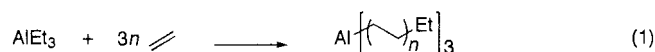


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Iron-Catalyzed Polyethylene Chain Growth on Zinc: Linear α -Olefins with a Poisson Distribution**

George J. P. Britovsek, Steven A. Cohen, Vernon C. Gibson,* Peter J. Maddox, and Martin van Meurs

Fifty years ago Ziegler and co-workers reported the *Aufbaureaktion* for alkylaluminum compounds.^[1] This reaction involves a stepwise insertion of ethylene into the Al–C bonds of, for example, triethylaluminum to give long-chain trialkylaluminum compounds [Eq. (1)]. Today, this chain-growth reaction is commercially exploited for the synthesis of linear α -olefins and primary alcohols from ethylene.^[2]

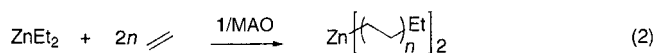
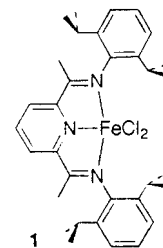


Subsequently, Ziegler and co-workers discovered the effect of transition metals such as colloidal nickel on this reaction, which suppressed chain growth to give only butene.^[3] The elucidation of this “nickel effect”, and the subsequent screening of the periodic table for the effects of other metals led to the discovery of the first transition metal catalyzed ethylene polymerization.^[4]

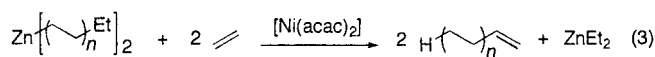
In their early reports,^[4] Ziegler and co-workers generally described the aluminum compound as the polymerization catalyst, with the transition metal compound functioning as the cocatalyst, and therefore considered the whole chain-

growth process to occur at the aluminum centers or, in other words, a transition metal catalyzed “*Aufbaureaktion*”. Later it was realized that in these polymerization systems, the polymer chain actually grows on the transition metal and not on the aluminum center. But, to complicate matters, in recent years it has been observed that, for certain early as well as late transition metal polymerization catalysts, under certain conditions, the polymer chain is transferred to the aluminum centers during the polymerization reaction, a process that is referred to as *chain transfer to aluminum*. This reaction is sometimes the only transfer process,^[5] but more often it occurs alongside the more common β -H transfer process.^[6–9] If chain transfer to aluminum constitutes the sole transfer mechanism, and the exchange of the growing polymer chains 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 transition metal catalyzed chain growth reaction on aluminum or, using Ziegler’s terminology, a transition metal catalyzed “*Aufbaureaktion*”. An attractive manifestation of this type of chain-growth reaction (catalyzed or uncatalyzed) is a Poisson distribution of main group alkyl products, as opposed to the Schulz–Flory distribution of olefinic products that arises when β -H transfer accompanies propagation.^[10]

Systems where these criteria are fulfilled, or are close to being fulfilled, have been described for transition metal and rare-earth metallocenes (on Al and Mg)^[11–14] and recently for half-sandwich complexes of chromium (on Al).^[16] Here we report the first highly active chain-growth process on zinc, catalyzed by bis(imino)pyridineiron catalyst **1** [Eq. (2)]. We also describe a nickel-catalyzed



displacement of the grown alkyl chain, in the presence of ethylene, to regenerate diethylzinc and to give a Poisson distribution of α -olefins [Eq. (3); acac = acetylacetonate].



In the absence of ZnEt_2 , a polymerization system containing **1** (5 μmol) and 100 equivalents of methylalumoxane (MAO) generates high molecular weight polyethylene with a broad molecular weight distribution (Table 1, Figure 1). A small amount of a low molecular weight fraction is also obtained, due to chain transfer to the AlMe_3 present in MAO. An increased proportion of low molecular weight material is obtained upon addition of 100 equivalents of ZnEt_2 (run 2, Table 1). At 500 equivalents of ZnEt_2 (2.5 mmol) a very narrow molecular weight distribution product results ($M_n = 700$, $M_w = 800$, $M_w/M_n = 1.1$). The polymer yield after hydro-

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Tabelle 1. Polymerization runs using **1** with various amounts of ZnEt₂.^[a]

Run	ZnEt ₂ [equiv]	Yield [g]	Activity [g mmol ⁻¹ h ⁻¹]	M _n	M _w	PDI	Vinyl chain ends	Saturated chain ends
1	0	3.01	1204	10000	192000	19.2	0.20	2.69
2	100	4.86	1944	3000	110000	36.8	0.18	8.05
3	500	3.51	1404	700	800	1.1	0.23	38.71

[a] Conditions: toluene solution, 5 μmol **1**, 100 equivalents of MAO, RT, 1 bar ethylene, 30 min.

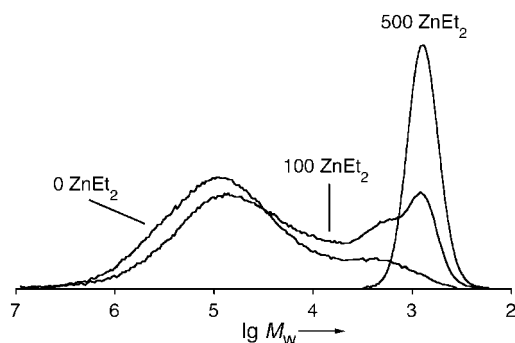


Figure 1. GPC traces of the polyethylene samples obtained by using different ratios of ZnEt₂ to catalyst system **1**/MAO.

lytic workup was 3.51 g, corresponding to an activity of 1404 g mmol⁻¹ h⁻¹ based on iron. Analysis of the polymer by NMR spectroscopy revealed a fully saturated linear alkane product.

The narrow molecular weight distribution is reminiscent of a living-polymerization system and lies in stark contrast to the broad molecular weight distribution typically observed with bis(imino)pyridineiron catalysts.^[9] The amount of polyethylene produced is 5 mmol (yield/M_n) corresponding to two alkyl chains per zinc center. This surprising result led us to conclude that long-chain dialkylzinc species had been produced by an iron-catalyzed chain-growth reaction on zinc, which after hydrolysis yielded linear alkanes. By contrast, the insertion of ethylene into a Zn–C bond in the absence of a catalyst is very slow and stops after one insertion.^[16, 17] The insertion of substituted alkenes into the Zn–C bond (carbocation) has been catalyzed by zirconium^[18] or palladium catalysts^[19] but also in these cases only a single insertion is generally observed.

During a typical polymerization experiment using **1**/MAO as the catalyst, but without diethylzinc (run 1, Table 1), the onset of polyethylene precipitation occurs within the first minute. In the presence of 500 equivalents of diethylzinc, the reaction solution remains clear for an extended period (ca. 15 min under the conditions used here) until an abrupt precipitation occurs when the solubility-limiting chain length (M_n ≈ 700) has been reached. Liquid samples were taken at two- to three-minute time intervals and, after hydrolysis, were analyzed by GC (Figure 2). The peak maximum of the Poisson distribution shifts to higher carbon number (*n*) with increased time, in an analogous fashion to the increase in M_n with time typical of living-polymerization systems.

Instead of hydrolysis, the grown alkyl chains can also be displaced from the zinc centers by an olefin-exchange reaction

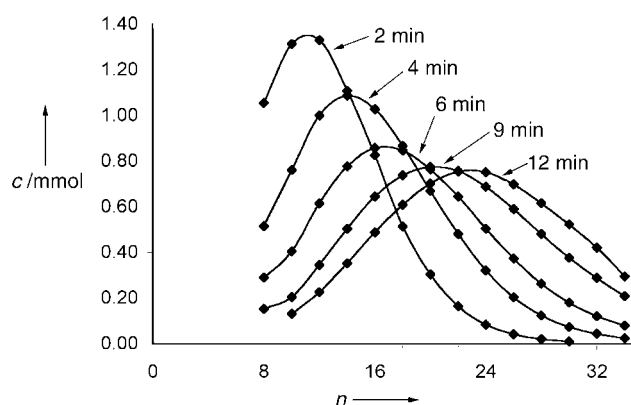


Figure 2. Alkane distributions obtained from the chain-growth reaction after different time intervals. *n* = carbon number.

that can be catalyzed by nickel complexes such as [Ni(acac)₂].^[20] After separation from the iron catalyst, the grown alkylzinc compounds were exposed to ethylene (1 bar) in the presence of 5% [Ni(acac)₂]. Analysis of the product by GC revealed clean formation of linear α-olefins, with a Poisson distribution of chain lengths.

To the best of our knowledge, these results represent the first observation of a catalyzed chain-growth reaction on zinc. Significantly, the chain-growth process occurs at an ethylene pressure of 1 bar and at room temperature, contrasting the more forcing conditions required for the uncatalyzed “Aufbaureaktion” (typically 100 °C, 100 bar ethylene). We are presently investigating the effect of other alkyl metal compounds in this reaction as well as other transition metal catalysts potentially suited to catalyzing the chain-growth reaction. Preliminary results indicate that Group 4 metallocenes and nickel α-diimine catalysts can also give rise to efficient chain transfer to zinc.

Experimental Section

2,6-Bis[1-(2,6-diisopropylphenyl)imino]ethylpyridineiron(II) chloride (1**)** was prepared according to an established procedure.^[11] MAO (10% in toluene) was obtained from Witco. Diethylzinc was used as a toluene solution (1.1M), obtained from Aldrich. Undecane was obtained from Aldrich and distilled over CaH₂ prior to use.

Chain transfer experiments: A catalyst solution was prepared from **1** (30 mg, 0.05 mmol), MAO (3 mL, 100 equiv), and toluene (22 mL). The clear orange solution was stirred for 5 min at room temperature. Aliquots of 2.5 mL of this solution (5 μmol **1**) were placed in four separate Schlenk flasks, each containing toluene (50 mL). After the addition of various amounts of ZnEt₂, (0, 100, and 500 equiv) the resulting yellow solutions were placed under ethylene (1 bar). The reactions were terminated after 30 min by the addition of dilute hydrochloric acid solution (1M). The products were filtered, washed with methanol, and dried at 50 °C in vacuum.

Chain-growth experiments: A catalyst solution was prepared from **1** (6 mg, 0.01 mmol), MAO (0.6 mL, 100 equiv), and toluene (24.4 mL). The clear orange solution was stirred for 5 min at room temperature. An aliquot of 2.5 mL of this solution (1 μmol **1**) was added to a ZnEt₂ solution (2.5 mL of 1.1M solution) in toluene (50 mL) under ethylene (1 bar). Time-dependent experiments were carried out by taking 1 mL samples (five in total) over a 12 minute period. The samples were immediately quenched with dilute HCl solution (1M), dried with MgSO₄, and filtered. Samples were analyzed by GC, using undecane as internal standard.

Displacement experiments: A chain-growth experiment was carried out using **1** (2 μmol) and ZnEt₂ (3.5 mL of a 1.1M solution in toluene) in toluene

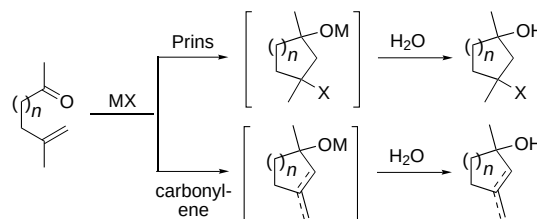
(50 mL) at room temperature and an ethylene pressure of 1 bar. After 8 min, the reaction mixture was transferred to another flask containing a slurry of dried silica (1.5 g) in toluene (10 mL) and MAO (1 mL). After stirring at room temperature for 15 min, the mixture was filtered into another flask containing $[\text{Ni}(\text{acac})_2]$ (90 mg, 0.35 mmol) in toluene. After the mixture had been stirred at room temperature for 30 min under an ethylene pressure of 1 bar, the reaction was quenched by the addition of dilute HCl (50 mL of a 1 M solution). After separation of the phases, the organic layer was dried over MgSO_4 and the product was analyzed by GC.

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Stereoselective Prins Cyclizations of δ,ϵ -Unsaturated Ketones to *cis*-3-Chlorocyclohexanols with TiCl_4 **

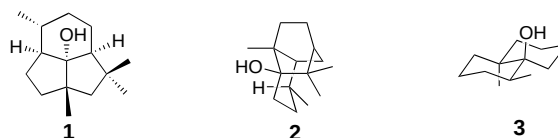
Chad E. Davis and Robert M. Coates*

The closely related Prins and carbonyl-ene cyclizations have proven to be useful transformations for forming five-membered, six-membered, and larger rings in the synthesis of carbocyclic natural products.^[1, 2] These similar annulation methods both involve initial electrophilic attack of an activated carbonyl group onto an olefin, followed by either nucleophilic capture or proton elimination (Scheme 1, MX = Lewis acid).



Scheme 1. Lewis acid mediated Prins and carbonyl-ene cyclizations of unsaturated ketones.

Although Lewis acid mediated Prins cyclizations of aldehydes^[1, 3] and trifluoromethyl ketones^[4, 5] are rather well documented in the literature, to our knowledge only a few examples of nucleophilic capture products from non-fluorinated ketones have been reported.^[6] This transformation would afford an attractive synthetic approach for the construction of hindered tertiary alcohols, a structural motif common in terpene natural products such as presilphiperfolan-8-ol (**1**), patchouli alcohol (**2**), and geosmin (**3**).^[7] Here we report TiCl_4 -mediated stereoselective Prins cyclizations of δ,ϵ - and ϵ,ζ -unsaturated ketones^[8] to *cis*-3-chlorocyclohexanols as well as comparisons with the corresponding reactions in which HCl is used.



A series of δ,ϵ -unsaturated ketones prepared by the Sakurai^[9] addition of allyl- or methallylsilanes to the requisite enone underwent cyclization in the presence of TiCl_4 (1.0 equiv) or HCl (0.9 equiv to large excess) in CH_2Cl_2 at

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