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Usama Hassan
College of Saint Benedict/Saint John's University, UHASSAN001@CSBSJU.EDU

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Synthesis and Modification of Phenol-Containing Catalysts for Ring-Opening Polymerization of Cyclic Esters

Usama Hassan, Kalista Jager, Anna Zeleny, Chris Schaller*

Department of Chemistry, College of Saint Benedict and Saint John's University, St. Joseph, MN 56374

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Introduction

- Ring-opening polymerization (ROP) of cyclic esters has become a key method in the synthesis of useful biodegradable materials such as poly(caprolactone), poly(lactide), and poly(menthide)

- These are employed in the biomedical and pharmaceutical fields as well as in day-to-day commodities.

- ROP of cyclic esters is also used in the synthesis of telechelic triblock copolymers that can be used to make thermoplastic elastomers (TPEs). TPEs are extensively used in the industrial field and consumer products such as soft grips on commonly used accessories, footwear, and pressure sensitive adhesives.[1]
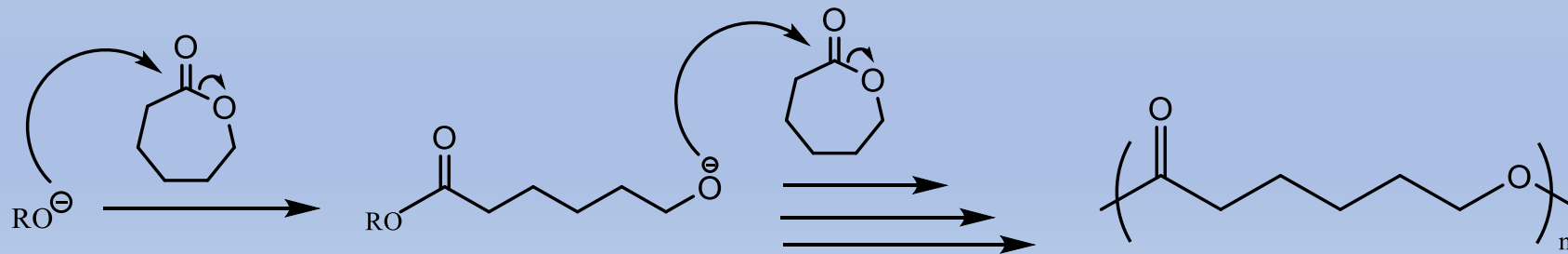
Scheme 1. General reaction scheme for ROP of cyclic esters, in this case caprolactone monomer

- There is a lot of interest in the development of new catalysts for carrying out ring-opening trans-esterification polymerization (ROTEP) of cyclic esters. Many classes of new catalysts exist. Among them are aluminum Schiff base complexes[2], cationic metal complexes[3], and compounds containing amines and N-heterocyclic carbenes.[4]

- Previous research students at our lab were able to develop an aluminum-based catalyst (**1**) that can successfully polymerize caprolactone, but not lactide. It contains a carbene unit, which has been found to be significantly useful in many applications such as homogeneous transition metal catalysis, organometallic materials, and its role as an organocatalyst.[5]

- The catalyst works faster than tin octoate and triethylaluminum but is unreliable as it decomposes over time. It has also been unsuccessful with diol initiators, which are needed for the synthesis of telechelic polymers that are used to develop triblock copolymers.

- The goal of this work is to modify the catalyst to increase its reliability as well as allow its usage with diol initiators.

Experimental

Polycaprolactone. A 15 mL pressure flask was charged with caprolactone (250 μL, 2.25 mmoles), benzyl alcohol (10 μL, 0.1 mmoles), and compound **1** (0.02 g, 0.038 mmoles) in the glove box. A clear solution was formed and stirred in an oil bath (120 ºC) for 30 minutes. Product was left to cool for 15 minutes to yield a white waxy solid (0.21 g, 1.84 mmoles, 82%). Degree of polymerization was evaluated by comparison of the integration for end group methylene at 5.12 ppm and repeating unit methylene at 3.65 ppm.

(PhenNHC)(THF)Al(Et)Br (**1**)**.** In a 20 mL vial in the glove box, imidazolium salt I (0.196 g, 0.404 mmoles) was dissolved in THF (10 mL). A triethylaluminum solution (0.43 mL, 1 M in heptane, 0.43 mmoles) was added via syringe. The reaction was left to stir overnight at room temperature. The solvent was removed in vacuo to yield a thick yellow (honey-colored) oil (no exact weight recorded to calculate percent yield). 1H-NMR (400 MHz, Benzene-D6) 0.64 (2H, q), 0.67 (3H, t), 1.27 (9H, s), 1.31 (2H, t), 1.5 (6H, s), 1.62 (3H, s), 1.64 (9H, s), 3.5 (2H, t), 5.4 (2H, s), 6.3 (2H, s), 6.4 (1H, s), 6.9 (1H, d), 7.5 (1H, d), 8.1 (1H, s).

(PhenNHC)Al(Et)Br (**2**)**.** In a 20 mL vial in the glove box, imidazolium salt I (0.404 g, 0.812 mmoles) was dissolved in toluene (14.5 mL). A triethylaluminum solution (0.86 mL, 1 M in heptane, 0.86 mmoles) was added via syringe. The reaction was left to stir overnight at room temperature. The solvent was removed in vacuo to yield a thick yellow (honey-colored) oil (0.315 g, 0.696 mmoles, 78%). 1H-NMR: (400 MHz, Benzene-D6) 0.629 (3H, t), 1.27 (9H, s), 1.5 (6H, s), 1.62 (3H, s), 1.64 (9H, s), 5.4 (2H, s), 6.3 (2H, s), 6.4 (1H, s), 6.9 (1H, d), 7.5 (1H, d).

(PhenNHC)Al(DMF)(Et)Br (3). In a 20 mL vial in the glove box, compound **1** (0.0501 g, 0.0817 mmoles) was dissolved in DMF (1 mL). The reaction was left to stir for 1.3 hrs at room temperature. The solvent was removed in vacuo to yield a yellow (honey-colored) oil (no exact weight recorded to calculate percent yield). 1H-NMR: (400 MHz, Benzene-D6) 0.64 (2H, q), 0.67 (3H, t), 1.28 (9H, s), 1.31 (2H, t), 1.5 (6H, s), 1.62 (3H, s), 1.64 (9H, s), 2.48 (6H, s), 5.4 (2H, s), 6.4 (2H, s), 6.9 (1H, d), 7.5 (1H, d), 9.57 (1H, s).

((PhenNHC)Al(THF)Br)$_2$1,4-butanediol (5). In a 20 mL vial in the glove box, compound **1** (0.0505 g, 0.0826 mmoles) was dissolved in toluene (2.5 mL). 1,4-butanediol (0.0055 g, 0.061 mmoles) was added. The reaction was left to stir for 2 hrs at room temperature. The solvent was evaporated in vacuo to yield a yellow oil (no exact weight recorded to calculate percent yield). 1H-NMR: (400 MHz, Benzene-D6) 1.27 (9H, s), 1.31 (2H, t), 1.5 (6H, s), 1.62 (3H, s), 1.64 (9H, s), 3.5 (2H, t), 4.88 (2H, s), 6.5 (1H, s), 6.9 (1H, d), 7.5 (1H, d), 8.3 (1H, s).

((PhenNHC)Al Br)$_2$1,4-butanediol (6). In a 20 mL vial in the glove box, compound **2** (0.137 g, 0.302 mmoles) was dissolved in toluene (2 mL). 1,4-butanediol (0.0114 g, 0.127 mmoles) was added. The reaction was left to stir for 2 hrs at room temperature. The solvent was removed in vacuo to yield a white solid (0.112 g, 0.12 mmoles, 75.5%). 1H-NMR: (400 MHz, Benzene-D6) 1.27 (9H, s), 1.5 (6H, s), 1.62 (3H, s), 1.64 (9H, s), 5.4 (2H, s), 6.3 (2H, s), 6.4 (1H, s), 6.9 (1H, d), 7.5 (1H, d).

Results & Discussion

- Compound **1** had been made previously in the lab, but polymerization with this catalyst proved unreliable, with apparent decomposition over time. The decomposition of aluminum catalyst **1** could have been caused by the loss of THF, so a series of compounds were made without the THF ligand.

- The resulting compounds were placed in neat caprolactone and heated for half an hour in order to assess their potential as catalysts for the ring-opening polymerization of esters. Comparison of the end group to the repeat unit was used to assess whether polymerization had occurred.
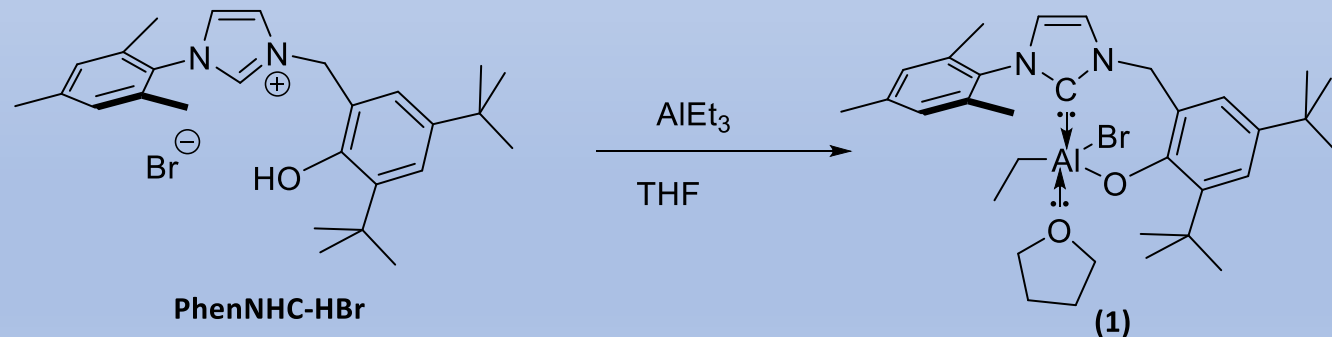
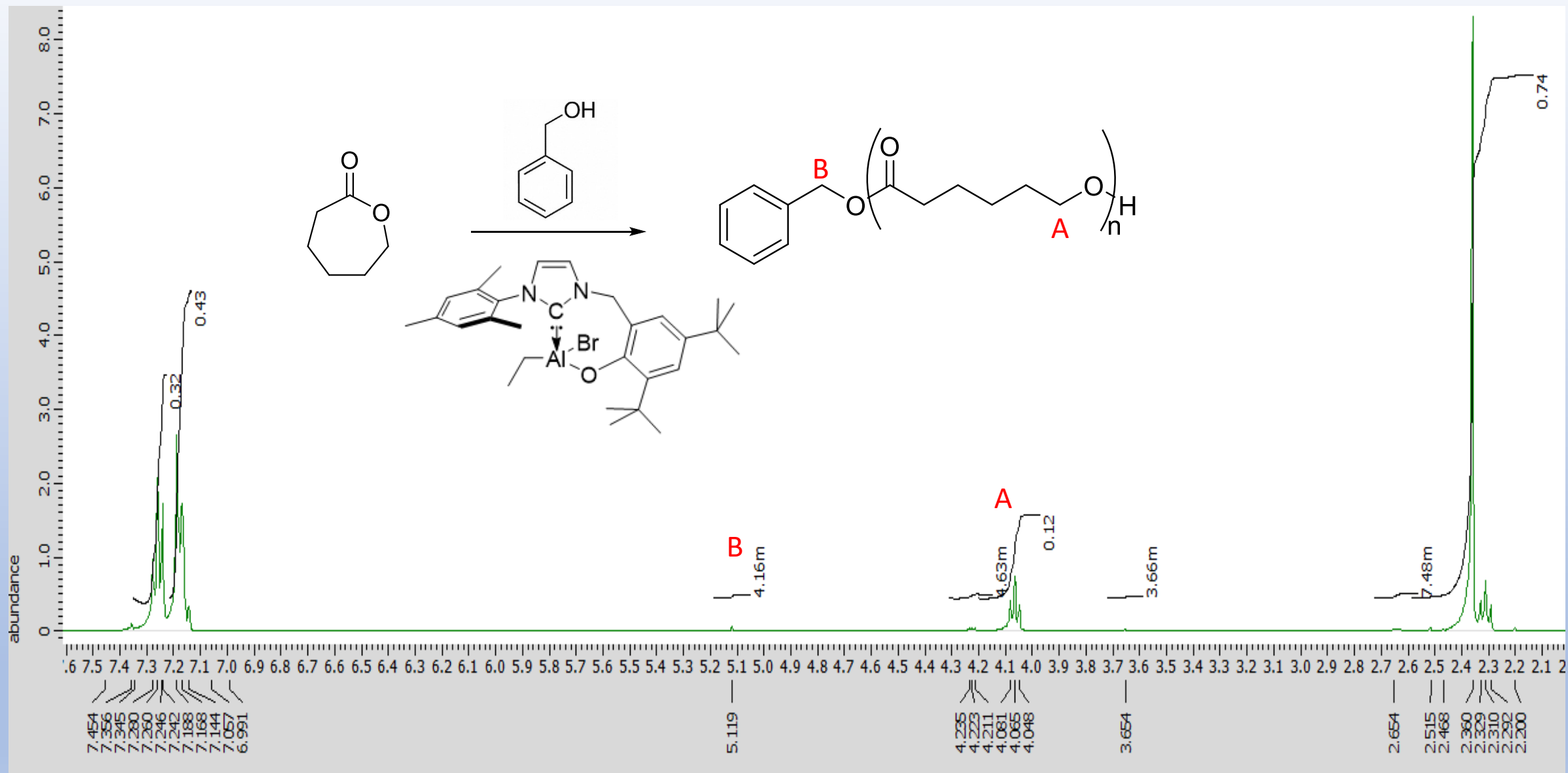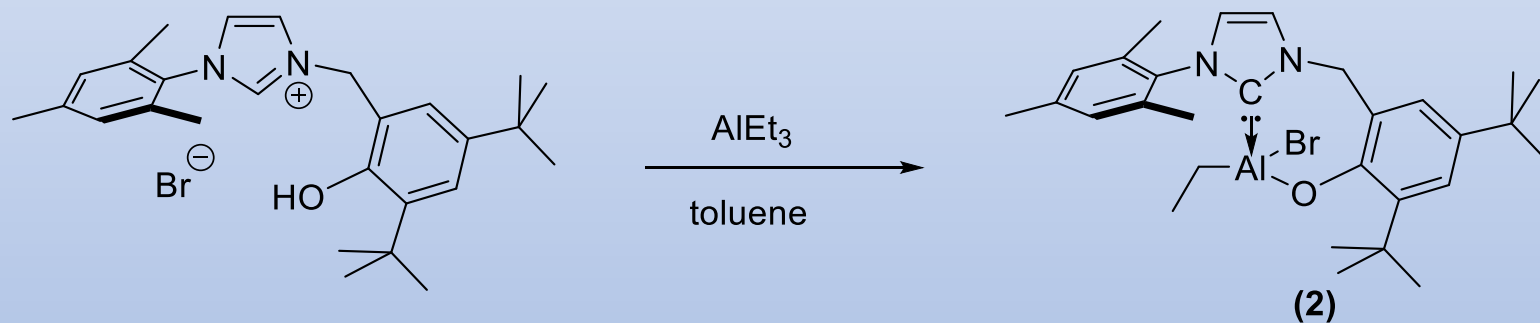**Scheme 2.** Synthesis of Aluminum-based catalyst from imidazolium salt under THF.

Figure 1. ^{1}H-NMR of polycaprolactone made using catalyst **2** and benzyl alcohol as the initiator

- Efforts were made to replace the THF with other solvents such as toluene and DMF to make complexes **2** and **3** respectively**.**

- As shown in Table 1, there was no significant difference in catalyst **3**'s ability to polymerize caprolactone compared to catalyst **1**.

- There is an improvement in catalyst **2**'s ability to polymerize caprolactone.

Scheme 3. Synthesis of aluminum catalyst from imidazolium salt under toluene
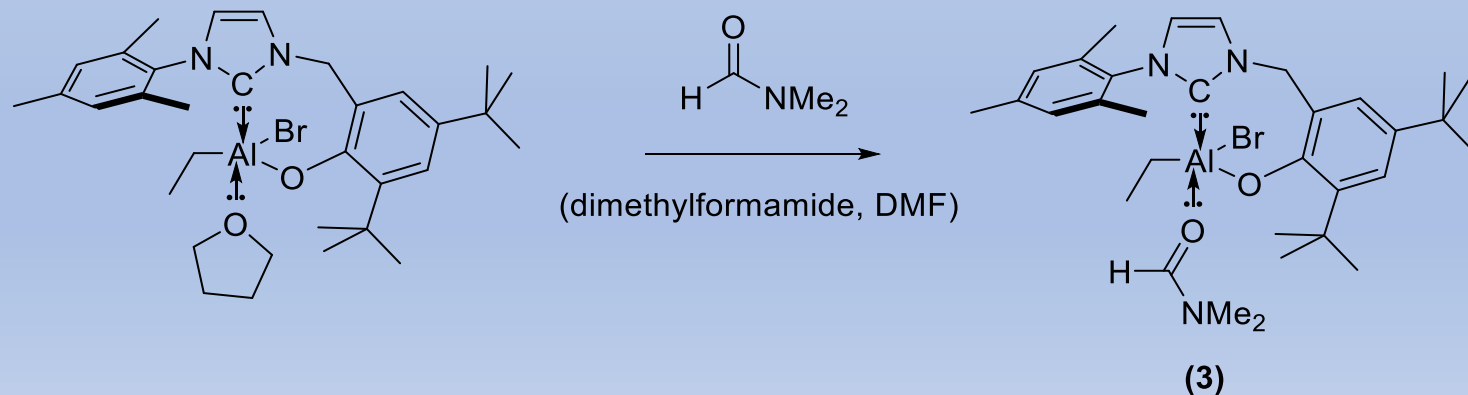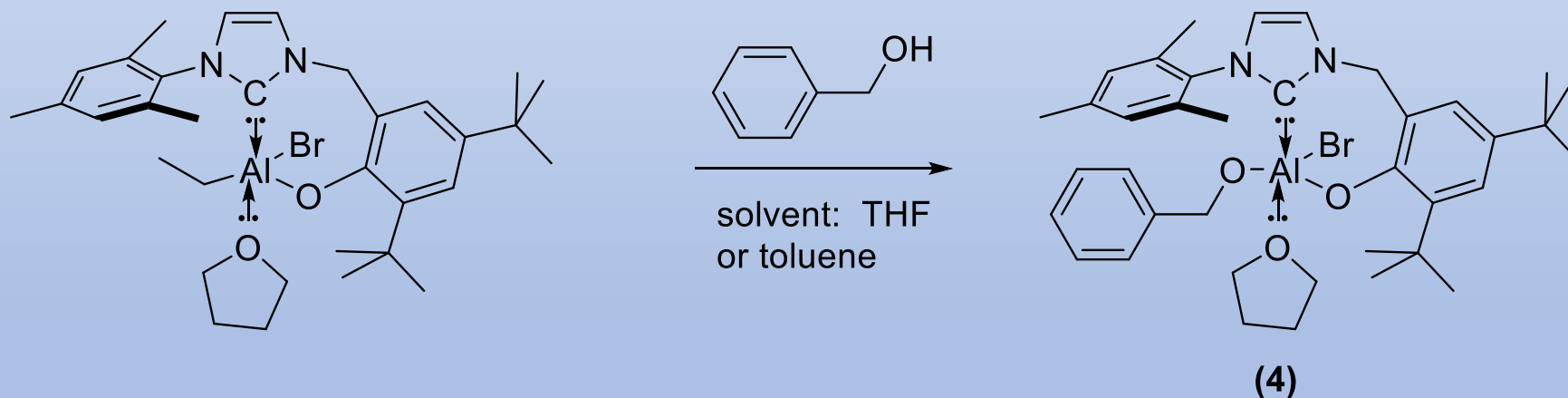
Scheme 4. Replacement of THF ligand with DMF

**Table 1.** Relationship between feed ratio and resulting degrees of polymerization for caprolactone

Catalyst/compound	Initiator	Feed Ratio	Degree of Polymerization (DP)
1	Benzyl Alcohol	23	16
		8	13
2	Benzyl Alcohol	40	35
		36	32
3	Benzyl Alcohol	23	18
		12	2
4	Benzyl Alcohol (embedded)	132	N/A
		125	N/A
5	1,4-butanediol (embedded)	81	80
		122	22
		164	91
6	1,4-butanediol (embedded)	85	87
		169	149
		241	162

- Decomposition could have also been caused by the ethyl ligand undergoing beta-elimination.

- Initiators were incorporated into the catalyst which allowed the ROP to proceed at a much faster rate.

- Benzyl alcohol as the first embedded initiator to make catalyst **4** was unsuccessful in polymerizing as Table 1 shows.


Scheme 5. Replacement of ethyl ligand with benzyl alcohol

- The second initiator that was attempted was 1,4-butanediol to yield compounds **5** and **6**. In this case, incorporation of the diol would allow the formation of a telechelic polymer.

- These resulted in the polymerization of caprolactone at a much shorter time compared to the other catalysts. However, they were still let to run about the same amount of time (~30 minutes).
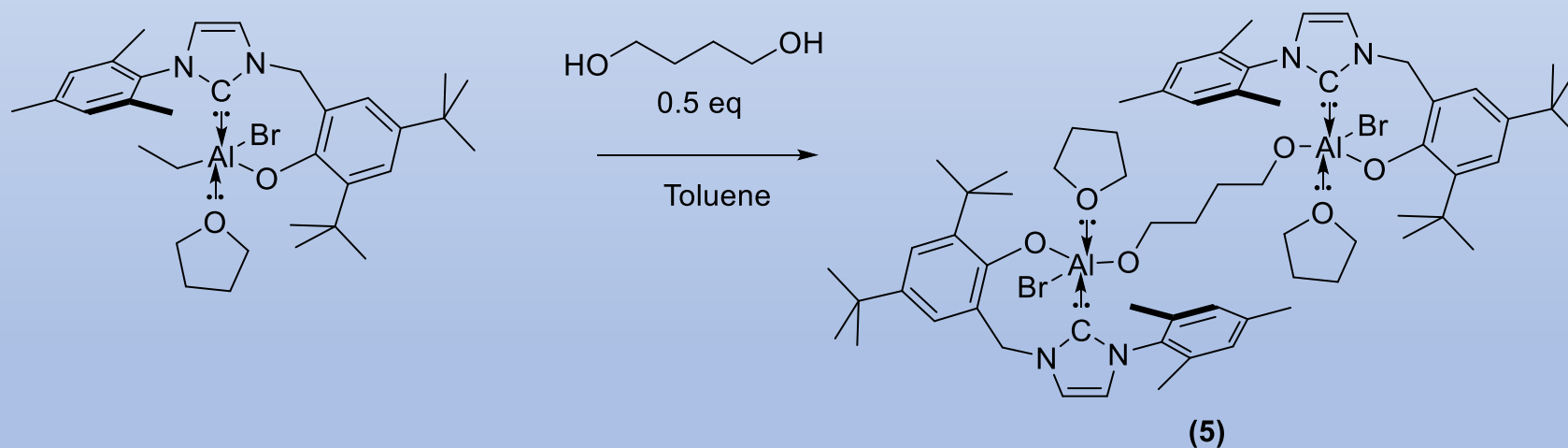
Scheme 6. Incorporation of 1,4-butanediol into catalyst in the presence of THF ligand
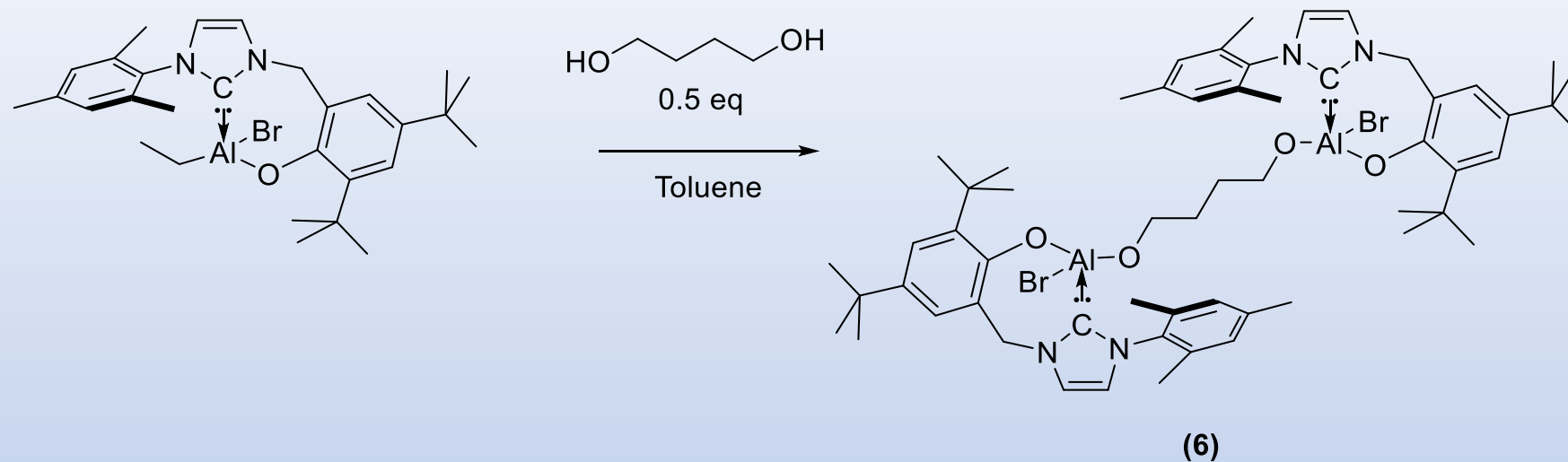
Scheme 7. Incorporation of 1,4-butanediol into catalyst under toluene (absence of THF ligand)

- As Table 1 suggests, there's not a definite control of degree of polymerization.

- It also seems that the higher the feed ratio, the less likely these catalysts can result in matching DP.

- In the future, it should be considered to have feed ratios ranging ~70-140 for catalysts **5** and **6**.

Conclusion and Future Work

- There was improvement in ROP of caprolactone with the use of catalyst **2** while others either worked just as well as the original or not at all.

- The catalyst was successful with 1,4-butanediol initiator once toluene was used as solvent.

- Catalysts synthesized with toluene as solvent show more controlled degrees of polymerization.

- In the future, ROP of caprolactone should be carried out using the modified catalysts to see if they end up decomposing as well since decomposition takes time.

- ROP of other cyclic esters such as lactide and menthide should be explored with developed catalysts.

Acknowledgements

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