ACS Catalysis
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Iron-Catalyzed Chain Growth of Ethylene: In Situ Regeneration of $ZnEt_2$ by Tandem Catalysis

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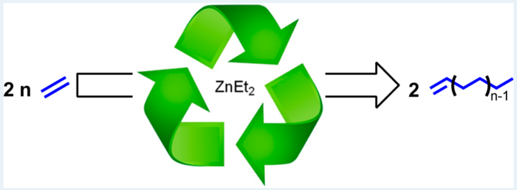
Ⓢ *Supporting Information*

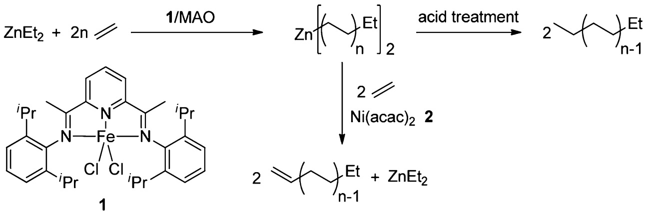
ABSTRACT: A dual catalyst system to implement in situ regeneration of $ZnEt_2$, the Chain Transfer Agent (CTA) in Catalyzed Chain Growth of ethylene (CCG), has been demonstrated. As in typical CCG systems, an Fe homogeneous catalyst is used to grow oligomeric chains that transfer rapidly to $ZnEt_2$. However, rather than liberating alkane products and destroying the expensive chain transfer agent via acid hydrolysis workup, a second Fe-alkyl catalyst, $(BiPy)_2FeEt_2$, has been introduced to regenerate $ZnEt_2$ via ethyl/alkyl exchange and liberate the oligomer chains as α-olefins via ß-hydride elimination. This improvement reduces the $ZnEt_2$ loading and leaves the chain growth catalyst competent, in contrast to $Ni(acac)_2$ shown to be unsuitable for in situ tandem catalysis. These findings greatly enhance the industrial viability of the chemistry.



KEYWORDS: *catalyzed chain growth, chain transfer, α-olefins, ethylene polymerization, tandem catalysis*

Remarkable control over polyolefins' microstructures, molecular weights, and polydispersity has been achieved due to the development of single-site polymerization catalysts.[1] Catalyzed chain growth (CCG) of ethylene and/or α-olefins offers such control, leading to polyolefin materials described by Sita as precision hydrocarbons (PHCs) with a broad range of potential commercial applications such as the production of lubricant base oils.[2a] Such a reaction proceeds via chain growth on main group alkyls (MgR_2, ZnR_2, AlR_3) catalyzed by lanthanide or transition metal complexes.[2] The bis(imino)-pyridine iron-(II) dichloride complex **1**, in combination with methylaluminoxane (MAO) as cocatalyst, was reported by Gibson to be highly active in the CCG reaction of ethylene with $ZnEt_2$ as chain transfer agent (CTA) (Scheme 1).[3] The reaction afforded a Poisson distribution of $Zn(oligomer)_2$ products, which after hydrolysis, yielded linear alkanes centered at C_{50}. Alternatively, a Poisson distribution of linear α-olefins was produced via a nickel-catalyzed chain displacement reaction from $Zn(oligomer)_2$. Despite great potential, this process comes with several hurdles to overcome. Importantly, the tandem chain growth/displacement experiment requires deactivation of the chain growth catalyst, **1**/MAO, prior to chain displacement and liberation of α-olefins.[3,4]

Scheme 1. Catalyzed Chain Growth of Ethylene on Zinc



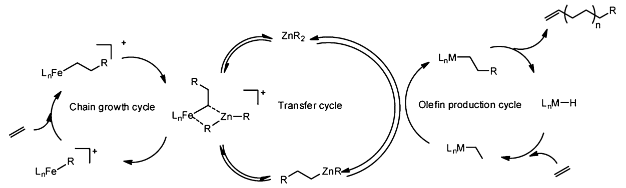
Furthermore, the use of stoichiometric amounts of expensive $ZnEt_2$ renders a potential process prohibitively expensive. An alternative to using smaller amounts of the CTA has been shown by Sita, who reported the synthesis of PHCs using a ternary living coordinative chain polymerization based on the combination of $ZnEt_2$ and Al^iBu_3 CTAs catalyzed by a hafnium catalyst. Chains are transferred rapidly and reversibly between Zn and Al centers allowing for the use of $ZnEt_2$ in amounts as low as 2 equiv/catalyst, although a large stoichiometric excess of aluminum alkyls is required.[2a,5] Another significant development in controlling the microstructure of polyolefins is the report of chain shuttling between two group IV olefin polymerization catalysts by Dow scientists, who leveraged chain transfer chemistry for the production of ethylene/α-olefin block copolymers (OBCs).[6] This process involves $ZnEt_2$ as the Chain Shuttling Agent (CSA) and is used for ethylene/1-octene copolymerization to afford block copolymers.

In order to circumvent the challenges of the Fe-catalyzed chain growth of ethylene, we envisioned the use of a dual catalyst system able to regenerate $ZnEt_2$ in situ without deactivation of the chain growth catalyst **1**, akin to Dow's chain shuttling process. However, our approach differs from that of Dow in the use of a catalyst effective in ß-hydride elimination and inactive in olefin polymerization. The one pot tandem catalytic cycle involves catalyzed chain growth (chain growth/chain transfer cycle) followed by an olefin production cycle (Scheme 2). As for CCG, the olefin production cycle relies on

Received: June 12, 2015
Published: June 17, 2015

DOI: 10.1021/acscatal.5b01231
ACS Catal. 2015, 5, 4363−4367

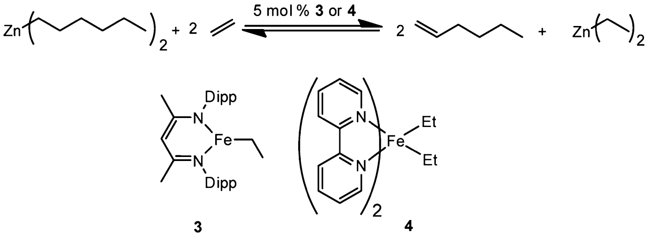
Scheme 2. One-Pot Tandem Catalytic Cycle



efficient chain transfer between Zn(oligomer)$_2$ and a M-Et species to give $ZnEt_2$ and M-oligomer, which readily releases the chain as an α-olefin via ß-H elimination and generates a M-H intermediate. Ethylene insertion into the M-H bond reforms the M-Et species, thus closing the cycle.

Previous reports have shown that efficient chain transfer between Fe and Zn species is governed by steric hindrance at the Fe center, as well as matching Zn−C and Fe−C bond strength.[4,7] Hence, two Fe-based organometallic complexes, NacNacFe-Et **3**,[8] and (Bipy)$_2$FeEt$_2$ **4**,[9] were selected for investigation as "transfer" catalysts. Before attempting catalysis, we investigated whether efficient chain transfer would occur between a ZnR_2 species and the selected "transfer" catalysts **3** or **4**. Accordingly, the complexes were tested in a chain displacement experiment with dihexylzinc under an ethylene atmosphere (Scheme 3) and monitored by ^{1}H NMR spectroscopy.

Scheme 3. Dihexylzinc Chain Displacement Probe Reaction Using 3 and 4 as Catalysts



Upon mixing dihexylzinc with 5 mol % of the paramagnetic complex **3** in C_6D_6, no change in the ^{1}H NMR spectrum was observed apart from broadening of the peaks. Upon exposure to ethylene, no reaction was observed after 2 h at room temperature. After heating the sample at 60 °C for 13 h, ethylene was consumed, and new broad peaks in the olefinic region (4−6 ppm) were observed.[10] Note that the starting catalyst **3** was still present in solution, indicating no apparent decomposition during the test experiment. Volatiles were vacuum transferred to another NMR tube and ^{1}H NMR spectroscopy indicated the presence of 1-hexene, which was also confirmed by GC analysis.[10] This result indicated that chain transfer occurred between the Fe and Zn species; however, elevated temperature was necessary to afford the α-olefin product most likely due to increased stability of the Fe-alkyl species. Indeed, NacNac ligands have been shown to stabilize highly reactive species.[11] Complex **4** is conveniently diamagnetic and allowed the reaction to be monitored by ^{1}H NMR spectroscopy. Upon mixing dihexylzinc with 5 mol % of **4** in C_6D_6, an upfield shift from 0.28 to −0.28 ppm was observed for the methylene protons on the carbon α to the Zn center (Figure 1). Exposing the solution to an ethylene atmosphere at room temperature resulted in ethylene consumption and appearance of olefinic protons at 4.99 and 5.76 ppm consistent with the formation of 1-hexene. In addition, a new broad peak was observed at −0.61 ppm.[10] Equilibrium conversion was reached within 42 h under these conditions and indicated that chain transfer of hexyl and ethyl chains occurred between the Zn and Fe centers, and implying that $ZnEt_2$ was regenerated (Figure 2).

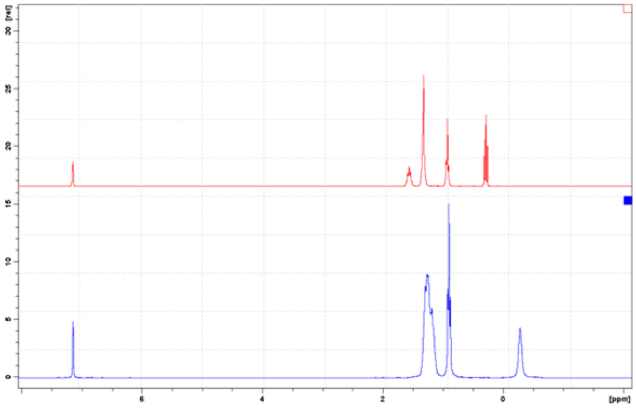


Figure 1. ^{1}H NMR spectra (C_6D_6, 300 MHz) of dihexylzinc (top) and in the presence of 5 mol % of **4** (bottom).

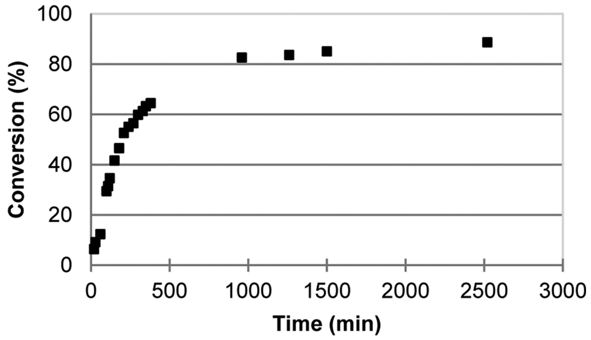
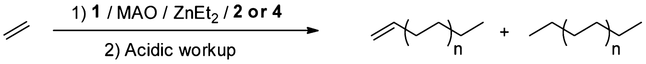


Figure 2. Conversion vs time plot of chain displacement of dihexylzinc catalyzed by 5 mol % of **4** under ethylene atmosphere.

On the basis of these observations, we decided to test **4** in catalysis by adding it to the typical Fe-catalyzed chain growth system. First, a typical chain growth experiment using, **1**/MAO/$ZnEt_2$, was carried out according to the established procedure reported by Gibson.[3] After 30 min, this procedure afforded a Poisson distribution of alkanes centered at C_{46} upon workup with acidified methanol (Table 1, Entry 1). Note that alkanes are generated upon acidic workup of the Zn-alkyls produced during the reaction. Upon repeating the reaction in the presence of 0.5 mol % of **4** relative to $ZnEt_2$, only liquids were formed, and no solids precipitated upon acidic methanol workup at the end of the reaction (Table 1, Entry 2). This result was in stark contrast to the benchmark experiment described above. The reaction was monitored over the period of 30 min by sampling at regular time intervals, with aliquots quenched in aqueous HCl and filtered through alumina prior to GC analysis while using nonane as internal standard.

GC analyses showed the presence of both alkanes and α-olefins and that over time the concentration of α-olefins increased at the expense of the concentration of alkanes (Figure 3a), indicating that tandem catalysis occurred. After 30 min, the product distribution consisted of 77 mol % α-olefins with a distribution centered at C_8. The aim of regenerating and

Table 1. Tandem Catalysis Experiments



entry	chain growth catalyst	transfer catalyst	$ZnEt_2$ (eq)[d]	toluene soluble fraction: yield (center of distribution[e])	toluene soluble fraction: α-olefin (mol %)[e]	toluene insoluble fraction: yield (center of distribution[e,f])	toluene insoluble fraction: α-olefin (mol %)[e,f]	activity (g/mmol/h)
1[a]	1	-	500	-	-	4.1 g (C_{46})	nd	1640
2[a]	1	4	500	1.14 g (C_8)	77	-	-	456
3[a]	1	4	250	1.09 g (C_8 + C_{18})	93	0.30 g (C_{24})	99+	556
4[a]	1	4	100	0.38 g (C_8)	94	0.87 g (C_{30} + C_{44})	80	500
5[a]	1	2	500	0.33 g (C_8)	16	3.3 g (C_{46})	nd	1452
6[b]	1	4	500	0.23 g (C_{20})	63	3.39 g (C_{50})	40	1448
7[c]	1	-	500	0.38 g[g]	-	-	-	152
8[a]	1	4	0	-	-	0.60 g (PE)	-	240

[a] Conditions: **1** (5 μmol), **4** or **2** (12.5 μmol), toluene (45 mL), MAO/**1** = 100, 30 min, C_2H_4 = 5 psig, reaction carried out for 30 min without temperature control followed by quenching with acidified methanol. [b] Conditions: **1** (5 μmol), **4** (5 μmol), toluene (45 mL), MAO/**1** = 100, 30 min, C_2H_4 = 5 psig reaction carried out for 30 min without temperature control followed by quenching with acidified methanol. [c] Conditions: **1** (5 μmol), bipyridine (12.5 μmol), toluene (45 mL), MAO/**1** = 100, 30 min, C_2H_4 = 5 psig reaction carried out for 30 min without temperature control followed by quenching with acidified methanol. [d] Equivalents relative to chain growth catalyst **1**. [e] Determined by GC. [f] Determined by ^1H NMR in d_{10}-xylene. [g] Schulz–Flory distribution.

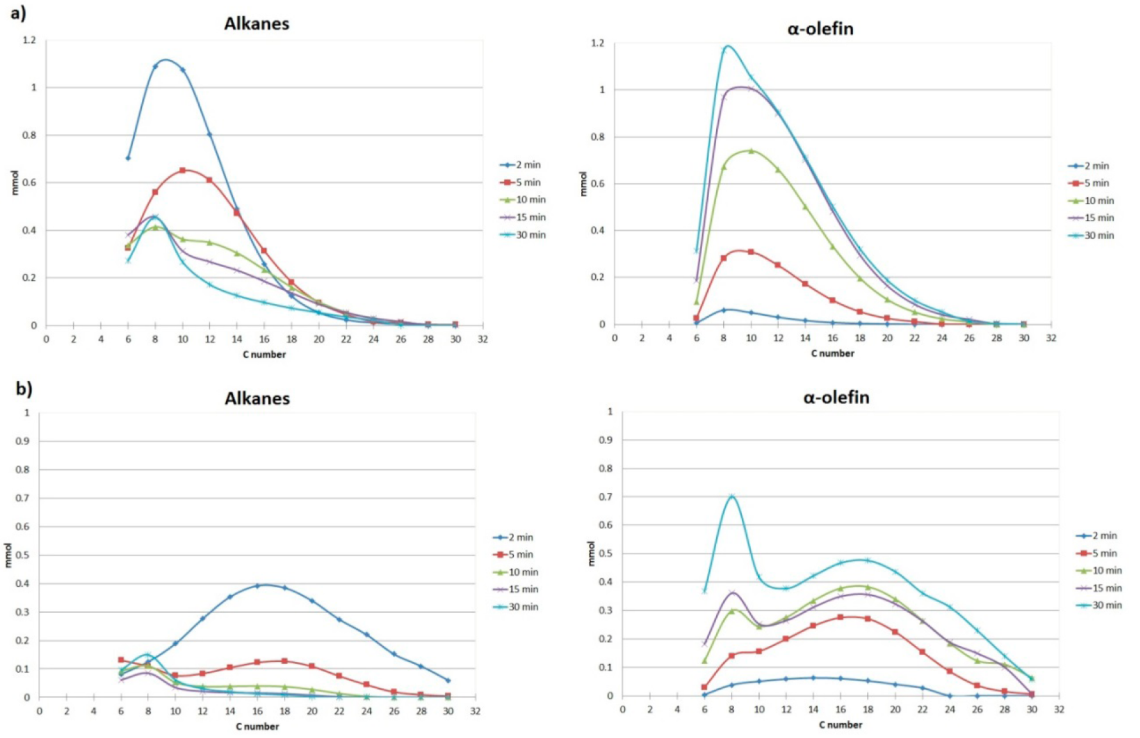


Figure 3. Alkanes and α-olefin distribution obtained from tandem catalysis experiments at the indicated time intervals: (a) Entry 2, 500 equiv of $ZnEt_2$ (b) Entry 3, 250 equiv of $ZnEt_2$.

recycling $ZnEt_2$ in situ is to decrease the amount of this expensive reagent required during catalysis, thus the amount of $ZnEt_2$ was halved to 250 equiv relative to **1** and resulted in a similar behavior (i.e., increase of α-olefins concentration at the expense of alkanes; Table 1, Entry 3). Most importantly, a bimodal distribution of α-olefins appeared over time, indicating that the regenerated $ZnEt_2$ re-entered the catalytic cycle (Figure 3b). Toluene insoluble solids recovered (0.30 g) upon quenching at the end of the reaction were analyzed by GC and NMR spectroscopy. High-temperature GC analysis of the solids revealed a Poisson distribution centered at C_{24}, while ^1H NMR spectroscopy indicated chains contained olefinic and methyl end groups confirming chain transfer and release of the chain via ß-H elimination.[10] Further lowering of the $ZnEt_2$ loading to 100 equiv relative to **1** increased the amount of solids to 0.87 g (Table 1, Entry 4) upon quenching. ^1H NMR analysis indicated a C_{38} average distribution consisting of 80 mol % α-olefin. Interestingly, high temperature GC analysis of the solids revealed a bimodal distribution with peaks centered at C_{30} and C_{44} (Figure 4). GC analysis of the toluene soluble fraction only shows traces of alkanes, and a C_8 centered α-olefins distribution.[10]

The original reports from Gibson indicate that $Ni(acac)_2$, **2**, can regenerate $ZnEt_2$ only following catalyst deactivation.[3,4]

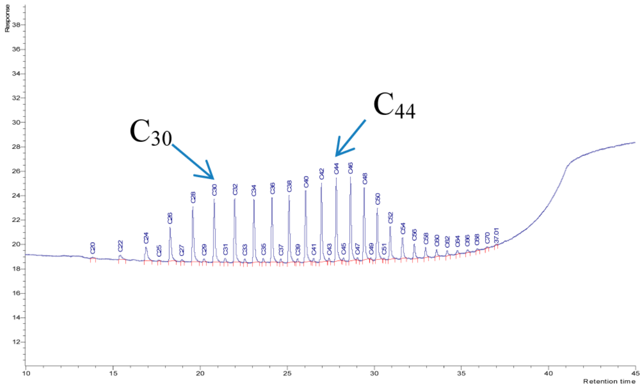


Figure 4. GC chromatogram of the solids obtained from tandem catalysis experiment, Table 1, entry 4 (100 equiv of $ZnEt_2$).

Thus, it was decided to benchmark **2** under identical conditions for the in situ recycling of $ZnEt_2$ (Table 1, Entry 5). In this instance, 3.3 g of solids were recovered along with a toluene soluble fraction of hydrocarbons centered at C_8 and consisting of 16 mol % α-olefins. In contrast to **4**, the α-olefin concentration did not increase with time suggesting little to no recycling of the chain transfer agent.[10] In addition, ^{1}H NMR spectroscopy of the solids did not show the presence of olefinic peaks and GC analysis revealed a C_{46} centered distribution nearly identical to that of the CCG benchmark experiment (Entry 1). All together, these results suggest that in contrast to $(BiPy)_2FeEt_2$, $Ni(acac)_2$ does not take part in tandem catalysis, presumably due to incompatibility with MAO as suggested in initial reports.[3,4] It also indicates that $Ni(acac)_2$ or the product of the reaction between $Ni(acac)_2$ and MAO do not affect the chain growth catalyst allowing for the typical catalyzed chain growth to occur.

Interestingly, the catalytic activity in the tandem experiments is reduced to about one-third of the original catalytic activity presumably due to interaction of free BiPy ligand with the chain growth catalyst. Indeed, one of the BiPy ligands in **4** is known to be loosely bound to the Fe center.[9] Decreasing the loading of the transfer catalyst **4** from 2.5 to 1 equiv relative to the chain growth catalyst **1** restored the catalytic activity and produced a hydrocarbon distribution centered at C_{50} consisting of about 40 mol % α-olefins (Table 1, Entry 6). Additionally, the toluene soluble fraction contained a distribution centered at C_{20} with 63 mol % of α-olefins. The detrimental effect of free BiPy on the catalytic activity was further demonstrated by the reduced activity of **1**/MAO in the presence of 2.5 equiv of BiPy (Table 1, Entry 7). The reaction produced a Schulz−Flory distribution of alkanes, indicating that free BiPy inhibits chain growth. The importance of $ZnEt_2$ in tandem catalysis was also investigated by carrying out an experiment without $ZnEt_2$ and resulted in the formation of fully saturated polyethylene (PE) in low activity (Table 1, Entry 8), indicating that chains do not transfer between the two iron centers.

From these results, it is apparent that the shape and position of the molecular weight distribution is highly dependent on the reaction conditions (i.e., amount of $ZnEt_2$ and ratio of catalysts **1** to **4**). Given that the rate of propagation on **1** and β-H elimination on **4** are independent of one another and the amount of Zn reagent, we anticipate that the relative rate of chain transfer reactions of **1** and **4** with Zn species will dictate the shape and position of the molecular weight distributions. This hypothesis will require further kinetic studies.

In conclusion, the Fe-catalyzed chain growth of ethylene producing Poisson distributions of alkanes reported by Gibson has been reinvestigated for the recycling of the chain transfer agent, $ZnEt_2$. It has been demonstrated that akin to $Ni(acac)_2$, simple Fe alkyl complexes also catalyze the conversion of $Zn(oligomer)_2$ to $ZnEt_2$ and α-olefins under an ethylene atmosphere. Most importantly, results presented here show that $ZnEt_2$ can be regenerated in situ without deactivation of the Fe chain growth catalyst in a tandem catalysis fashion using the iron "transfer" catalyst, $(BiPy)_2FeEt_2$. In contrast, $Ni(acac)_2$ is not suitable under the reaction conditions reported here. The dual catalyst system presented here offers the possibility to lower the loading of $ZnEt_2$. In addition, the product distribution is tunable and offers a wide range of target products in the synthesis of precision hydrocarbons. Application of this strategy to other Catalyzed Chain Growth systems as well as optimization of the reaction conditions such as temperature, pressure, ratio of catalysts are currently the focus of our efforts. Furthemore kinetic studies will shade light on the origins of the bimodal distribution and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01231.

Experimental details, NMR spectra and GC traces (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Russell Taylor and Dr. Glenn Sunley for helpful discussions and Joanne Medcalf for GC analyses.

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