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Enhancing α-Diimine Catalysts for High-Temperature Ethylene Polymerization

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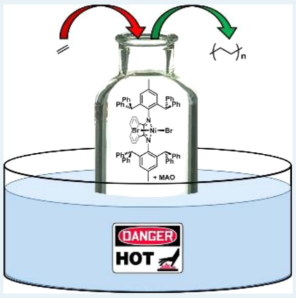
Supporting Information

ABSTRACT: Sterically demanding 2,6-bis(diphenylmethyl)-4-methylaniline was condensed onto acenaphthenequinone via an aminoalane intermediate and metalated using nickel(II) dibromide dimethoxyethane adduct to yield bis[(2,6-dibenzhydryl-4-methylimino) acenaphthene]dibromo nickel(II). This α-diimine precatalyst was examined for high-temperature ethylene polymerization and proved to be thermally robust at temperatures as high as 90 °C, demonstrating enhanced activity as compared with related catalysts. Furthermore, the resultant polymers displayed increased melting transitions as compared with those produced using catalysts with identical *N*-aryl moieties appended to nonacenaphthenequinone-derived ligand backbones.



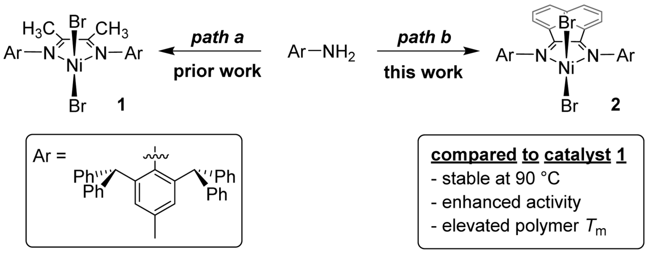
KEYWORDS: *polyethylene, nickel, α-diimine, catalysis, high temperature, coordination polymerization*

Annually, polyolefins account for over 50% of the polymers produced within the United States, providing affordable alternatives to traditional materials, such as wood, metal, and glass.[1] Ziegler and Natta originally pioneered the field of olefin polymerization with the development of heterogeneous group IV catalysts; however, the development of homogeneous, single-site catalysts has since revolutionized the field, enabling researchers to gain greater mechanistic understanding, to enhance catalytic control, and to produce designer polyolefins.[2] During this period, perhaps one of the most pivotal advancements was the development of late-transition metal-based catalysts by Brookhart and co-workers. These Ni- and Pd-based catalysts permitted the incorporation of polar comonomers[3] and have facilitated the production of high-molecular-weight polyethylene with topologies ranging from highly linear to hyperbranched.[4]

One of the most widely studied classes of Ni- and Pd-based catalysts is those bearing α-diimine ligands, and despite their numerous potential advantages, a major impediment to their commercialization has been their poor thermal stability at the elevated temperatures required for industrially used gas-phase polymerizations (70−110 °C).[5] To address this, many studies have been published concerning the elucidation of α-diimine derived catalyst's decomposition pathways; however, their full extent is not completely understood.[6] As an example, cationic Pd-based catalysts are known to rapidly undergo C−H activation of their ligand substituents, potentially hindering further polymerization.[7]

Advancements in Ni and Pd α-diimine catalysts' thermal stability have been reported through various modifications of ligand backbone and *N*-aryl substituents.[8] For example, catalysts bearing camphorquinone-derived ligands have shown moderate stability up to 80 °C,[9] whereas *N*-aryl modifications, such as the use of cyclophane-based ligands, have resulted in catalysts with high turnover frequencies and enhanced thermal stability.[10] More recently, benzhydryl-derived ligand frameworks were investigated,[11] and in an effort to further advance this area, we have reported the use of Ni-based catalyst **1**, which demonstrated exceptional thermal stability (Scheme 1).[12] This catalyst was readily synthesized from inexpensive, commercial starting materials, demonstrated impeccable thermal stability up to 90 °C, and produced polyethylene molecular weights exceeding 500 kg/mol. To the best of our knowledge, this catalyst represents the most thermally stable α-diimine-based catalyst reported to date.

Scheme 1. Development of Sterically Encumbered Precatalysts



Encouraged by these results, we began to further investigate the effects that ligand backbone structure have on this class of sterically encumbered catalysts, placing emphasis on enhancing polyethylene melting temperatures and mechanical properties, improving catalytic activity, and increasing or maintaining thermal stability. To accomplish this, we sought to utilize the

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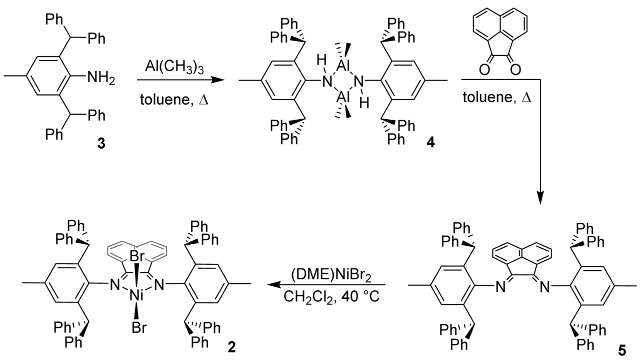
popular acenaphthene-based backbone; however, at the conclusion of our previous report, we were unable to successfully condense 2 equiv of 2,6-bis(diphenyl-methyl)-4-methylaniline onto acenaphthenequinone using common synthetic methodologies. More recently, we have discovered that conversion of this bulky aniline derivative into an aminoalane intermediate provides a useful strategy to overcome this limitation.[9] Thus, we herein report the synthesis, activity, and stability of bis[(2,6-dibenzhydryl-4-methylimino)-acenapthene]dibromo nickel(II) (**2**) for the polymerization of ethylene at elevated temperatures (Scheme 1).

Initial strategies to condense 2 equiv of aniline derivative **3** onto acenaphthenequinone via acid-catalyzed routes yielded only monocondensed products, which was consistent with previous literature reports.[11c,13] Attempts using the "template method" of Rosa and co-workers, which has been used with other sterically hindered diimines, also exclusively formed singly condensed monoimine product.[14] Ultimately, the synthesis of diimine ligand **5** was realized in ~10% yield via reaction of **3** with trimethylaluminum to form aminoalane **4**, followed by subsequent addition of acenaphthenequinone (Scheme 2). This methodology relies on the thermodynamic driving force of Al−O bond formation and has been previously used for the formation of *α*-diimine ligands bearing electron-deficient *N*-aryl substituents, as well as with sterically encumbered diimine backbones.[15] Last, ligand **5** was metalated using nickel(II) dibromide dimethoxyethane adduct to form precatalyst **2**.[16]

Scheme 2. Synthesis of Precatalyst 2



Ethylene polymerizations with precatalyst **2** were performed using polymethylaluminoxane-improved performance (PMAO-IP) (a product of Akzo Nobel) as an activator. Initial studies using low ethylene pressure (15 psi) revealed that high-molecular-weight material could be obtained with consistently low molecular weight distributions across a wide range of temperatures (M_w/M_n = 1.11−1.33) (Table 1). Low-temperature polymerizations (Table 1, entry 1) produced highly linear polyethylene, as evidenced by differential scanning calorimetry measurements (T_m = 127 °C), and as the reaction temperature was increased, the resultant polyethylene showed a correlated and expected decrease in the melting temperature due to the increased extent of chain-walking.

To further investigate catalyst stability at elevated temperatures and ethylene pressures, polymerizations were conducted from 80−100 °C at 100 psi of ethylene pressure (Table 2). The molecular weight of the resultant polymers reached ~500 kg/mol, with the highest molecular weights observed at 80 and 90 °C after 20 min of polymerization (Table 2, entries 4 and 8).[17] The molecular weight distributions observed were relatively narrow ($M_w/M_n \leq 1.82$) and the polymers displayed higher melting transitions than those obtained with catalyst **1** (58−67 °C vs 37−46 °C), suggesting a decrease in branching content. This was quantitatively confirmed by NMR spectroscopy, which showed that polymers produced using catalyst **2** contained 43−60 branches per 1000 carbons as opposed to catalyst **1**, which produced 63−75 branches per 1000 carbons. In addition, the polymers produced using catalyst **2** contained mostly methyl branches (see Supporting Information), which is consistent with results obtained using catalyst **1**.

Table 1. Low Pressure Ethylene Polymerizations Using Catalyst 2.[a]

entry	T_{rxn} (°C)	yield (mg)	TOF[b] (h^{-1})	M_n[c] (kg/mol)	M_w/M_n[c]	T_m[d] (°C)
1	−40[e]	64	463	74	1.27	127
2	−20	31	901	35	1.33	112
3	0	29	843	58	1.13	92
4	20	82	2352	85	1.10	83
5	40	181	5198	78	1.17	74
6	60	151	4340	85	1.11	67
7	80	287	8256	102	1.33	54
8	100	193	5557	64	1.32	53

[a]Polymerization conditions: [**2**] = 5.0 μmol, 100 mL of toluene, 15 psi, 15 min, and 100 equiv of PMAO-IP. [b]Turnover frequency (TOF) = mol of ethylene/(mol of cat. × h). [c]Determined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene. [d]Determined by differential scanning calorimetry, second heating. [e]60 min.

Unlike catalyst **1**, which produced polyethylene with molecular weights up to 600 kg/mol,[12] lower molecular weight material was obtained using catalyst **2** at 90 °C (491 kg/mol). This strongly indicated that although still catalytically active, chain transfer may have occurred to a greater extent, thereby limiting ultimate molecular weights. This hypothesis was further supported by the observation of moderately broadened molecular weight distributions as compared with those obtained when using catalyst **1**. This result was not surprising because catalysts bearing alkyl backbones have been shown to produce higher-molecular-weight polymers, and it is consistent with previous investigations into backbone effects on polymerization activity and behavior.[6a,9]

The plot of turnover frequency (TOF) versus time for catalyst **2** clearly indicates that at 100 °C, the catalyst begins to decompose, showing a 15% decrease in turnover frequency after just 10 min (Figure 1a).[18] However, the activity of catalyst **2** remained constant at 80 and 90 °C and displayed TOFs ~1.4 times greater than those observed for catalyst **1**. Similarly, a plot of productivity versus time (Figure 1b) showed a linear increase in productivity at 80 and 90 °C, whereas after only 10 min at 100 °C, the productivity of catalyst **2** decreases, as evidenced by its decreased slope. These data clearly indicate that the acenaphthyl-based catalyst **2** does *indeed* demonstrate higher TOFs while maintaining thermal stability up to 90 °C. In addition, higher polyethylene melting temperatures and lower branching content was observed for catalyst **2** than was witnessed using catalyst **1**.

In conclusion, the use of synthetically simple dibenzhydryl as ortho *N*-aryl substituents on nickel(II) *α*-diimine catalysts **1** and **2** has been shown to impart remarkable thermal stability. Similarly to catalyst **1**, catalyst **2** displayed impeccable thermal stability up to 90 °C. However, in contrast, catalyst **2** does exhibit TOFs 1.4 times greater than catalyst **1**, produced

Table 2. High-Temperature Ethylene Polymerizations Using Catalyst 2[a]

entry	T_{rxn} (°C)	time (min)	yield (mg)	TOF[b] (× 10^3 h^{-1})	M_n[c] (kg/mol)	M_w/M_n[c]	T_m[d] (°C)	branches/1000 carbons[e]
1	80	5	327	97	287	1.25	66	43
2	80	10	740	105	392	1.43	67	43
3	80	15	1063	105	514	1.59	66	47
4	80	20	1481	111	534	1.70	63	45
5	90	5	442	132	269	1.41	62	49
6	90	10	779	116	409	1.56	64	46
7	90	15	1086	108	489	1.56	62	61
8	90	20	1633	123	491	1.71	60	53
9	100	5	453	135	260	1.45	59	52
10	100	10	904	135	314	1.66	60	56
11	100	15	1203	119	329	1.78	58	56
12	100	20	1520	114	354	1.82	58	51

[a] Polymerization conditions: [2] = 1.4 μmol, 100 mL of toluene, 100 psi, and 400 equiv of PMAO-IP. [b] Turnover frequency (TOF) = mol of ethylene/(mol of cat. × h). [c] Determined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene. [d] Determined by differential scanning calorimetry, second heating. [e] Determined using ^{1}H NMR spectroscopy.

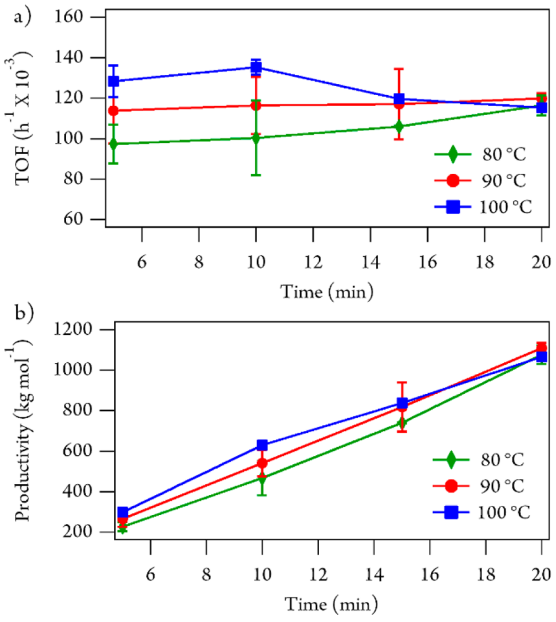


Figure 1. Plots of (a) turnover frequency (TOF) versus time and (b) productivity versus time for catalyst **2** at 80 °C (green), 90 °C (red), and 100 °C (blue).

polyethylene with melting temperatures increased by ~20 °C, and yielded fewer branches per 1000 carbons than polymers made with catalysts bearing alkyl substituted backbones.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of **2** and **5** and all high temperature polymerization data points. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) Attempts to grow single crystals were unsuccessful; however, the precatalyst was characterized by elemental analysis, see the SI.

(17) Similarly to catalyst 1, polymerization reactions extending beyond 20 min were performed; however, precipitation of polymer from solution became problematic, hindering reproducibility and making TOF and productivity calculations unreliable.

(18) Several polymerization at each data point were run, and the average with standard deviation are reported in the plots.