DETERMINING THE EFFECTS OF A LEWIS ACID IN THE PRODUCTION OF COPOLYMERS OF ETHYLENE AND METHYL ACRYLATE

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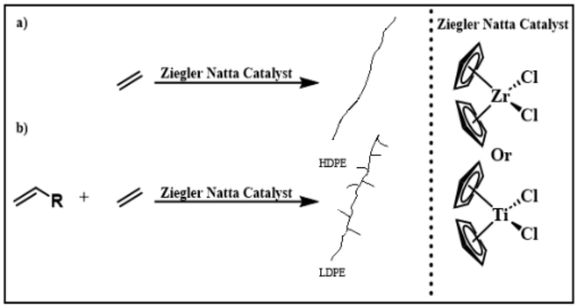
Abstract

Polyethylene (PE) is a ubiquitous polymer with many applications, but there is a constant need to develop new polymers to meet future challenges. Copolymers of ethylene and polar monomers are examples of plastics that are highly sought after to address some of these goals. The Brookhart α-diimine Pd/Ni catalysts have been comprehensively studied to prepare ethylene/methyl acrylate co-polymers. However, low incorporation of the polar monomer remains a challenge due to formation of a stable chelate with the Lewis basic moiety of the polar monomer. To disrupt this resting chelate state, we have installed a pendant Lewis acid on a Brookhart α-diimine type catalyst to establish an intramolecular second coordination sphere to increase polar monomer incorporation in ethylene copolymers. These newly prepared copolymers can then serve as starting points for tailoring post-synthetic modifications to fit emerging industrial needs.

Introduction and Background

Aeronautics is the first "A" in NASA which encompasses space and terrestrial airborne travel. On average, 38 Boeing 737-8 MAX airplanes with an empty weight of 65,952kg are produced a month, which will inevitably consume 2000kg of fuel per hour when flying.[1–3] In aiming to make these flights greener, NASA has recently started the initiative Hi-Rate Composite Aircraft Manufacturing (HiCAM).[4] This project seeks to switch the primary component of plane parts to plastic; reducing the amount of fuel that is required to reach their destinations, by reducing material weight and affording greener air travel.[4]

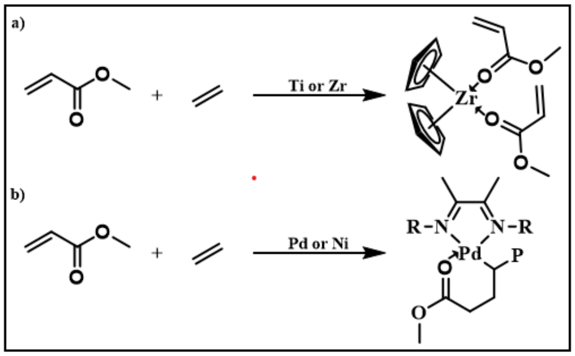
In 2022, 436 million metric tons of different plastic derivatives were traded globally.[5] Of this amount produced, it is estimated that 27% is strictly PE.[6] That is around 117.72 mt of PE plastic being produced worldwide. Commonly, PE plastics fall into one of two categories: high density polyethylene (HDPE) or low density polyethylene (LDPE) (**Scheme 1)**.[7] HDPE is strictly made with ethylene as the monomer, resulting in long straight chain polymers.[8] Conversely, LDPE is routinely made with ethylene and larger α-olefins as comonomers leading to branch points in the polymer backbone.[8] Commercial production of these polymers primarily utilize Ziegler Natta or Phillips catalysts, which account for 90% of the total PE produced globally.[8]



Scheme 1. a) Formation of HDPE from ethylene.[7] b) Formation of LDPE from ethylene and larger α olefin.[7]

However, due to the demands of society for new plastic materials, research in the polymeric field is heavily dominated by producing new materials with divergent properties. One avenue to prepare new polymers for commercial use is to incorporate functional group containing monomers in copolymers as a site for post synthetic modification to occur.[9,10] A particularly attractive plastic for this application is the copolymer of ethylene and methyl acrylate (MA). The incorporation of

MA into PE changes the polymer's characteristics such as glass transition state (Tg), tacticity (t), number-average molecular weight (M_n), and weight average molecular weight (M_w) through funcationalization.[11,12] Unfortunately, utilization of the Ziegler Natta and Phillips catalyst is not possible.[13] The metal center of these catalysts bind to the Lewis basic oxygen within MA diminishing the "living" nature of these polymerizations and hindering further propagation from occurring (**Scheme 2a**).[14] To this end, new catalyst were developed with less oxophilic metal centers in hopes of preventing the diminished reactivity caused by MA addition during polymerization coined as Brookhart-type α-diimine catalysts.[15] Brookhart-type α-diimine catalysts bear nickel and palladium metal centers which have become standard in incorporating MA into PE copolymers.[16] However, it was found that the use of nickel and palladium metal centers still led to limited incorporation of MA, which can be attributed to three key factors: **1)** a continued poisoning of the metal center by the MA, **2)** fast termination reactions, such as β-hydride elimination leading to chain walking, and **3)** chelate formation which blocks coordination sites for further propagation (**Scheme 2b**).[17–19]



Scheme 2. a) Formation of a stable metal chelate on Ziegler Natta catalyst due to methacrylate incorporation.[14] b) Formation of a stable metal chelate on a Brookhart-type α-diimine catalyst due to methacrylate incorporation.[32]

To address these issues, new methodologies focus on ligand design to modify the sterics and electronics of the nickel and palladium metal centers within the catalyst.[19–23] One such ligand design is the phosphine sulfonate class distinguished by a strongly σ donating phosphine moiety and a very weakly σ donating sulfonate moiety (**Figure 1a**).[24] It is generally agreed upon that the nonsymmetric framework of this ligand blocks β-hydride elimination producing linear copolymers of ethylene and MA which bear high mol% of MA.[24,25] However, most of the incorporated MA monomers are found as blocks within the backbone rather than being spread out evenly throughout the polymer.[24] It has also been shown that modified versions of the diimine ligand can influence MA incorporation.[16] The Chen group installed pendant morpholine groups into the backbone of the diimine ligand as a way to initiate a second coordination sphere strategy through a Lewis basic interaction to disrupt chelate formation (**Figure 1b**).[19] The pendant morpholine groups were added to bind to the metal center of the catalyst faster than MA oxygen, but not as quickly as the ethylene.[19] Thereby, limiting chelate formation and inhibiting the rate of β-hydride elimination to prevent undesired branching and termination of the polymer, resulting in higher mol% incorporations of MA.[19] Thus, highlighting a positive correlation in utilizing a second sphere interaction.

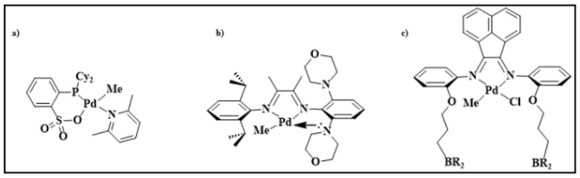
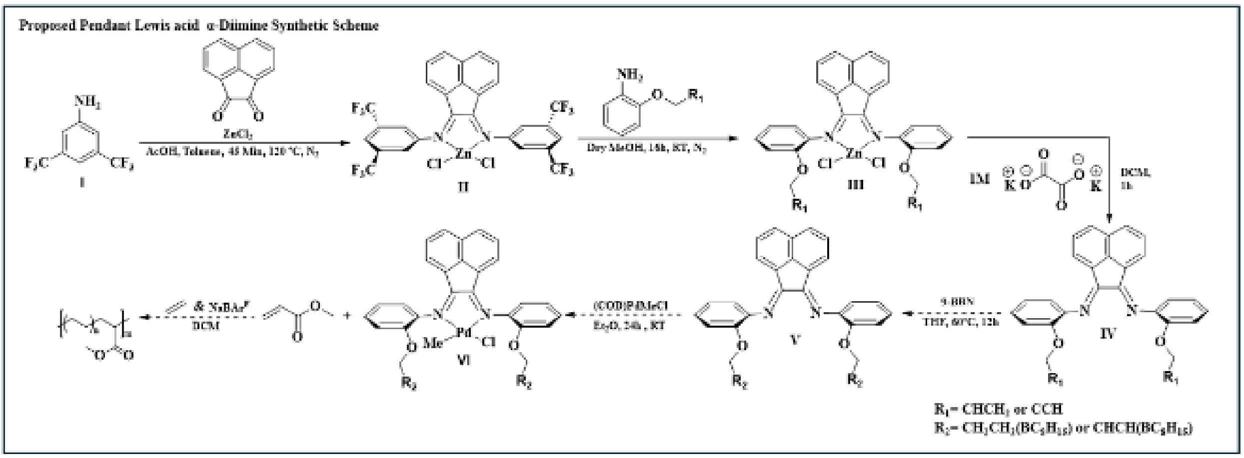


Figure 1. a) The Nozaki phosphine catalyst providing for 50 mol% incorporation of methyl acrylate as linear copolymer.[24] b) Cheng's α-diimine catalysts allowing for 7.5 mol% methyl acrylate at terminal ends of branched copolymer.[19] C) Proposed pendant Lewis acid α-diimine catalysts.

Addition of exogenous Lewis acids has also been studied using these same



Scheme 3. Proposed pendant Lewis acid catalyst synthesis.

catalyst.[26,27] The Harth group investigated the use of excess AlCl$_3$ in solution with a standard iPr-Brookhart diimine catalyst to influence the rate of polymerization intermolecularly.[26] The Lewis acid promoted isomerization of terminal alkenes to internal alkenes in 1-hexene polymerizations, resulting in an increase of branching within the polymer.[26] However, when copolymerizing 1-hexene and polar monomers in the presence of AlCl$_3$ low rates of polar monomer incorporations were observed.[26] Similarly, the Chen group integrated Lewis acid B(C$_6$F$_5$)$_3$ onto a Brookhart diimine ligand to influence the rate of polymerization intramolecularly.[27] However, the B(C$_6$F$_5$)$_3$ was appended as an adduct to a ketone within the ligand preventing additional adduct formation with MA to disrupt any polar monomer chelation due to the boron center already being occupied.[27] Though, the adduct formation near the metal center did allow for long alkyl chain polar monomers to be proficiently incorporated.[27] Here it is **proposed installation of pendant Lewis acidic boron moieties on conventional Brookhart-type α-diimine catalysts will serve as a location for second-coordination-sphere adduct formation to occur between the boron and the oxygen of incorporated MA monomers. This will disrupt the formation of the thermodynamically favored chelate and allow for further propagation and enhanced incorporation of MA within the copolymer (Figure 1c).**

Results and Discussion

Considerable progress has been made towards preparing the pendant Lewis acid Brookhart α-diimine catalyst. First, the scaffolding of the original Brookhart α-diimine catalyst was examined to provide a blueprint for our proposed synthesis scaffolding (**Scheme 3**).[28,29] In designing our aniline for the condensation, the top priority was identifying a substrate which possessed a free olefin as a site to install the boron moiety via a hydroboration. Initial results utilizing ortho alkene functionalities such as 2-vinyl aniline in the traditional pathway proved futile as no diimine was formed; presumably due to reversible hydrolysis of the diimine. However, upon switching to a more amenable ether-based alkene/alkyne moiety on the aniline (**Scheme 3, III**), progress was made leveraging the insolubility of the synthesized diimines in the reaction solvent to prevent any degradation due to hydrolysis. This allowed us to prepare diimine (**IV**) via this condensation pathway. Moreover, the single crystal X-Ray structures

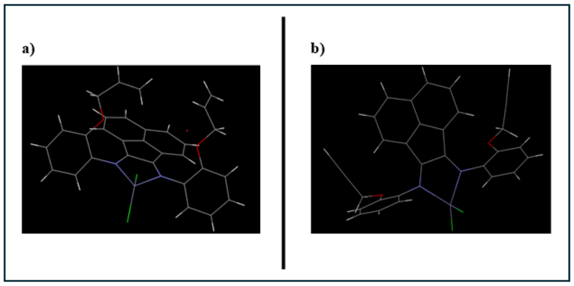


Figure 2. a) Crystal structure of Zn-alkene diimine. b) Crystal structure of Zn-alkyne diimine.

of the Zn-complexes were obtained to verify the exact structure **Figure 2**.

With this ligand and other related variations in-hand, we are now working to carry out hydroboration of the alkene. Initial results indicate that this step is synthetically challenging. However, this reaction is widely used in organic synthesis so many iterations of this process are known and will be screened to successfully obtain the desired hydroborated product (**Scheme 3**).

Conclusions and Future Work

Upon synthesizing the pendant Lewis acid catalyst, progress towards making PE and ethylene/MA copolymers will proceed. It is expected that minimal to no change will be observable when utilizing the pendant Lewis acid to make PE. However, it is proposed that the steric bulk of appended arms of the diimine ligand could influence branching of the produced polymer.[30,31] Brookhart found that changing the size of the aryl groups arms from methyl groups to bulkier isopropyl groups dropped branching of the PE polymer from 106/1000C to 100/1000C (branches per carbons).[30] Akin to Brookhart's findings, the Takeuchi group found that upon moving to an even larger dinuclear α-diimine Pd(II) complex bearing a bridging xanthene diimine ligand branching dropped to as low as 55/1000C.[31]

Conversely when moving into the copolymerization of ethylene and MA, the appended Lewis acid arm should act to disrupt formation of the six membered chelate between the metal center and the MA carbonyl (**Scheme 4**). The appended borons have two modes to disrupt formation of the chelate by adduct formation: **1)** after the olefin of MA has been added into the polymer chain which prevents any kind of chelation, and **2)** when the incorporated MA chelate pops off metal center due to the chelate existing as a reversible thermodynamic equilibrium of 15.2 kcal/mol.[32] Thereby, disrupting the reformation of the chelate and opening a coordination site for continued propagation.

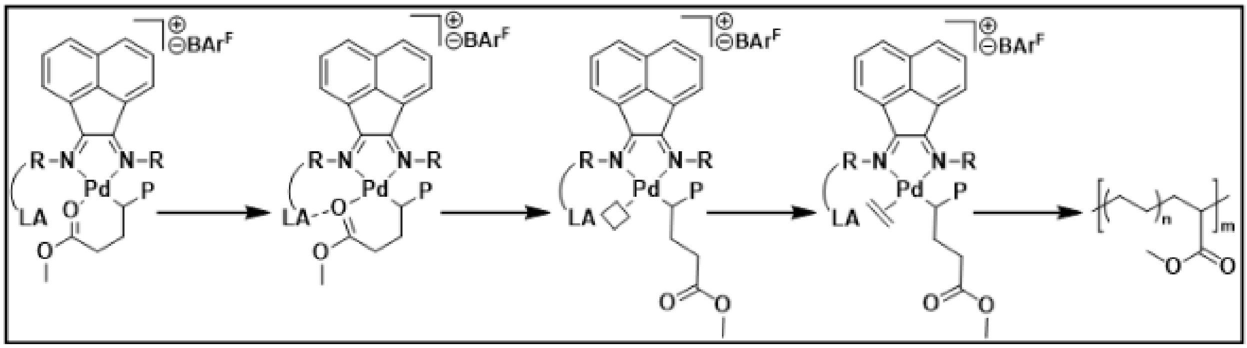
In summary, steps have been taken towards synthesis of a new category of polymerization catalyst to assist in polar monomer incorporation within ethylene polar monomer copolymers. Initial results indicate that traditional α-diimine catalyst synthesis pathways are incompatible when trying to install terminal olefins for hydroboration. However, upon leveraging the solubility of Zn-complexed diimines, the diimine ligands were isolated.

Experimental

General Experimental

General Methods: Unless otherwise stated, all reactions were carried out in oven (130°C) dried glassware under an inert atmosphere using standard Schlenk techniques and conducted at ambient temperature (25°C, rt).

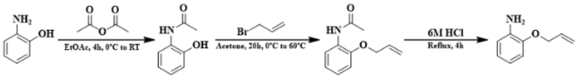
Chemicals: All reagents were used as received from commercial sources without further purification. Unless otherwise stated, all solvents were degassed with nitrogen for 30 minutes before use after being passed through activated alumina columns in a solvent purification system.



Scheme 4. Representative Lewis acid assisted breaking of the metal chelate.

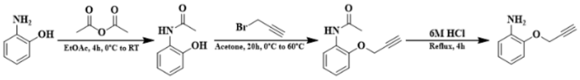
NMR: All 1H NMR and 13C spectra were acquired on either a 400 or 600 MHz Bruker Avance spectrometer. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. Chemical shifts are reported in parts per million (ppm), with the residual solvent protons used as internal calibration standards.

General synthesis of ortho alkene aniline



2-(allyloxy)aniline was synthesized according to literature.[33]

General synthesis of ortho alkyne aniline

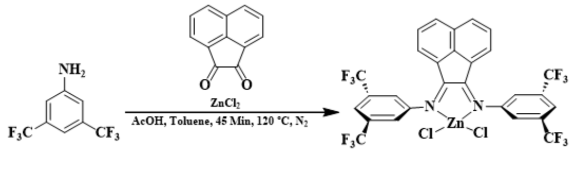


2-(2-Propyn-1-yloxy)benzenamine was synthesized following a modified literature procedure.[33] To a solution of 2-hydroxyacetanilide (2.92 g, 19.3 mmol, 1 eq.) and K_2CO_3 (42.67 g, 19.3 mmol, 1 eq.) in anhydrous acetone (7 mL) was added dropwise Propargyl bromide solution 80 wt. % in toluene (2.23 g, 1.72 mL, 19.3 mmol, 1 eq.) at 0 °C. The mixture was warmed to reflux and stirred for 20 h. The organic phase was extracted with diethyl ether (2× 50 mL), washed with H_2O (50 mL), with a solution of NaOH (10%) and dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography.

A solution of N-(2-(propynoxy) phenyl) acetamide (3.51g, 18.57 mmol, 1 eq.) in 6 M HCl (4.46 mL) was refluxed for 4h. The mixture was basified with 4 M sodium hydroxide solution until pH =14. This basified solution was extracted with EtOAc (2 × 20 mL) and dried over anhydrous Na_2SO_4. The organic solvent was evaporated, and the crude product was purified by flash column chromatography.

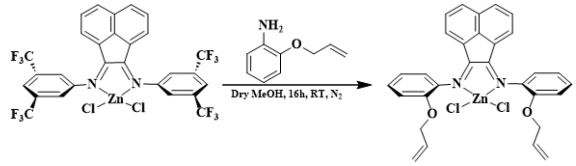
Synthesis of Ligand

CF_3-$ZnCl_2$ BIAN



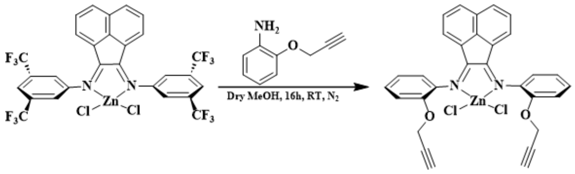
CF_3-$ZnCl_2$ was synthesized according to literature.[34]

Alkoxy-$ZnCl_2$ BIAN



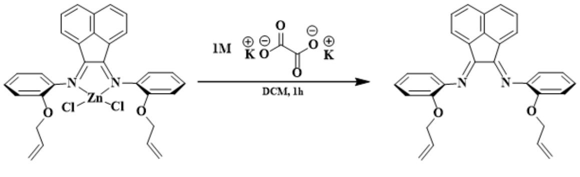
Alkoxy-$ZnCl_2$ BIAN was synthesized following a modified literature procedure. First, solid CF_3-$ZnCl_2$ (2.80 g, 3.78 mmol, 1 eq.) was suspended in dry methanol (20 mL). After that, 2-(allyloxy)aniline (1.69 g, 11.3 mmol, 3 eq.) was added and the mixture was stirred at room temperature for 16h under a nitrogen atmosphere. The orange precipitate was filtered off, washed with diethyl ether, and dried in vaccuo.[35]

Propynoxy-$ZnCl_2$ BIAN



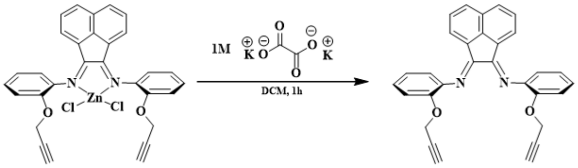
Propynoxy-$ZnCl_2$ BIAN was synthesized following a modified literature procedure. First, solid CF_3-$ZnCl_2$ (2.80 g, 3.78 mmol, 1 eq.) was suspended in dry methanol (20 mL). After that, 2-(2-Propyn-1-yloxy)benzenamine (1.67 g, 11.3 mmol, 3 eq.) was added and the mixture was stirred at room temperature for 16h under a nitrogen atmosphere. The orange precipitate was filtered off, washed with diethyl ether, and dried in vaccuo.[35]

Alkoxy BIAN



Alkoxy BIAN was synthesized following a modified literature procedure. First, Alkoxy BIAN (0.32 g, 0.55 mmol, 1 eq.) was suspended in 11 mL dichloromethane and 1M potassium oxalate. The mixture was stirred for an hour. The organic layer was extracted with H_2O and brine, dried over $MgSO_4$, and dried in vaccuo.[35]

Propynoxy BIAN



Propynoxy BIAN was synthesized following a modified literature procedure. First, Propynoxy BIAN (0.32 g, 0.55 mmol, 1 eq.) was suspended in 11 mL dichloromethane and 1M potassium oxalate solution (3 mL). The mixture was stirred for an hour. The organic layer was extracted with H_2O and brine, dried over $MgSO_4$, and dried in vaccuo.[35]

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