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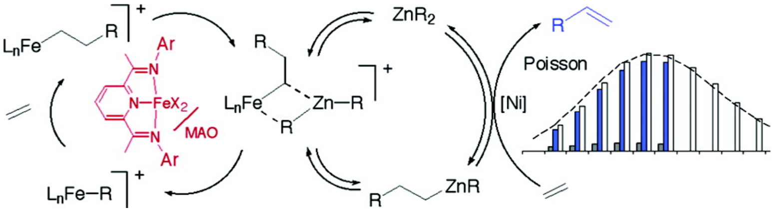

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Iron Catalyzed Polyethylene Chain Growth on Zinc: A Study of the Factors Delineating Chain Transfer *versus* Catalyzed Chain Growth in Zinc and Related Metal Alkyl Systems

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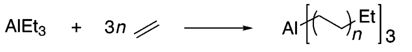
Abstract: The bis(imino)pyridine iron complex, [{2,6-(MeC═N-2,6-$^{i}Pr_2C_6H_3)_2C_5H_3N$}$FeCl_2$] (**1**), in combination with MAO and $ZnEt_2$ (> 500 equiv.), is shown to catalyze polyethylene chain growth on zinc. The catalyzed chain growth process is characterized by an exceptionally fast and reversible exchange of the growing polymer chains between the iron and zinc centers. Upon hydrolysis of the resultant ZnR_2 product, a Poisson distribution of linear alkanes is obtained; linear α-olefins with a Poisson distribution can be generated via a nickel-catalyzed displacement reaction. Other dialkylzinc reagents such as $ZnMe_2$ and $Zn^{i}Pr_2$ also show catalyzed chain growth; in the case of $ZnMe_2$ a slight broadening of the product distribution is observed. The products obtained from $Zn(CH_2Ph)_2$ show evidence for chain transfer but not catalyzed chain growth, whereas $ZnPh_2$ shows no evidence for chain transfer. The Group 13 metal alkyl reagents AlR_3 (R = Me, Et, octyl, ^{i}Bu) and GaR_3 (R = Et, ^{n}Bu) act as highly efficient chain transfer agents, whereas $GaMe_3$ exhibits behavior close to catalyzed chain growth. $Li^{n}Bu$, $Mg^{n}Bu_2$ and BEt_3 result in very low activity catalyst systems. $SnMe_4$ and $PbEt_4$ give active catalysts, but with very little chain transfer to Sn or Pb. The remarkably efficient iron catalyzed chain growth reaction for $ZnEt_2$ compared to other metal alkyls can be rationalized on the basis of: (1) relatively low steric hindrance around the zinc center, (2) their monomeric nature in solution, (3) the relatively weak Zn−C bond, and (4) a reasonably close match in Zn−C and Fe−C bond strengths.

Introduction

Half a century ago, Ziegler and co-workers reported the *Aufbaureaktion* for aluminum alkyls.[1] This reaction involves a stepwise insertion of ethylene into the aluminum carbon bonds of, for example, triethyl aluminum (TEA) to give long-chain aluminum trialkyls (eq 1). For this insertion to occur, an ethylene pressure of 50−300 bar has to be maintained. By reducing the pressure to 10 bar and increasing the reaction temperature to 300 °C, the long-chain alkyl groups can be displaced from aluminum as α-olefins, thereby regenerating triethyl aluminum (eq 2).[2] This chain growth reaction is still commercially exploited today for the synthesis of linear α-olefins (Alfen Process) and primary alcohols from ethylene.[3,4]

Soon after, Ziegler discovered the effect of nickel on this reaction, which suppressed chain growth to give only butenes.[5]



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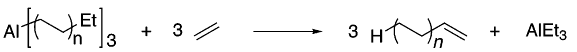

(2)

The elucidation of this “nickel effect” and the subsequent screening of the periodic table for the effects of other metals led to the discovery of the first transition metal catalyzed ethylene polymerization.[6] Since then, many more catalysts, both homogeneous and heterogeneous, have been discovered for the polymerization and oligomerization of α-olefins and the search for new catalyst systems still continues, driven by the desire to obtain greater control over the polymerization reaction and to discover and develop new materials with improved performance parameters. During the past decade, enormous advances have been made in this area, in particular the discovery of highly active late transition metal catalysts.[7,8] In addition, considerable progress has been made toward the understanding of the various branching and chain transfer mechanisms that can occur during metal-mediated polymerization reactions.

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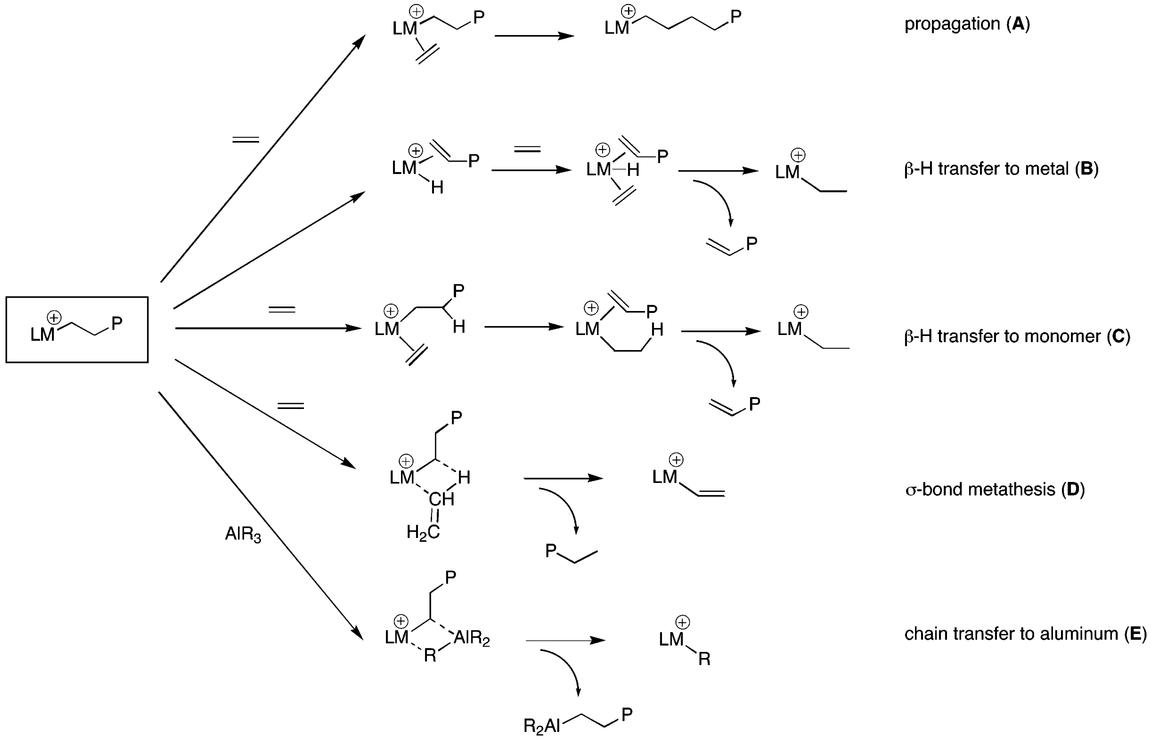
Scheme 1



Chain Transfer Mechanisms. A polyolefin chain, defined by its chain length, the nature of the end-groups and the amount of branching, is the product of the relative rates of chain propagation, chain transfer and chain branching during the polymerization reaction. In the absence of any transfer mechanism, the polymerization system is termed a living polymerization system, but more commonly transfer reactions are operating which will limit chain growth and, in the case of β-H transfer for example, generate polyolefin chains with an unsaturated end-group. The mechanism of β-H transfer is reasonably well understood and is believed to occur either by a *β-H transfer to metal* mechanism via a metal hydride intermediate (**B**), or a direct *β-H transfer to monomer* mechanism (**C**, Scheme 1).[9−13] An analogous *β-methyl transfer* mechanism is sometimes observed in propylene polymerization.[14,15] A third, less common, transfer mechanism is *σ-bond metathesis* (**D**), which has been observed in several early transition metal systems.[16−24]

Advances in polymer analysis techniques, especially NMR, have enabled detailed end-group analysis of polyolefin chains. In some cases, where a transition metal based pre-catalyst and an aluminum based cocatalyst are used as the catalyst system, fully saturated polyolefin chains have been observed, which have been attributed to a chain transfer mechanism involving transfer of the chain to aluminum, or *chain transfer to aluminum* (**E**). The mechanism of this chain-transfer process is believed to occur via an exchange of the growing polymer chain on the transition metal with an alkyl group of the aluminum alkyl of the cocatalyst, most likely via a bimetallic intermediate as shown in Scheme 1 (E). The occurrence of chain transfer to aluminum in ethylene polymerization has been observed for many catalyst systems throughout the transition series, including early transition metal systems,[9,25−30] chromium-based catalysts,[31−33] and late transition metal systems based on iron,[34−36] and nickel,[37]

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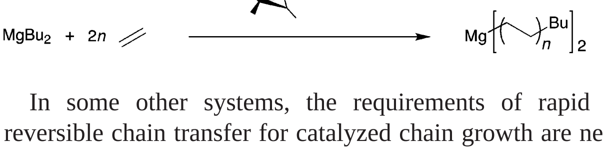
as well as lanthanides[38] and actinides.[39] Importantly, this chain transfer process is not limited to aluminum; other Group 13, as well as Group 2, 12, and 14 alkyls including boron (BEt_3),[40] beryllium ($BeEt_2$),[41,42] magnesium (MgR_2),[43−45] and zinc and cadmium alkyls (ZnR_2 and CdR_2)[46−54] have been used as chain transfer agents in the polymerization of olefins. In fact, the aforementioned σ-bond metathesis process may also be viewed as a chain transfer process, but involving C−H bonds rather than M−C bonds. In addition, silanes (Si−H bond)[55−58] and dihydrogen (H−H bond)[59] are known to act as chain transfer agents and may be viewed as members of a related family of chain transfer agents. The extent to which a chain transfer process occurs during the polymerization reaction will depend on the reaction conditions, the nature of both the transition metal catalyst and the transfer agent and their relative concentrations. However, a common result of all chain transfer agents is a reduction of the polymer molecular weight and the formation of fully saturated polyolefin chains upon hydrolytic workup.

Catalyzed Chain Growth. In his early reports on ethylene polymerization, Ziegler generally described the aluminum component as the polymerization catalyst, with the transition metal compound functioning as the cocatalyst, and therefore considered the whole chain growth process to occur at the aluminum centers or, in other words, a transition metal catalyzed Aufbaureaktion.[6] Later it was realized that in these polymerization systems, the polymer chain actually grows on the transition metal and not on the aluminum center. However, as outlined above, for certain early as well as late transition metal polymerization catalysts, under appropriate conditions, the growing polymer chain can be transferred to the aluminum center during the polymerization reaction. In cases where chain transfer to aluminum has been observed as the dominant chain transfer process, the rate of chain propagation is generally very much higher than the rate of chain transfer. In several metallocene systems for example, quantitative kinetic analysis has indicated a difference of at least 3−4 orders of magnitude between the rate of propagation and the rate of chain transfer to aluminum.[25,60,61] However, if chain transfer to aluminum constitutes the sole transfer mechanism and the exchange of the growing polymer chain between the transition metal and the aluminum centers is *very fast and reversible*, the polymer chains will appear to be growing on the aluminum centers. This can then reasonably be described as a *catalyzed chain growth* reaction on aluminum or, using Ziegler's terminology, a transition metal catalyzed Aufbaureaktion. (*Catalyzed chain growth* is distinct from *catalytic chain growth*, the latter referring to metal-catalyzed olefin insertion into a growing alkyl chain.) An attractive manifestation of this type of chain growth reaction is a Poisson distribution of product molecular weights, as opposed to the Schulz−Flory distribution that arises when β-H transfer accompanies propagation. Interestingly, from a mechanistic point of view, the catalyzed chain growth process of olefins is analogous to the polymerization of epoxides to narrow molecular weight polyethers in the presence of alcohols as chain transfer agents.[62−64]

Only a few cases have been reported in which the requirements for catalyzed chain growth are fulfilled. Samsel and Eisenberg reported in 1993 a chain growth reaction on aluminum catalyzed by an actinide metallocene in combination with a cocatalyst.[39] Their most efficient catalyst, $Cp^*_2ThCl_2$ in combination with 500 equiv. isobutylaluminoxane (IBAO) as cocatalyst (eq 3), gave an activity of 500 g/mmol·h·bar for the chain growth on TEA (7300 equiv.) at 95 °C and 7 bar ethylene pressure. No high molecular weight polyethylene was observed and the oligomers obtained from the chain growth reaction followed a Poisson distribution. Mortreux et al. have shown that lanthanocenes, for example $Cp^*_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$, catalyze the chain growth reaction of ethylene with magnesium dialkyls to give long chain dialkylmagnesium compounds with a Poisson distribution of alkyl chains (eq 4).[65,66]



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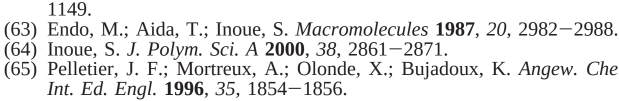

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In some other systems, the requirements of rapid and reversible chain transfer for catalyzed chain growth are nearly

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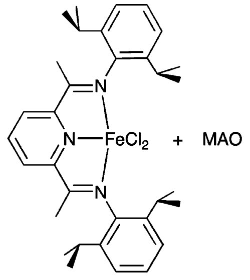
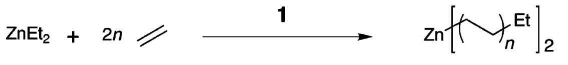
fulfilled, and the product distribution then deviates from a perfect Poisson distribution. For example, the half-sandwich hafnium complex, (η^5-indenyl)$HfCl_3$, activated with 800 equiv. MAO at 80 °C and 6 bar ethylene pressure in neat TEA (8000 equiv.), produced short alkyl chains grown on aluminum with an activity of 300 g/mmol•h•bar. However, the distribution of the chain growth products in this system did not fit a Poisson distribution but rather one that is more accurately described by a Schulz−Flory distribution. As a result, at the end of the reaction the shortest grown chains (butyl) predominate and 50% of the ethyl groups from TEA have not reacted at all. Another drawback of this system is the persistent formation of polyethylene as a side-product, comprising at least 10 wt % of the total product. More recently, half sandwich chromium(III) complexes,[31,32,67] and triazacyclononane chromium(II) complexes[33] have been used to catalyze chain growth on trialkyl aluminum.

We have recently reported a remarkably efficient catalyzed chain growth reaction on zinc using the bis(imino)pyridine iron(II) dichloride complex **1**, in combination with MAO as cocatalyst (eq 5).[68,69] This was the first time a catalyzed chain growth reaction had been observed using zinc alkyls. The reaction afforded a Zn(polymer)$_2$ product with an activity of 1400 g/mmol•h•bar and, after hydrolysis, yielded a Poisson distribution of linear alkanes. We have also shown that the polymer chains can be displaced from Zn(polymer)$_2$ via a nickel catalyzed displacement reaction to give linear α-olefins with a Poisson distribution (eq 6), thus making the overall reaction a catalyzed zinc-based alternative to the Alfen Process. Here we report the details of our investigations into this catalyzed chain growth system, the effect of a variety of other main group alkyl reagents on the iron-catalyzed process, and our understanding of the factors that are important in favoring metal-catalyzed chain growth processes.





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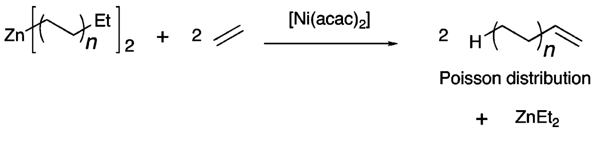

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Results

Aluminum Alkyl Compounds. Previous studies on the effect of different MAO concentrations on the polymerization behavior of bis(imino)pyridine iron dichloride **1** have shown that an increase in the MAO concentration leads to an increased amount of a lower molecular weight fraction in the polymer product. The high and low molecular weight fractions can be separated by toluene Soxhlet extraction. The lower molecular weight fraction was shown (by NMR) to be fully saturated, its formation being ascribed to chain transfer to aluminum, most likely due to free trimethyl aluminum (TMA) present in MAO.[36,70,71] The higher molecular weight polymer is mainly vinyl terminated due to β-H transfer, indicating that, under these conditions, two transfer processes are operating simultaneously. With a view to obtaining a better understanding of this chain transfer process, and to making chain transfer to aluminum the sole chain transfer process, we decided to explore the effect of varying the concentrations of a number of aluminum alkyl reagents. The solid polymer fraction and the toluene soluble oligomer fraction have been analyzed separately by GPC and GC respectively, and the combined results are summarized in Table 1. The resultant polymers generally possess broad and often bimodal distributions, hence M_n, M_w, and PDI parameters are of limited value. Some representative traces are shown in Figure 1. All other GPC traces can be found in the Supporting Information.

As can be seen from Table 1 (runs 1.2−1.8) and Figure 1, increasing the concentration of trimethyl aluminum (TMA) or triethyl aluminum (TEA) resulted in the formation of a low molecular weight polymer fraction ($M_n \approx 1000$) with a relatively narrow polydispersity, in addition to a high molecular weight fraction with a very broad polydispersity. This behavior is similar to the observations made when increasing the amount of MAO for this catalyst,[36] but, unlike MAO, the addition of more than 500 equiv. of TMA or TEA has very little effect on the product distribution and leads to a slight decrease in activity at higher concentrations. A similar trend is seen for trioctyl aluminum (TOA, runs 1.9−1.10), but polymerization activities are already significantly lower at relatively low amounts (500 equiv.). The bulkier triisobutyl aluminum (TIBAL, runs 1.11−1.13) appears to behave differently in that, initially at lower concentrations a bimodal distribution is observed, but at higher concentration, a nearly monomodal distribution with a slightly higher molecular weight ($M_n \approx 3000$) is seen. Similar observations have been reported recently for **1** in combination with TEA or TIBAL, but without MAO activation.[72,73] Diethyl aluminum ethoxide (Et_2AlOEt) also causes a slight decrease in activity but has very little effect on the polymer distribution, whereas chlorinated aluminum alkyls such as Me_2AlCl and Et_2AlCl and $^iBu_2AlH$ (DIBAL-H) deactivate the catalyst system.

Analysis of the polymer end-groups by ^1H and ^{13}C NMR spectroscopy allowed further insight in to the polymerization mechanism. From Table 1 it can be seen that more saturated chain ends and very little vinyl termination is observed in all cases compared to run 1.1, indicating that β-H termination is only a minor transfer mechanism and that virtually all of the polymer chains are terminated via chain transfer to aluminum. The number of Al-alkyl groups that have actually engaged in

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Table 1. Chain Transfer Experiments with **1**/MAO and Various Aluminum Alkyl Reagents[a]

run	**1** μmol	Al alkyl (equiv.)	yield[b] (g)	activity (g/mmol·h·bar)	M_n[c]	M_w[c]	PDI[c]	methyl chain ends [d]	vinyl chain ends [d]	isobutyl chain ends [e]	$(Al–R)_{ext}$ mmol (%)[f]
1.1	5	none	3.8	1500	10000	199000	19	2.3	0.6		
1.2	5	TMA (500)	2.5	1000	490	34060	69	25.5	0		5 (69)
1.3	5	TMA (1000)	2.6	1040	490	36800	75	24.8	0		6 (39)
1.4	5	TMA (2000)	2.1	840	470	59700	128	24.4	0		6 (18)
1.5	5	TEA (380)	2.7	1100	1500	382000	263	15.2	0.2		4 (77)
1.6	5	TEA (950)	3.4	1400	1500	351000	238	14.0	0.2		9 (60)
1.7	5	TEA (1900)	3.3	1300	2200	669000	304	11.9	0.2		13 (45)
1.8	5	TEA (3800)	2.3	900	2000	632000	319	11.0	0		13 (22)
1.9	5	TOA (500)	2.0	800	1100	44000	39	20.4	0.3		4 (56)
1.10	5	TOA (1000)	2.2	900	700	86000	118	27.5	0.3		6 (42)
1.11	2	TIBAL (1000)	2.0	2000	3100	397000	129	3.4[e]	0.2	1.9	0.5 (8)
1.12	2	TIBAL (2500)	1.8	1800	2400	39000	16	3.9[e]	0.1	1.7	0.5 (3)
1.13	2	TIBAL (5000)	1.4	1400	2700	122000	45	4.8[e]	0.1	1.9	0.3 (1)
1.14	10	DIBAL-H (500)	0.5	94	2600	7200	2.7	5.6[e]	0	2.8	0.2 (1)
1.15	5	$AlEt_2OEt$ (1000)	2.4	1000	21000	104000	5	3.4	0.7		*g*
1.16	5	$AlMe_2Cl$ (500)	0								
1.17	5	$AlEt_2Cl$ (500)	0								

[a] Conditions: Schlenk flask test, MAO = 100 eq, 1 bar ethylene, r.t., 30 min, toluene solvent (50 mL). [b] Yield is total yield: solid polymer + oligomeric products (determined by GC). [c] Determined by GPC. [d] Determined by ^{1}H NMR, given per 1000 carbon atoms. [e] Determined by ^{13}C NMR. [f] Defined as the percentage of alkyl groups that has been extended with at least 1 inserted ethylene, determined by NMR analysis of the polymer and GC analysis of the oligomers. [g] No significant chain transfer to aluminum observed.

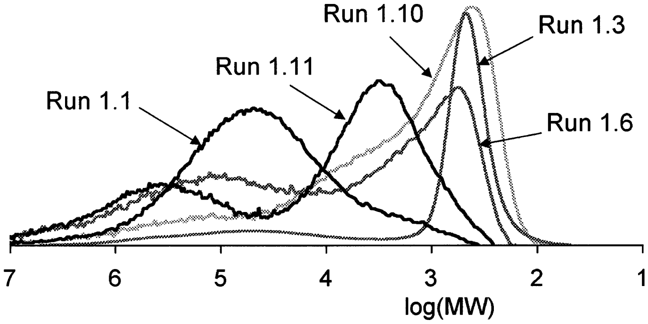

Figure 1. Effect of various AlR_3 compounds on the molecular weight distribution of the PE products obtained using **1**/MAO.

chain transfer $(Al-R)_{ext}$ can be calculated using the formula given below, which takes into account both solid polymeric material and the toluene soluble oligomers. (Note that these calculations are only a rough estimate as there is a relatively large error in the determination of M_n for low molecular weight polyethylene and in addition, the small amounts of β-H transfer and chain transfer to TMA present in MAO are not taken into account.)

$$(Al-R)_{ext} = \frac{\text{yield(polymer)}}{Mn} + \sum \frac{\text{yield(oligomer)}}{\text{M(oligomer)}}$$

For low concentrations of TMA or TEA (runs 1.2 and 1.5), 69% of all Al-methyl and 77% of all Al-ethyl bonds respectively have undergone chain extension or, conversely, 20−30% remain after 30 min. As expected, the percentage of unreacted Al-alkyl bonds increases as the amount of TMA or TEA is increased. Considering the total amount of Al-methyl or Al-ethyl bonds converted in runs 1.2−1.4 (5, 6, and 6 mmol) and runs 1.5−1.8 (4, 9, 13, and 13 mmol) a maximum appears to have been reached. In other words, although the amount of TEA in run 1.8, for example, has been doubled compared to run 1.7, the total number of Al-ethyl bonds that have reacted has remained the same. These results show that both TMA and TEA are efficient chain transfer agents, but that there is an upper limit to the number of Al-alkyl bonds that can be involved in chain transfer. In addition, there is a consistent formation of high molecular weight polymer in all experiments, the origin of which is unclear at this stage.

In the case of TIBAL, the degree of chain transfer to the aluminum centers arising from TIBAL as opposed to those arising from TMA (from MAO) could be determined by ^{13}C NMR spectroscopy since this readily differentiates between methyl and isobutyl end-groups. The number of fully saturated linear polymer chains due to chain transfer to TMA (from MAO) indicated that the percentage chain growth on TMA was near 100% (based on 35 mol % free TMA present in MAO, as specified by the supplier). The number of polymer chains containing an isobutyl chain end revealed that only 8% of all Al-^{i}Bu groups had reacted and that, even at higher TIBAL concentrations, the number of extended chains arising from Al-^{i}Bu bonds remained approximately constant. These results show that aluminum isobutyl groups are much poorer chain transfer agents than linear alkyls.

Other Metal Alkyl Compounds. As outlined in the introductory section, other metal alkyl reagents have previously been employed as chain transfer agents in olefin polymerization, usually with the aim of reducing the molecular weight of the polyolefin or functionalizing the chain ends. To explore the chain transfer activity of other metal alkyls in the polymerization of ethylene, a series of experiments has been carried out using **1**/MAO in conjunction with a variety of other metal alkyl reagents. The results are summarized in Table 2; selected GPC traces are shown in Figure 2. Addition of 500 equiv. Li^{n}Bu or Mg^{n}Bu$_2$ to the catalyst system **1**/MAO (runs 2.2 and 2.3) resulted in a dramatic decrease in activity and the small amounts of polymer obtained were not analyzed further. Of the other Group 13 metal alkyls that have been investigated, BEt_3 also gave very low polymer yield and was not pursued. Gallium alkyls on the other hand, such as $GaMe_3$, $GaEt_3$, and $GaBu_3$ are efficient chain transfer agents, as can be seen from runs 2.5−2.7 in Table 2. In the case of $GaEt_3$ and $GaBu_3$, the GPC data indicates that a similar product distribution is obtained with these gallium alkyls as were obtained for aluminum alkyls (cf.

Table 2. Chain Transfer Experiments with 1/MAO and Various Metal Alkyl Reagents[a]

run	metal alkyl (equiv.)	yield (g)	activity (g/mmol·h·bar)	M_n[b]	M_w[b]	PDI[b]	methyl chain ends[c]	vinyl chain ends[c]	$(M–R)_{ext}$ (%)
2.1	none	3.8	1500	10000	199000	19.1	2.3	0.6	
2.2	Li^nBu (500)	0	0	nd	nd	nd	nd	nd	
2.3	Mg^nBu_2 (500)	0.14	60	nd	nd	nd	nd	nd	
2.4	BEt_3 (500)	0.15	60	nd	nd	nd	nd	nd	
2.5	$GaMe_3$ (520)	2.9	1160	400	500	1.2	29.6	0	89
2.6	$GaEt_3$ (500)	3.18	1270	900	150000	177	13.6	0	79
2.7	Ga^nBu_3 (500)	1.9	760	900	31000	32.8	12.7	0	46
2.8	$SnMe_4$ (560)	0.9	360	4400	54000	12.2	5.9	0.2	2
2.9	$PbEt_4$ (500)	2.16	900	10000	65000	6.4	3.0	0.4	2
2.10	$ZnEt_2$ (500)	3.51	1400	700	800	1.1	38.7	0.2	100

[a] Schlenk flask test, **1** (5 μmol), MAO (100 equiv.), 1 bar ethylene, r.t., 30 min, toluene solvent (50 mL). [b] Determined by GPC. [c] Determined by ^1H NMR, given per 1000 carbon atoms.

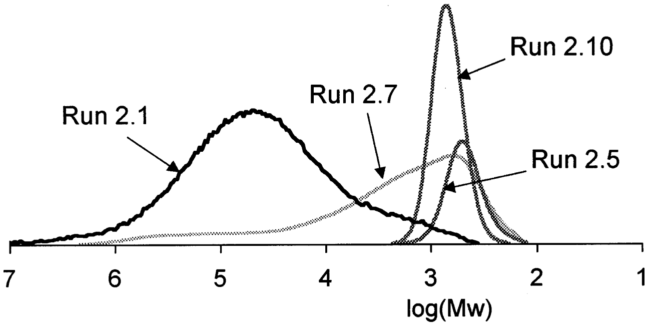

Figure 2. Effect of various metal alkyl compounds on the molecular weight distribution of the PE products obtained using **1**/MAO.

Table 3. Catalyzed Chain Growth Versus Time for $ZnEt_2$, $AlEt_3$, and $GaMe_3$[a]

(a) $ZnEt_2$

run	time (min.)	yield (g)[b]	activity (g/mmol·h·bar)	$(Zn–Et)_{ext}$ mmol (%)	X_t[c]	M_n[c]
3.1	2	1.26	18900	6.77 (97)	5.1	170
3.2	4	1.63	12300	7.19 (100)	6.7	220
3.3	6	1.75	8750	6.72 (96)	8.1	260
3.4	9	2.02	6720	6.75 (96)	9.8	310
3.5	12	2.14	5360	6.71 (96)	10.9	340
3.6	15	1.93	3860	5.98 (85)	11.0	340
3.7	18	1.87	3110	5.74 (82)	11.3	350

(b) $AlEt_3$

run	time (min.)	yield (g)[b]	activity (g/mmol·h·bar)	$(Al–Et)_{ext}$ mmol (%)	k
3.8	1	0.56	6780	5.51 (38)	0.55
3.9	3	1.1	4400	8.57 (60)	0.71
3.10	5	1.25	3000	9.22 (64)	0.75
3.11	7	1.28	2200	9.34 (65)	0.76
3.12	9	1.27	1690	8.95 (62)	0.77
3.13	11	1.28	1390	9.28 (64)	0.76

(c) $GaMe_3$

run	time (min.)	yield (g)[d]	activity (g/mmol·h·bar)	$(Ga–Me)_{ext}$ mmol (%)
3.14	2	0.01	210	0.14 (1)
3.15	4	0.03	230	0.25 (2)
3.16	8	0.26	980	1.28 (11)
3.17	10	0.34	1030	1.54 (13)
3.18	12	0.47	1180	2.04 (17)
3.19	14	0.51	1100	2.17 (18)
3.20	16	0.52	970	2.17 (18)

[a] Conditions: **1**/MAO/$ZnEt_2$ 2/200/3500 μmol, 1 bar ethylene, r.t., toluene solvent (50 mL) in a jacketed round-bottom flask. **1**/MAO/$AlEt_3$ 2/200/4000 μmol, 1 bar ethylene, r.t., toluene solvent (50 mL) in a Schlenk flask. **1**/MAO/$GaMe_3$ 2/200/4000 μmol, 1 bar ethylene, r.t., toluene solvent (50 mL) in a Schlenk flask. [b] Yield of toluene soluble oligomeric alkanes, determined by GC. [c] Determined from the Poisson distribution that fits best the experimental data.

$GaEt_3$, run 2.6 in Fig. S6 and $AlEt_3$, run 1.6 in Figure 1). Trimethyl gallium (run 2.5) appears to behave differently: no high molecular weight polymer, but only a low molecular weight, fully saturated polyethylene fraction with a rather narrow PDI of 1.2 is obtained. This low polydispersity, combined with the high percentage of extended Ga methyl units is indicative of catalyzed chain growth. A smaller decrease in catalyst activity was observed with Group 14 metal alkyls such as $SnMe_4$ or $PbEt_4$ (runs 2.8 and 2.9). Analysis of these polymer products showed that only very little chain transfer to Sn or Pb had occurred.

When 500 equiv. $ZnEt_2$ were added, the activity remained high and a dramatically different polymer product was obtained (run 2.10). From the GPC trace (Figure 2), it can be seen that a low molecular weight fully saturated product was formed with a very narrow PDI of 1.1. The yield of 3.51 g, and the number average molecular weight of $M_n = 700$, indicate that approximately 5 mmol of polymer chains were generated which, based on 2.5 mmol $ZnEt_2$, corresponds to 2 chains per zinc. All the $ZnEt_2$ had been converted to $Zn(polymer)_2$ which, after hydrolysis, yielded two fully saturated polymer chains, indicating a highly efficient catalyzed chain growth process. During the course of the reaction, the solution remained clear until the solubility-limiting chain length ($M_n \approx 700$, ca. 50 carbon atoms per chain) was reached, whereupon the product $Zn(polymer)_2$ precipitated from solution.

Catalyzed Chain Growth Versus Time. In catalyzed chain growth, chain transfer is reversible and much faster than chain propagation. One of the characteristics of a catalyzed chain growth process is that the product distribution follows a Poisson distribution and that M_n increases with time, as opposed to a Schulz-Flory distribution where M_n does not change during the polymerization. To verify that a truly catalyzed chain growth process is operating, samples were taken from the reaction mixtures during a growth experiment using $ZnEt_2$, $AlEt_3$, and $GaMe_3$ and, after hydrolysis, analyzed by GC (Table 3 and Figure 3). From the molar product distributions shown in Figure 3a it can be seen that for $ZnEt_2$, the maximum of the oligomer distributions shifts to higher carbon number with time, similar to an increase in M_n. Curve fitting analysis[74] (see Supporting Information) shows an excellent fit between the experimentally obtained alkane distribution and the distribution calculated using the Poisson formula, as shown for run 3.2 in Figure 4a. A 'best'

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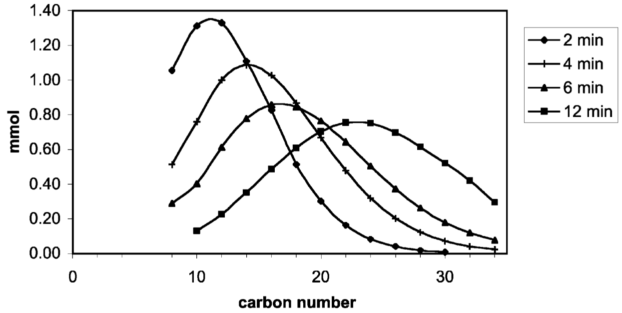
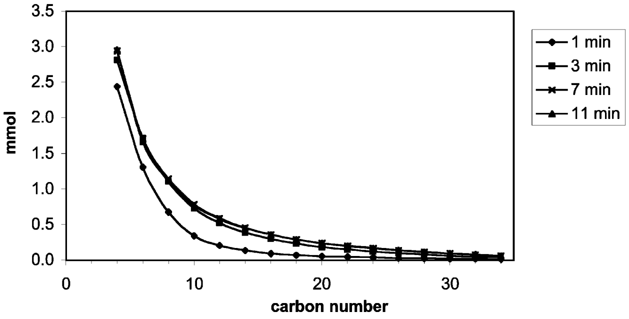
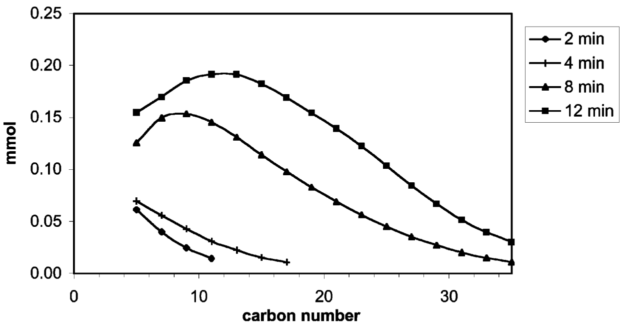


a) $ZnEt_2$ (see Table 3a)



b) $AlEt_3$ (see Table 3b)

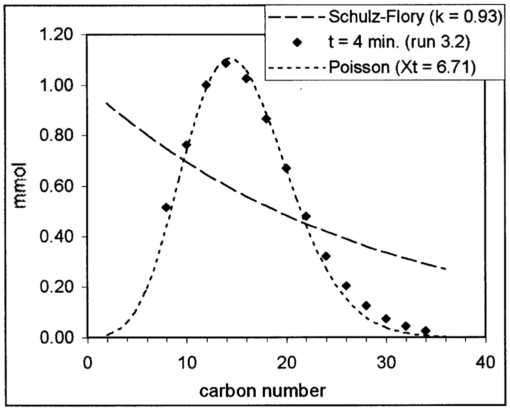


c) $GaMe_3$ (see Table 3c)

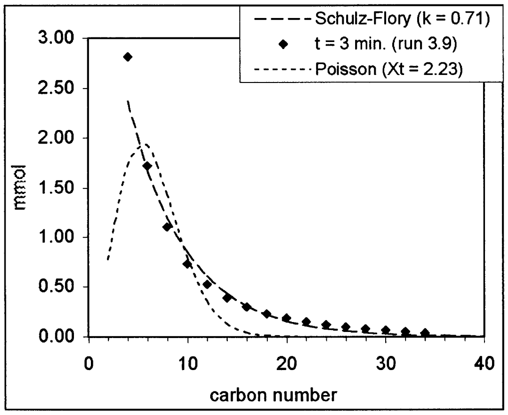
Figure 3. Molar distributions of linear alkanes at different time intervals: (a) $ZnEt_2$; (b) $AlEt_3$; and (c) $GaMe_3$.

Schulz−Flory fit is also shown for comparison. From this analysis, growth factors X_t can be determined for each distribution, which are given in Table 3a. The growth factor X_t corresponds to the average number of ethylene molecules inserted into each zinc-ethyl bond. The percentage chain growth is near 100%, although after 15 min some insoluble product (C > 34) is formed which is lost in the GC analysis and consequently the yield is decreased. With $AlEt_3$ on the other hand, the molar distributions of linear alkanes obtained upon hydrolysis after various time intervals are markedly different (Figure 3b). The maximum is always at the beginning and curve fitting analysis shows that this distribution fits exactly with a Schulz−Flory distribution (Figure 4b). These results show that, although chain transfer to aluminum is the dominant transfer process during this period, the reversible chain transfer process is not sufficiently fast relative to chain propagation to afford the Poisson distribution characteristic of catalyzed chain growth.

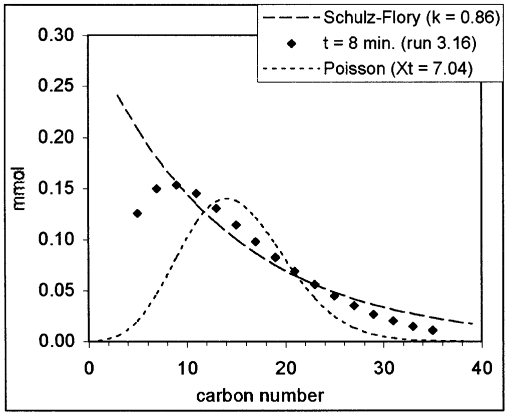
In the case of $GaMe_3$, the product distribution appears to be intermediate and the experimental data fit neither a Poisson nor a Schulz−Flory distribution (see Figure 3c and 4c). The percentage chain growth is much lower and only reaches about 20% after 15 min (Table 3c). Although, at first sight, the GPC data for $GaMe_3$ indicate a very similar behavior to $ZnEt_2$ (Table 2, run 2.5 versus 2.10), these time dependent experiments show that the distribution deviates from a Poisson distribution and is therefore not a simple catalyzed chain growth reaction.



a) $ZnEt_2$



b) $AlEt_3$



c) $GaMe_3$

Figure 4. Experimental distribution curve fitting analysis with best Poisson and Schulz−Flory fit: (a) $ZnEt_2$; (b) $AlEt_3$; and (c) $GaMe_3$.

A plot of the growth factors versus time for the $ZnEt_2$ reaction (Table 3a) showed that the activity of the polymerization system decreased as the experiment proceeded (Figure 5). The activity over the first two minutes (Table 3, run 3.1) was extremely high with one gram of ethylene being incorporated within this time. This explains the initial large exotherm. The experiment was performed in a jacketed round-bottom flask with water-cooling, but this did not prevent the temperature rising by almost 15 °C within 30 s. The activity decreased rapidly, probably due

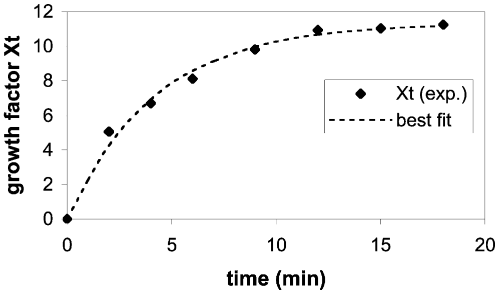


Figure 5. Catalyzed chain growth on zinc: change in X_t over time.

Table 4. Product Distribution at Different $ZnEt_2$ Concentrations[a]

run	$ZnEt_2$ (mmol)	yield (g)	yield (mmol)	$(Zn–Et)_{ext}$ (%)	activity (g/mmol·h·bar)	X_t[b]
4.1	2.2	0.81	4.22	96	2420	5.7
4.2	3.3	0.85	6.17	94	2540	3.7
4.3	4.4	0.92	7.75	88	2760	2.9
4.4	6.6	0.98	10.32	78	2950	1.9

[a] Conditions: Schlenk flask test, **1**/MAO = 2/200 μmol, 1 bar ethylene, r.t., toluene solvent (50 mL) for 10 min. [b] Determined from the Poisson distribution that fits best with the experimental data.

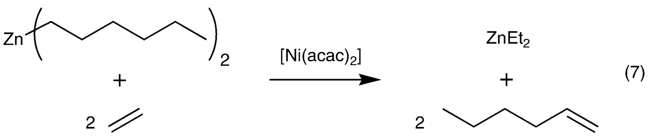
to the internal rise in temperature; it was found that this system had a substantially lower activity at 60 °C (∼200 g/mmol·h·bar) than at room temperature. Due to this lack of precise temperature control and the consequent change in ethylene concentration during the reaction, the reported activity numbers and growth factors are necessarily estimates. The experimentally obtained growth factors in Figure 5, can be fitted to a mathematical equation assuming an exponential decay of the amount of active catalyst. This affords a catalyst half-life of approximately 3 min under these conditions.

Variations in the Zinc/Iron Ratio. The remarkably high activity of the catalyst system **1**/MAO in the presence of $ZnEt_2$ led us to examine the effect of the diethylzinc-to-catalyst ratio, to determine the limits of activity for this catalyst system. The amount of diethylzinc was varied from 2.2 to 6.6 mmol and, after 10 min, the reaction was terminated and the product distribution was analyzed by GC. As can be seen from the results shown in Table 4 and Figure 6, catalyst activity was still very high at a high Zn:Fe ratio of 3300 (run 4.4). At this higher diethyl zinc concentration, the catalyst would need to convert more diethyl zinc to higher dialkyl zinc within the same amount of time (10 min) and consequently the average chain length of the grown dialkyl zinc will be shorter, resulting in a reduction of the calculated growth factor X_t. In addition, the number of Zn−Et bonds that have not been extended is increased (Table 4).

Other Zinc Alkyl Reagents. To explore the generality of the chain growth reaction on zinc catalyzed by **1**/MAO, we have investigated the series of alkyl zinc reagents shown in Table 5. It can be seen that $ZnMe_2$ and Zn^iPr_2 behaved more or less the same as $ZnEt_2$. Linear, fully saturated polyethylene was obtained with high activity and selectivity. In the case of $ZnMe_2$, GC analysis of the toluene soluble fraction showed that, as expected, only odd-numbered chains were obtained, but with a slightly higher polydispersity. In the case of Zn^iPr_2 the polymer chains contained one methyl and one isopropyl chain end and again a PDI of 1.1 was observed. Overlapping Me and ^tBu signals in ^1H NMR spectra and overlapping ^tBu and polyethylene backbone signals in ^{13}C NMR spectra precluded a detailed analysis of the product obtained using Zn^tBu_2. A combination of equimolar amounts of $ZnEt_2$ and Zn^tBu_2 resulted in catalyzed chain growth only on $ZnEt_2$. After hydrolysis and analysis by GC, only linear end-groups and no ^tBu end-groups were observed, indicating that only the Zn−ethyl bonds engaged in catalyzed chain growth in this case. $ZnPh_2$ gave a much lower activity and only high molecular weight polyethylene was formed (run 5.5). No phenyl endgroups, and therefore no chain transfer or catalyzed chain growth was observed under the conditions used. When dibenzylzinc ($ZnBn_2$) was used as the metal alkyl, a polymer with a bimodal molecular weight distribution and an excess of methyl over phenyl end groups was obtained (run 5.6). Soxhlet extraction of this product with toluene over 2 days resulted in a fairly good separation of the two fractions. ^1H NMR analysis showed that the low molecular weight fraction (M_n = 900, M_w = 1400, PDI = 1.6) possessed a methyl-to-phenyl ratio of 2.3:1 whereas the high molecular weight fraction (M_n = 84 000, M_w = 536 000, PDI = 6.4) had a methyl-to-phenyl ratio of 12:1. Some chain transfer to zinc apparently occurs with $ZnBn_2$, and the excess methyl end groups are likely to arise from chain transfer reactions either with TMA (from MAO) or with $ZnMe_2$ generated from methyl exchange between $ZnBn_2$ and TMA.

In the presence of a functionalized dialkyl zinc reagent, for example $Zn(CH_2CH_2COOEt)_2$ (run 5.7), **1**/MAO was completely inactive, possibly due to the coordinating property of the ester group since **1**/MAO/$ZnEt_2$ was also deactivated by the addition of 2000 equiv. ethyl acetate. In the presence of 500 equiv. EtZnCl, no active system is generated with **1**/MAO (run 5.8), similar to the case of Et_2AlCl (run 1.17).

Nickel Catalyzed Chain Displacement. A potentially useful feature of the catalyzed chain growth reaction on diethyl zinc is the presence of a reactive carbon−zinc bond at the end of the polymer chain, allowing further derivatization of the product. Instead of hydrolyzing the long-chain dialkyl zinc product, the grown alkyl chains can also be displaced from the zinc center by an olefin-exchange reaction, which can be catalyzed by nickel complexes such as $[Ni(acac)_2]$.[75,76] As a model reaction for the displacement of α-olefins from dialkyl zinc, the displacement of 1-hexene from dihexyl zinc was studied (eq 7).



(7)

The reaction was carried out at room temperature under 1 bar ethylene pressure and catalyzed by 5 mol % $[Ni(acac)_2]$. GC analysis of samples taken during this reaction showed that after 4 h 90% of the hexyl groups had been displaced, yielding 1-hexene and diethyl zinc (Figure 7). A longer reaction period did not result in a higher conversion, suggesting that an equilibrium distribution between dihexyl zinc and diethyl zinc had been reached.

A tandem experiment was carried out, whereby an iron catalyzed chain growth reaction on zinc was followed by a nickel catalyzed chain displacement reaction. Deactivation of the iron catalyst prior to the addition of the nickel catalyst was

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Table 5. Chain Transfer Experiments with 1/MAO and Various Zinc Alkyl Reagents[a]

run	Zn alkyl (equiv.)	yield (g)	activity (g/mmol·h·bar)	M_n[b]	M_w[b]	PDI[b]	methyl chain ends[c]	vinyl chain ends[c]	other chain ends
5.1	$ZnEt_2$ (500)	3.51	1400	700	800	1.1	38.7	0.2	
5.2	$ZnMe_2$ (500)	2.8	1100	800	1000	1.3	34.3	0.3	
5.3	Zn^iPr_2 (540)	1.9	800	600	700	1.1	16.4[d]	0	21.7[d] (^{i}Pr)
5.4	Zn^tBu_2 (480)	2.58	1040	5200	530000	102	11.2[e]	0	
5.5	$ZnPh_2$ (520)	0.16	60	1700	463000	265	14.8	0	
5.6	$ZnBn_2$ (500)	1.62	320	2700	365000	133	8.8	0	3.5 (Ph)
5.7	ZnR_2[f] (540)	0	0						
5.8	EtZnCl (500)	0	0						

[a] Schlenk flask test, **1**/MAO = 5/500 μmol, 1 bar ethylene, r.t., 30 min, toluene solvent (50 mL). [b] Determined by GPC. [c] Determined by ^1H NMR, given per 1000 carbon atoms. [d] Determined by ^{13}C NMR, given per 1000 carbon atoms. [e] Combined methyl and ^{t}Bu end groups. [f] Bis[2-(ethoxycarbonyl)ethyl]zinc.

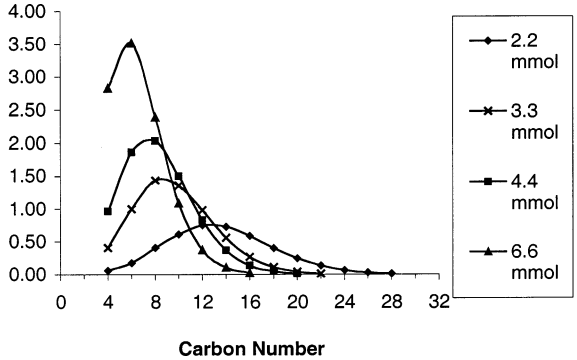

Figure 6. Molar weight distributions of linear alkanes at various $ZnEt_2$ concentrations.

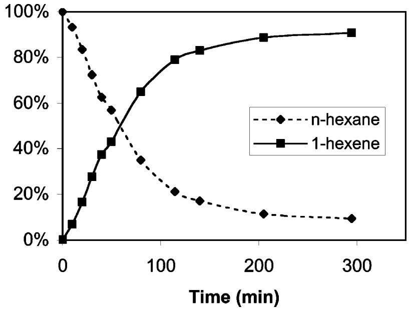

Figure 7. Nickel catalyzed displacement of dihexylzinc with ethylene.

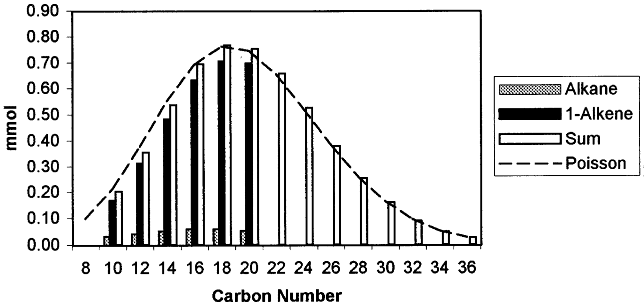

Figure 8. Molecular weight distribution of 1-alkenes obtained from a tandem catalyzed chain growth/displacement experiment.

achieved by adding a small amount of THF. Figure 8 shows the alkene and alkane distribution obtained from this experiment; it can be seen that 1-alkenes were obtained with >90% selectivity. Only a small amount (≈ 10 mol %) of alkanes was formed due to hydrolysis of residual zinc alkyls. Separation by GC of the alkane and alkene fraction higher than C20 was not possible and only the total amount is given. The resultant α-olefins possessed a near perfect Poisson distribution.

Discussion

General Considerations. The uncatalyzed insertion of alkenes, including ethylene, into a Zn−C bond is generally slow and only single insertions have previously been observed.[77−79] It has been shown that this insertion reaction can be catalyzed by zirconium[80] or palladium[81] complexes, but again only a single insertion is observed. The iron catalyzed chain growth reaction described here, provides a method for very fast multiple insertions of ethylene into a Zn−C bond. The efficient formation of long chain dialkyl zinc compounds from $ZnEt_2$ and ethylene can be understood in terms of a fast propagation reaction (**A**, Scheme 1) combined with an *even faster* and *reversible* alkyl exchange process between iron and zinc (**E**, with ZnR_2 instead of AlR_3). This situation is known as catalyzed chain growth and results in the formation of linear alkanes (after hydrolysis) with a Poisson distribution. Modeling studies have indicated that a Poisson distribution is only achievable when the rate of chain transfer is at least ca. 100 times faster than the rate of propagation. The question arises: why is the exchange between iron and zinc so fast and why not, for example, for the combination Fe−Al? To rationalize these observations, we need to examine more closely the nature of the catalyst resting state and the relative barriers for chain propagation versus chain transfer.

The metal alkyl species $L_nM{-}R$, where R is the growing polymer chain (Scheme 1) is generally believed to be the active species in metal catalyzed olefin polymerization reactions. Such a highly reactive species is most likely a transition state or perhaps a high energy intermediate and the catalyst resting state will be a more coordinatively saturated species, arising from solvent, monomer, intramolecular C−H bond interactions (agostic) or interactions with the cocatalyst. For example, in Group 4 metallocene catalyst systems, activated by MAO, the catalyst resting state is believed to be a cationic bimetallic Zr−Al species: $[L_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me{-}MAO]^-$.[82,83] Indeed, several stable hetero-bimetallic complexes of this type have been isolated for Group 4 metals,[83−88] lanthanides[89−93] and late

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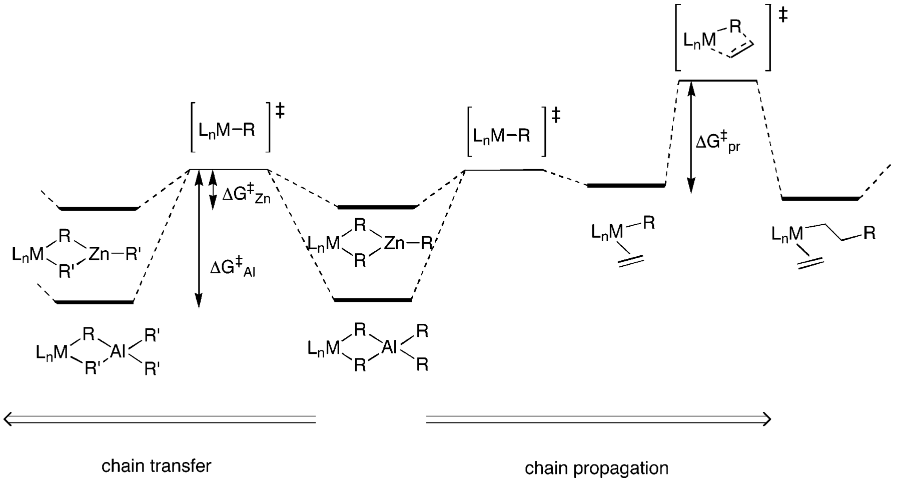
Scheme 2



transition metals.[94] Also for bis(imino)pyridine iron catalyst systems there is NMR evidence for the existence of bimetallic Fe−Al species.[95−98] From these observations, we may safely assume that in polymerization systems where chain transfer reactions with the aluminum cocatalyst occur, the catalyst resting state is likely to be a bimetallic, neutral or cationic, complex of the form $L_nM(\mu\text{-}R)_2AlR_2$.

Chain propagation and chain transfer to aluminum are believed to arise from this hetero-bimetallic $L_nM(\mu\text{-}R)_2AlR_2$ species via a substitution reaction with ethylene or AlR'_3, respectively, as depicted in the energy diagram shown in Scheme 2. These substitution reactions can occur either by a dissociative (via an iron alkyl intermediate), an associative or an interchange mechanism (only transition states). A dissociative or dissociative-interchange mechanism is most likely, as the resting state $L_nM(\mu\text{-}R)_2AlR_2$ is a coordinatively saturated species. In addition, large amounts of trialkyl aluminum lead to a decrease in polymerization activity, both in the case of iron (see Table 1) as well as for metallocenes.[83] For simplicity, we have shown the interchange mechanism, where L_nM-R represents a transition state, rather than an intermediate. The important barriers are the barrier for olefin insertion, $\Delta G^‡_{pr}$, and the barrier for chain transfer to aluminum, $\Delta G^‡_{Al}$. The relative heights of these barriers will determine the outcome of the polymerization reaction. If $\Delta G^‡_{Al} > \Delta G^‡_{pr}$, the resting state will be too stable and no polymerization will occur. This is the case for most stable bimetallic M−Al complexes mentioned previously. Also note that the $\Delta G^‡_{Al}$ for $Me_2Al(\mu\text{-}Me)_2AlMe_2$ has been determined to be 71 kJ/mol,[99] and that chain propagation as in the Ziegler Aufbau process is only observed under high-temperature and high-pressure conditions. If $\Delta G^‡_{Al} \approx \Delta G^‡_{pr}$, both polymerization and chain transfer to aluminum will occur, which is the situation observed in many polymerization systems. The third case $\Delta G^‡_{Al} < \Delta G^‡_{pr}$ will eventually lead to catalyzed chain growth, provided the difference is sufficiently large.

Bis(imino)pyridine Iron/MAO−Dialkyl Zinc System. The addition of 500 equiv. of diethyl zinc to the bis(imino)pyridine iron/MAO catalyst system results in a color change from orange to yellow-green, which is believed to be due to the formation of a bimetallic Fe−Zn complex (see eq 8). Zinc alkyls are generally monomeric and stable hetero bimetallic alkyl-bridged complexes involving zinc are very much rarer compared to aluminum. Only an ill-defined methyl-bridged ruthenium−zinc complex,[100] and a phenyl-bridged gold−zinc complex have been reported.[101] To date, we have not succeeded in isolating an iron−zinc species. However, the self-exchange of alkyl groups in dialkyl zinc species is common,[102] and diphenyl zinc is dimeric in the solid state.[103] Alkyl exchange reactions have also been reported to occur between zinc alkyls and other metal alkyls, such as boron,[104,105] aluminum[46] and cadmium,[99,106] Although four-centered bimetallic alkyl bridged complexes have not been isolated, they are reasonably invoked as intermediates in these reactions.

We propose that at high $ZnEt_2$ concentrations (>500 equiv.) the equilibrium reaction shown in eq 8 is shifted to the right,

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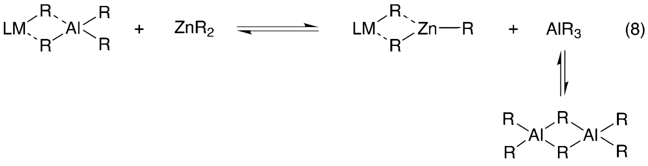
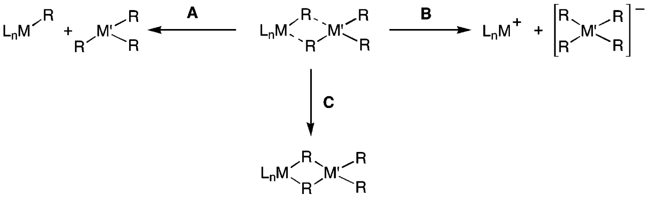


(8)

generating an alkyl bridged Fe−Zn complex. An additional driving force will be the tendency of trialkyl aluminum species to dimerize (71 kJ/mol for TMA). At lower $ZnEt_2$ concentrations, the two Fe−Al and Fe−Zn species are in equilibrium and an intermediate situation is indeed observed at, for example, 100 equiv.[68] The resulting four-centered Fe−Zn species will be less stable and higher in energy compared to the Fe−Al species, resulting in a lower activation barrier $\Delta G^{\ddagger}_{Zn}$, as shown in Scheme 2. As mentioned previously, statistical modeling has indicated that for efficient catalyzed chain growth to occur, the rate of chain transfer has to be about 100 times faster than chain propagation, which corresponds to a $\Delta\Delta G^{\ddagger} \approx 11$ kJ/mol between $\Delta G^{\ddagger}_{pr}$ and $\Delta G^{\ddagger}_{Zn}$. DFT calculations have previously given an estimate of $\Delta G^{\ddagger}_{pr} \approx 10$ kJ/mol,[107] which suggests that $\Delta G^{\ddagger}_{Zn}$ is probably very small indeed, which is in line with the extremely fast rates observed.

Scheme 3



Other Metal Alkyls. The effect of other metal alkyl compounds on the ethylene polymerization reaction, catalyzed by the bis(imino)pyridine iron/MAO system, may thus be rationalized in terms of the reactivity of the bimetallic catalyst resting state. The reactivity of the Fe−Al or Fe−Zn or any other hetero-bimetallic species will be determined by two main factors: the steric repulsion between the two metal fragments and the relative metal−carbon bond strengths. A fine balance between these factors is needed to generate a catalyst resting state which is stable, yet highly reactive. Three alternative scenarios for the interaction of a coordinatively unsaturated transition metal alkyl with a trivalent main group alkyl species can be envisaged as shown in Scheme 3. We shall discuss these in the context of steric effects and thermodynamic bond strengths.

(i) Steric Effects. There appears to be a direct correlation between the size of the ligand on the transition metal and the extent of observed chain transfer to aluminum. Both for early as well as late metal systems, significant amounts of chain transfer to aluminum are only observed when bulky ligands are employed.[108] In addition, catalyzed chain growth has only been observed with metal catalysts containing bulky ligands, such as 2,6-diisopropylphenyl or mesityl substituted bis(imino)-pyridine iron catalysts, in combination with dialkyl zinc, or pentamethylcyclopentadienyl lanthanide and actinide based systems with magnesium or aluminum alkyls, respectively. These bulky ligands are believed to destabilize the ground-state bimetallic species, i.e., disfavor the formation of too stable an adduct between the transition metal alkyl and the chain transfer agent (pathway **C** in Scheme 3). In addition, bulky ligands may also stabilize the transition state, the free metal alkyl species. Both effects will reduce the barrier $\Delta G^{\ddagger}_{Al}$ or $\Delta G^{\ddagger}_{Zn}$ and consequently increase the rate of chain transfer.

The steric requirements of the chain transfer reagent are also important. If we consider the results summarized in Table 5, the reactions involving $ZnMe_2$, $ZnEt_2$ or Zn^iPr_2, all show similar behavior. In all cases, catalyzed chain growth is observed, albeit with a slightly lower activity for Zn^iPr_2. From this it is clear that even long chain dialkyl zinc compounds are able to do very fast chain transfer to zinc, since no deviation from a Poisson distribution is observed at high growth factor. With dibenzyl zinc; some chain transfer to zinc occurs, as phenyl end-groups are observed, but efficient chain transfer is now probably affected by steric effects. Zn^tBu_2 appears to be too bulky and does not interfere with the polymerization reaction. This is situation **A** in Scheme 3, where the adduct formation is unstable. The much lower activity of $ZnPh_2$, which is dimeric in the solid state,[103] and the absence of phenyl end-groups may be attributed to the formation of relatively stable phenyl bridged adducts between iron and zinc (situation **C**).

For Group 13 metal alkyls, being trialkyls, one would expect steric effects to become more pronounced. No chain transfer to boron is observed when using BEt_3, which may be due to the small size of the boron atom and the steric repulsion that would result between alkyl groups in the bridged structure, for the same reason that boron trialkyls are monomeric. For aluminum alkyls, trimethyl aluminum, triethyl aluminum and at least the next few aluminum trialkyls are predominantly dimeric in solution. A significant activation energy (ca. 71 kJ/mol for TMA) is required for the dissociation of the dimer before exchange can occur.[99] However, this does not seem to present any major obstacle as both $AlMe_3$ and $AlEt_3$ show significant amounts of chain transfer to aluminum (runs 1.1−1.8, Table 1). Even longer chain aluminum alkyl compounds such as $AlOct_3$, which is monomeric in solution, show appreciable amounts of chain transfer. Only small amounts of chain transfer are observed with the much bulkier Al^iBu_3. In none of the Fe−Al combinations are the conditions for catalyzed chain growth fulfilled. The addition of dialkyl aluminum chlorides leads to catalyst deactivation, probably due to the formation of a stable chloro bridged Fe−Al complex. Gallium is similar in size to zinc and gallium alkyls are also monomeric in solution. Chain transfer to gallium is observed with $GaMe_3$, $GaEt_3$ and Ga^nBu_3 and catalyzed chain growth conditions are almost achieved in the case of $GaMe_3$, as we have shown in Figures 3 and 4. Comparing the results between $AlMe_3$, $GaMe_3$, and $ZnMe_2$ it appears that steric effects are not the only important criteria. We believe that the compatibility of metal carbon bond strengths is also important, which we address in the following section.

Group 14 metal alkyl compounds such as tin or lead tetraalkyls are monomeric in solution and no self-exchange of alkyl groups is generally observed. The formation of five-coordinate alkyl bridged bimetallic intermediates required for alkyl exchange, will be sterically unfavorable. However, alkyl exchange with aluminum alkyls has been claimed,[109] and small

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Table 6. Bond Dissociation Energies (BDEs) for Homoleptic Metal Alkyl Compounds (in kJ/mol)[a]

	B	Al[b]	Ga	Sn	Pb	Zn
methyl	373	283	259	227	162	184
ethyl	355	265	240	206	140	155
propyl	360	270	na	207	na	167
butyl	355	274	244	205	na	163

[a] BDEs for organometallic compounds are available in the literature,[115] but the values shown have been recalculated from experimentally determined heats of formation (ΔH_f) for the metal alkyl compounds MR_n,[116,117] using the standard formation enthalpies for the metal (M)[116] and the more recent values for alkyl radicals (R).[110] There is only very limited information available on the formation enthalpies for lithium and magnesium alkyls since these compounds are neither monomeric in the gas phase nor in solution. [b] Values are for monomeric AlR_3.

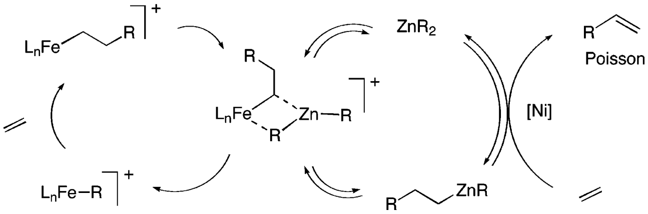
amount of chain transfer are observed when $SnMe_4$ and $PbEt_4$ are used as chain transfer agents (runs 2.8 and 2.9).

(ii) Metal−Carbon Bond Strengths. The second factor that will affect the reactivity of the hetero bimetallic catalyst resting states are the relative metal−carbon bond strengths. The average bond dissociation energies (BDEs) required for the homolytic cleavage of the metal carbon bond in the various metal alkyl compounds investigated here are collected in Table 6. It can be seen that boron−carbon bonds are among the strongest element-carbon bonds whereas zinc−carbon bonds are relatively weak. However, it is not the absolute bond strength that is important, but rather the compatibility of the metal−carbon bond strength within the transition metal alkyl and the main group alkyl that is important. There is little literature data available for the metal−carbon bond strengths in olefin polymerization catalysts,[115] but they are expected to be relatively weak for olefin insertion to occur. The only information available on iron carbon bonds suggests that they are slightly weaker than zinc carbon bonds.[110]

The bis(imino)pyridine iron/MAO catalyst system is significantly deactivated when using 500 equiv. BEt_3 (run 2.4). We believe that this is due to the formation of relatively stable borate $[BR_4]^-$ complexes, due to the mismatch between the weak iron carbon bond and the strong boron carbon bond (pathway **B** Scheme 3). This may also apply, to some extent, to aluminum. It is noteworthy that methyl migration from an iron center to $AlMe_3$ has been observed to form a stable, ionic iron(II) complex containing the $[AlMe_4]^-$ aluminate anion.[111] For zinc, the formation of zincate complexes is only seen in highly ionic alkaline-earth metal complexes of the type $[M(ZnR_3)_2]$.[112,113] The gallium carbon bond is only a little weaker than the aluminum carbon bond, but aluminum alkyls are dimeric and require additional dissociation energy for exchange reactions to occur. Higher metal alkyls of Group 13 (GaR_3 and InR_3) are essentially monomeric in solution and alkyl exchange reactions are generally fast.[99] Lead−carbon bond strengths are comparable to zinc−carbon bond strengths, but the lack of chain transfer using $PbEt_4$ is most reasonably attributed to steric congestion around the tetrahedral lead center.

For the metals listed in Table 6, the metal−carbon bonds are generally stronger in the case of methyl compared to ethyl or higher alkyls. This trend has also been seen for transition metal and rare earth metal alkyls.[114] The results described here have shown that only in the case of diethyl zinc and higher dialkyl zinc reagents, perfect Poisson distributions are obtained, indicating a very fast alkyl exchange between iron and zinc. The slightly stronger zinc-methyl bond is likely to be responsible for the deviation from a perfect Poisson distribution (PDI = 1.3) observed with $ZnMe_2$, due to a slower chain growth reaction from Zn-methyl to Zn-propyl. This is analogous to slow initiation within the context of a living polymerization system.

Scheme 4



Summary

In conclusion, we have carried out the first detailed examination of the factors that are important for differentiating between *chain transfer to metal* and *catalyzed chain growth* processes, the latter affording the technologically desirable Poisson distribution of products. The remarkably efficient catalyzed chain growth reaction for diethyl zinc compared to other metal alkyls can be rationalized on the basis of: (1) relatively low steric hindrance around the zinc center, (2) their monomeric nature in solution, (3) the relatively weak Zn−C bond, and importantly (4) a reasonably close match in Zn−C and Fe−C bond strengths. When combined with a nickel-catalyzed displacement reaction, the iron-catalyzed chain growth process on zinc can be used to convert ethylene to a Poisson distribution of linear α-olefins. The key components of the process: C−C bond formation on iron, facile and reversible exchange of oligomer/polymer chains between iron and zinc, and the nickel catalyzed olefin displacement reaction, are summarized in Scheme 4. We are currently investigating other monomers, such as propylene, for catalyzed chain growth as well as the effect of zinc alkyls on other polymerization catalyst systems.

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Supporting Information Available: Experimental procedures, formulas and methods used for Schulz−Flory and Poisson distributions and additional GPC data. This material is available free of charge via the Internet at http://pubs/acs.org.

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