Video Article

Ethylene Polymerizations Using Parallel Pressure Reactors and a Kinetic Analysis of Chain Transfer Polymerization

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Abstract

We demonstrate a method for high-throughput catalyst screening using a parallel pressure reactor starting from the initial synthesis of a nickel α -diimine ethylene polymerization catalyst. Initial polymerizations with the catalyst lead to optimized reaction conditions, including catalyst concentration, ethylene pressure and reaction time. Using gas-uptake data for these reactions, a procedure to calculate the initial rate of propagation (k_p) is presented. Using the optimized conditions, the ability of the nickel α -diimine polymerization catalyst to undergo chain transfer with diethylzinc (ZnEt_2) during ethylene polymerization was investigated. A procedure to assess the ability of the catalyst to undergo chain transfer (from molecular weight and ^{13}C NMR data), calculate the degree of chain transfer, and calculate chain transfer rates (k_e) is presented.

Video Link

The video component of this article can be found at <http://www.jove.com/video/53212/>

Introduction

Polyolefins are an important class of industrial polymers with uses in thermoplastics and elastomers. Significant advances in the design of single-site catalysts for the production of polyolefins has led to the ability to tune molecular weight, polydispersity, and polymer microstructure, which leads to a wide range of potential applications.¹⁻³ More recently, chain transfer and chain shuttling polymerizations have been developed to give an additional route to modify the properties of the polymer without having to modify the catalyst.^{4,6} This system employs a single-site transition metal catalyst and a chain transfer reagent (CTR), which is typically a main group metal alkyl. During this polymerization, the growing polymer chain is able to transfer from the catalyst to the CTR, where the polymer chain remains dormant until it is transferred back to the catalyst. Meanwhile, the alkyl group that was transferred to the catalyst can initiate another polymer chain. In a chain transfer polymerization, one catalyst can initiate a greater number of chains compared to a standard catalytic polymerization. The polymer chains are terminated with the chain transfer metal; therefore further end-group functionalization is possible. This system can be used to change the molecular weight and molecular weight distribution of polyolefins,⁷ to catalyze Aufbau-like alkyl chain growth on main group metals,⁸ and for the synthesis of specialty polymers involving multicatalyst systems, such as block copolymers.^{9,10}

Chain transfer polymerizations have been observed most commonly with early transition metals (Hf, Zr) and alkylzinc or alkylaluminum reagents, although examples exist across the transition metal series.^{5,7,8,11-16} In typical early transition metal catalyst systems, chain transfer is fast, efficient and reversible leading to narrow molecular weight distributions. Chain transfer/shuttling has been observed in mid-to-late transition metals (e.g. Cr, Fe, Co and Ni) with group 2 and 12 metal alkyls, although the rates of transfer are highly variable compared to early metals.^{4,7,17-19} Two main factors are apparently necessary for efficient chain transfer: a good match of metal-carbon bond dissociation energies for the polymerization catalyst and chain transfer reagent, and an appropriate steric environment to promote bimolecular formation/breakage of alkyl-bridged bimetallic intermediates.²⁰ In the case of late transition metals, if the catalyst does not contain enough steric bulk, beta-hydride (β -H) elimination will be the dominant termination pathway and will generally out-compete chain transfer.

Herein we report on a study of bimetallic chain transfer from nickel to zinc in a bis(2,6-dimethylphenyl)-2,3-butanediimine-based catalyst system with diethylzinc (ZnEt_2) through small-scale high-throughput reactions. Chain transfer will be identified by examining changes in the molecular weight (M_w) and dispersity index of the resulting polyethylene through gel-permeation chromatography analysis. Chain transfer will also be identified through ^{13}C NMR analysis of the ratio of vinyl to saturated chain ends as a function of chain transfer agent concentration. An in-depth kinetic analysis of the rates of propagation and chain transfer will also be presented.

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS) before use. Several of the chemicals used in these syntheses are acutely toxic and carcinogenic, while several are pyrophoric and ignite in air. Please use all appropriate safety practices when performing these

reactions including the use of engineering controls (fume hood, glovebox) and personal protective equipment (safety glasses, gloves, lab coat, full length pants, closed-toe shoes). Portions of the following procedures involve standard air-free handling techniques.

1. Preparation of [bis(2,6-dimethylphenyl)-2,3-butanediimine]NiBr₂,²¹⁻²⁵

- Preparation of bis(2,6-dimethylphenyl)-2,3-butanediimine: (α -diimine)
 - Dissolve 2,3-butanedione (1.0 ml, 11 mmol) and 2,6-dimethylaniline (2.8 ml, 23 mmol) in 20 ml of methanol in a 100 ml round bottom flask.
 - Add formic acid (0.4 ml, 11 mmol) and stir the reaction at room temperature until the diimine precipitates (typically 1-2 hr, but can be left overnight). If a precipitate does not form, concentrate the reaction mixture using a rotary evaporator and cool in an ice bath.
 - Filter the reaction mixture using glass frit and filter flask and wash the yellow solid with 20 ml of cold methanol and dry *in vacuo*.
Note: ¹H NMR (500 MHz, CD₂Cl₂): δ 7.06 (d, J = 7.6 Hz, 4H), 6.92 (t, J = 7.5 Hz, 2H), 2.00-1.99 (m, 19H).
- Preparation of (1,2-dimethoxyethane)NiBr₂: DME-NiBr₂
 - Under a nitrogen atmosphere, combine anhydrous nickel bromide (NiBr₂, 15 g, 0.069 mol), triethylorthoformate (30 ml, 0.185 mol) and methanol (100 ml) in a 2-neck round-bottom flask fitted with a reflux condenser and rubber septum on a Schlenk line under a nitrogen atmosphere.
 - Reflux the brown reaction mixture under a nitrogen atmosphere until a green solution forms. This typically takes 2-3 hr, however this reaction can be left refluxing overnight if necessary.
 - After allowing the mixture to cool, concentrate the reaction mixture using the vacuum pump on the Schlenk line to form a dark green gel.
 - Cannula transfer an excess 1,2-dimethoxyethane (DME, 100 ml) onto the green gel, which instantly forms orange solid. Once all the DME is added, heat the reaction at 85 °C for an additional 2 hr until a light orange reaction mixture forms. Cool the reaction to room temperature, at which point a light-orange solid precipitates.
 - Remove the reflux condenser from the reaction flask and replace with a Schlenk frit connected to a second Schlenk receiving flask under a nitrogen atmosphere. Rotate the entire apparatus by 180° causing the orange reaction mixture to enter the Schlenk frit and filter the reaction mixture.
 - Remove the original reaction flask and place a septum on the Schlenk frit. Cannula transfer DME (100 ml) and then pentane (100 ml) to wash the DME-NiBr₂. Dry the orange solid *in vacuo* and bring into the glovebox.
Note: DME-NiBr₂ can be stored indefinitely under a nitrogen atmosphere at room temperature. When left open to the atmosphere, it forms a green, hydrated gel.
- Preparation of [bis(2,6-dimethylphenyl)-2,3-butanediimine]NiBr₂: ([α -diimine]NiBr₂)
 - In the glovebox, combine DME-NiBr₂ (1.0 g, 3.2 mmol) and bis(2,6-dimethylphenyl)-2,3-butanediimine (1.1 g, 3.8 mmol) in a 50 ml round bottom flask.
 - Add 20 ml of dichloromethane and stir overnight at room temperature.
 - Filter the reaction mixture with a glass frit and filter flask. Wash the brown solid with 75 ml of dichloromethane and dry *in vacuo*.
Note: This nickel catalyst can be stored indefinitely in an inert-atmosphere glovebox at room temperature. It is also insoluble in most solvents, so standard characterizations were not performed.

2. Preparation of Catalytic Stock Solutions

- Preparation of [[α -diimine]Ni(CH₃)]⁺ [MAO]⁻ stock solution
 - Prepare a 1.0×10^{-3} M catalyst stock solution by adding 0.0041 g of [α -diimine]NiBr₂ (8.0×10^{-6} mol) into a vial with 7.5 ml of toluene.
 - To the stirred nickel suspension, add 0.50 ml of 30% methylaluminoxane (MAO) in toluene and stir for 1 min. The color will change from a brown suspension to a blue-green solution. This solution can be stored at -30 °C for up to 6 hr and used in subsequent polymerizations.
Note: Methylaluminoxane is pyrophoric and will smoke in air. It should only be used in an inert-atmosphere glovebox and care should be taken when removing contaminated syringes/glassware from the glovebox. Typically, the syringes and glassware are washed with toluene in the glovebox and placed in a metal can, separate from Kimwipes or any other flammable substances. The contaminated toluene is capped in a vial and removed from the glovebox with the metal can. These items are transferred to the fume hood where they open to air and allowed to slowly quench behind the protective glass.
- Preparation of ZnEt₂ stock solution
 - Prepare a 1.2 M solution by dissolving 0.25 ml of ZnEt₂ in 1.75 ml toluene.
Note: Diethylzinc is pyrophoric and will ignite in air. It should only be used in an inert atmosphere glovebox and care should be taken when removing contaminated syringes/glassware from the glovebox. Typically, the syringes and glassware are washed with toluene in the glovebox and placed in a metal can, separate from Kimwipes or any other flammable substances. The contaminated toluene is capped in a vial and removed from the glovebox with the metal can. These items are transferred to the fumehood where they open to air and allowed to slowly quench behind the protective glass.

3. Catalytic Polymerizations Using a Parallel Pressure Reactor

- Pressure Scope
 - Set up all polymerization reactions in a parallel pressure reactor with overhead stirring housed in an N₂ atmosphere glovebox. Program the polymerization in the software: indicate total reaction volume (3.0 ml), the purge gas (N₂), the desired reaction gas (ethylene), the desired pressure (15-150 psi), and the desired reaction time (1 hr).

Note: A Biotage Endeavor Parallel Pressure Reactor with a separate computer capable of monitoring the gas uptake was used for polymerizations. All polymerizations were done at least three times to ensure accuracy and reproducibility. Using this type of reactor several variables can be adjusted within a single experiment or over the course of multiple experiments including: the reaction gases, pressure, temperature, time, solvent, volume, catalyst, or chain transfer reagent. By doing eight reactions at a time with real-time gas uptake, catalytic reactions are efficiently tested. In this case, the reaction vials have a maximum volume of 5 ml, therefore a volume of 3 ml was chosen to account for the formation of polymer. Also, standard concentrations, pressures and times were based of literature conditions.²¹ These polymerizations can all be done in individual pressure reactors or even on a Schlenk line, however it is more difficult to achieve higher pressures or gas uptake for the reactions.

2. Insert glass liner reaction vials into the eight wells. Use the depth tool to ensure the glass liners are at the appropriate height. Insert the blade impellers into the overhead assembly.
3. Fill the reaction vials according to **Table 1**:

Reaction Vessel	Pressure (psi)	Catalyst Vol. (ml)	ZnEt ₂ Vol. (ml)	Toluene Vol. (ml)
1	15	0	0	3
2	15	0.1	0	2.9
3	30	0	0	3
4	30	0.1	0	2.9
5	60	0	0	3
6	60	0.1	0	2.9
7	150	0	0	3
8	150	0.1	0	2.9

Table 1. Reaction conditions for the pressure scope reactions.

4. Ensure the O-rings are properly seated in the metal grooves and carefully place the overhead stirring assembly on the base and screw down in an alternating fashion. Ensure all screws are tight and press start in the software. Monitor the reaction *via* gas uptake measurements.
5. After 1 hr of polymerization, remove the reaction vials from the glove box and precipitate polyethylene with the addition of 5% hydrochloric acid in methanol, remove solvent and dry *in vacuo*. Mass the polymer to obtain the yield and compare to the ethylene consumption during the reaction.
6. Calculate the activity of the catalyst, which is the mass of polymer formed per mole of catalyst, per hour of polymerization.
7. Analyze the molecular weight and dispersity index of the dried polyethylene using high temperature Gel Permeation Chromatography (GPC). Dissolve 0.002 g of the polymer in 2 ml 1,2,4-trichlorobenzene at 135 °C. Run the GPC according to manufacturer's protocol. Note: An Agilent PL-GPC 220 High Temperature GPC/SEC system was used at 135 °C and data was fit using polystyrene standards to analyze the molecular weight of the polymer.
8. Analyze the degree of branching, the branch type and the end group type of the dried polyethylene using high-temperature ¹³C NMR. Dissolve 0.050-0.080 g of the polymer in 0.5 ml of tetrachloroethane-d₂ (C₂D₂Cl₄) at 130 °C. Run the samples on a 600 MHz NMR at 130 °C for at least 2,000 scans. Assign polymer branching according to the literature.²⁶⁻²⁸ Note: An Agilent/Varian 600 MHz spectrometer at 130 °C was used for ¹³C NMR analysis.

2. Chain Transfer Polymerization

1. Following the same procedures and analysis as Section 3.1, fill the reactor and program the software according to the parameters in **Table 2**:

Reaction Vessel	Pressure (psi)	Catalyst Vol. (ml)	ZnEt ₂ Vol. (ml)	Toluene Vol. (ml)
1	60	0.1	0	2.9
2	60	0.1	0.005	2.9
3	60	0.1	0.01	2.89
4	60	0.1	0.015	2.89
5	60	0.1	0.025	2.88
6	60	0.1	0.042	2.86
7	60	0.1	0.06	2.84
8	60	0.1	0.085	2.82

Table 2. Reaction conditions for the chain transfer polymerization reactions.

2. In addition, calculate the moles of chains extended due to the presence of ZnEt₂ and the number of chains initiated per mole of catalyst based on the following equations.⁷

$$(M-R)_{\text{Extended}} = \frac{\text{Yield}_{\text{Polymer}}}{M_n} \quad (1)$$

$$\text{Chains}_{\text{Initiated}} = \frac{(M-R)_{\text{Extended}}}{\text{Moles}_{\text{Catalyst}}} \quad (2)$$

$(M-R)_{\text{Extended}}$ - moles of chains extended due to the presence of ZnEt_2 (mol)

$\text{Yield}_{\text{Polymer}}$ - Mass of polymer formed (g)

M_n - Number average molecular weight of the polymer from GPC (g/mol)

$\text{Chains}_{\text{Initiated}}$ - Number of chains initiated per mole of catalyst

$\text{Moles}_{\text{Catalyst}}$ - Moles of catalyst used in the polymerization

3. Make a plot of the number chains initiated versus the concentration of ZnEt_2 .

4. Kinetic Analysis of Polymerizations: Rates of Chain Transfer and Propagation

1. Rate of Propagation (k_p)
 1. For each run where only $[\alpha\text{-diimine}]\text{NiBr}_2$ is present, make a plot of ethylene consumption versus time.
 2. Fit the initial ethylene gas uptake in the linear region to obtain the initial rate. In the case of **Figure 2a**, the traces were fit from 500 to 2,000 sec.
 3. Use the average of the slopes to obtain the rate of propagation (k_p) for the particular catalyst at the desired pressure.
2. Rate of chain transfer (k_e)
 1. Estimate the concentration of ethylene, $[\text{C}_2^-]$, in 3.0 ml of toluene from the average gas uptake (solubility) by finding the number of moles of gas consumed in the reactors that do not contain catalyst.
 2. Make a Mayo plot of $1/M_n$ (from the molecular weight data obtained from the GPC) versus $[\text{ZnR}_x]/[\text{C}_2^-]$ (from the concentration of ZnEt_2 placed in the reactor).^{7, 29}
 3. Fit the data to a linear line based on the Mayo equation. Multiply the slope by 28, the molecular weight of ethylene, to obtain the ratio of the rate of chain transfer to the rate of propagation (k_e/k_p).

$$\frac{1}{M_n} = \frac{1}{M_n^0} + \frac{k_e \cdot [\text{ZnR}_x]}{k_p \cdot 28 \cdot [\text{C}_2^-]} \quad (3)$$

M_n - Number average molecular weight of the polymer from GPC with ZnEt_2

M_n^0 - Number average molecular weight of the polymer from GPC without ZnEt_2

k_e - Rate of chain transfer

k_p - Rate of propagation

$[\text{ZnR}_x]$ - Concentration of ZnEt_2 in the reaction

$[\text{C}_2^-]$ - Concentration of ethylene in the reaction

28 - The molecular weight of ethylene

4. Multiply k_e/k_p by k_p obtained in the previous section to get the rate of chain transfer k_e .

Representative Results

The ethylene gas consumption versus time is presented in **Figure 1** for the different ethylene pressures tested. This data is used to determine optimized reaction conditions. The ethylene gas consumption versus time is presented in **Figure 2A** for the catalyst alone samples, which is used to calculate the rate of propagation (k_p). **Figure 2B** shows gel permeation chromatography (GPC) traces for chain transfer polymerizations with 0-1,000 equivalents of diethylzinc. The GPC is used to calculate the molecular weight (M_n) and dispersity ($\mathcal{D}$) of the polymer samples, which is presented in **Table 1**. **Figure 3** shows ^{13}C NMR of the polyethylene samples, with **3A** showing the spectra of the full series and **3B** showing a zoomed in spectrum with the peaks labeled. The molecular weight data is used to calculate the number of chains initiated (**Figure 4A** and **Table 1**) and the Mayo plot (**Figure 4B**). The fit of the Mayo plot is used to calculate the ratio of the rate of chain transfer to the rate of propagation (k_e/k_p), which is used to calculate the rate of chain transfer (k_e).

Figure 1: Ethylene consumption versus time at selected pressures.

Figure 2: (A) Ethylene consumption versus time for catalyst [α-diimine]NiBr₂ at 60 psi ethylene. The slope of the linear region was used to calculate k_p . (B) GPC traces of polymer obtained from catalyst [α-diimine]NiBr₂ activated with MAO in the presence of ZnEt₂ (0-1,020 eq.) in 1,2,4-trichlorobenzene at 135 °C. Figure adapted from reference ²⁰.

Figure 3: (A) ^{13}C NMR in $\text{C}_2\text{D}_2\text{Cl}_4$ at 130°C of polyethylene from $[\alpha\text{-diimine}]\text{NiBr}_2$ activated with MAO. The concentration of ZnEt_2 increases from bottom to top. (B) ^{13}C NMR in $\text{C}_2\text{D}_2\text{Cl}_4$ at 130°C of polyethylene from $[\alpha\text{-diimine}]\text{NiBr}_2$ activated with MAO with 1,020 eq. ZnEt_2 . Polyethylene peak assignments showing saturated end groups labeled S_x .²⁸ Figure adapted from reference²⁰. [Please click here to view a larger version of this figure.](#)

Figure 4: (A) Average polymer chains initiated per nickel catalyst versus the amount of ZnEt₂ for [α-diimine]NiBr₂ over 3 runs. The error bars represent the standard deviation. (B) Mayo plot of the catalyst ligand steric effects on ethylene polymerization with [α-diimine]NiBr₂ and ZnEt₂, and calculations of k_e/k_p and k_e . Figure adapted from reference²⁰.

Entry	Equiv. ZnEt ₂ ^a	Yield (g)	Activity (g * mol ⁻¹ * hr ⁻¹ * 10 ⁻⁵)	M _n (x 10 ⁻⁵) ^b	Đ	Mol (Zn-R) _{ext} (x 10 ⁷) ^c	Chains/Ni ^d
1	0	0.199	19.9	1.52	2.37	-	13.1
2	60	0.18	18	1.31	2.56	13.8	13.8
3	120	0.299	29.9	1.12	2.41	26.7	26.7
4	180	0.216	21.6	0.953	2.46	22.7	22.7
5	300	0.178	17.8	0.689	2.39	25.8	25.8
6	500	0.189	18.9	0.506	2.17	37.2	37.2
7	720	0.179	17.9	0.406	2.08	44.1	44.1
8	1,020	0.268	26.8	0.278	2.16	96.4	96.4

Table 3: Data for ethylene polymerizations with the [α-diimine]NiBr₂ catalyst and ZnEt₂. All values are the average of at least 3 runs. Conditions: 1 x 10⁻⁷ moles catalyst, 500 equivalents of MAO, 60 psi ethylene, room temperature, 1 hr, toluene solvent (3.0 ml). ^aEquivalents of ZnEt₂ based on the amount of catalyst. ^bDetermined by GPC. ^cDefined as the number of ethyl groups that has been extended with ethylene, determined by GPC. ^dThe number of chains initiated per total molar amount of polymerization catalyst.

Discussion

A methyl-substituted cationic [α-diimine]NiBr₂ ethylene polymerization catalyst activated with MAO was examined for its competency for ethylene chain transfer polymerizations. The reactions were monitored *via* gas uptake measurements to determine the rate and extent of polymerization and catalyst lifetime, and the molecular weight of the resultant polymers were determined *via* gel permeation chromatography (GPC). Initially, the nickel catalyst was tested over a range of ethylene pressures (from 15-225 psi) to determine optimal conditions for this system in the absence of ZnEt₂. Using a 3.33 x 10⁻⁵ M reaction solution of catalyst (0.1 ml of the catalyst stock solution and 3.0 total reaction volume), a pressure of 60 psi of ethylene was found to produce an optimal combination of catalyst lifetime and ethylene consumption. It is important that the catalyst is active for the entire polymerization while also producing significant amounts of polyethylene for analysis. **Figure 1** shows the ethylene consumption versus time at 4 selected pressures of 15, 30, 60 and 150 psi. At pressures of 15 and 30 psi, the ethylene consumption is linear over the time period tested, indicating an active catalyst, however small amounts of polymer are produced, which could complicate characterization. At 150 psi, the initial gas consumption is linear, and a significant amount of polymer is produced. However, it reaches a saturation point 25 min into the run, indicating an inactive catalyst. At 60 psi, the gas consumption is linear and a significant amount of polymer is produced allowing for easy isolation and characterization of the sample. Using the optimal conditions at 60 psi, multiple polymerizations were attempted to probe the reproducibility of the system in addition to the initial rate of propagation (k_p). **Figure 2A** shows the ethylene uptake for four runs under identical conditions. From the initial slope (from 500 to 2,000 sec), k_p was calculated to be 0.00319 M⁻¹ sec⁻¹.

Chain transfer polymerizations were tested in the presence of excess molar equivalents (0 to 1,020 equiv.) of ZnEt₂ holding all other conditions constant. In the cases where polymerization was successful, catalyst systems that underwent chain transfer were identified by a *reduction* of M_n as the concentration of main group ZnEt₂ increased. **Figure 2B** shows the GPC traces moving to longer retention times as a function of

increasing $[ZnEt_2]$, where the longer retention times indicate a polymer with a lower molecular weight. **Table 3** also lists the M_n of the produced polyethylene indicating successful chain transfer from Ni to Zn. The polymerization activity and molecular weight dispersity did not systematically vary across all $[ZnEt_2]$ (**Table 3**). In addition, the polymer microstructure determined from the ^{13}C NMR in **Figure 3A** remains constant over the range $[ZnEt_2]$. **Figure 3B** shows only saturated chain ends are present (marked S_x) indicating chains terminated on the Zn. Vinyl chain ends (at 111 and 136 ppm) would be expected from chain termination on the Ni due to β -H elimination, however these peaks are not present in this sample.^{20, 28} This data proves successful chain transfer from Ni to Zn and disproves competing side reactions involving the catalyst and chain transfer reagent that could alter the resulting polymer. Analysis of the polymer microstructure is also important because a change in the polymer microstructure could be indicative of a change in the nature of the catalyst species, which would make kinetic comparison impossible.

The amount of chain transfer can be quantified in two ways: first, as the amount (mol) of main group metal alkyl groups extended (equation 1),⁷ and second, by examining the number of chains initiated per total molar amount of polymerization catalyst (equation 2). **Figure 4A** shows a plot of the number of chains initiated versus the concentration of $ZnEt_2$. This catalyst systems shows a linear dependence on the number of polymer chains generated per Ni and the $[ZnEt_2]$. This type of plot can be used to compare the degree of chain transfer across different catalyst systems to determine ideal matches; for example multiple catalysts and the same chain transfer agent or multiple chain transfer agents and a single catalyst.

Mayo plot analysis of the catalytic system can reveal the relative rates of chain transfer with Zn (k_e) to propagation (k_p) based on the Mayo equation (equation 3). Fitting **Figure 4B** reveals $k_e/k_p = 0.00355$ for $[\alpha\text{-diimine}]NiBr_2$. The absolute rates of chain transfer (k_e) in these systems, calculated from k_p in the absence of $ZnEt_2$, yields $k_e = 1.14 \times 10^{-5} M^{-1} sec^{-1} \pm 4.42 \times 10^{-7}$. Using this type of kinetic analysis, it is straightforward to determine how the system is affected by addition of chain transfer agent, whether it is the rate of propagation, chain transfer or both. However, Mayo plot kinetic analysis is limited to systems that undergo chain transfer polymerizations.

We have demonstrated the ability of a $[\alpha\text{-diimine}]NiBr_2$ polymerization catalyst to undergo chain transfer with metal alkyls during ethylene polymerization. Although chain transfer from Ni to Zn is slower than many previously reported systems, using high-throughput screening and straightforward kinetic analysis it will be possible to study a large number of late transition metals, ligand frameworks and metal combinations in a short amount of time. With the data obtained from high-throughput chain transfer polymerizations and prudent catalyst system design, it will be possible to finely tune and exploit chain transfer with late transition metal complexes to produce new polymers, efficient routes to common polymers and specialty block copolymers.

Disclosures

The authors declare no competing financial interest.

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References

- Gibson, V. C., Spitzmesser, S. K. Advances in Non-Metallocene Olefin Polymerization Catalysis. *Chem. Rev.* **103** (1), 283-316 (2002).
- Coates, G. W. Precise Control of Polyolefin Stereochemistry Using Single-Site Metal Catalysts. *Chem. Rev.* **100** (4), 1223-1252 (2000).
- Resconi, L., Cavallo, L., Fait, A., Piemontesi, F. Selectivity in Propene Polymerization with Metallocene Catalysts. *Chem. Rev.* **100** (4), 1253-1346 (2000).
- Valente, A., Mortreux, A., Visseaux, M., Zinck, P. Coordinative Chain Transfer Polymerization. *Chem. Rev.* **113** (5), 3836-3857 (2013).
- Sita, L. R. Ex Uno Plures ("Out of One, Many"): New Paradigms for Expanding the Range of Polyolefins through Reversible Group Transfers. *Angew. Chem., Int. Ed.* **48** (14), 2464-2472 (2009).
- Kempe, R. How to Polymerize Ethylene in a Highly Controlled Fashion? *Chem. Eur. J.* **13** (10), 2764-2773 (2007).
- van Meurs, M., Britovsek, G. J. P., Gibson, V. C., Cohen, S. A. Polyethylene Chain Growth on Zinc Catalyzed by Olefin Polymerization Catalysts: A Comparative Investigation of Highly Active Catalyst Systems across the Transition Series. *J. Am. Chem. Soc.* **127** (27), 9913-9923 (2005).
- Wei, J., Zhang, W., Sita, L. R. Aufbaureaktion Redux: Scalable Production of Precision Hydrocarbons from AlR_3 ($R=Et$ or iBu) by Dialkyl Zinc Mediated Ternary Living Coordinative Chain-Transfer Polymerization. *Angew. Chem., Int. Ed.* **49** (10), 1768-1772 (2010).
- Arriola, D. J., Carnahan, E. M., Hustad, P. D., Kuhlman, R. L., Wenzel, T. T. Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization. *Science*. **312** (5774), 714-719 (2006).
- Mazzolini, J., Espinosa, E., D'Agosto, F., Boisson, C. Catalyzed chain growth (CCG) on a main group metal: an efficient tool to functionalize polyethylene. *Polymer Chemistry*. **1** (6), 793-800 (2010).
- Britovsek, G. J. P., Cohen, S. A., Gibson, V. C., van Meurs, M. 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. *J. Am. Chem. Soc.* **126** (34), 10701-10712 (2004).
- Gibson, V. C. Shuttling Polyolefins to a New Materials Dimension. *Science*. **312** (5774), 703-704 (2006).
- Chenal, T., Ollonde, X., Pelletier, J.-F., Bujadoux, K., Mortreux, A. Controlled polyethylene chain growth on magnesium catalyzed by lanthanidocene: A living transfer polymerization for the synthesis of higher dialkyl-magnesium. *Polymer*. **48** (7), 1844-1856 (2007).

14. Busico, V., Cipullo, R., Chadwick, J. C., Modder, J. F., Sudmeijer, O. Effects of Regiochemical and Stereochemical Errors on the Course of Isotactic Propene Polyinsertion Promoted by Homogeneous Ziegler-Natta Catalysts. *Macromolecules*. **27** (26), 7538-7543 (1994).
15. Annunziata, L., Duc, M., Carpentier, J.-F. Chain Growth Polymerization of Isoprene and Stereoselective Isoprene-Styrene Copolymerization Promoted by an ansa-Bis(indenyl)allyl-Yttrium Complex. *Macromolecules*. **44** (18), 7158-7166 (2011).
16. Kretschmer, W. P., *et al.* Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution. *Chem. Eur. J.* **12** (35), 8969-8978 (2006).
17. Britovsek, G. J. P., Cohen, S. A., Gibson, V. C., Maddox, P. J., van Meurs, M. Iron-Catalyzed Polyethylene Chain Growth on Zinc: Linear α -Olefins with a Poisson Distribution. *Angew. Chem., Int. Ed.* **41** (3), 489-491 (2002).
18. Xiao, A., *et al.* A Novel Linear-Hyperbranched Multiblock Polyethylene Produced from Ethylene Monomer Alone via Chain Walking and Chain Shuttling Polymerization. *Macromolecules*. **42** (6), 1834-1837 (2009).
19. Simon, L. C., Mauler, R. S., De Souza, R. F. Effect of the alkylaluminum cocatalyst on ethylene polymerization by a nickel-diimine complex. *J. Polym. Sci. A Polym. Chem.* **37** (24), 4656-4663 (1999).
20. Hue, R. J., Cibuzar, M. P., Tonks, I. A. Analysis of Polymeryl Chain Transfer Between Group 10 Metals and Main Group Alkyls during Ethylene Polymerization. *ACS Catalysis*. **4** (11), 4223-4231 (2014).
21. Johnson, L. K., Killian, C. M., Brookhart, M. New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and α -Olefins. *J. Am. Chem. Soc.* **117** (23), 6414-6415 (1995).
22. Ittel, S. D., Johnson, L. K., Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **100** (4), 1169-1204 (2000).
23. Bautista, R., *et al.* Synthesis and Diels-Alder Cycloadditions of exo-Imidazolidin-2-one Dienes. *J. Org. Chem.* **76** (19), 7901-7911 (2011).
24. Rulke, R. E., *et al.* NMR study on the coordination behavior of dissymmetric terdentate trinitrogen ligands on methylpalladium(II) compounds. *Inorg. Chem.* **32** (25), 5769-5778 (1993).
25. Ward, L. G. L., Pipal, J. R. Anhydrous Nickel (II) Halides and their Tetrakis (Ethanol) and 1,2-Dimethoxyethane Complexes. *Inorg. Syntheses*. **13**, 154-164, (1972).
26. Galland, G. B., de Souza, R. F., Mauler, R. S., Nunes, F. F. ¹³C NMR Determination of the Composition of Linear Low-Density Polyethylene Obtained with [η³-Methallyl-nickel-diimine]PF₆ Complex. *Macromolecules*. **32** (5), 1620-1625 (1999).
27. Cotts, P. M., Guan, Z., McCord, E., McLain, S. Novel Branching Topology in Polyethylenes As Revealed by Light Scattering and ¹³C NMR. *Macromolecules*. **33** (19), 6945-6952 (2000).
28. Wiedemann, T., *et al.* Monofunctional hyperbranched ethylene oligomers. *J. Am. Chem. Soc.* **136** (5), 2078-2085 (2014).
29. Mayo, F. R. Chain Transfer in the Polymerization of Styrene: The Reaction of Solvents with Free Radicals¹. *J. Am. Chem. Soc.* **65** (12), 2324-2329 (1943).