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Alternating Copolymerization of Cyclohexene Oxide with Cyclic Anhydrides catalyzed by Chiral Alkyl Aluminum Compounds

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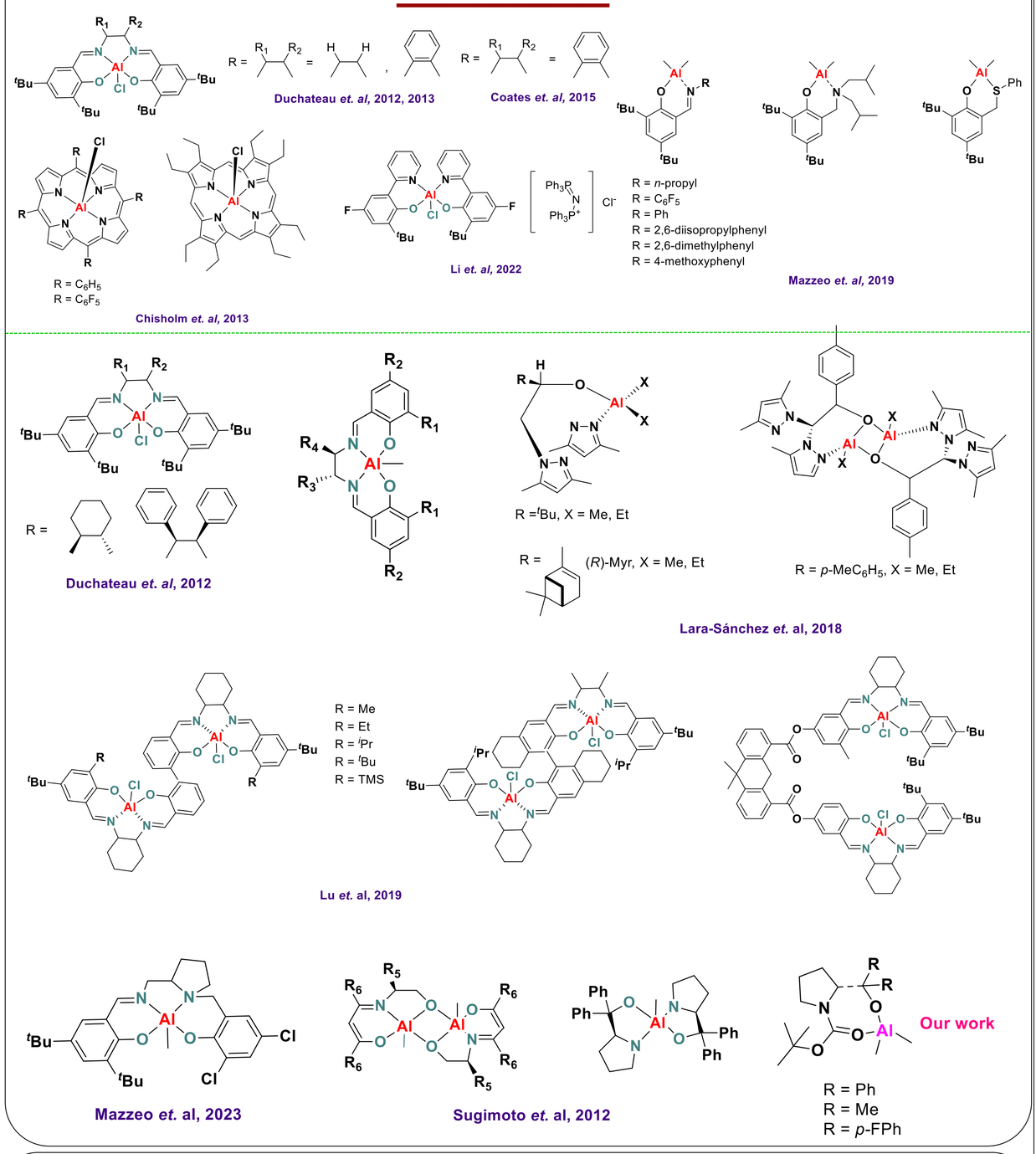
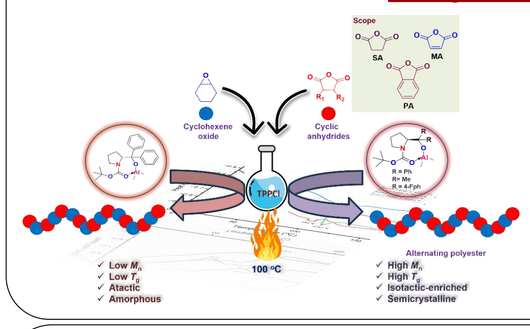
Abstract

The most commercially successful aliphatic polyester today namely polylactide (PLA) has found applications in packaging materials, biomedical devices and a variety of commodity consumer products. Unfortunately, regular PLA shows a moderate glass transition temperature (T_g = 50-60 °C).[1] Hence it is a poor alternative to glassy petroleum-based polymers such as polystyrene (T_g = 100 °C). Aliphatic and aromatic alternating polyesters have found to be the suitable alternatives of synthetic petroleum-based polymers as they are biodegradable and biocompatible.[2] The alternating polyester can be synthesized by the ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides. The ROCOP of cyclohexene oxide (CHO) with anhydrides to give fully alternating polyesters has grabbed the research interests of researchers globally due to their high glass transition temperature.[3] The respective polymers have been extensively used as plastics, fibers and films for engineering, packaging and biomedical materials.[4] To date there are numerous reports for the ROCOP of epoxides and cyclic anhydrides using metal complexes containing achiral ligands and the use of chiral metal complexes in this area is unexplored. We synthesized chiral monomeric (*S*) and (*R*) isomer of aluminum complexes and investigated their catalytic activity towards ROCOP of CHO and cyclic anhydrides (Phthalic anhydride, succinic anhydride and maleic anhydride) to produce fully alternating polyesters. The polymerizations were carried out under various conditions and from this study we made a correlation of the selectivity, molecular weight (M_n) and polydispersity ($Đ$) of the synthesized polyesters with changing the catalyst chirality. These Al(III) compounds with an ionic cocatalyst show notable catalytic activity producing alternating polyester with TOF up to 80 h^{-1}, high selectivity (polyester linkages > 80%) and moderate to high T_g. The catalytic activities of the two enantiomers of the Al(III) compounds have been investigated, where the (*S*)-isomer is found to be more active towards the ROCOP.

Introduction

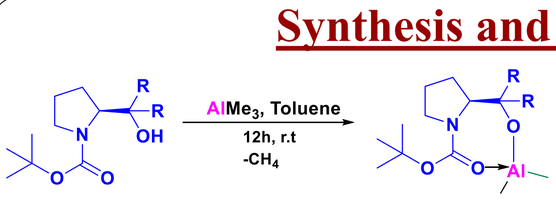


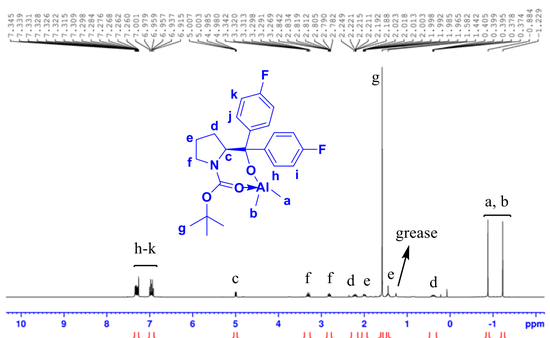
Objective of the work

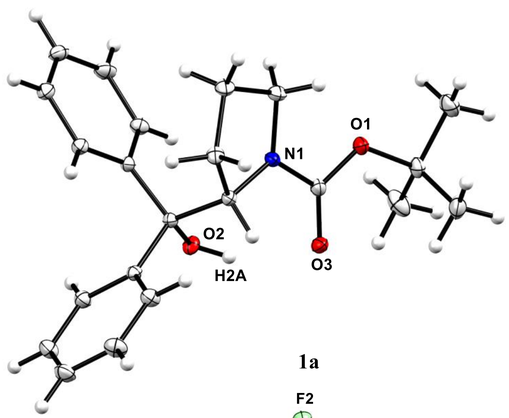


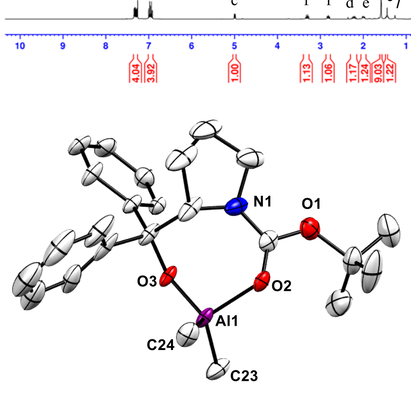
- To study the catalytic activity of chiral catalyst containing aluminum towards ring-opening copolymerization (ROCOP) of cyclohexene oxide (CHO) with cyclic anhydrides.
- To achieve well-defined biodegradable copolymers with desired microstructures and thermal properties.

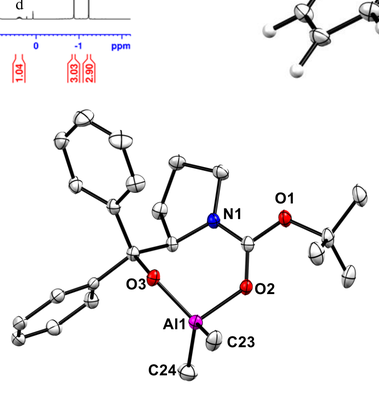
Synthesis and crystal structure

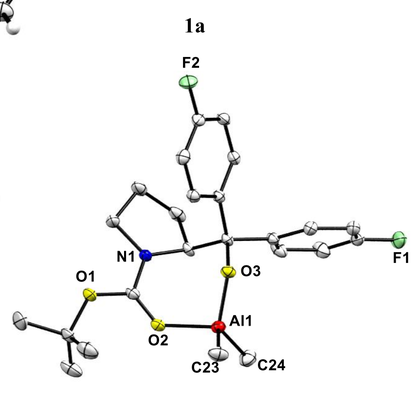








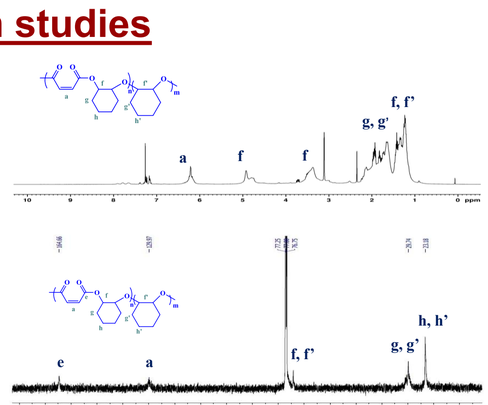




Polymerization studies

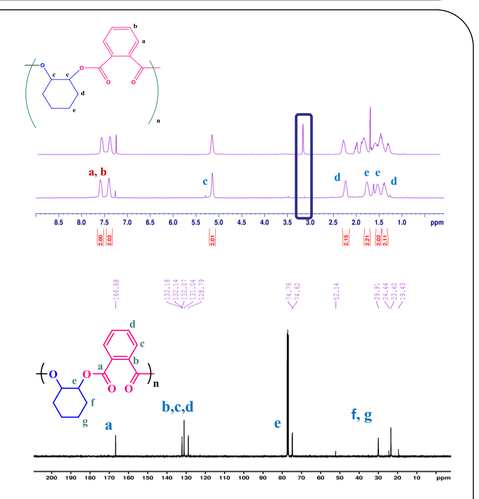
ROCOP of CHO with Maleic anhydride (MA)

Entry	Catalyst	Cocatalyst	Solvent	Time (h)	PA conv. (%)	Ester linkage (%)	M_n (g/mol)	PDI
1	2a	-	-	5	-	-	-	-
2	2a	TPPCl	-	5.5	71	24	3057	1.23
3	2b	TPPCl	-	4	75	26	3324	1.29
4	2c	TPPCl	-	3.5	73	27	3152	1.25
5	2d	TPPCl	-	7	55	15	2846	1.78
6	2a	TPPCl	Toluene	8	68	58	2968	1.14
7	2c	TPPCl	Toluene	8	70	67	3025	1.12
8	2d	TPPCl	Toluene	8	52	16	2633	1.19



ROCOP of CHO with Phthalic anhydride (PA)

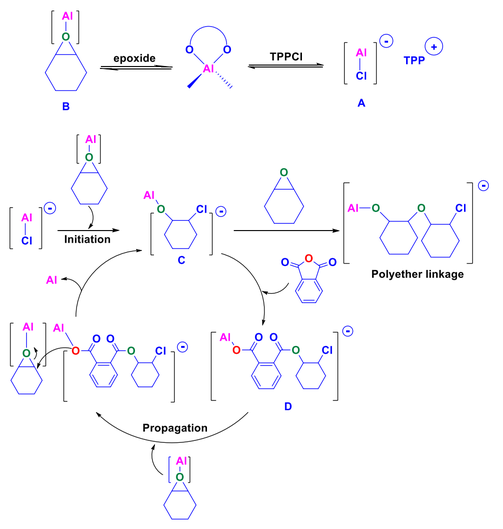
Entry	Catalyst	Cocatalyst	Solvent	Time	Temp. (°C)	PA conv. (%)	Ester linkage (%)	M_n (g/mol)	PDI	TOF (h^{-1})
1	2a	-	-	10 min	100	17	4	27879	1.56	102
2	2a	TPPCl	-	2 h	100	>99	77	7490	1.18	49.5
3	2a	PPNCl	-	1.5 h	100	78	34	5085	1.25	52
4	2a	TBAB	-	2 h	100	52	16	71597	1.92	16
5	2b	TPPCl	-	1.75 h	100	>99	86	9589	1.23	57
6	2c	TPPCl	-	1.25 h	100	99	81	6803	1.18	79
7	2d	TPPCl	-	2.5 h	100	93	26	2808	1.14	279
8	2a	TPPCl	Toluene	2.5 h	100	99	77	7550	1.10	40
9	2b	TPPCl	Toluene	3 h	100	>99	72	9602	1.16	33
10	2c	TPPCl	Toluene	1.75 h	100	99	57	7883	1.19	56
11	2d	TPPCl	Toluene	4 h	100	99	53	5049	1.33	40
12	2a	TPPCl	-	3.5 h	80	>99	72	2553	1.18	21
13	-	TPPCl	-	6 h	100	>99	74	2930	1.26	12

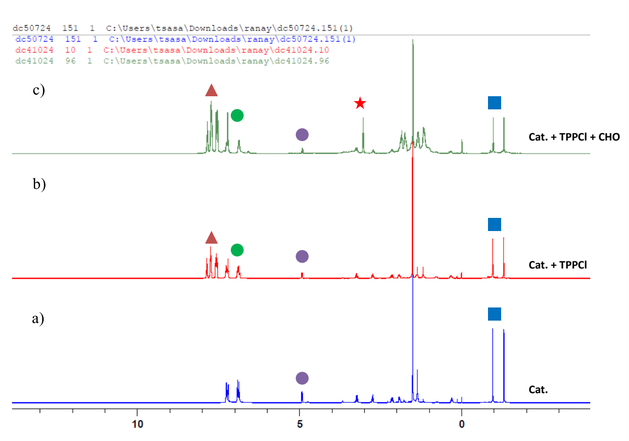


ROCOP of CHO with Succinic anhydride (SA)

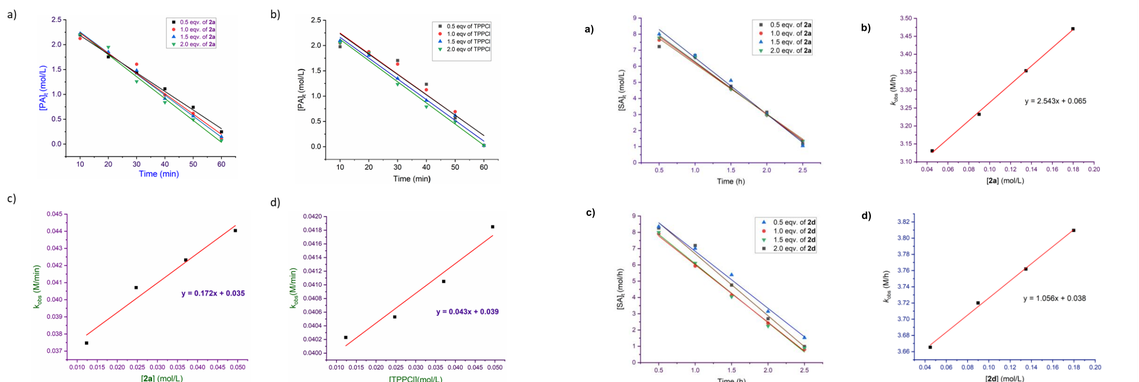
Entry	Catalyst	Cocatalyst	CHO:PA	Time (h)	PA conv. (%)	Ester linkage (%)	M_n (g/mol)	PDI
1	2a	-	110:100	6	-	-	-	-
2	2a	TPPCl	110:100	3	95	86	2026	1.45
3	2b	TPPCl	110:100	3	95	79	2202	1.42
4	2c	TPPCl	110:100	3	95	85	2196	1.52
5	2d	TPPCl	110:100	3	95	85	2210	1.50
6	2a	TPPCl	400:100	3	79	58	2047	1.55
7	2d	TPPCl	400:100	3	80	67	2036	1.63

Mechanistic studies

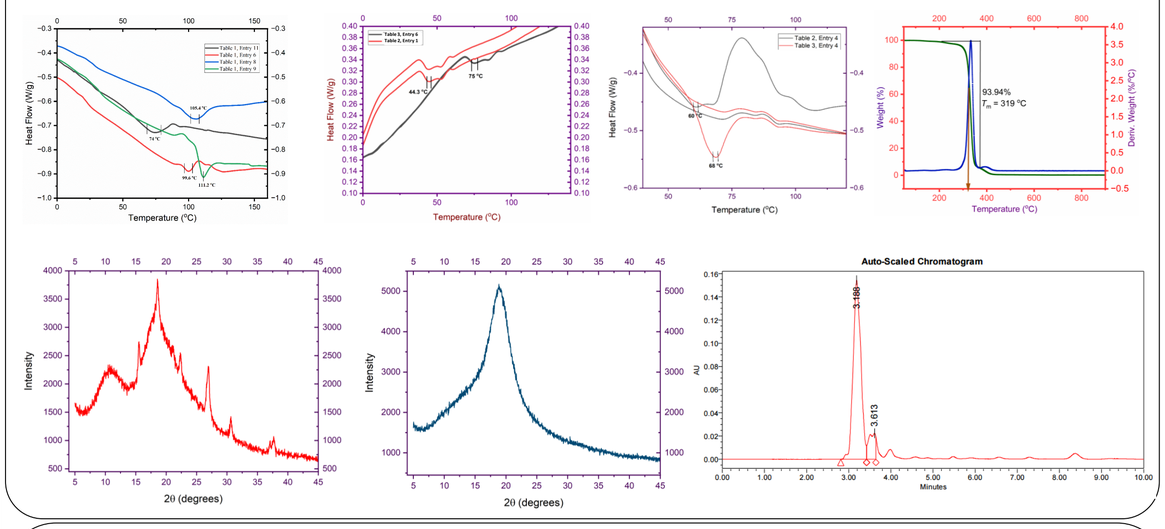




Kinetic studies



Thermal studies



Conclusions

- We synthesized both (*R*) and (*S*) isomers of chiral alkyl Al(III) compounds.
- The catalytic activity of the compounds depend upon the electronic environment as well as the chirality where the (*R*) isomer is found to be more active towards ROCOP.
- The rate of the (S)-isomer (2a) is almost three times and 2.4 times higher than the rate of the (R)-isomer (2d) for CHO/PA and CHO/SA copolymerization, respectively.
- The reactivity of PA is higher than SA towards ROCOP could be attributed to the ring strain.
- The ionic cocatalyst TPPCl initiates the ROCOP reaction through the coordination of chloride ion to the Al(III) center.
- The copolymer produced from 2a was isotactic-enriched with semicrystalline in nature. On the contrary, 2d was found to produce atactic amorphous polyester with a comparatively low T_g value.

References

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3. M. Schutze, S. Dechert and F. Meyer, *Chem. Eur. J.*, 2017, **23**, 16472-16475.

Acknowledgement

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