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Communications to the Editor

Polyethylenes with Uni-, Bi-, and Trimodal Molecular Weight Distributions Produced with a Single Bis(phenoxy−imine)zirconium Complex

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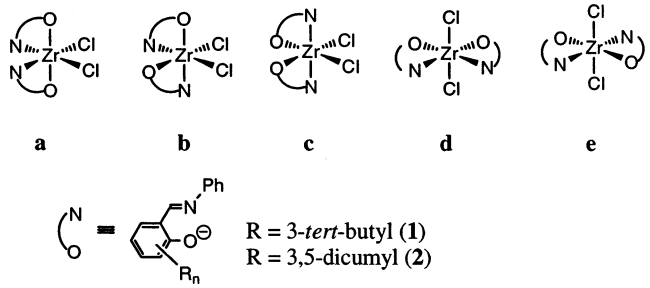
Since metallocene catalysts have emerged, chemically homogeneous polyolefins can be produced with high efficiency, which are characterized by narrow molecular weight distributions (MWDs). In contrast, conventional heterogeneous catalysts produce polyolefins with broad MWDs. Chemical homogeneity in comonomer distribution tremendously improves the mechanical and optical properties of polyolefins.[1] However, there is a strong demand for broader MWDs to meet the requirement for good resin processability. Industrially, cascade polymerization processes are often employed to increase MWD. Considerable efforts have also been made to control MWD by using more than two polymerization catalysts[2] or using acid−base equilibrium in the system.[3] Broad MWDs are sometimes observed in single-site organometallic catalysts as a result of nonstationary polymerization conditions[4] or unexpected multisite character,[5] most of which are inexplicable and uncontrollable.

We have been exploring a new family of group 4 transition metal complexes bearing two phenoxy−imine ligands (FI Catalysts) for olefin polymerization.[6] FI Catalysts potentially possess five isomers arising from coordinating modes of ligands in an octahedral geometry (Chart 1),[6a,e] which may result in multiple active species under appropriate conditions. Here, we describe a novel methodology for the syntheses of polyethylenes with controlled uni-, bi-, and trimodal molecular weight distributions using a single FI Catalyst.

Chart 1



Synthesis of **1** was already reported,[6a,e] and **2** was synthesized by a similar method. Both complexes were fully characterized by X-ray analysis (**1**),[6a,e] FD-MS (**1** and **2**), and elementary analysis (**1** and **2**). Complex **1** or **2** in conjunction with MAO at 25 °C yields polyethylene with much higher activity than an early metallocene catalyst, Cp_2ZrCl_2 (Table 1). To our surprise, unimodal MWD was observed for **1** and trimodal MWD for **2**. By varying the polymerization temperature between 0 and 75 °C, **2** deliberately produces polyethylenes with uni-, bi-, and trimodal MWDs (Figure 1).

The trimodal peaks were deconvoluted to three symmetric peaks using mathematical calculations. Each peak has a reasonable M_w/M_n (∼2.0), suggesting single-site polymerization mechanism.[7] On the other hand, polyethylenes produced with **1** over the same temperature range maintained narrow unimodal MWDs. The multimodal polyethylenes formed with **2** are linear, and the polymerization time has little influence on the activities and MWDs (runs 4, 9, 10 and 7, 11, 12). These observations eliminated the possibilities that the vinyl-terminated polymer, which accumulates with reaction time, was incorporated into the main chain later in the

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Table 1. Ethylene Polymerizations with Complexes 1 and 2[a]

run	cat.	T_p (°C)	TOF[b]	M_w[c] ($\times 10^3$)	M_w/M_n[c]	area ratio of GPC peaks[d]
1	**1**	0	2920	7.0	2.06	100/0/0
2	**1**	25	5150	7.6	2.06	100/0/0
3	**1**	75	950	8.1	2.38	100/0/0
4	**2**	0	9460	5.3	2.03	100/0/0
5	**2**	20	8750	7.5	2.34	98/2/0
6	**2**	25	9520	28.0	8.64	94/5/1
7	**2**	40	5950	133.2	24.80	68/21/11
8[e]	**2**	75	260	136.7	15.89	40/39/21
9[f]	**2**	0	9420	5.6	2.10	100/0/0
10[g]	**2**	0	7220	5.5	2.03	100/0/0
11[f]	**2**	40	6260	93.9	21.61	76/16/8
12[g]	**2**	40	4130	231.8	42.63	63/22/15
13[h]	**2**	40	4220	152.7	29.42	66/23/11
14[i]	**2**	40	3940	131.7	28.17	71/17/12
15	Cp_2ZrCl_2	25	280	636.0	2.31	100/0/0

[a] Standard conditions: 100 L/h of ethylene, 250 mL of toluene, 0.02 μmol of precatalyst, 62 500 equiv of MAO, polymerization time 5 min. [b] In s^{-1}. [c] Determined by GPC at 145 °C using polyethylene calibration. [d] Deconvoluted by SC-8010 (Tosoh Corp.), in low/medium/high molecular weight peaks. [e] 0.2 μmol of precatalyst, 6250 equiv of MAO. [f] Polymerization time 3 min. [g] Polymerization time 8 min. [h] 12 500 equiv of MAO. [i] 312 500 equiv of MAO.

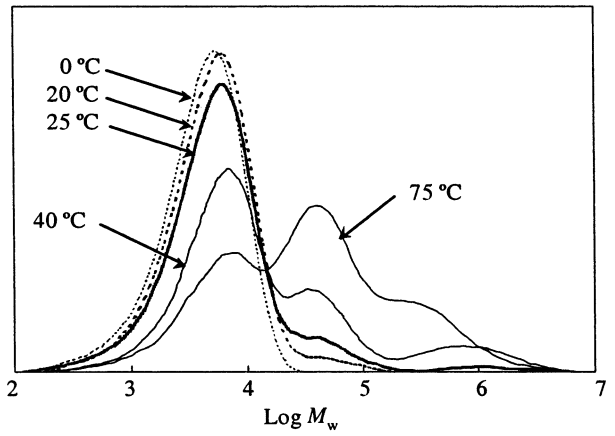

Figure 1. GPC elution curves of polyethylenes produced with complex **2** at various temperatures (runs 4−8 in Table 1).

reaction and that catalyst decay caused the multimodal MWD. Changing Al/Zr ratio (runs 7, 13, 14) caused no obvious effect on MWD, which suggests that neither a chain transfer to MAO nor acid−base interaction between MAO and the heteroatoms of the ligands[3] is responsible for determining MWD. Alkylation or reduction of the imine function by alkylaluminum or by intramolecular alkyl group migration from the metal center, both of which were observed for related systems,[6a,e,8] was excluded due to the fact that a benzylic proton did not appear in the ^{1}H NMR spectra even with MAO at 75 °C. Meanwhile, FI Catalysts potentially possess five isomers arising from coordinating modes of ligands in an octahedral geometry (Chart 1).[6a,e] At −25 °C, the ^{1}H NMR spectrum of **1** was well-resolved with three sets of signals in an approximately 5:1:1 intensity ratio.[9] With temperature increase, the main signal remains relatively sharp with a slight downfield shift while the two minor sets of signals are significantly broadened at 25 °C. At 50 °C, all signals are broadened, and the two minor sets of signals are coalesced into one set of broad signals. The spectra are reversibly reproduced over the temperature range examined. The molecular structure of **1** calculated with DFT, which is consistent with the X-ray analysis data, revealed that

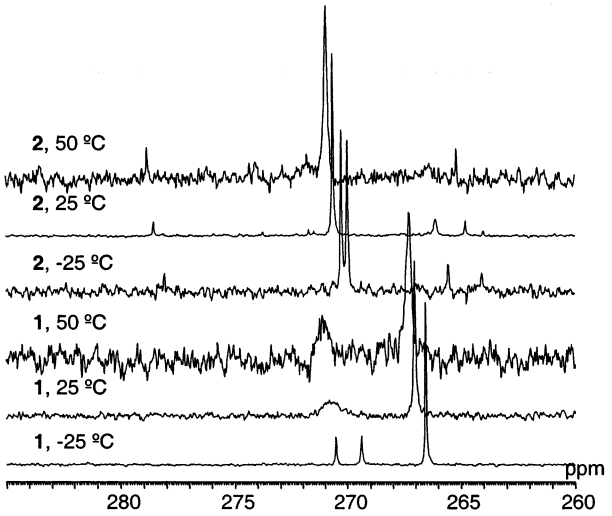

Figure 2. ^{15}N NMR spectra of complexes **1*** and **2*** in $C_2D_2Cl_4$.

isomer **a** in Chart 1 (**1a**) is more stable, because of effectively reduced steric and electronic repulsion by locating shorter O−Zr bonds trans, than the isomer **1b** by 20 kJ mol^{-1}, **1c** by 25 kJ mol^{-1}, **1d** by 33 kJ mol^{-1}, and **1e** by 37 kJ mol^{-1}.[6a,e] Therefore, we preliminarily assigned the main signal to **1a** and the minor paired signals to **1b**, which is the only isomer that has chemically nonequivalent phenoxy−imine ligands. Although the ^{1}H and ^{13}C NMR spectra of **2** are complicated, the spectra suggested that there were at least two imine protons. To avoid complexity of the spectra, ^{15}N NMR experiments were conducted with ^{15}N-enriched precatalysts (**1*** and **2***). For both **1*** and **2***, the spectra were reversible, and no decomposition was observed over the temperature range examined. At −25 °C, complex **1*** exhibited one main signal and two minor signals in an approximately 5:1:1 intensity ratio (Figure 2).

With temperature increase, the main signal was slightly downfield shifted and broadened and the two minor signals coalesced into one broad signal, which is consistent with ^{1}H NMR data. As for **2***, there are two main signals in almost equal intensities around 270 ppm and three minor signals at −25 °C.[10] Upon heating, the main two signals coalesce and form one relatively sharp signal at 25 °C. At 50 °C, one of the minor signals (266 ppm) significantly broadens. Assuming that the nitrogen chemical shifts in the same configuration for **1*** and **2*** are similar, the paired main signals (∼270 ppm) and the one minor signal (∼266 ppm) of **2*** mentioned above are related to three signals for **1***. Therefore, in the case of **2***, the configuration **b** is more stable than the configurations **a** (**b**/**a** = 88/12 at −25 °C), which is highly unusual for an early transition metal complex. The coalescence of paired peaks means that the exchange of the two nitrogens, one trans to a chlorine and the other trans to an oxygen, is fast relative to the NMR time scale and indistinguishable probably through a nitrogen dissociation mechanism.[11] Judging from the NMR data, configuration **b** is more fluxional than configuration **a** because peak broadening (and coalescence) takes place at a lower temperature while peaks from configuration **a** remain relatively sharp. Although the mechanism causing multimodality is still elusive since the NMR experiments are conducted with the precatalysts and the conditions are different from

those for polymerizations (solvent, concentration, temperature), we propose that the highly fluxional character especially for an unusual cis-N, cis-O, cis-Cl arrangement is connected to multimodal MWDs of polymers produced. Further studies of dynamic structures of the real active species are in progress.

In summary, we have demonstrated that FI Catalysts are capable of producing uni-, bi-, and trimodal polyethylenes in a controlled manner with very high activities. The results described herein together with our previous reports show that FI Catalysts create polyethylenes with nearly monodispersed molecular weight distributions ($M_w/M_n < 1.10$)[6a,f,g] to controlled multimodal molecular weight distributions ($M_w/M_n > 20$).

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Supporting Information Available: Detailed experimental procedures and spectroscopic data of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) A typical example of peak deconvolution (run 8, Table 1). Peak 1, top 24.70 min, $M_w = 391 \times 10^3$, $M_w/M_n = 1.90$. Peak 2, top 28.07 min, $M_w = 48.8 \times 10^3$, $M_w/M_n = 1.49$. Peak 3, top 32.27 min, $M_w = 8.5 \times 10^3$, $M_w/M_n = 2.51$. Total (calculated for deconvoluted peaks), $M_w = 104.7 \times 10^3$, $M_w/M_n = 13.77$. Total (calculated for the real elution curve), $M_w = 136.7 \times 10^3$, $M_w/M_n = 15.89$.

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(9) ^{1}H NMR for the main isomer in $C_2D_2Cl_4$: δ 8.09 (s, 2H; HC=N), 7.36 (dd, ^3J(H,H) = 8.0 Hz, 2H; 3-*tert*-butylsalicylidene 6-H), 7.07 (d, ^3J(H,H) = 7.5 Hz, 2H; 3-*tert*-butylsalicylidene 4-H), 7.01 (m, 4H; Ph 3-H), 6.97 (d, ^3J(H,H) = 7.0, 2H; Ph 4-H), 6.94 (m, 4H, Ph 2-H), 6.78 (t, ^3J(H,H) = 7.5 Hz, 2H; 3-*tert*-butylsalicylidene 5-H), 1.21 (s, 18H; *tert*-butyl).

(10) Some minor signals might arise from an impurity because a small amount of monochloride, $[N^*-O]_3ZrCl$, was observed in FD-MS.

(11) Rapid racemization of related compounds was observed. For example: Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282 and references therein.

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