Selective Synthesis of Al-Terminated Polyethylenes Using a Bis(Phenoxy-Imine)Zr Complex with Methylalumoxane

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Received February 9, 2005

Revised Manuscript Received April 21, 2005

Al-terminated polyethylenes (Al-PEs) are useful precursors for end-functionalized PEs and PE- and polar polymer-based block and graft copolymers, which are expected to exhibit new or innovative material properties.[1−4] The most reasonable synthetic procedure for Al-PEs would be a direct synthesis by chain transfer to the aluminum species, which is used as a cocatalyst during the course of the polymerization.[1,5] However, the selective preparation of Al-PEs is generally difficult because homogeneous olefin polymerization catalysts often favor β-H transfer over chain transfer to aluminum for ethylene polymerization. Therefore, the development of a catalyst that can produce Al-PEs selectively is a challenge in the field of polymerization catalysis and polymer synthesis.[6]

Recently, on the basis of a ligand-oriented catalyst design concept,[7,8] we developed bis(phenoxy-imine) early transition metal complexes (known as FI catalysts), which form a variety of unique polyolefinic materials including a wide array of block copolymers from ethylene and α-olefins.[9−12] As part of our investigations into catalysis using FI catalysts, we studied the chain transfer processes of Zr-FI catalysts, resulting in the discovery of a Zr-FI catalyst system that exclusively provides Al-PEs.

In this paper, we introduce the chain transfer behavior of two structurally related Zr-FI catalysts. The first of these favors β-H transfer, leading to vinyl-terminated PEs,[10] whereas the other prefers chain transfer via transmetalation to selectively form Al-PEs, representing the first example of an FI catalyst system where chain transfer to aluminum is the predominant chain transfer mechanism. Additionally, we describe the preparation of Al-PEs with a wide range of molecular weights and narrow-to-broad molecular weight distributions using the Zr-FI catalyst that unusually favors the chain transfer to aluminum route.

To obtain some insight into the influence of the substituent attached to the imine-N on the chain transfer behavior, comparative ethylene polymerization experiments were conducted with structurally relevant Zr-FI catalysts **1** (R = phenyl) and **2** (R = 2-isopropylphenyl),[10] using an methylalumoxane (MAO) activator at 25 °C under atmospheric pressure (entries 1 and 2, Table 1). These catalyst systems exhibited extremely high productivities (**1**: 116 kg of PE/(mmol of cat. h); **2**: 66 kg of PE/(mmol of cat. h)) and produced highly linear PEs (branching less than 1 per 1000 carbon atoms, IR analyses). The molecular weight distributions of the PEs obtained are 2.38 (**1**) and 2.02 (**2**), as expected for polymers formed through single-site catalysis.

The Zr-FI catalyst **2** system afforded a PE (M_w 90 000) with a noticeably higher molecular weight (by a factor of 10) than **1**/MAO (M_w 9300). Considering that molecular weight is determined by the comparative rate of chain propagation and chain transfer, the increased molecular weight (**2**/MAO) is ascribed to the fact that the steric congestion exerted by the isopropyl group on the aryl ring reduces the rate of chain transfer more significantly than that of chain propagation.

End-group analyses by ^{1}H NMR as well as IR (910 cm^{-1}) show that the PE formed with **1**/MAO contains 94% vinyl-terminated chain ends, indicative of a marked preference for β-H transfer as the chain termination mechanism. This chain transfer behavior is the same as that for the Zr- and Ti-FI catalysts/MAO systems elucidated previously.[11,13] Notably, the same analysis of the PE produced with **2**/MAO revealed no detectable levels of unsaturation, which probably suggests that the only chain transfer process that is in operation for the **2**/MAO system is chain transfer to aluminum, leading to the exclusive formation of Al-PEs. This is the first example of an FI catalyst that favors chain transfer to aluminum as the termination pathway. These facts suggest that the isopropyl group on a catalytically active species originating from **2**/MAO is located at a strategic place that effectively suppresses β-H transfer and, at the same time, does not mitigate chain transfer to aluminum. The above results illustrate that a minor change in the ligand structure can have a dramatic effect on chain transfer processes.

A decrease in the MAO concentration will lead to a decrease in the rate of chain transfer to aluminum, presumably resulting in the formation of Al-PEs with higher molecular weights. As anticipated, a decrease in the MAO concentration led to the production of higher molecular weight PEs (e.g., M_w 716 000), which substantially consist of saturated polymer chains (IR analyses) (entries 3 and 4, Table 1). The narrow molecular weight distributions (M_w/M_n 2.02−2.61) suggest that the rate of chain transfer to aluminum is virtually constant under the given conditions.

Conversely, Al-PEs with lower molecular weights (M_w 10 200−36 800, M_w/M_n 1.97−2.22) were obtained by adding trimethylaluminum (TMA) to the polymerization medium as a chain transfer agent (Table 2). An increase in the TMA concentration resulted in a decrease in catalytic activity, which is probably due to catalyst decay caused by the ligand migration that is induced by TMA.[14]

Interestingly, studies on the effect of reaction time demonstrated that Al-PEs with narrow-to-broad molecular weight distributions (M_w 36 800−201 400, M_w/M_n 2.04−5.88) can be produced by varying the polymerization time (Table 3). End-group analysis by IR shows that the PEs produced are fully saturated (below the detectable level). As can be seen in Tables 1−3, Al-PEs having low-to-very high molecular weights and narrow-to-broad molecular weight distributions are available by using the **2**/MAO system.

The production of the broad molecular weight distribution PEs is probably due to the fact that depletion of the available alkylaluminum for the chain transfer

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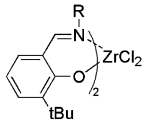
10.1021/ma050289a CCC: $30.25
Published on Web 05/14/2005

Table 1. Ethylene Polymerization Results for Complexes 1 and 2 with Methylalumoxane (MAO)[a]



Complex
1: R = phenyl
2: R = 2-isopropylphenyl

entry	complex	MAO (mmol)	Al/Zr	yield (g)	activity[b]	M_X [c] $\times 10^{-3}$	M_w/M_n	chain-end group vinyl/methyl
1	**1**	1.250	2500	4.85	116	9.3	2.38	47/53
2	**2**	1.250	2500	2.76	66	90.0	2.02	0/100
3	**2**	0.625	1250	2.73	66	159.0	2.26	0/100
4	**2**	0.250	500	2.41	58	716.0	2.61	0/100

[a] Polymerization conditions: toluene 250 mL, complex **1** or **2** 0.5 μmol, ethylene 0.1 MPa, 25 °C, polymerization time 5 min. [b] In kg of PE/(mmol of cat. h). [c] Determined by gel permeation chromatography using polyethylene calibration.

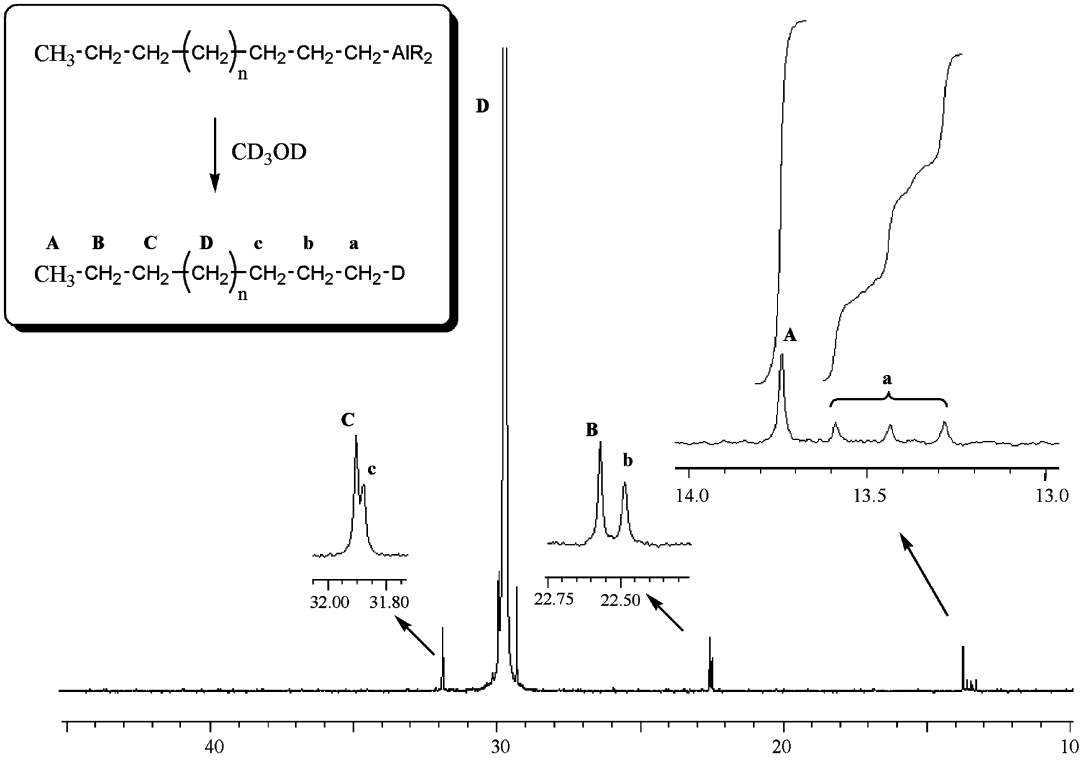


Figure 1. ^{13}C NMR spectrum of the polyethylene obtained with deuterolytic workup: ((i) complex **2**/methylalumoxane, ethylene 0.1 MPa, 25 °C; (ii) CD_3OD, 10−25 °C; see the Supporting Information) (Table 2, entry 7).

Table 2. Ethylene Polymerization Results with Complex 2/Methylalumoxane (MAO)/Trimethylaluminum (TMA)[a]

entry	TMA (mmol)	Al/Zr	yield (g)	activity[b]	M_w [c] $\times 10^{-3}$	M_w/M_n [c]
1	0.000	500	2.41	58	716.0	2.61
2	0.200	900	2.48	60	36.8	2.04
3	0.375	1250	2.09	50	28.3	2.22
4	1.000	2500	1.88	45	18.6	1.97
5	2.250	5000	1.63	39	13.3	2.05
6	3.500	7500	1.42	34	11.9	1.99
7	6.000	12500	1.07	26	10.2	2.12

[a] Polymerization conditions: toluene 250 mL, complex **2** ([1-(2′-*i*PrC$_6$H$_3$NCH)-3-*t*BuC$_6$H$_3$O]$_2$ZrCl$_2$,Table 1, caption) 0.5 μmol, MAO 0.250 mmol, ethylene 0.1 MPa, 25 °C, polymerization time 5 min. [b] In kg of PE/(mmol of cat. h). [c] Determined by gel permeation chromatography using polyethylene calibration.

Table 3. Effect of Polymerization Time on the Performance of Complex 2/Methylalumoxane (MAO)/Trimethylaluminum (TMA)[a]

entry	time (min)	yield (g)	activity[b]	M_w [c] $\times 10^{-3}$	M_w/M_n [c]
1	5	2.48	60	36.8	2.04
2	15	6.67	53	62.5	2.84
3	30	10.16	41	201.4	5.88

[a] Polymerization conditions: toluene 250 mL, complex **2** ([1-(2′-*i*PrC$_6$H$_3$NCH)-3-*t*BuC$_6$H$_3$O]$_2$ZrCl$_2$, Table 1, caption) 0.5 μmol, MAO 0.250 mmol, TMA 0.200 mmol, ethylene 0.1 MPa, 25 °C, polymerization time 5 min. [b] In kg of PE/(mmol of cat. h). [c] Determined by gel permeation chromatography using polyethylene calibration.

reaction as the polymerization proceeds decreases the rate of chain transfer to aluminum. Additionally, the rate of chain transfer to aluminum may also decrease with polymerization time as the catalyst becomes increasingly embedded in the Al-PE that is produced.

Finally, the formation of Al-PEs with **2**/MAO was confirmed by a deuterium-labeling experiment. Deuterolytic workup of the polymerization mixture (entry 7, Table 2) gives a PE whose ^{13}C NMR spectrum is displayed in Figure 1, which exhibits a 1:1:1 triplet derived from a deuteriomethyl end group ($-CH_2D$) centered at 13.44 ppm. The relative peak intensity between the $-CH_3$ (A) and $-CH_2D$ (a) end groups indicates that approximately 92% of the PE chains are terminated with a deuteriomethyl end group, further confirming the highly selective formation of Al-PEs.[15]

The Al-PEs can be transformed using established methods to a wide array of functionalized PEs and PE- and polar polymer-based block and graft copolymers.[16]

In summary, we have shown that a Zr-FI catalyst incorporating a 2-isopropylphenyl group on the imine-N favors chain transfer to aluminum and selectively yields Al-PEs. This represents a rare example of a molecular catalyst that predominantly undergoes chain transfer to aluminum as the chain transfer mechanism. Using this catalyst system, various molecular weight Al-PEs with narrow-to-broad molecular weight distributions that are useful intermediates for functional PEs have been successfully synthesized. Further studies into the effects of varying the substituents attached to the imine-N's on the chain transfer processes are presently in progress and will be reported in due course.

Acknowledgment. The authors thank Prof. T. Shiono (Hiroshima University), Mr. A. Valentine, and Dr. M. Onda for fruitful discussions and suggestions.

Supporting Information Available: Detailed experimental procedures and gel permeation chromatography charts for entries 1−3 in Table 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The selectivity obtained (92%) is lower than expected on the basis of IR analysis, which is probably due to the presence of a contaminant possessing reactive H (such as moisture) during the workup process.

(16) We are currently investigating chain transfer agents such as $ZnEt_2$ other than Al-based compounds for ethylene polymerization with bis(phenoxy-imine)Zr complexes (Zr-FI catalyst), and results will be reported in due course.

MA050289A