Self-Induced Short Chain Branching in Homopolymers and 1-Hexene Copolymers of Ethylene Produced with Amido Functionalized ansa Half-Sandwich Complexes as Catalysts

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ABSTRACT: Amido *ansa* 3-substituted indenyl complex precursors can be activated with methylaluminoxane and used for prepolymerization with ethylene to give a heterogeneous catalyst for olefin polymerization. Homo polymerization of ethylene with 1-(3-pent-4-enylindenylidene) dimethylsilyl'-butylamidotitaniumdichloride (1), 1-(3-hex-5-enylindenyl-idene)dimethylsilyl'butylamidotitanium-dichloride (2), and 1-(3-pent-4-enylindenylidene) (oct-7-enyl)methylsilyl'butyl-amidotitaniumdichloride (3) produces polyethylenes that contain ethyl branches. The ethyl branching in the polymers made with complexes 1 and 2 is barely above the ^{13}C NMR detection limit, but the level observed in the polymer made with complex 3 is 17 times greater. Copolymerization of ethylene and 1-hexene using prepolymerized 3 yields copolymers containing both ethyl and butyl branches. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 734–739, 2006

Key words: *ansa* half-sandwich complexes; titanium; ethylene polymerization; copolymerization; branching; bimodal polyethylene

INTRODUCTION

The market for linear low density polyethylenes[1] continues to grow rapidly, especially the market for polymers made with metallocene catalysts.[2,3] This growth is due to the excellent balance of polymer properties that metallocene based resins possess for blown and cast films.[4] The observed balance of film properties is a result of the narrow molecular weight distribution and uniform short chain branching found in these resins. For some metallocene and nickel based resins, a percentage of the short chain branching can be self-induced.[5–7] Similar behavior has also been observed for polymers made with amido functionalized *ansa* half-sandwich[8,9] catalysts.

Here we characterize homopolymers and 1-hexene copolymers of ethylene made from amido functionalized *ansa* 3-substituted indenyl catalyst precursors **1, 2,** and **3** (see Fig. 1). All the complex precursors[10,11] were prepolymerized in the presence of methylaluminoxane (MAO) and ethylene to form heterogeneous catalysts.

EXPERIMENTAL

All air sensitive work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. The solvents toluene and pentane were purified by distillation over Na/K alloy. Deuterated solvents such as CDCl$_3$ were dried over molecular sieves (300 pm), degassed, and stored under inert gas atmosphere.

Methylaluminoxane (MAO) was supplied by Albemarle, Baton Rouge, as 10% solution in toluene.
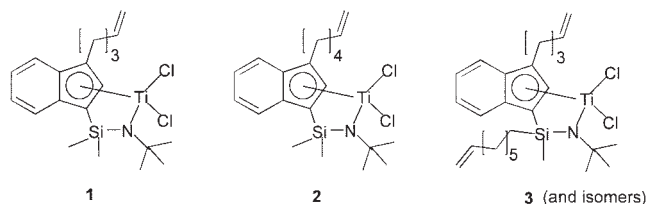
NMR spectroscopy

The NMR sample was prepared by dissolving a polyethylene in 1,2,4-trichlorobenzene in a 10-mm tube at 125°C to form a 15 wt % solution. The ^{13}C NMR experiment was carried out with NOE and a Waltz proton decoupler on Varian Inova 500 MHz or Varian Unity 300 MHz spectrometers at 125 MHz and 75 MHz, respectively. To ensure good long term lock stability, deuterated 1,4-dichlorobenzene was used as a lock solvent. Chemical shift values were referenced against the $\delta + \delta +$ main backbone methylene peak of the polymer, which was set at 30.00 ppm.

High temperature gel permeation chromatography

The polymers were measured with a Millipore Waters high temperature gel permeation chromatography

Figure 1 Amido functionalized ansa 3-substituted indenyl catalyst precursors.

TABLE I
Ethylene Homopolymers

Complex	Hydrogen bar	M_w	M_n	M_w/M_n	Density g/cm^3	Butyl branches (mole %)
1	0.68	738	77.9	9.5	0.9391	0.03
2	0.68	727	78.9	9.2	0.9404	0.03
3	0.68	782	35.5	22	0.9297	NA
4	1.05	266	14.9	18	0.9425	0.52

(HT-GPC) 150C apparatus. Four successive columns filled with crosslinked polystyrene were used for separation. The pore diameter of the individual particles was 500 Å, 1.000 Å, 10.000 Å, and 100.000 Å. For detection a RI Waters 401 refractometer was used. Degassed 1,2,4-trichlorobenzene was the eluent (flow rate 1 mL/min). The polymer samples were dissolved in boiling 1,2,4-trichlorobenzene. The measurements were conducted at 150°C. The apparatus was calibrated using a polystyrene calibration standard.

Synthesis of prepolymerized catalysts

Eighty milligrams of the corresponding catalyst precursor was activated with MAO (10% in toluene) (M:Al = 1:250) and stirred for 10 min. Subsequently, 1.5 g silica gel (water content < 1 weight %) was added and stirred for additional 10 min. An ethylene pressure of 0.2 bar was applied and polymerized until 1 g polyethylene was produced. The produced prepolymerized catalyst was filtered and the residue was dried *in vacuo.*

Polymerization reactions

A 1-gallon reactor was charged with 150 mg of heterogenized catalyst and hydrogen was added to the reactor from a 300 mL vessel (0.68 bar H$_2$-pressure) at normal pressure. Two liters isobutane were added and the autoclave was thermostated at 90°C. For copolymerizations, the respective amount of monomer was added. Subsequently, an ethylene pressure of 10 bar was applied. The mixture was stirred for 1 h and the reaction was terminated by releasing the pressure in the autoclave. The obtained polymer was dried *in vacuo.*

RESULTS AND DISCUSSION

After activating the amido functionalized *ansa* half-sandwich catalyst precursors with MAO, a small amount of ethylene was added to the solution. A precipitate of polyethylene containing copolymerized catalyst precursor was formed as depicted in Scheme 1. The heterogenized catalyst was used for polymerization without further activation.[12–14]
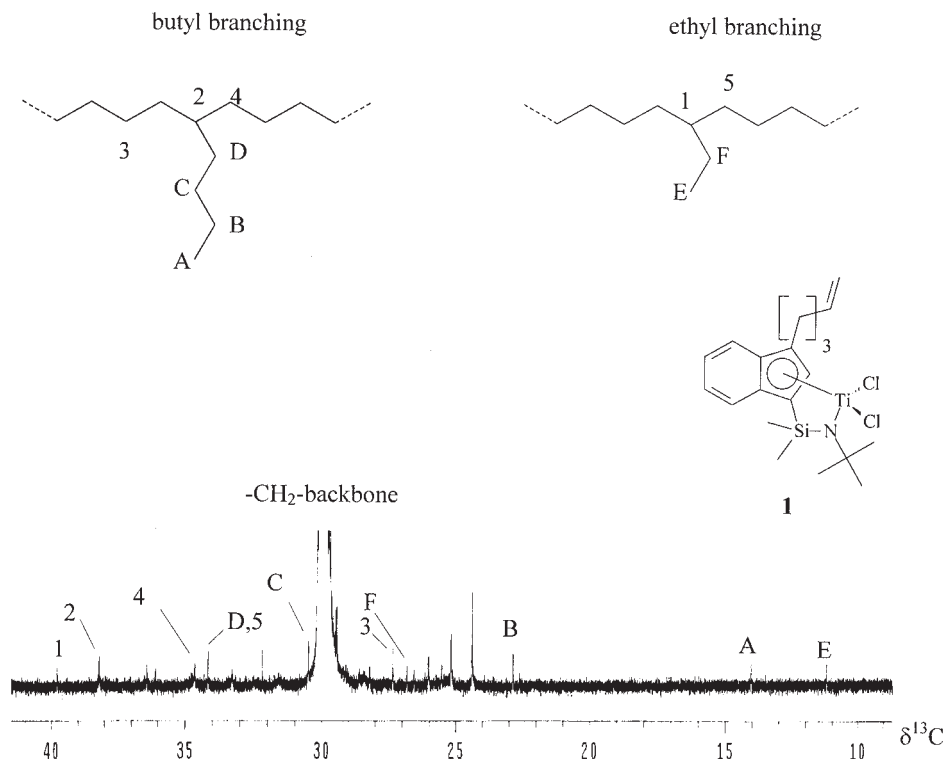
Ethylene homopolymers

Catalyst precursors **1, 2,** and **3** were prepolymerized to form heterogeneous olefin polymerization catalysts and then used to prepare homopolymers of ethylene. The polymerizations were conducted at 90°C, with continuous ethylene feed to maintain the reactor pressure at 31.6 bar. Before starting the polymerization reactions, hydrogen from a 0.3-L vessel was added to the reactor. The resulting polymers were characterized by GPC, ^{13}C NMR, and gradient density column measurements (see Table I).

The GPC's for resins made with all three complexes at 0.68 bar hydrogen pressure were similar in weight average molecular weight, but the resin made with complex **3** had a number average molecular weight that was only half of the other resins. The similar M_w's and polydispersity indices M_w/M_n of the first two resins in Table I suggest that they should have similar densities as observed. The resin made with complex **3** has a higher polydispersity index, which would normally lead to a higher density. However, a significantly lower density is observed suggesting this resin contains self-induced short chain branching even though no comonomer was added to the reactor. To determine the branching content of resins made with
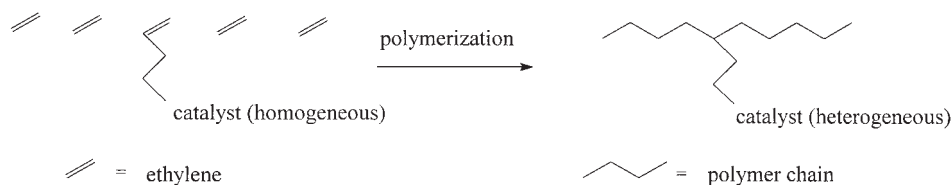
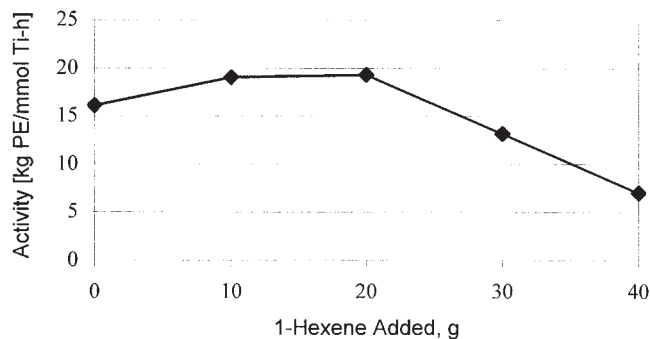**Scheme 1** Prepolymerization of a self-immobilizing catalyst.

Figure 2 High temperature $^{13}C\{^1H\}$ NMR-spectrum of polyethylene obtained in the presence of the prepolymerized catalyst precursor **1** (at 90°C, 10 bar ethylene pressure).

these complexes, the ^{13}C NMR spectra were obtained (see Fig. 2).

While homopolymer made with complexes **1** and **2** contained ethyl branches just above the detection limits of the measurement, homopolymer made with complex **3** contained 17 times the amount of ethyl branching.

Ethylene/1-hexene copolymers

To determine the effect of comonomer on the degree of self-induced ethyl branching, a series of polymers was made at varying 1-hexene concentrations. The polymerization runs were made at 80°C to reduce the tendency for the lower density polymers (higher 1-hexene containing polymers) to go into solution and foul the reactor. The productivities of these polymerization runs are compared in Figure 3. As the amount of 1-hexene added is increased, the productivity increases slightly [15] and then decreases significantly. It is not known if the decrease at higher 1-hexene levels is caused by poisons or some other effect.

The melt index (MI), high load melt index (HLMI), GPC, and gradient density column measurements of the corresponding resins are found in Table II.

As the 1-hexene concentration in the reactor is increased, the M_w of the resin decreases linearly (see Fig. 4). This behavior with increasing concentrations of

Figure 3 Dependency of the polymerization productivity of complex 3 on the 1-hexene concentration.

TABLE II
Ethylene/1-Hexene Copolymers Made with Prepolymerized Complex 3

1-Hexene added (g)	MI (dg/min)	HLMI/ MI	M_w (kg/mol)	M_n (kg/mol)	M_w/ M_n	Density (g/cm³)
0	0.17	87	266	14.9	18.0	0.9425
10	0.12	103	223	10.3	21.7	0.9352
20	0.10	105	206	11.8	17.4	0.9285
30	0.67	46	106	13.7	7.7	0.9161
40	1.33	33	86.7	25.8	3.4	0.9151
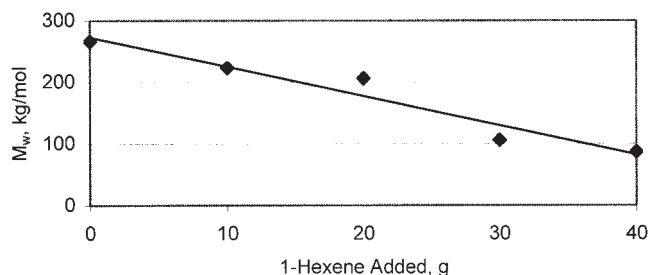
Figure 4 The dependence of M_w on the concentration of 1-hexene.

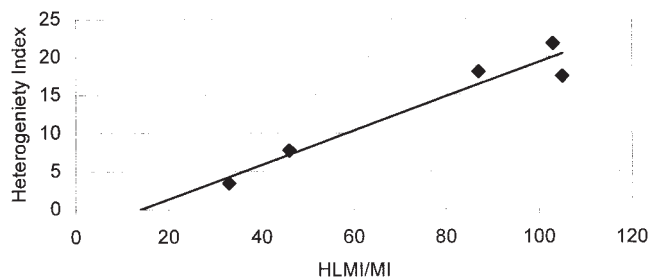**Figure 6** The effect of comonomer concentration on resin density.

comonomer is observed frequently with single-site catalysts.[16,17] The MI of the resin increases correspondingly as expected, but the experimental error is significantly higher, especially at the lower 1-hexene levels.

In the literature, and especially in the patent literature, the shear stress response, HLMI/MI, is assumed to be an indicator of the breadth of the molecular weight distribution. As the MI and HLMI of different resins are subject to many changes besides molecular weight changes, it is seldom appropriate to make this assumption. In the current study, even though the catalyst remains unchanged, the M_w is changing significantly in response to the amount of 1-hexene in the reactor. This suggests that in this special case one might expect the heterogeniety indices and shear stress responses to vary linearly as is observed (see Fig. 5).
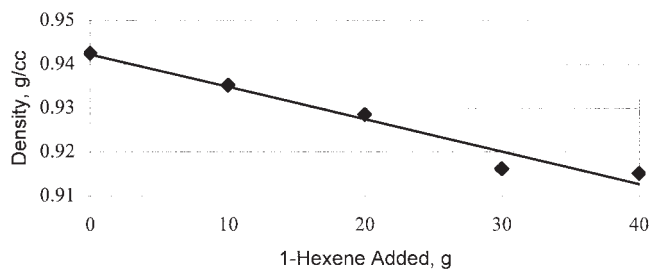
As expected, the density varies indirectly with the comonomer level in the reactor (see Fig. 6).

Branching in the copolymers

The ^{13}C NMR spectrum of an ethylene/1-hexene copolymer has a rather typical peak assignment.[18] The most important peaks in the spectrum are assigned according to the nomenclature proposed by Carman[19] in the related study of ethylene–propylene copolymers. Greek letters were used to designate the proximity of each methine carbon relative to the backbone

methylene carbon of interest. The scheme of branches and polymer backbone are shown in Figure 7.

The ethyl branches of ethylene/1-butene copolymers were generated *in situ* during polymerization. Evidence of their existence is clear in the ^{13}C NMR spectrum. The ethyl branch tertiary carbons, CH [EBE] triads, show a resonance at 39.8 ppm and corresponding $\alpha\delta_b+$ and $\beta\delta_b+$ peaks are found at 34.1 ppm and 27.4 ppm, respectively. Two carbon atoms: $1B_b$ and $2B_b$ are centered at 26.8 and 11.2 ppm.

Similarly, the resonances of ethylene/1-hexene branches are found in typical positions. Tertiary CH[EHE] at 38.3 ppm. $\alpha\delta_h+$ and $\beta\delta_h+$ 34.2 ppm, 27.3 ppm respectively. The carbon $4B_h$ is centered at 34.2 ppm in the vicinity of the $\alpha\delta_b+$ carbon. One can notice in close vicinity at 33.9 ppm the resonance that belongs to methylene carbon atoms associated with vinyl end groups.[20] The other carbon atoms, e.g., $2B_h$, $1B_h$, are found at 23.4 ppm and 14.1 ppm, respectively.

Figure 5 Correlation between the polydispersity index (polydispersity) and shear stress response for the copolymers.

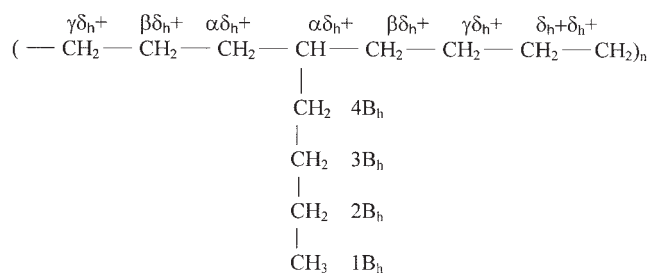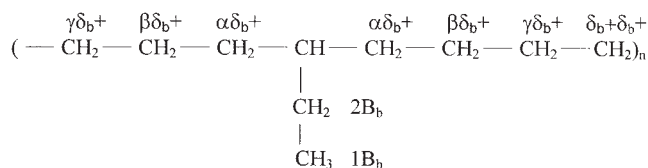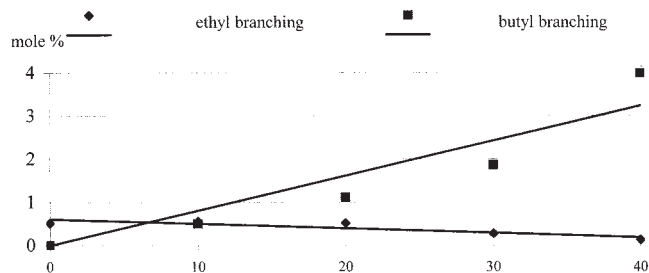**Figure 7** The ethylene/1-hexene copolymer (A); and the ethylene/1-butene copolymer (B) with nomenclature according to Carman.[19]

Figure 8 Butyl and ethyl branching in ethylene/1-hexene copolymers for different amounts of comonomer added to the polymerization reactor.

The spectrum shows also terminal end groups (CH_3 and next to them CH_2) at well known positions.

We performed a quantitation of short chain branches based on the analysis of particularly triads, their clustering always considering necessary relationship between triads.[18]

The copolymers that were obtained with different amounts of comonomer from prepolymerized complex **3** were investigated with ^{13}C NMR spectroscopy in regard to possible branching. The HT ^{13}C NMR spectra reveal a dependency of the frequency of the ethyl and butyl branchings on the added amount of 1-hexene. The correlation is illustrated in Figure 8.

The higher the 1-hexene/ethylene molar ratio in the polymerization medium, the higher the butyl branch content of the resin as more comonomer inserts into the polymer chain. However, unlike previous studies, the ethyl branch content also varies with the 1-hexene concentration in the polymerization reactor. The number of ethyl branches per 1000 carbon atoms decreases, from 0.52–0.12 mol %, with increasing 1-hexene. This 77% decrease in ethyl branching with increased hexene concentration was not observed previously with metallocene catalysts. In the metallocene experiments, increasing 1-hexene concentration had no effect on the amount of self-induced ethyl branches. The decrease in ethyl branching as more 1-hexene is added strongly suggests, as previously hypothesized, that the origin of the ethyl branching is a result of an isomerization reaction at the active polymerization center and not the result of 1-butene formation followed by instant incorporation into the growing polymer chain. The latter mechanism would not be expected to vary with

3a

3b
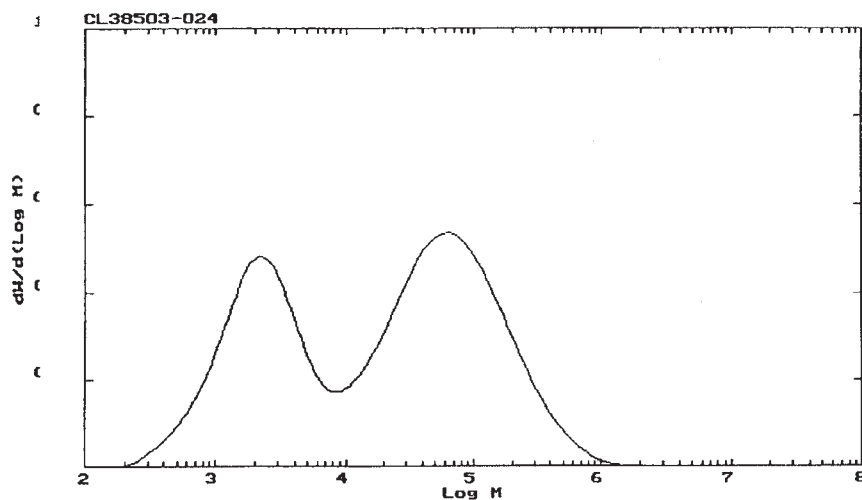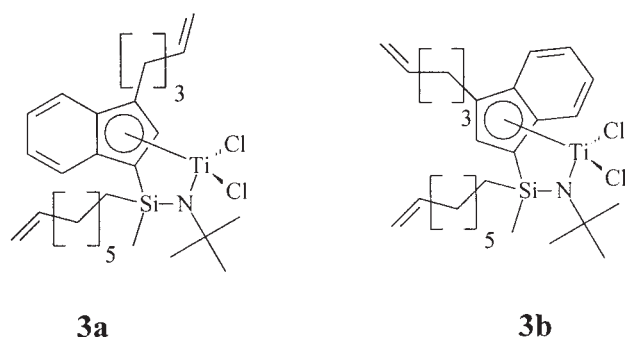
Figure 9 HT-GPC-diagram of 1-hexene-copolymer obtained with 3a/b as self-immobilized catalyst.

the concentration of 1-hexene. On the other hand, the molecular weight distribution clearly shows that the nature, if not number, of the amido active centers is changing with 1-hexene concentration, which could well account for changes in the rate of formation of the ethyl branches.

The complex nature of prepolymerized complex **3** is illustrated by running the copolymerization reaction at different hydrogen levels. Dropping the hydrogen concentration in the reactor changes the resin produced from a narrow molecular weight distribution to a clearly bimodal distribution. In earlier work, diastereomer amido complexes, such as **3**, were shown to give bimodal polymers[11] due to the presence of the isomer mixtures. The current results are consistent with the earlier work. Each diastereomer, **3a** and **3b,** may produce a different M_w resin and the two resins can be differentiated by HT-GPC (see Fig. 9). Clearly the observance of the bimodal distribution is dependent upon reactor conditions.

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