Synthesis and Characterization of a Mono-Isopropyl-Substituted Tetramethylene-Tethered *Bis*[*N*-(*N*'-Butylimidazolium) as a Pre-Catalyst for Application in Ring-Opening Polymerization of *ε*-Caprolactone

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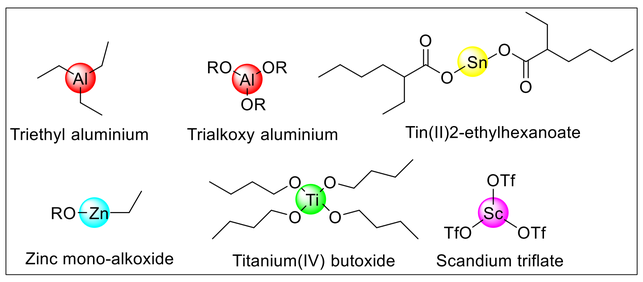
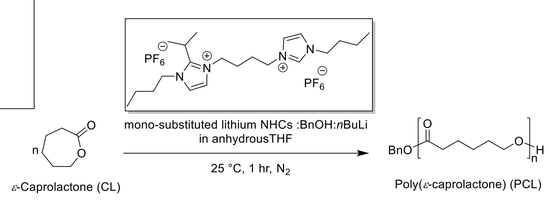
Abstract

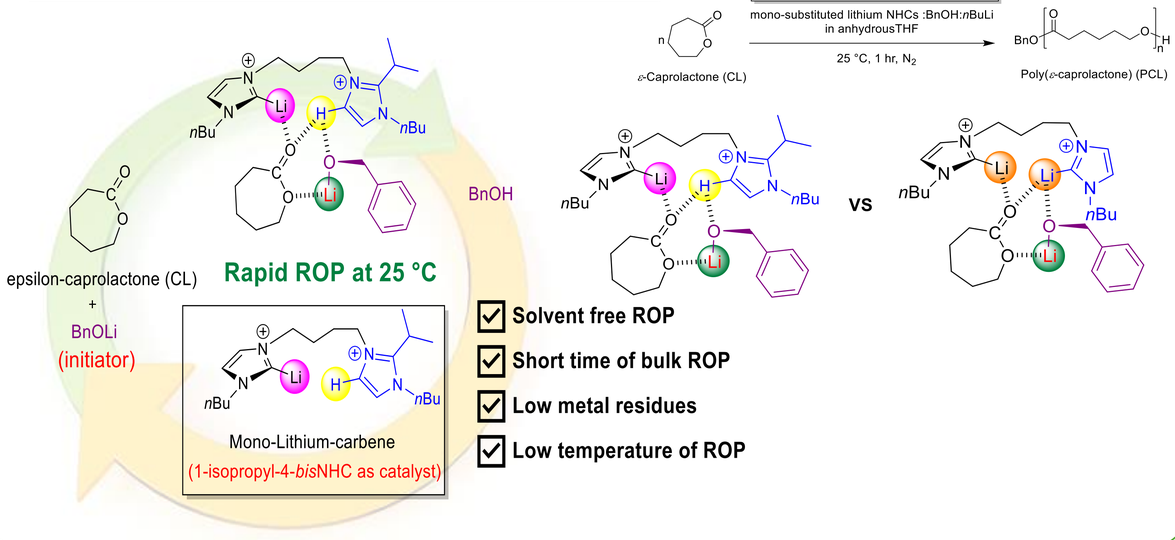
Ring-opening polymerization (ROP) of *ε*-caprolactone is a fundamental approach for synthesizing biodegradable polyesters. However, the widespread use of heavy metal catalysts in industrial applications raises concerns regarding potential metal contamination in the final product. To address this issue, this study explores the catalytic potential of [1,4-*bis*[Bim][PF_6]] as an alternative organocatalyst. The catalytic efficiency of mono-substituted lithium *N*-heterocyclic carbene (NHC) complexes was evaluated at varying catalyst-to-monomer ratios, comparing substituted and non-substituted catalysts. Polymerization kinetics were assessed by monitoring temperature variations, which increased progressively throughout the reaction and analyzing the correlation between polymerization rate and heat emission. Additionally, gel permeation chromatography (GPC) was employed to determine molecular weight distributions. The findings indicate that the iso-propyl monosubstituted lithium NHC catalyst exhibits a lower polymerization rate than its non-substituted counterpart. However, the resulting polymer is expected to achieve a higher molecular weight.

Introduction



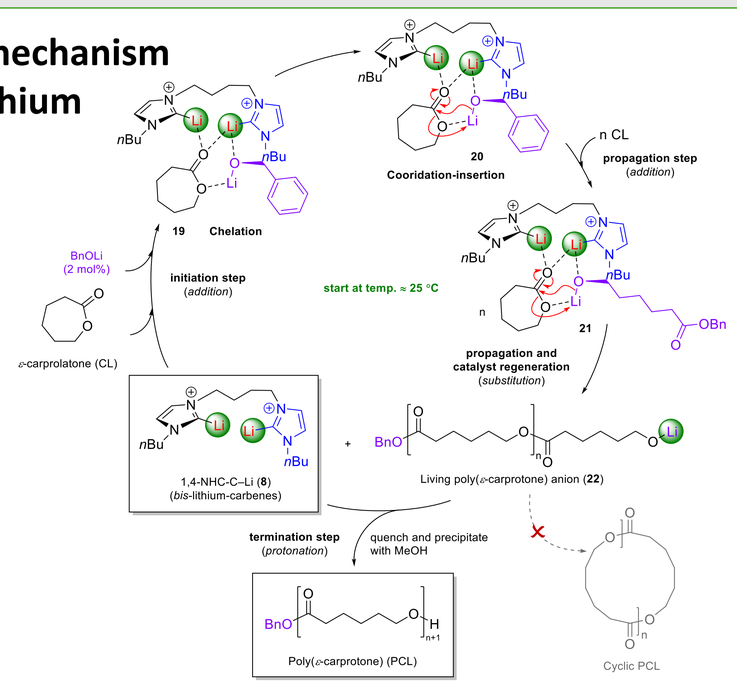
- ☒ High temperature of ROP
- ☒ Heavy metal residues
- ☒ Long time of ROP 2-24 hr

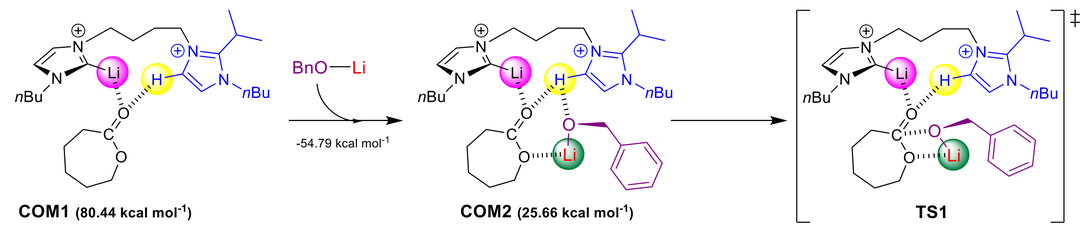




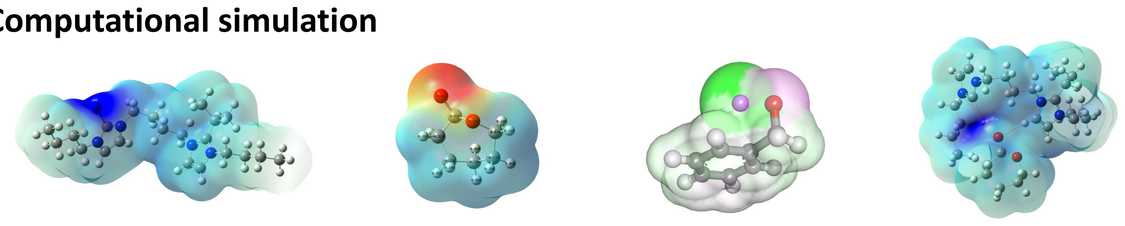
- ☑ Solvent free ROP
- ☑ Short time of bulk ROP
- ☑ Low metal residues
- ☑ Low temperature of ROP

Propose ROP mechanism using Mono-lithium NHC complex as catalysts



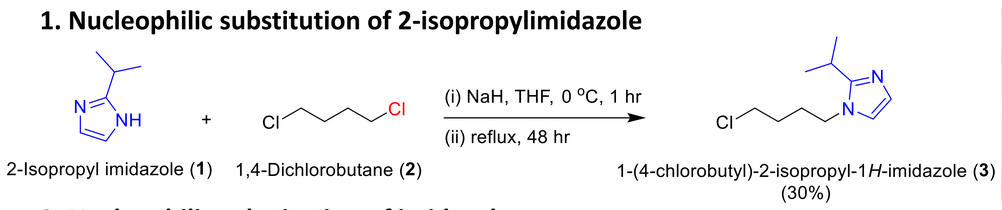


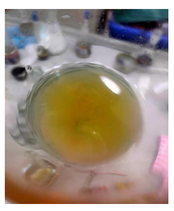
Computational simulation



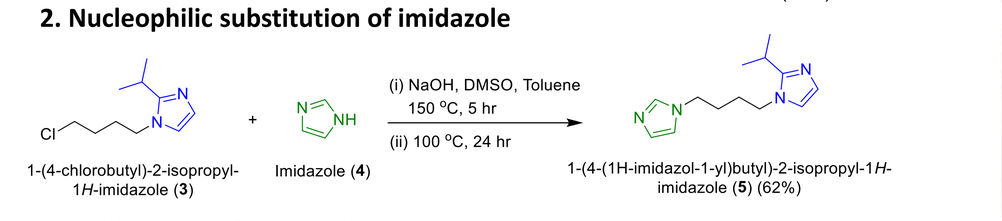
Catalysts Synthesis Procedure

1. Nucleophilic substitution of 2-isopropylimidazole

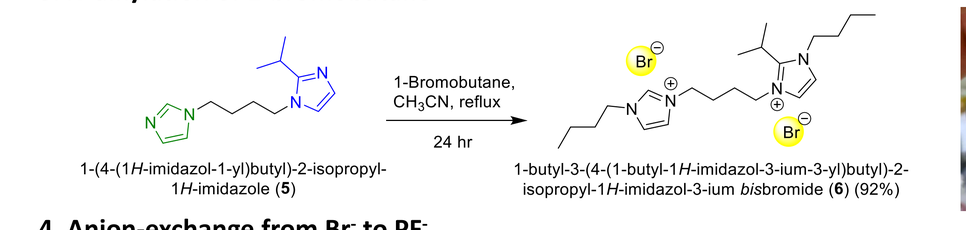




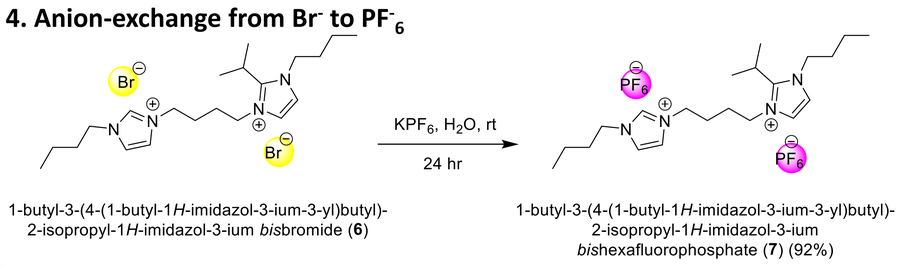
2. Nucleophilic substitution of imidazole

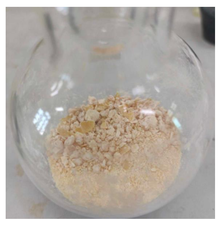


3. *N*-alkylation of 1-bromobutane

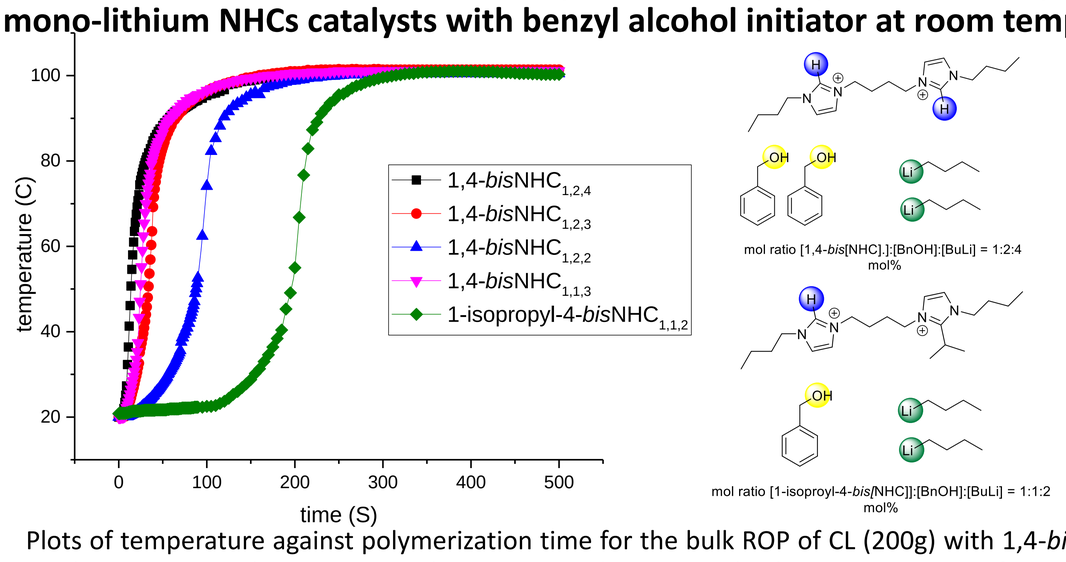


4. Anion-exchange from Br^- to PF^-_6



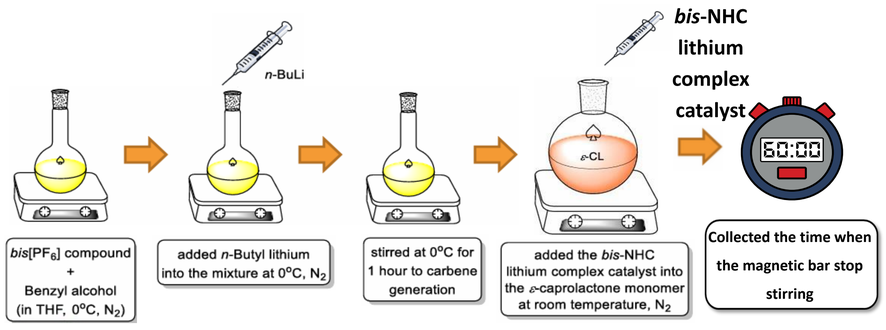


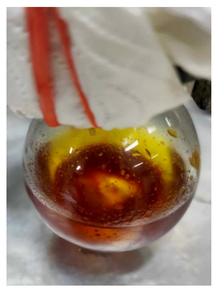
Kinetic studies of the ROP of *ε*-caprolactone catalyzed by the synthesized mono-lithium NHCs catalysts with benzyl alcohol initiator at room temperature



Plots of temperature against polymerization time for the bulk ROP of CL (200g) with 1,4-*bis*$NHC_{1,2,4}$, 1,4-*bis*$NHC_{1,2,3}$, 1,4-*bis*$NHC_{1,2,2}$, 1,4-*bis*$NHC_{1,1,3}$, and 1-isopropyl-4-*bis*$NHC_{1,1,2}$ at 20 °C for 500 s.

Generation of Mono-lithium NHC complex as catalysts for ROP





Conclusion

The experimental results indicate that 1-isopropyl-4-*bis*NHC, at a catalyst:BnOH:BuLi ratio of 1:1:2, exhibits a lower reaction rate than 1,4-*bis*LiNHC across all studied ratios. Despite its slower reaction rate, it is expected to produce the highest molecular weight polymer due to the extended polymerization time. Additionally, the study revealed that the reaction mechanism of 1-isopropyl-4-*bis*NHC differs entirely from that of unsubstituted 1,4-*bis*LiNHC. This distinction may aid in the future development of more efficient catalysts.

Acknowledgement

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References

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[2] D.E. Kamber, W. Jeong, R.M. Waymouth, J.L. Hedrick, *Chemical Reviews*, **2009**, *109(11)*, 5437–5474.

[3].A. McGonagle, M.G. Coleman, C.N. Bowman Free-Radical Polymerization and Ring-Expansion of a Cubane Acrylate: a Unique Low-Shrink Polymer. Macromolecules 2006, 39, 244–249.