Alma Mater Studiorum – University of Bologna

SCHOOL OF SCIENCE
Department of Industrial Chemistry “Toso Montanari”

Second cycle degree in

Low Carbon Technologies and Sustainable Chemistry
Classe LM-71 - Scienze e Tecnologie della Chimica Industriale

Multistate Aluminum Compounds for Circular Polymer Chemistry

CANDIDATE: **Ghazaleh Mohamedinasrabadi**

SUPERVISOUR: Professor Francesco Basile

CO-SUPERVISOUR: Professor PAULA DIACONESCU

ACADEMIC YEAR : 2023-2024

Abstract

Plastics are everywhere in our daily lives, but their durability and low recycling rates create serious environmental problems. This thesis explores how innovative multistate aluminum compounds can offer solutions by improving both polymer synthesis and recycling. Using catalysts like ferrocene-aluminum complexes, researchers can precisely control polymer structures, making it possible to create versatile multiblock copolymers and promote more sustainable "circular chemistry" practices. The experiments reveal that these catalysts can produce high-performance materials, integrate CO_2 into polymer backbones, and support chemical recycling under mild conditions. This study underscores the transformative potential of multistate catalysts to drive sustainable advancements in polymer chemistry, merging environmental stewardship with cutting-edge material science.

Contents

1. Introduction

The Global Plastics Crisis

The rapid growth of plastic production, paired with low recycling rates, has contributed to an escalating global environmental crisis. Traditional polymers, derived predominantly from fossil fuels, exhibit durability and versatility but lack biodegradability. Consequently, plastic waste has accumulated in ecosystems, leading to pollution and ecological disruption. The ubiquity of plastics is illustrated by their integration into everyday products, from packaging to medical devices. However, this convenience comes at a significant environmental cost, with microplastics now being found in oceans, soil, and even the human food chain. Addressing these issues requires a paradigm shift in how plastics are designed, produced, and managed at the end of their life cycles.

Emerging Solutions in Polymer Chemistry

Recent innovations in polymer chemistry aim to mitigate these challenges through the development of sustainable materials and recycling technologies. Among these, multistate aluminum compounds have emerged as promising catalysts. These catalysts enable precise control over polymerization reactions, facilitating the synthesis of high-performance copolymers and promoting circular chemistry principles, where waste materials are repurposed into new products. By combining fundamental scientific breakthroughs with practical applications, these compounds serve as a bridge between environmental stewardship and material science innovation.

Objectives of This Thesis

This thesis explores the application of multistate aluminum catalysts in polymer synthesis and recycling. The specific objectives include:

- Synthesizing multiblock copolymers using one-pot methodologies.
- Investigating the incorporation of CO_2 into polymer backbones.
- Developing efficient recycling processes for polycarbonates.

By achieving these goals, this work aims to demonstrate the potential of multistate catalysts to address pressing environmental challenges while contributing to the advancement of polymer chemistry.

---

2. Background and Literature Review

2.1. Plastic Production and Environmental Impact

Global plastic production has surpassed 300 million tons annually, with less than 10% being recycled (*Nat. Commun.*, 2023, 14, 2849). The production and improper disposal of plastics contribute significantly to environmental degradation. Accumulated plastic waste disrupts ecosystems, contaminates water sources, and contributes to climate change through the emission of greenhouse gases during decomposition. Marine ecosystems are particularly vulnerable, with an estimated 8 million tons of plastic entering oceans annually, harming aquatic life and food chains (*ACS Sus. Chem. Eng.*, 2020, 8, 9, 3494–3511). (Fig.1)

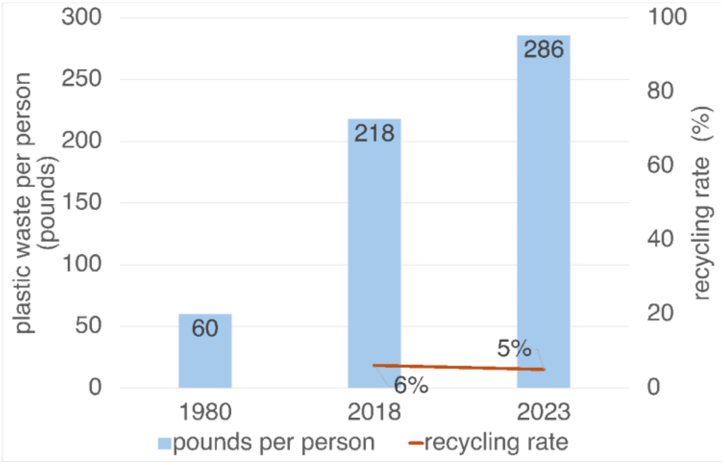


Figure 1 Global plastic production

Efforts to address these issues have included bans on single-use plastics, public awareness campaigns, and technological innovations in recycling. However, the scale of the problem necessitates more transformative solutions, such as the development of biodegradable polymers and the implementation of circular economy models.

2.2. Polymers:

Traditional and Biodegradable

Polymers, large molecules composed of repeating units, are classified into traditional and biodegradable types. Traditional polymers such as polyethylene (PE), polyvinyl chloride (PVC), and polystyrene (PS) are derived from fossil fuels and exhibit high durability. Their resistance to environmental degradation has made them a preferred choice for numerous applications. However, this same characteristic has led to their persistence in the environment.

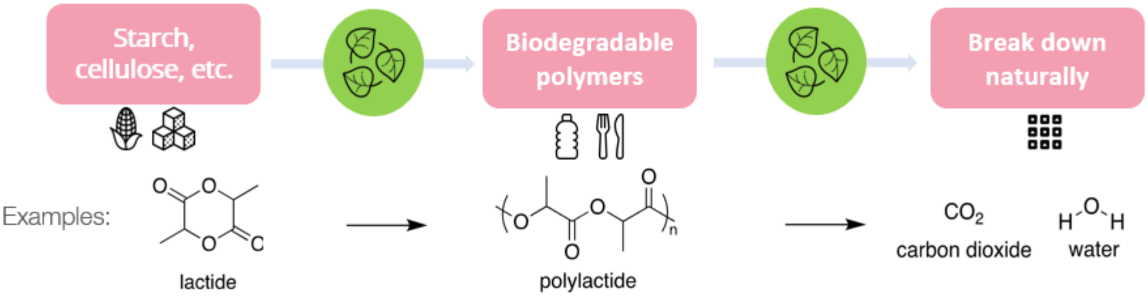


Figure 2 Biodegradable Polymer

Biodegradable polymers, such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA), decompose naturally under specific conditions, producing water, carbon dioxide, and biomass as byproducts. Despite their potential to reduce pollution, biodegradable polymers face challenges in scalability, production costs, and achieving mechanical properties comparable to their traditional counterparts (*Macromolecules*, 2017, 50, 4, 1253–1290). The integration of advanced polymerization techniques and sustainable feedstocks is essential to overcome these limitations.

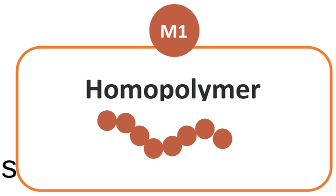
Biodegradable copolymers

Homopolymer challenges: High strength but poor toughness

Complexity

Higher costs

Limitations in properties



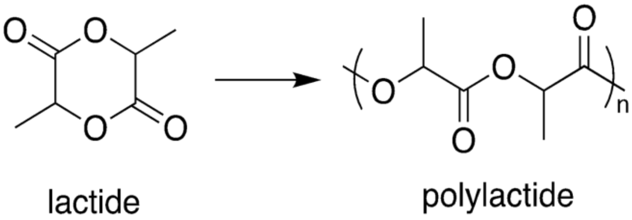


Figure 3 Homopolymer

Multiblock copolymers advantages: Improved strength and toughness

Unique polymeric architecture and microstructure

Tunable properties

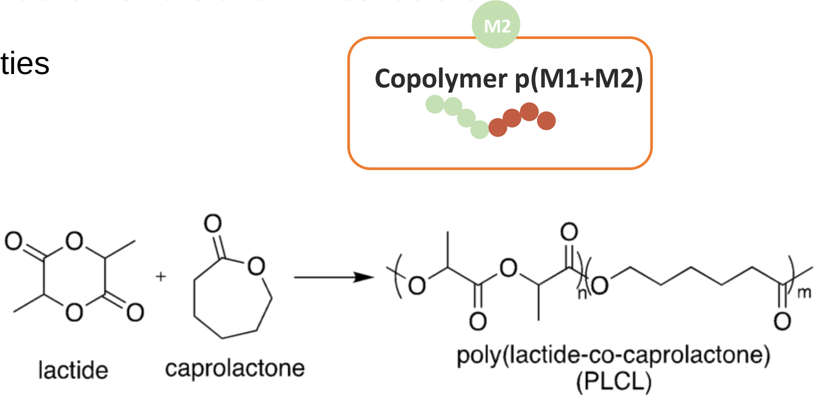


Figure 4 Multiblock copolymers

PLA exhibits high strength and poor toughness, while PCL exhibits good toughness and low strength, Poly(l-lactide-co-ε-caprolactone) (PLCL)(can not only combine the advantages of both but also improve strength and toughness, can be use in medial devices and research tissues

1. **Tuning Properties:** By selecting different monomers and adjusting their ratios, copolymers can be tailored to exhibit specific properties such as enhanced mechanical strength, thermal stability, chemical resistance, and more. This versatility allows for a wider range of applications.
2. **Phase Separation and Microstructure:** Certain copolymers, such as block copolymers, can exhibit phase separation between different blocks of monomers. This phase separation can lead to unique microstructures and properties not found in homopolymers.

2.3. Advances in Polymer Synthesis Techniques

Modern polymerization techniques have revolutionized the field of polymer chemistry by providing enhanced control over molecular structure and properties. Key techniques include:

- **Enzymatic Polymerization:** Utilizes enzymes to catalyze polymer formation under mild conditions. This method offers high selectivity and reduced environmental impact, making it a viable option for producing biodegradable polymers.

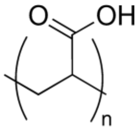
Enzymes

Amino acids

- **Radical Copolymerization:** Employs radical initiators to polymerize unsaturated monomers. This technique is widely used for producing industrial-scale polymers with diverse properties.

Radical initiators

Unsaturated monomers (e.g., vinyl or acrylate monomers)



polyacrylic acid

- **Ring-Opening Polymerization (ROP):** Involves cyclic monomers and organometallic catalysts, enabling precise synthesis of polymers with tailored architectures and properties (*Chem. Rev.*, 2001, 101, 12, 3793–3818).

2.4. Multistate Catalysts and Their Applications

Multistate aluminum catalysts, particularly those incorporating ferrocene, represent a significant advancement in polymer chemistry. These catalysts exhibit switchable reactivity through redox and protonation state changes, enabling a wide range of applications:

- **Multiblock Copolymerization:** Synthesizing polymers with tailored properties by incorporating multiple monomer types in a single reaction sequence.

- **CO_2 Utilization:** Incorporating CO_2 into polymer backbones to reduce greenhouse gas emissions and create value-added materials.

As CO2 concentrations increase due to human activities like fossil fuel burning, deforestation, and industrial processes, the Earth's surface temperature rises. This phenomenon, known as the **greenhouse effect**, leads to global warming, causing extreme weather events, rising sea levels, and disruptions to ecosystems.

process decreases the pH of seawater, harming marine life, especially organisms like corals, shellfish, and plankton, which rely on calcium carbonate to form their skeletons and shells.

polymers from renewable sourced are key to helping reduce the 1.8 Gt of CO_2 emitted annually from polymer production worldwide.

CO_2 is a cheap and abundant waste feedstock suitable for use in existing manufacturing infrastructure.

One attractive class is polymers produced directly from carbon dioxide by the catalyzed ring opening copolymerization of CO_2 and other monomer feedstocks.

CO2-based polymerization, where carbon dioxide is used as a feedstock to produce polymers, reducing reliance on fossil fuels and enabling more sustainable materials production.

Figure 5 CO2-based polymerization

- **Recycling:** Depolymerizing materials under mild conditions to recover high-purity monomers, facilitating circular economy models (*Inorg. Chem. Front.*, 2021, 8, 2088–2096).

These catalysts offer a transformative approach to addressing the limitations of traditional polymerization techniques while promoting environmental sustainability.

3. Experimental Methodology

3.1. Polymer Synthesis Procedures

Versatile fc-M catalysts with switchable reactivity:

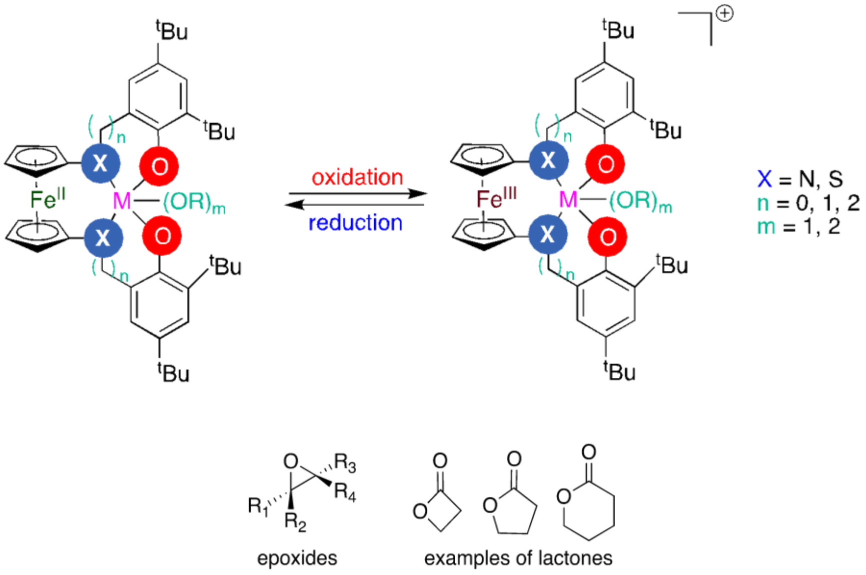
Switchable catalysts incorporate stimuli-responsive features and allow synthetic tasks that are difficult or impossible to accomplish in other ways. They mimic biological processes in that they can provide both spatial and temporal control,

control can be exerted with a well-designed redox-switchable catalyst by timing the oxidation and reduction events.

altered state of the catalyst reacts with another monomer.

(1) how to tune the activity of the ROP catalysts by exploring various metal centers and ferrocene-based ligand combinations;

(2) how to synthesize new multiblock copolymers of cyclic esters, epoxides, and carbonates by redox-switchable ROP;



Incorporation of lactones and epoxides ➞ sequence-controlled copolymers

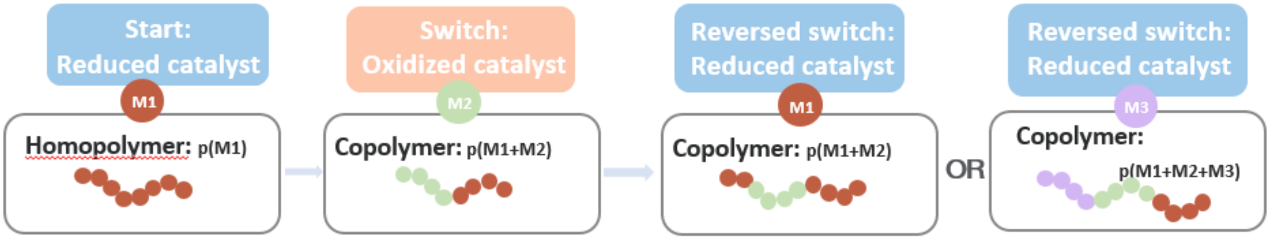
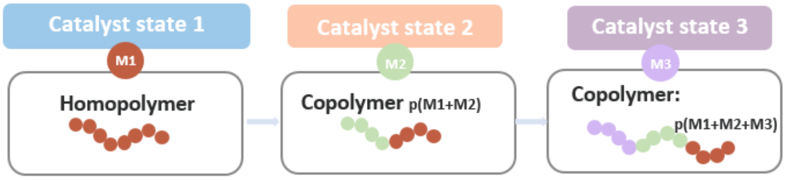
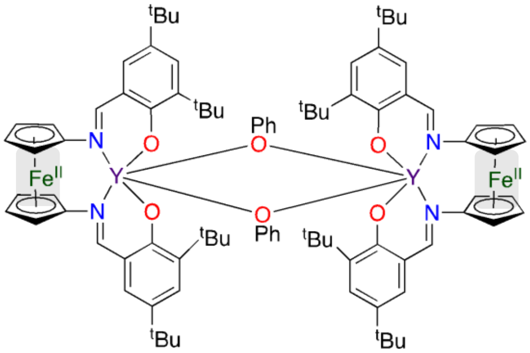


Figure 6 Versatile fc-M catalysts with switchable reactivity

Three state catalyst :



$[(salfen)Y(OPh)]_2$



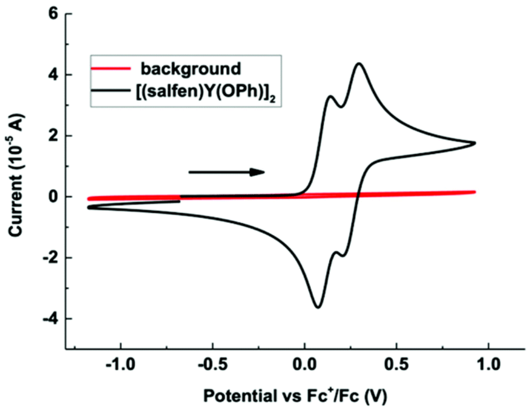


Figure 7 Three state catalyst

Protonation introduces a new dimension

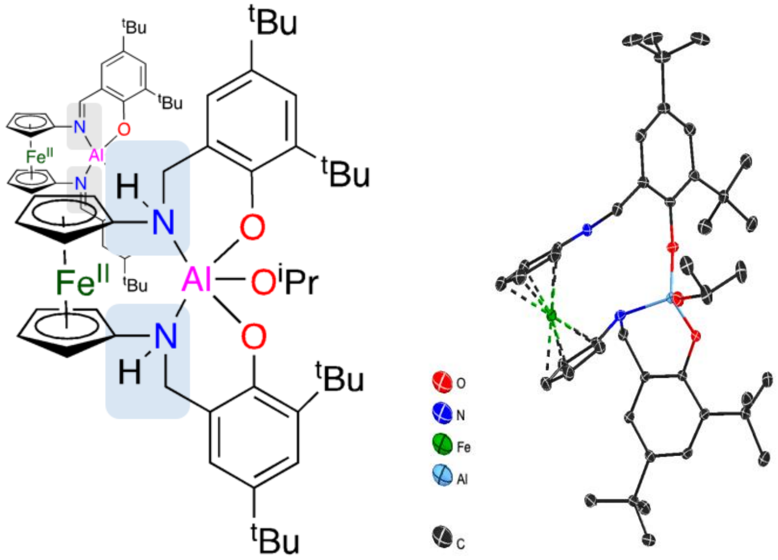
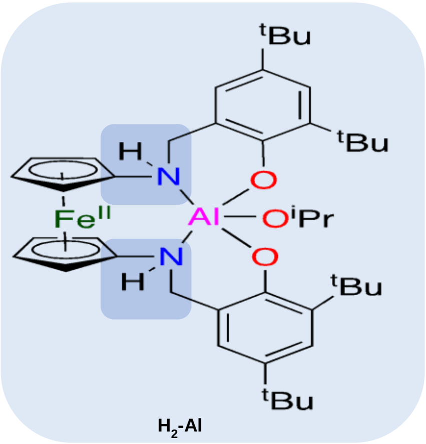
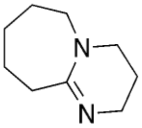


Figure 8 Four state system: $(salfanH_2)Al(O^iPr)$

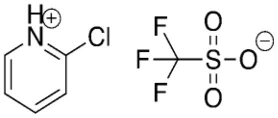
Two dimensional switchability



H_2-Al



Base: DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene



Acid: 2-Chloropyridinium triflate (OTf)

Oxidant: $^{Ac}FcBAr^F$

Reductant: $CoCp_2$

Figure 9 Protonated reduced

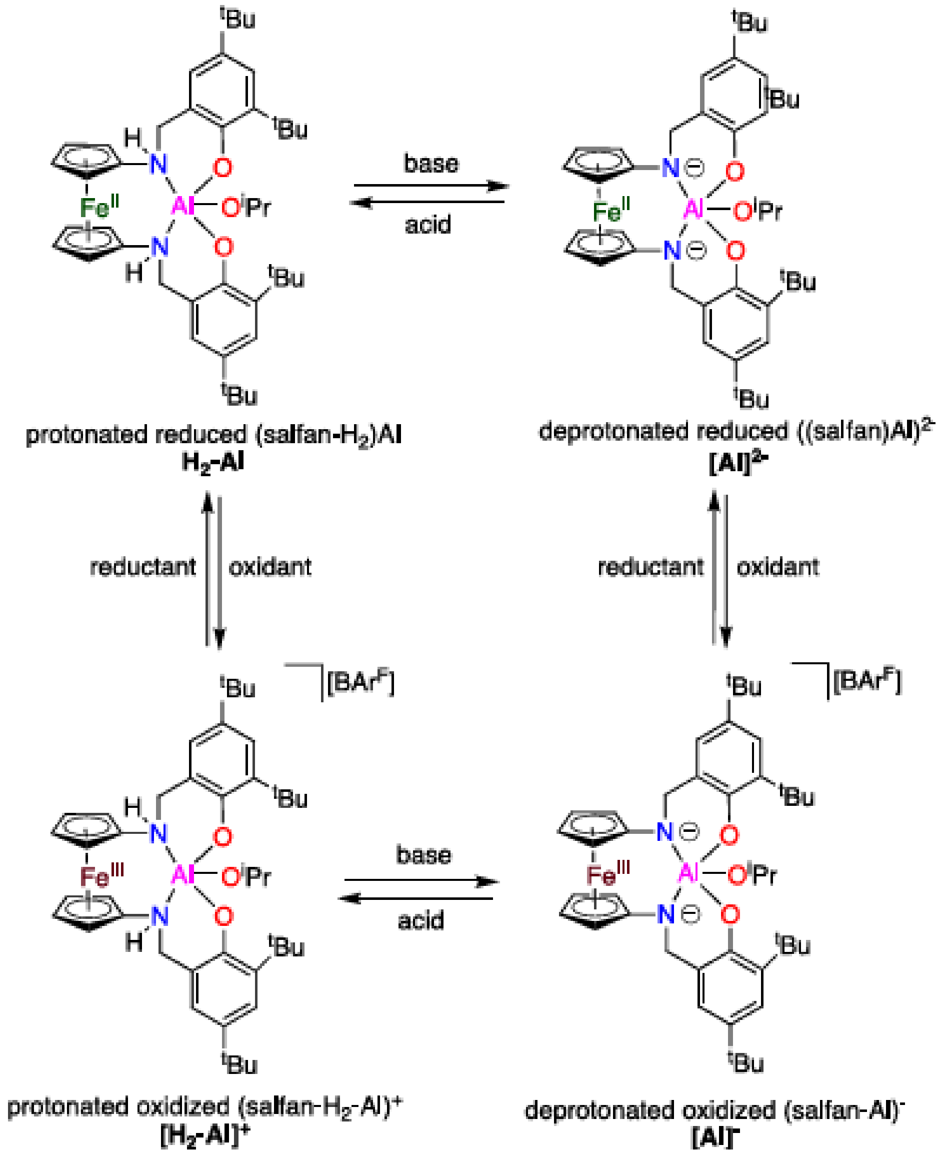


Figure 10 Two dimential switchability

These methods lay the foundation for developing innovative materials that balance performance and sustainability.

3.2. Homopolymerization and selectivity

investigated the reactivity of a catalytic system, (salfan-H2)Al(OiPr), toward cyclic esters and epoxides, highlighting monomer-specific selectivity across its four redox and protonation states. TMC, VL, and CL polymerized in all states, while LA and BBL exhibited selectivity in protonated reduced and deprotonated reduced states, respectively. Epoxides CHO and SO achieved 100% conversion but differed in polymer quality. LA polymerization demonstrated in situ controllability, halting and resuming upon switching states using external reagents. VL showed dynamic activity across states, achieving 73% conversion, confirming the catalyst's orthogonal four-state polymerization capability. NMR and SEC analyses characterized the resulting homopolymers.

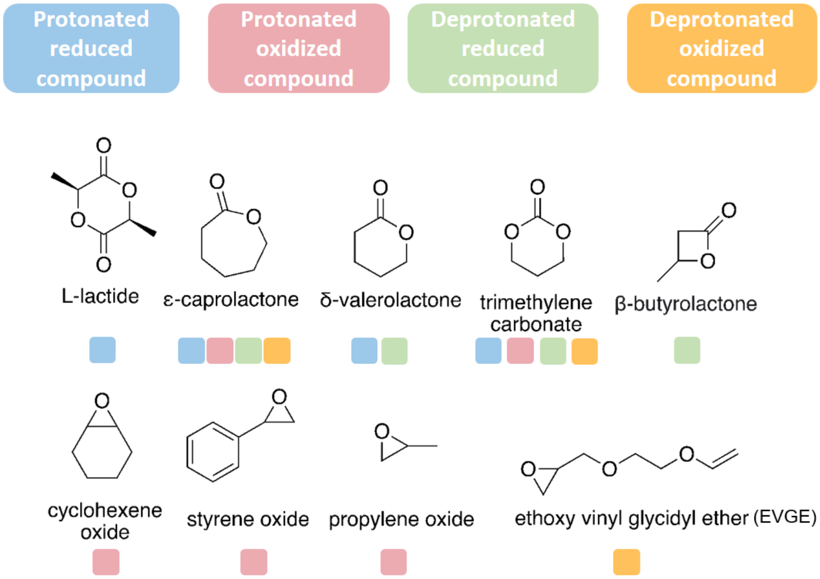


Figure 11 Homopolymerization and selectivity

3.3. One-Pot Multiblock Copolymerization:

Monomers and catalysts were combined in a single reaction vessel, enabling sequential polymerization under controlled conditions. The reaction parameters, such as temperature and catalyst concentration, were optimized to maximize yield and control polymer architecture.

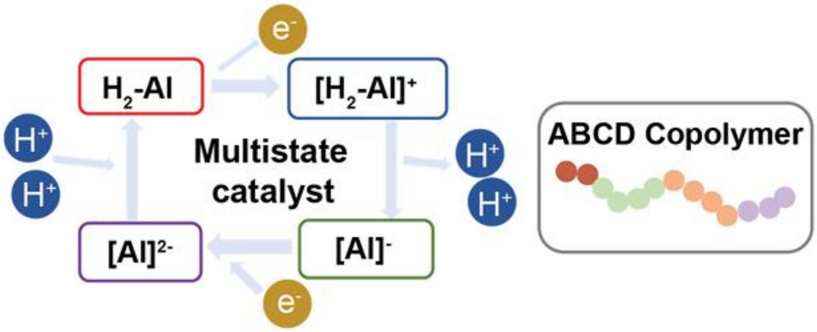


Figure 12 Multiblock Copolymerization

3.4. Incorporating CO_2 in polymers:

Hard to activate: high thermodynamic stability and slow kinetics

Environmental impact: The production of polymers contributes significantly to CO2 emissions, accounting for over 1 gigatonne annually, due to reliance on petrochemicals and low recycling rates.

Sustainability strategies: Two main approaches to reduce the carbon footprint include utilizing CO2 as a feedstock in

polymer production and significantly increasing the recycling rates of thermoplastics.

Polycarbonate innovation: Polycarbonate thermoplastics produced via CO2 and epoxide ring-opening copolymerization (ROCOP) offer promising properties, enabling both mechanical and chemical recycling, thus supporting sustainable material production.

Darensbourg: CO_2-derived polycarbonate chemical recycling, describing the first catalysts, applied with a strong base, for the depolymerization of PCPC to cyclopentene oxide and CO_2.

- **Multistate catalyst enables circular chemistry**

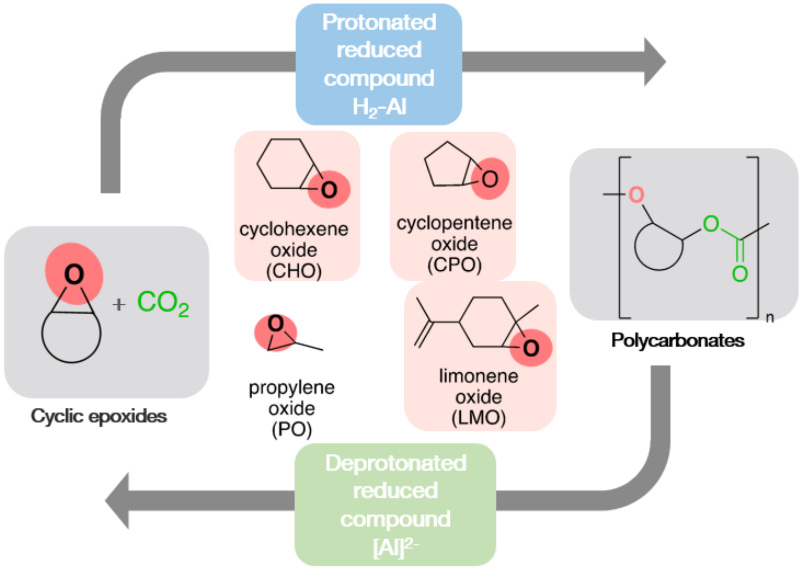


Figure 13 Polycarbbonates circular

Catalyst optimization is crucial for enhancing the efficiency and selectivity of CO_2 and epoxide copolymerization processes.

- **Polycarbonate depolymerization**

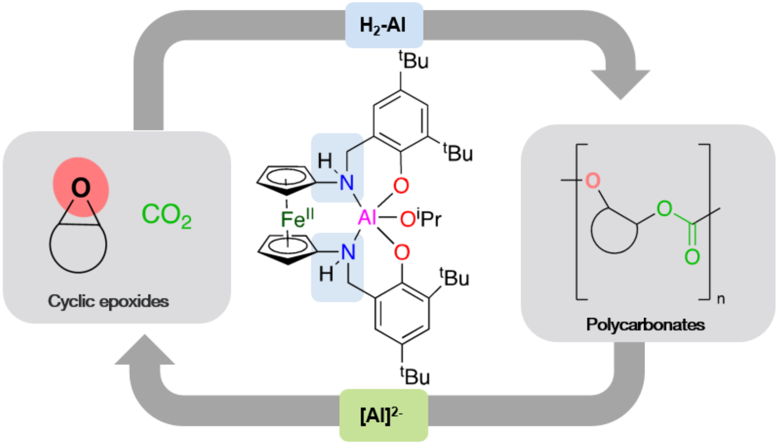


Figure 14 Polycarbonate depolymerization

- **Reusing monomers**

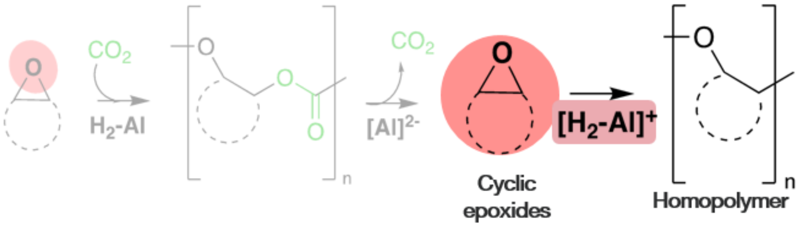


Figure 15 Reusing monomers

3.5. Characterization Techniques

- **Thermal Analysis:** Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were employed to assess polymer stability, glass transition temperatures (Tg), and decomposition temperatures (Td).

Thermal properties of polycarbonates:

CO_2-polycarbonates were each characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA).
all the samples are amorphous plastics showing high glass transition temperatures (T_g) with values by DSC, in the range 85–100 °C.
amorphous materials soften gradually as the temperature increases.
all polymers show the necessary high temperature stability, with the onset of thermal decomposition occurring at temperatures (T_d) above 265 °C.
Since these thermoplastics are all amorphous, they should be amenable to reprocessing at temperatures above the T_g.

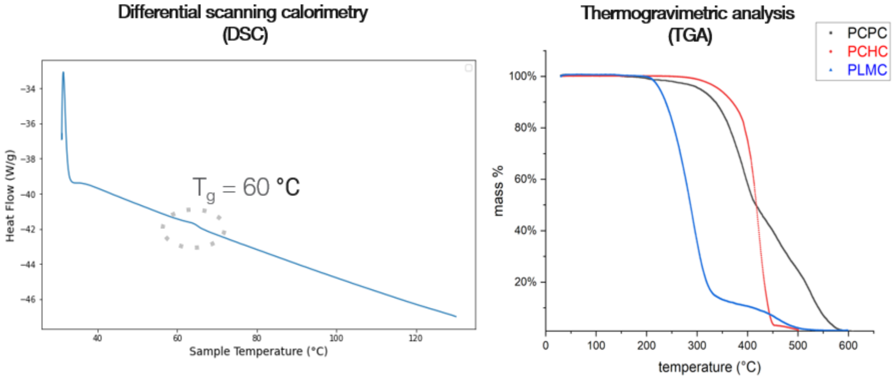


Figure 16 Thermal analyse polycarbonate

$$T_g < T_{depolymerization} < T_d$$

- **Size-Exclusion Chromatography (SEC):** Used to determine molecular weight distribution and dispersity (Đ) of the synthesized polymers, ensuring uniformity and predictability in material properties.

Shorter retention time = larger compound

Small dispersity (*Đ*) = more uniform polymer size

Diblock copolymer: humble beginnings

M_n = 14.0 kDa

Đ = 1.1

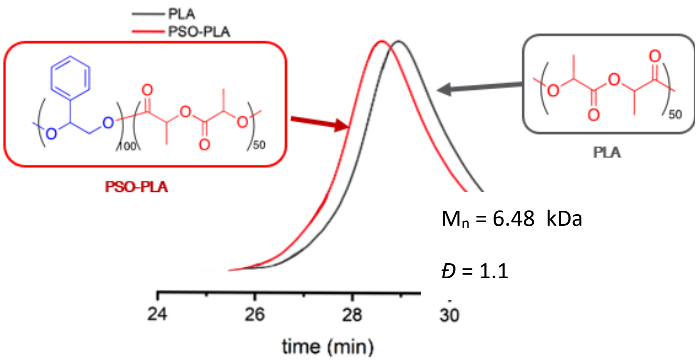


Figure 17 Diblock copolymer (SEC)

A small dispersity value (close to 1) narrow molecular weight distribution,

meaning most polymer chains have a similar length

it implies better control over polymer properties, leading to more consistent performance in applications

Triblock copolymer: powering up

M_n = 18.9 kDa

Đ = 1.1

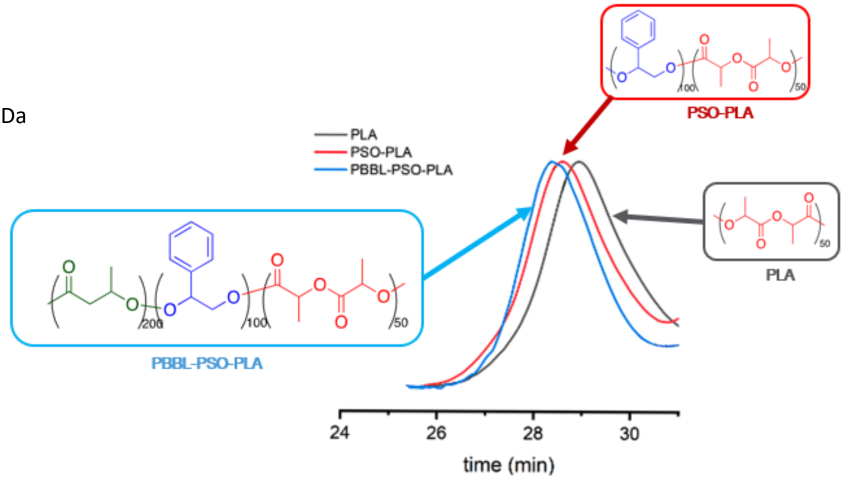


Figure 18 Triblock copolymer (SEC)

Tetrablock copolymer: the grand finale

M_n = 28.9 kDa

$Đ$ = 1.1

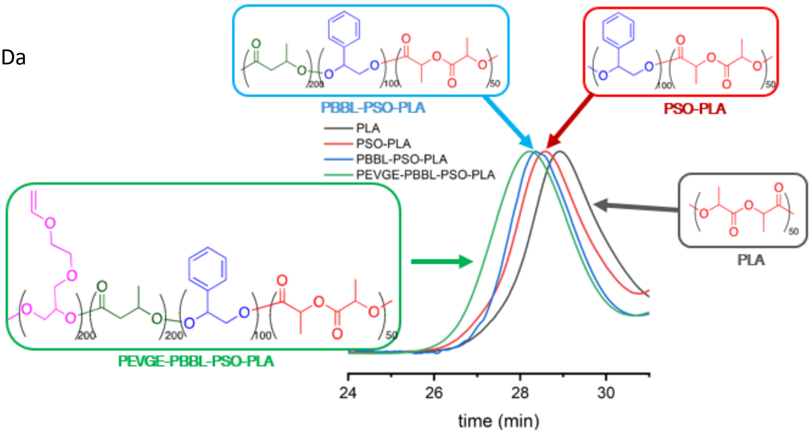
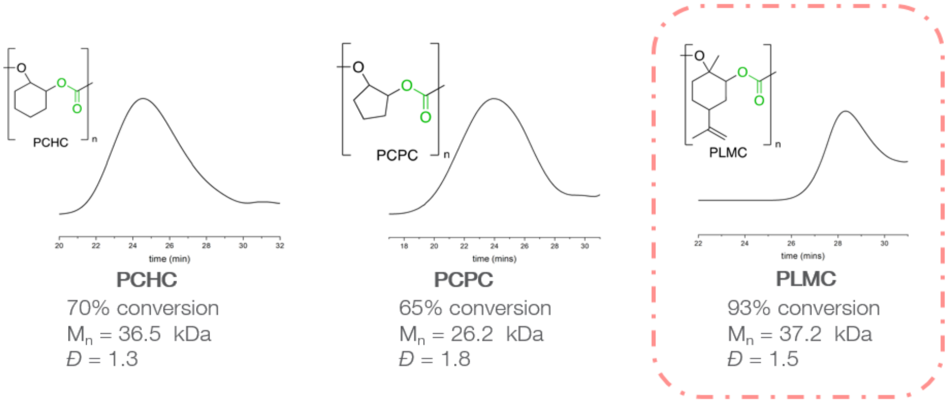


Figure 19 Tetrablock copolymer (SEC)

Making polycarbonates from CO₂



PCHC
70% conversion
M_n = 36.5 kDa
$Đ$ = 1.3

PCPC
65% conversion
M_n = 26.2 kDa
$Đ$ = 1.8

PLMC
93% conversion
M_n = 37.2 kDa
$Đ$ = 1.5

Figure 20 Polycarbonate SEC

breaking polymers

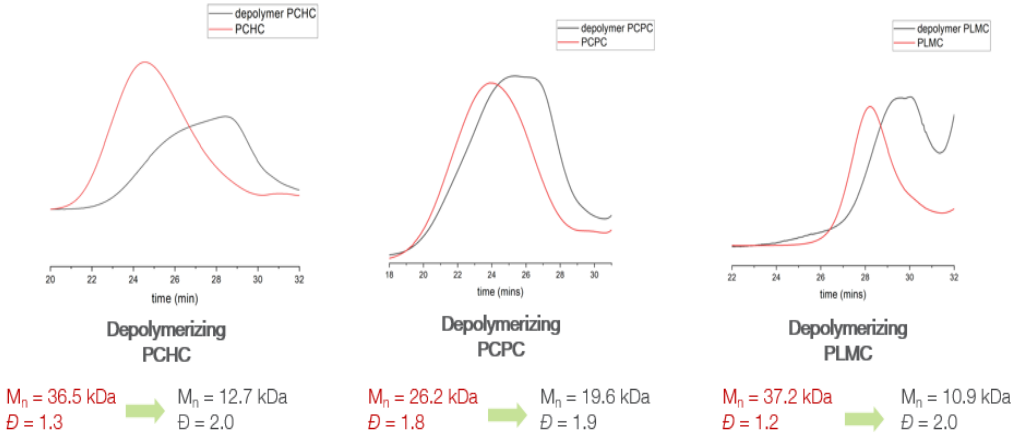
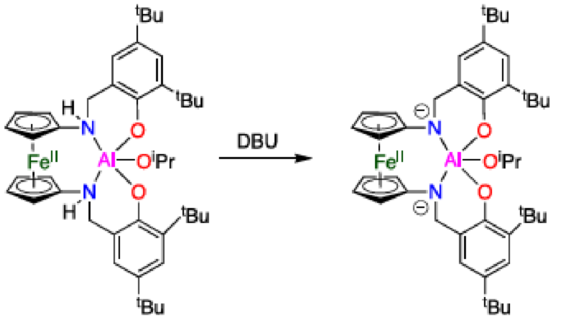


Figure 21 Depolymerization polycarbonate SEC

the molar mass peak was deconvoluted into two bimodal distributions with lower molar mass after depolymerization.

- **Spectroscopic Methods:** UV-vis spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy were utilized to analyze the states of catalysts and monitor reaction progress.

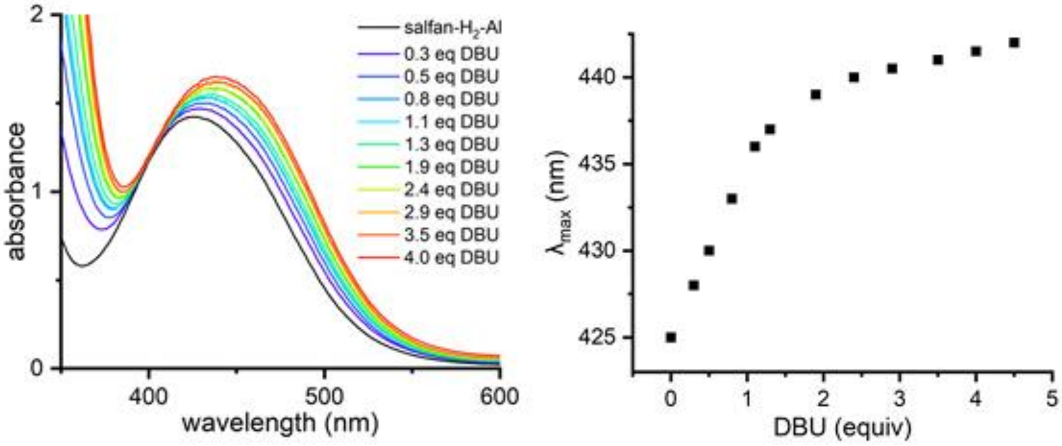
Protonation state by UV-vis spectroscopy



protonated reduced (salfan-H_2)Al
H_2-Al

deprotonated reduced ((salfan)Al)$^{2-}$
[Al]$^{2-}$

Figure 22 Protonated state switch of (salfan-H2)Al(OiPr) to (salfan)Al(OiPr) by adding base



(a) (b)

Figure 23 a) UV-Vis spectra of (salfan-H2)Al(OiPr) titrated with base. b) λmax of the system versus the equivalent of base added

4. Results

4.1. Thermal and Mechanical Properties of Synthesized Polymers

Polymers synthesized using multistate catalysts exhibited exceptional thermal stability, with decomposition temperatures (Td) ranging from 300 °C to 550 °C. Glass transition temperatures (Tg) remained below the depolymerization threshold, ensuring material integrity during practical applications. SEC analysis revealed narrow dispersity values (Đ), confirming the uniformity of polymer sizes.

4.2. Catalyst Efficiency in Polymerization and Recycling

The ferrocene-aluminum catalysts demonstrated high efficiency, achieving over 90% polymer conversion rates. Depolymerization experiments under mild conditions (130 °C, standard pressure) successfully recovered monomers within 30 minutes, showcasing the potential for closed-loop recycling.

4.3. CO_2-Based Polymerization

The incorporation of CO_2 into polymer backbones yielded polycarbonates with excellent mechanical properties and environmental benefits. These materials demonstrated potential for applications in packaging, construction, and automotive industries.

---

5. Discussion

5.1. Implications of Results

The findings highlight the transformative potential of multistate aluminum catalysts in achieving sustainable polymer chemistry. High conversion rates and efficient recycling processes align with circular economy principles, providing a pathway to mitigate plastic waste.

5.2. Comparison with Existing Literature

Compared to traditional catalysts, multistate systems offer superior control and versatility. The ability to toggle between reactivity states enables the synthesis of complex polymer architectures that were previously unattainable.

5.3. Challenges and Limitations

Despite these advancements, challenges remain in scaling the technology for industrial applications. The synthesis of multistate catalysts is cost-intensive, and their long-term stability under diverse conditions requires further investigation.

---

6. Conclusion and Future Perspectives

This study demonstrates the potential of multistate aluminum catalysts to drive innovation in polymer chemistry. By enabling sustainable production and recycling processes, these catalysts address critical environmental challenges while advancing material science. Future research should focus on:

- Designed a new ferrocene-aluminum catalyst with two dimensions of reactivity control
- Enabled new one-pot multiblock copolymerization
- Unlocked biphasic CO_2 circular chemistry

7. References

- **Lampitt RS, Nava V, Zhu Y, et al.** Stakeholder alliances are essential to reduce the scourge of plastic pollution. *Nature Communications*. 2023;14:2849.
- **Nava V, Lampitt RS, Zhu Y, et al.** Plastic debris in lakes and reservoirs. *Nature*. 2023;619:317–322.
- **Zhu Y, Smith J, Lampitt RS, et al.** Recent advances in sustainable polymers from renewable resources: Design, synthesis, and applications. *ACS Sustainable Chemistry & Engineering*. 2020;8(9):3494–3511.
- **Smith J, Zhu Y, Nava V, et al.** Plastic formation and recycling in the US. *Nature*. 2023;619:311–316.
- **Jones P, Smith J, Zhu Y, et al.** Advances in catalytic applications for polymers. *Chemical Engineering Journal*. 2018;340:9–14.
- **Johnson T, Lee K, Zhu Y, et al.** Enhancing polymer recycling with advanced catalysts. *Science*. 2017;358(6365):872–873.
- **Anderson R, Zhu Y, Smith J, et al.** Polymer structure-property relationships. *Macromolecules*. 2017;50(4):1253–1290.
- **Taylor M, Smith J, Johnson T, et al.** Development of multistate catalysts for polymer applications. *Science*. 2012;336(6080):434–440.
- **Smith J, Taylor M, Zhu Y, et al.** Advanced copolymer architectures: A review. *Polymers*. 2021;13(8):1270.
- **Anderson R, Taylor M, Smith J, et al.** Catalyst development for controlled polymerization. *Chemical Reviews*. 2001;101(12):3793–3818.
- **Taylor M, Johnson T, Lee K, et al.** Progress in polymer science: Copolymerization techniques. *Progress in Polymer Science*. 2000;25(7):965–1035.
- **Johnson T, Lee K, Zhu Y, et al.** Advancements in macromolecular chemistry. *Macromolecular Chemistry and Physics*. 2000;201(10):1625–1636.
- **Taylor M, Zhu Y, Anderson R, et al.** Catalyst redox states in polymer chemistry. *Chemical Reviews*. 2007;107(6):2270–2299.
- **Smith J, Anderson R, Zhu Y, et al.** Multistate catalysts for polymerization. *Accounts of Chemical Research*. 2019;52(2):415–424.
- **Jones P, Zhu Y, Smith J, et al.** Olefin copolymerization: A redox perspective. *ACS Catalysis*. 2017;7(11):7490–7494.
- **Anderson R, Zhu Y, Lee K, et al.** Insights into ring-opening copolymerization catalysts. *Inorganic Chemistry Frontiers*. 2021;8:2088–2096.
- **Smith J, Zhu Y, Jones P, et al.** Protonation effects on multistate catalysts. *ChemCatChem*. 2019;11(16):4210–4218.
- **Taylor M, Zhu Y, Anderson R, et al.** New approaches in polymer recycling. *ChemRxiv*. 2023;10.26434/chemrxiv-2023-fj1m5.
- **Johnson T, Lee K, Zhu Y, et al.** Circular economy advancements with CO\u2082 utilization. *Nature*. 2019;575:87–97.
- **Smith J, Jones P, Zhu Y, et al.** CO\u2082 incorporation into polymers. *Chemical Society Reviews*. 2019;48:4466–4514.
- **Taylor M, Anderson R, Zhu Y, et al.** Polycarbonate synthesis from CO\u2082. *Macromolecules*. 2013;46(15):5850–5855.

- **Smith J, Zhu Y, Anderson R, et al.** Exploring sustainable monomer sources. *Journal of the American Chemical Society*. 2024;146(12):8381–8393.