monomers with varying side-chain lengths.

## Investigation

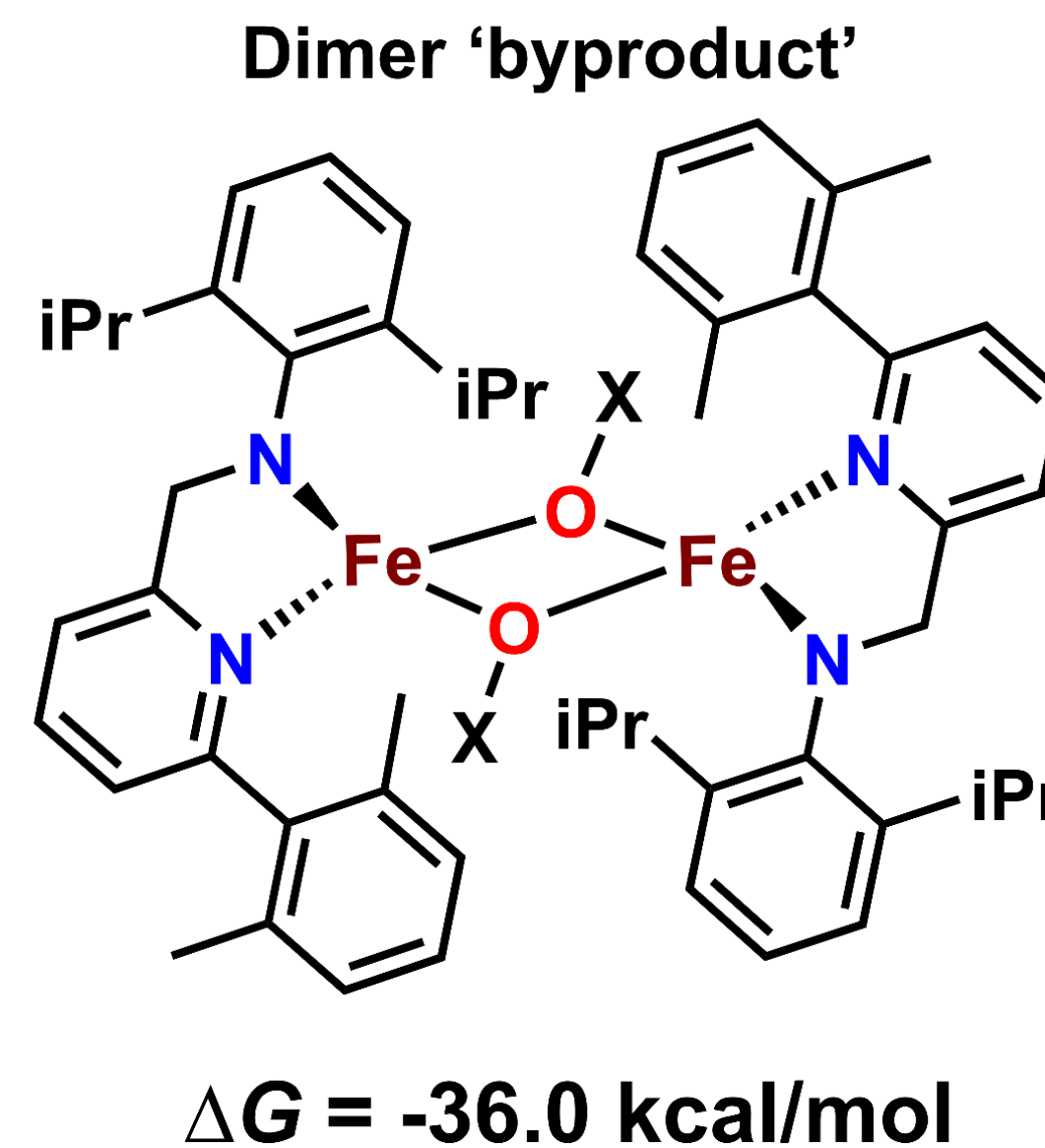
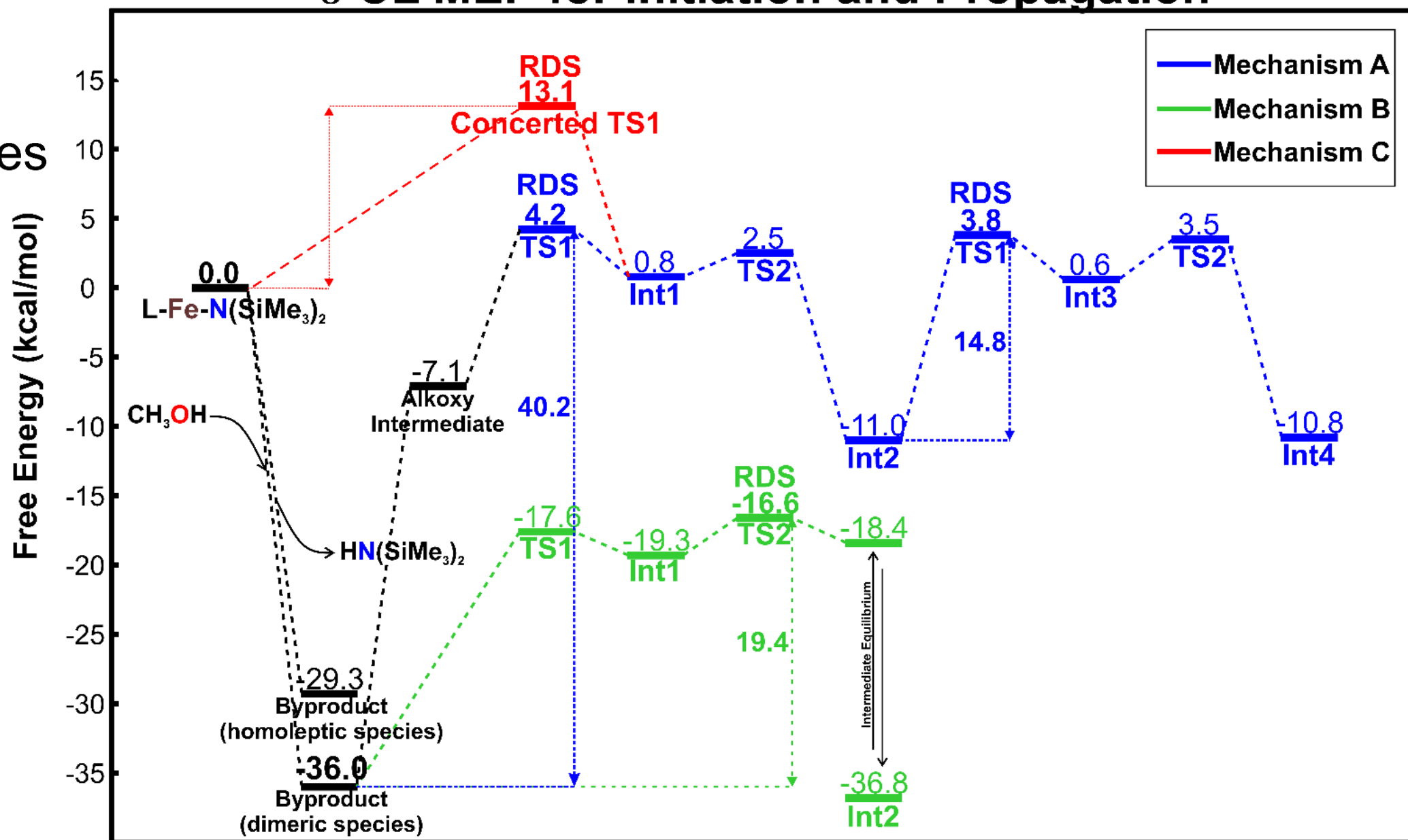


- Pseudo first-order kinetics observed for all monomer
- Induction time for all monomers (ε-CL is the only exception)
- Formation of a light blue precipitate during early stages



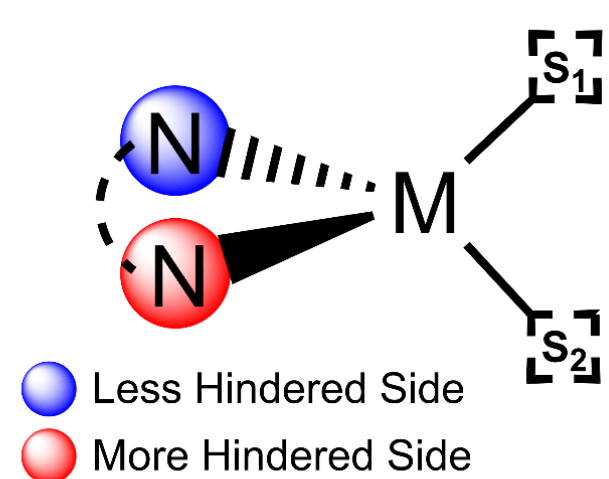
## DFT Approach

$\epsilon$ -CL MEP for Initiation and Propagation



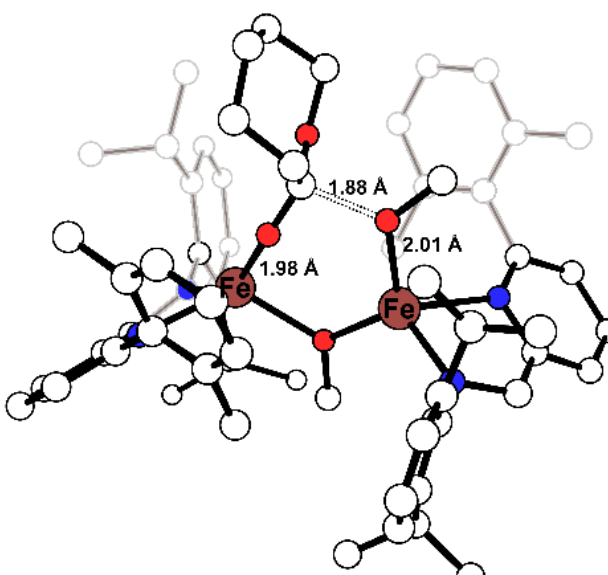
### Fe(II) Catalyst - Intricacy

- Two Diastereotopic Coordination Sites



- Fe(II)  $d^6$  electronic configuration (low-spin and high-spin states)

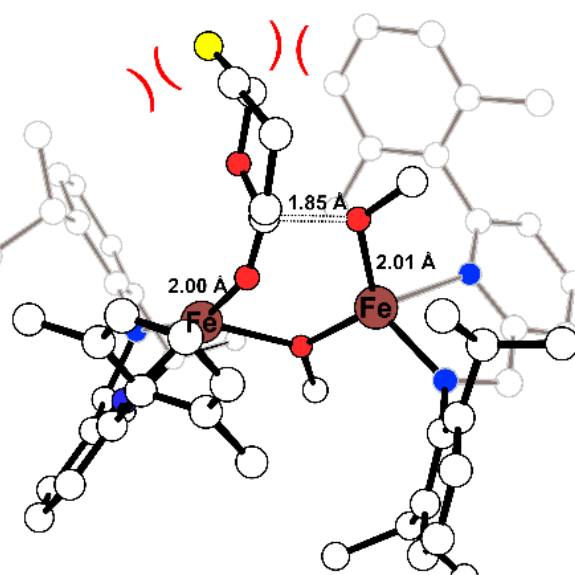
### TS1 on Dimer $\epsilon$ -Caprolactone



$\Delta G^\ddagger = 18.4$  kcal/mol w.r.t. to dimer

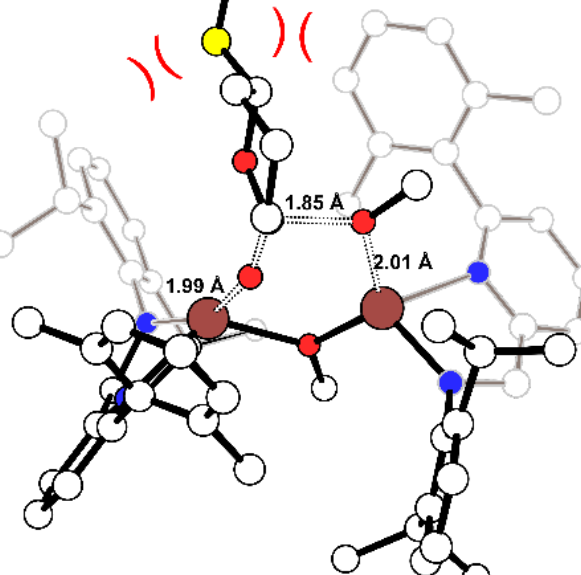
### Dimeric Iniziation

### TS1 on Dimer $\delta$ -S-Hexalactone



$\Delta G^\ddagger = 22.6$  kcal/mol w.r.t. to dimer

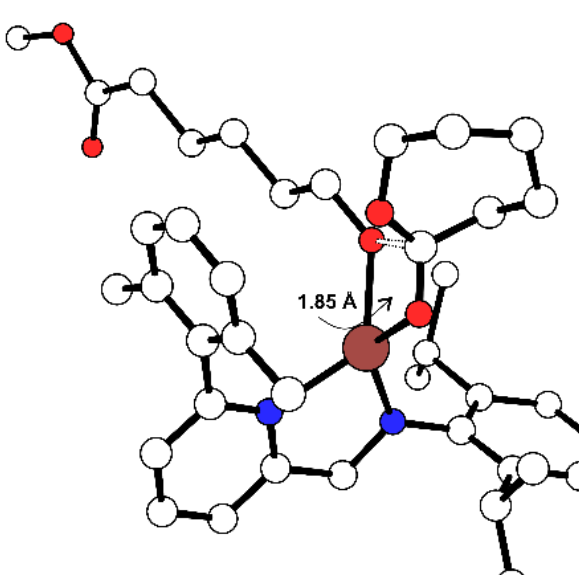
### TS1 on Dimer $\delta$ -S-Nonalactone



$\Delta G^\ddagger = 21.7$  kcal/mol w.r.t. to dimer

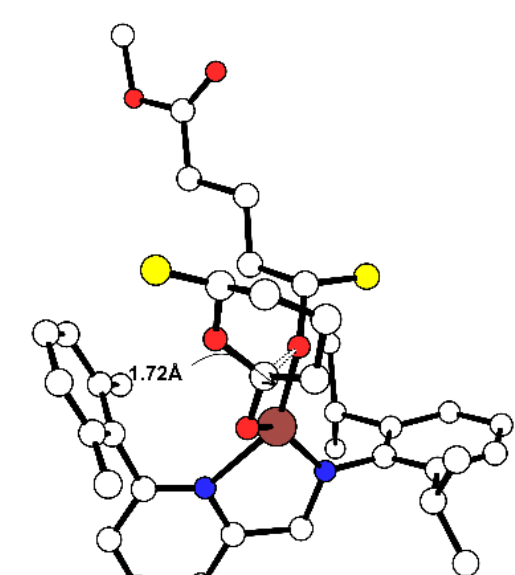
### Propagation on Mononuclear Species

### TS1' $\epsilon$ -Caprolactone



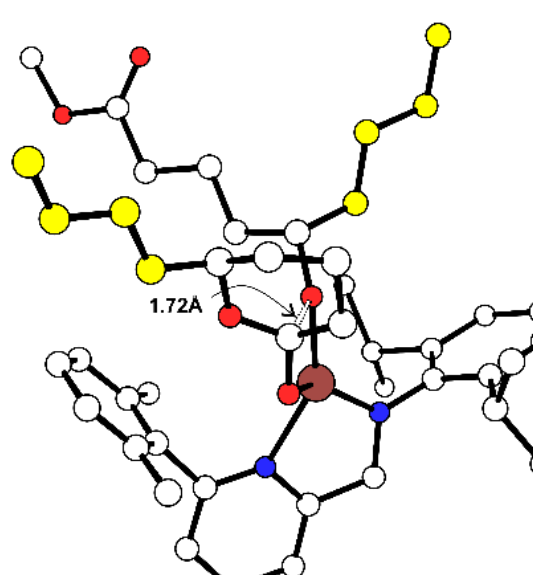
$\Delta G^\ddagger = 14.8$  kcal/mol w.r.t. to Int2

### TS1' $\delta$ -S-Hexalactone



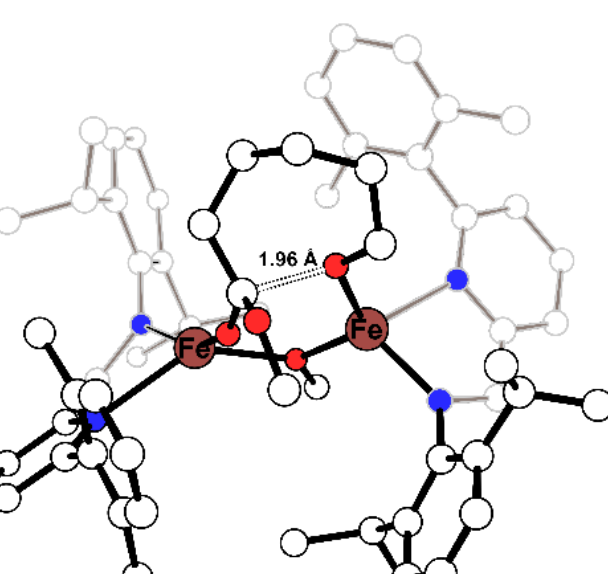
$\Delta G^\ddagger = 15.0$  kcal/mol w.r.t. to Int2

### TS1' $\delta$ -S-Nonalactone



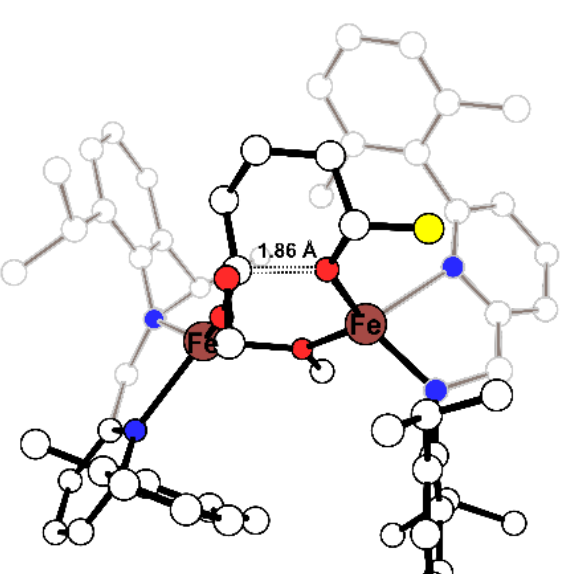
$\Delta G^\ddagger = 16.7$  kcal/mol w.r.t. to Int2

### TS2 on Dimer $\epsilon$ -Caprolactone



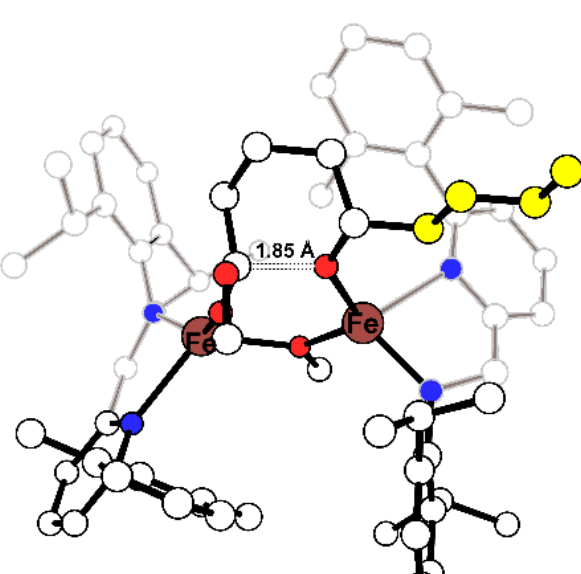
$\Delta G^\ddagger = 19.4$  kcal/mol w.r.t. to dimer

### TS2 on Dimer $\delta$ -S-Hexalactone



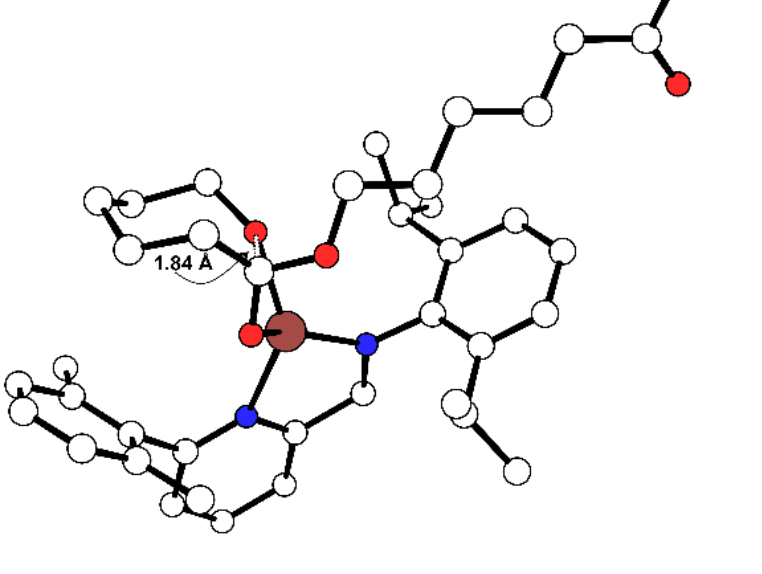
$\Delta G^\ddagger = 20.6$  kcal/mol w.r.t. to dimer

### TS2 on Dimer $\delta$ -S-Nonalactone



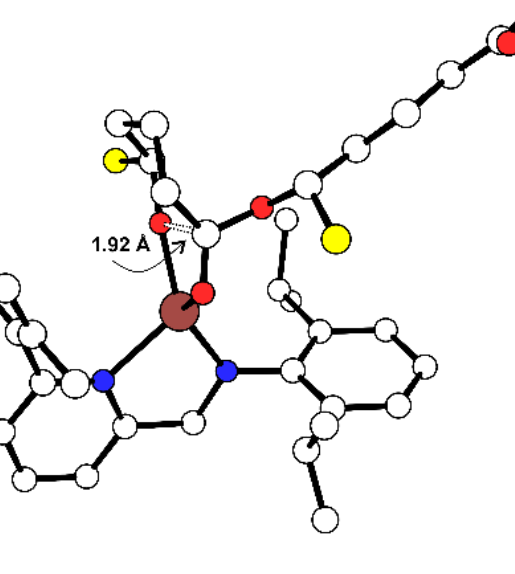
$\Delta G^\ddagger = 19.5$  kcal/mol w.r.t. to dimer

### TS2' $\epsilon$ -Caprolactone



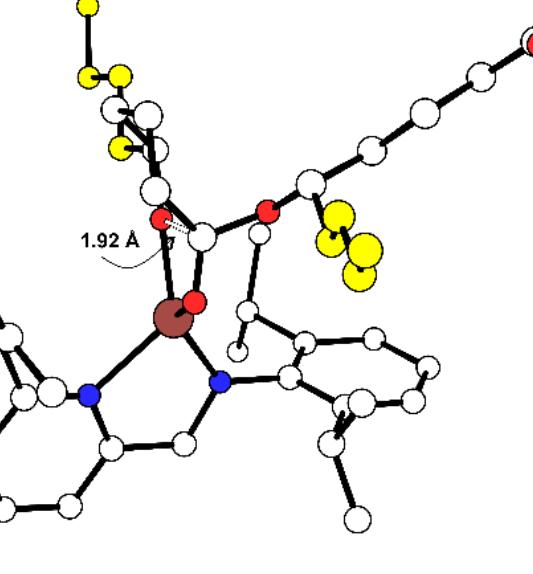
$\Delta G^\ddagger = 14.5$  kcal/mol w.r.t. to Int2

### TS2' $\delta$ -S-Hexalactone



$\Delta G^\ddagger = 16.2$  kcal/mol w.r.t. to Int2

### TS2' $\delta$ -S-Nonalactone



$\Delta G^\ddagger = 18.6$  kcal/mol w.r.t. to Int2

1) Dimeric species could initiate polymerization

2) Induction period could be due to the difficulty for substituted monomers with bulky side groups

1) Intramolecular interactions involving the pendant group of the monomer and its backbone

2) Intramolecular interactions involving the pendant group of the growing chain and its backbone

## Conclusion

- ✓ The potential use of novel monomers for the synthesis of innovative materials has been explored.
- ✓ A recently synthesized catalyst enabled the successful polymerization of monomers that are typically challenging to polymerize.

- ✓ DFT calculations allowed for the rationalization of reactivity trends based on the structural features of monomers.
- ✓ Computational analysis provided further mechanistic insights, revealing alternative reaction pathways beyond those classically accepted.

## References

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- Schneiderman, D. K. & Hillmyer, M. A. Aliphatic Polyester Block Polymer Design. *Macromolecules* **49**, 24192428 (2016).
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