



# Branched polyethylene with an ( $\alpha$ -diimine) nickel catalyst

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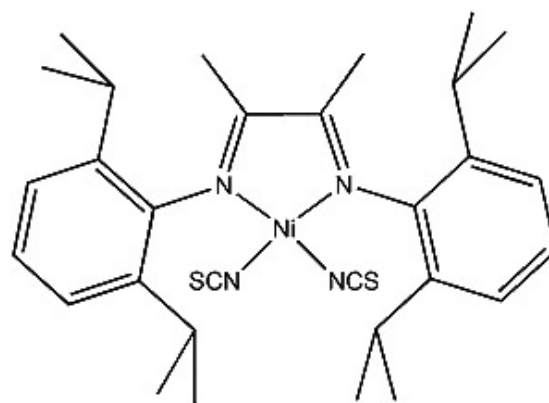
*Polymerizing ethylene using a nickel ( $\alpha$ -diimine) complex and ethylaluminum sesquichloride generates materials with tunable properties.*

Investigation of short-chain branching (SCB) in linear low-density polyethylenes (LLDPEs) and of long-chain branching (LCB) in low-density polyethylenes (LDPEs) has gained increasing importance over the last decade because of the outstanding mechanical and rheological (flow) properties of branched materials. Although flow properties and overall polymer processing behavior are largely influenced by molecular weight distribution (MWD), the existence of branched structures and the respective branching distributions exert important beneficial effects on film-blowing processes.<sup>1,2</sup>

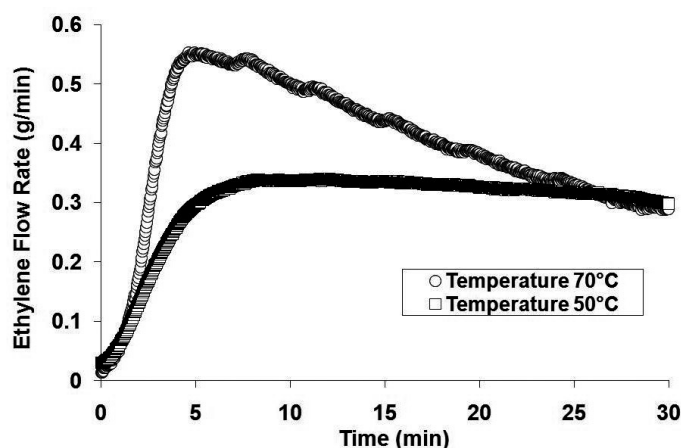
LCB does not occur when conventional Ziegler-Natta catalysts are used to perform the polymerizations. However, some metallocene catalysts can incorporate LCBs into polymer chains even at mild conditions, through reincorporation of vinyl-terminated macromonomers.<sup>2</sup> To produce SCBs without comonomers, multidentate ligands are used to coordinate the active metal atom and to allow for 'running' of the active center along the polymer chain. As these catalysts can produce both SCBs and LCBs simultaneously, they offer opportunities for generating new polyolefin grades.<sup>3,4</sup> However, such catalysts usually require the use of MAO (methyl aluminoxane) as cocatalyst, which can be very dangerous and expensive.

In this work, we investigated the polymerization of ethylene with a nickel ( $\alpha$ -diimine) complex<sup>5</sup> (see Figure 1) activated by ethylaluminum sesquichloride (EASC). The cocatalyst was selected in accordance with a preliminary investigation performed to replace MAO for an alternative and cheaper cocatalyst.<sup>6</sup> In particular, we observed that the analyzed catalyst system leads to production of polyethylenes with SCBs and LCBs simultaneously. Moreover, final polymer properties respond to modification of the operating variables, allowing for production of distinct grades at the plant site.

We performed a set of preliminary experiments to evaluate the cocatalyst and temperature effect on the polymerization reactions. We used MAO, aluminum diethyl monochloride (DEAC), and EASC as cocatalysts in the temperature range of 25–75°C. We observed that all three



**Figure 1.** ( $\alpha$ -Diimine) nickel catalyst used to perform ethylene polymerizations.<sup>5</sup> Ni: Nickel. SCN: Thiocyanate. NCS: Isothiocyanate.



**Figure 2.** Ethylene consumption rates at different temperatures. (○): Run 1. (□): Run 8.

cocatalysts could activate the nickel complex, showing that MAO could be replaced by conventional alkylaluminum compounds to promote the

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**Table 1.** Polymerization data. Al: Aluminum. Ni: Nickel. E: Ethylene. molC: Moles of catalyst. Mw: Weight-average molecular weight. Mn: Number-average molecular weight. EASC: Ethylaluminum sesquichloride. gP: Grams of polymer. \*: Performed in triplicate.

Runs	[E] (mol/l)	P (bar)	Al/Ni	Temp (°C)	Cocatalyst	Catalyst activity (10 <sup>5</sup> gP/molC/h)	Mw (10 <sup>3</sup> Dalton)	Mn (10 <sup>3</sup> Dalton)	Mw/Mn
<b>R1(*)</b>	0.3	3.4	250	50	EASC	11.5±2	216±5	96±8	2.3±0.1
<b>R2</b>	0.2	3.4	350	30	EASC	9.5	304	124	2.5
<b>R3</b>	0.2	3.4	150	30	EASC	8.3	301	108	2.8
<b>R4</b>	0.2	3.0	350	70	EASC	12.0	116	52	2.2
<b>R5</b>	0.2	3.0	150	70	EASC	14.3	130	68	1.9
<b>R6</b>	0.4	1.8	350	30	EASC	8.0	273	121	2.3
<b>R7</b>	0.4	1.8	150	30	EASC	8.5	309	125	2.5
<b>R8</b>	0.4	5.8	350	70	EASC	40.0	154	64	2.4
<b>R9</b>	0.4	5.8	150	70	EASC	35.0	180	58	3.1

**Table 2.** Branch frequencies of polyethylene samples obtained. See Tables 1 and 2 for information about polymerization conditions. The number of branches is represented (in moles) per mole of ethylene in the polymer (mole percent).

	R1	R2	R4	R5	R6	R7	R8	R9	R10
<b>Methyl</b>	23.8	21.6	21	19.4	19.5	22	24	18.9	19.4
<b>Ethyl</b>	4.8	3.1	2.2	2	5.7	3.7	2	2.9	4
<b>Propyl</b>	3.1	2.8	2.3	1	0.3	3.1	1.1	0.9	1.1
<b>Butyl</b>	1.7	1.3	0.7	1.6	3.3	1.3	1.2	1.5	2
<b>Amyl</b>	1.7	1.3	0.7	1.4	0.6	1.3	1.9	0.8	2
<b>Long</b>	8.3	6.4	4.9	7.1	11.8	8.6	5.6	7.7	9.4
<b>Isobutyl</b>	0.5	0.6	0.6	1.5	2.7	0.3	1.4	0	4.2
<b>2-Methyl-hexyl</b>	1.1	0.5	0.6	0	0.05	0.5	0.3	0.5	0.3
<b>Total of branches</b>	45	37.7	33	34	43.9	40.9	37.4	33.3	42.4

activation of the catalyst precursor. This is very important for development of commercial processes, as EASC is much less expensive and much safer to handle at a plant site than MAO.

Tables 1 and 2 show some of our experimental results. Catalyst activities can be very high, and molecular weight averages are within the range of commercial interest. Increasing the ethylene concentration enhances catalyst activity because of higher propagation rates. The increase in catalyst activity with temperature could be attributed to formation of additional active catalyst sites and to the larger activation energies for monomer propagation than for catalyst deactivation,<sup>7</sup> as Figure 2 clearly shows. Polymerization temperature exerts the most important effects on the final average molecular weights of the obtained polymer samples, indicating that chain transfer to alkylaluminum and to monomer are less important than spontaneous chain transfer.

The polyethylene samples obtained presented large amounts of short alkyl branches and LCBs with six or more carbons. The presence of SCBs with one to five carbons is due to sequential ethylene insertions and catalyst isomerizations. However, this cannot explain the high amount of LCBs in the polymer samples, indicating that macromonomer reincorporation takes place. Table 2 shows that the catalysts we studied can produce both short and long branches simultaneously, whose relative frequencies respond to modification of the operating variables, making it possible to tune the polymer properties at the plant site by adjusting operating conditions.

In summary, our work analyzed the effects of polymerization variables on the catalyst activities and molecular properties of polyethylene



samples prepared with an ( $\alpha$ -diimine) nickel catalyst. We showed that this catalyst can produce both short and long branches simultaneously, using EASC as a cocatalyst. In addition, we found that the polymer properties respond to modification of the operating variables, with practical implications. The next step will involve evaluating the rheological properties of the materials obtained in order to tune the polymer properties to desired application performance.

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