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Articles

Linear or Branched Polyethylenes from Supported Aryloxytitanium(IV)−Cyclopentadienyl Complexes

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ABSTRACT: The reaction of titanium−piano stool complexes (**1**−**4**) with poly(styrene-*r*-4-hydroxystyrene) afforded immobilized aryloxycyclopentadienyl complexes ((**5**−**8**), macroligated catalyst). These macroligated catalysts have low solubility in toluene, indicative of chemical cross-linking. The formation of chemical cross-links is attributed to the titanium being ligated with two aryloxy units. Elemental analysis and ^{13}C NMR have confirmed the presence of the mono- and bis(aryloxy) components in these macroligated catalysts. In conjunction with MAO as the cocatalysts, the macroligated catalysts have been used for ethylene homopolymerization. The resulting polymers were either linear polyethylene or polyethylene having exclusively butyl short chain branches (SCBs). The formation of SCBs was found to be dependent on the cyclopentadienyl substituents, the influence exerted by the polymeric macroligand, and the nature of the cocatalysts. The thermal transitions and apparent crystal sizes as determined by wide-angle X-ray diffraction and ^{13}C NMR are consistent with polyethylene having butyl short chain branches evenly distributed along the polymer backbone.

Introduction

Numerous efforts are being directed toward the synthesis of single site catalysts (SSCs) for the polymerization of olefins to afford branched polyethylenes. There are now several known SSCs that copolymerize ethylene and α-olefins to produce branched copolymers with uniform comonomer distributions across the entire molecular weight range and tunable levels of commoner incorporation. An alternative method for the production of branched polyethylenes utilizing only ethylene as monomer can be achieved by judicious choice of catalyst(s) and reaction conditions. The use of Ni- or Pd-based cationic or neutral complexes affords polyethylenes with tunable branch content via a chain isomerization mechanism.[1] Multicomponent catalyst systems can be utilized where one catalyst oligomerizes ethylene to α-olefins (or vinyl macromers) and a second catalyst is employed to copolymerize the α-olefin formed in situ with ethylene to afford branched polyethylenes.[2,3] Recently, there have been reports of branched polyethylene synthesis by the use of Ti and/or Zr catalysts in conjunction with an aluminum or boron cocatalyst. Polyethylene with a significant amount of ethyl branches has also been observed with MAO as the cocatalysts for certain zirconocenes, and this has been attributed to the formation of 1-butene in the product feed and subsequent copolymerization with ethylene.[4,5] During ethylene homopolymerization the interaction between the metal cation (Ti and Zr) and the cocatalyst anion (borates) has been tuned to afford α-olefins in situ, which are subsequently copolymerized with ethylene.[6,7] Branched polyethylene having exclusively butyl branches can be prepared using monocyclopentadienyl titanium-trimethyl/B(C_6F_5)$_3$. This catalyst combination is apparently producing 1-hexene in situ, by an ethylene trimerization reaction, which is then copolymerized with ethylene to afford branched polyethylene.[8] Altering of the primary ligand sphere around catalysts provides one pathway to generate branched polyethylene in ethylene homopolymerizations. For single site catalysts that are covalently bound to a support questions arise as to what influences the nature of the support will have on catalyst performance and the properties of the resulting polymer. Synthetic schemes to support piano stool complexes on functionalized polystyrene supports have been developed in order to study the influence of the modified catalyst architecture on the catalyst performance and the properties of the resulting polyolefin.

Results and Discussion

Poly(styrene-*r*-4-hydroxystyrene) (HPS)[9] of 70 000 M_w having 0.3 mol % of hydroxyl groups was prepared for use as the macroligand. The reaction of complexes **1**−**4** (Figure 1) with HPS in toluene at 60 °C for 2 days (Scheme 1, reaction stoichiometries are in Table 1) forms a viscous reaction mixture that ultimately results in a polymeric gel having low solubility in toluene. The initial reaction of **1**−**4** with HPS affords monoaryloxycyclopentadienyltitanium(IV) dichloride, form **A**, the hydrochloric acid formed as the byproduct of the reaction of the Ti−Cl with the hydroxyl groups on the HPS was removed in vacuo. The low solubility observed is indicative of the formation of bis(aryloxy)cyclopentadi-

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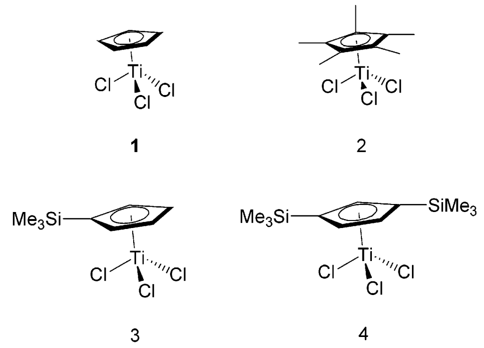


Figure 1. Precursor catalysts.

Table 1. Elemental Composition of the Supported Catalysts

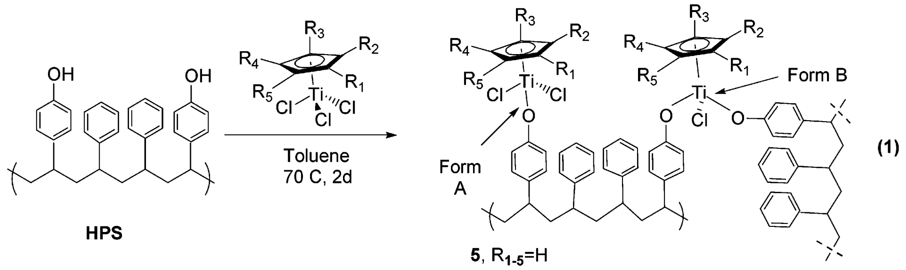
precursor catalyst (mmol)	macroligand (OH mmol)	supported catalysts	elemental analysis (found) Ti:Cl:Si
1 (0.5)	3.0	**5**	1:1.5:n.d.
2 (0.4)	3.1	**6**	1:1.3:n.d.
3 (0.3)	3.0	**7**	1:1.7:1
4 (0.3)	3.0	**8**	1:1.8:2

enyltitanium(IV) chloride, form **B**, which serves to chemically cross-link the polymer. The net result of the reaction is formation of macroligated catalysts **5**−**8** immobilized on polystyrene. Elemental analyses of the Ti:Cl mole ratio of complexes **5**−**8** was performed, and the experimentally determined values were in the range 1:1.5−1.7 (Table 1). These values are intermediate between those expected for forms **A** and **B** and are indicative of the presence of both forms. The probability of formation of a tris(aryloxy)cyclopentadienyltitanium(IV) species is considered to be quite low on the basis of steric factors. Analyses by NMR on **5**−**8** swollen with C_6D_6 were performed to further quantify the formations of forms **A** and **B**. There are not sufficient chemical shift differences in the ^{1}H NMR and ^{13}C NMR spectra for **5**−**7** to differentiate between the two forms. However, the ^{13}C NMR of **8** has two resonances for $Si(CH_3)_3$ at δ −0.2 and δ 1.5 which are attributed to the formation of form **A** and form **B**, respectively. The ratios of **8A** to **8B** determined by elemental analysis and ^{13}C NMR are in good agreement. Related observations have been made by Xu et al. for $CpTiCl_3$ supported on hydroxyl-containing styrene terpolymers. Following activation by MAO, ESR spectra were recorded for Ti(III) species that were then assigned to the presence of monoaryloxy and bis(aryloxy), (both inter- and intrachain ligation) macroligated catalyst centers during styrene polymerization.[10] Ethylene polymerization was performed using complexes **5**−**8** in conjunction with MAO as the cocatalyst in toluene at room temperature. Experimental conditions, the polymerization yield, molecular weights (M_w), melting points (T_m), enthalpy of fusion (ΔH_f), and degree of crystallinity of the polymers are shown in Table 2. Under comparable Al:Ti ratios, **6** and **7** showed similar activities for the production of polyethylene, and these catalysts are more active than **5**, with **8** being the least active. The molecular weights of the polyethylenes produced range from high for those prepared using **7** and **8** to moderate for those prepared by **5** and **6**.

Complex **5** afforded polyethylene of unimodal molecular weight distribution as seen from the GPC. The thermal analysis of the polymer showed a melting point of 121.5 °C in the first and the second melt cycles. The physical characteristics of the polyethylene are fully consistent with the formation of a polyolefin from a SSC, and the depression in melting point is indicative of short chain branches. The carbon resonances were assigned as 14.27 ($1B_4$, CH_3, EHE), 22.92 ($2B_4$), 23.41 ($\delta\delta$), 27.21 ($\beta\delta$, EHEE+EEHE), 29.58 ($3B_4$, EHE), 29.98 ($\delta\delta$, EEE), 30.45 ($\gamma\delta$, HEEE+EEEH), 34.10 ($4B_4$, EHE), 34.41 ($\alpha\delta$, EHEE+EEHE), 38.04 (CH, methine).[11] From ^{13}C NMR, exclusively butyl branches were observed at 1.5 mol % incorporation (see Figure 2). An explanation for the exclusive formation of butyl branches is the in situ formation of 1-hexene by a selective trimerization of ethylene. The catalytic trimerization of ethylene is promoted by the presence of Ti(II), which is known to result from the reduction of Ti(IV) precursors by reaction with MAO.[12] The 1-hexene generated is then subsequently copolymerized with ethylene to afford short chain branches (SCB) in polyethylene.[8]

To further investigate the importance of the macroligand supported catalysts in generating SCB in ethylene polymerizations, a series of control experiments were performed. Pretreatment of HPS with an excess of MAO results in formation of aluminum aryloxides. The subsequent addition of **1** along with ethylene results in the formation of polyethylene with a T_m of 132.0 °C and fewer than four branches per 1000 C atoms as determined by ^{13}C NMR. This result is in agreement with the known solution polymerization behavior of **1**/MAO. Apparently, the attachment of titanium to the macroligand in complex **5** is retained after activation with the MAO cocatalysts during the polymerizations of ethylene. Nonbridged complexes (cyclopentadienyl)-mono(phenoxy)titanium(IV) and (cyclopentadienyl)-mono(phenoxy)titanium(IV) activated by MAO afforded HDPE from ethylene homopolymerization. These results are in line with those reported by Nomura for structurally similar catalyst structures.[13,14] The material characterization reported for the polyethylenes produced by Nomura are limited to molecular weight analysis. No determination of the presence, or absence, of short chain

Scheme 1. Synthesis of Macroligated Catalysts



5, R_{1-5}=H
6, R_{1-5}=CH_3
7, R_1=$Si(CH_3)_3$, R_2-R_5=H
8, R_1=R_3=$Si(CH_3)_3$, R_2=R_4=R_5=H

Table 2. Ethylene Homopolymerization Using Macroligated Catalyst in Conjunction with MAO

entry	catalyst	Al:Ti	yield (mg)	activity (kg/(mol of Ti h atm))	$T_m{}^a$ (°C)	$\Delta H_f{}^a$ (J/g)	% crystallinity^b	$M_w{}^c$	PDI^c
1	**5**	632	348	16	121.5	43.60	14.8	52 050	1.7
2	**6**	847	110	45	130.1	79.41	27.2	33 390	2.3
3	**7**	995	331	43	134.0	86.4	29.5	498 750	1.6
4	**8**	1612	50	8	129.1	45.37	15.5	204 500	1.8

[a] DSC second scan with a heating and cooling rate of 10 °C/min. [b] Calculated with respect to a polyethylene single crystal, $\Delta H_f = 293$ J/g. [c] Determined through GPC at 135 °C in trichlorobenzene (TCB) using light scattering detectors calibrated with PS standards.

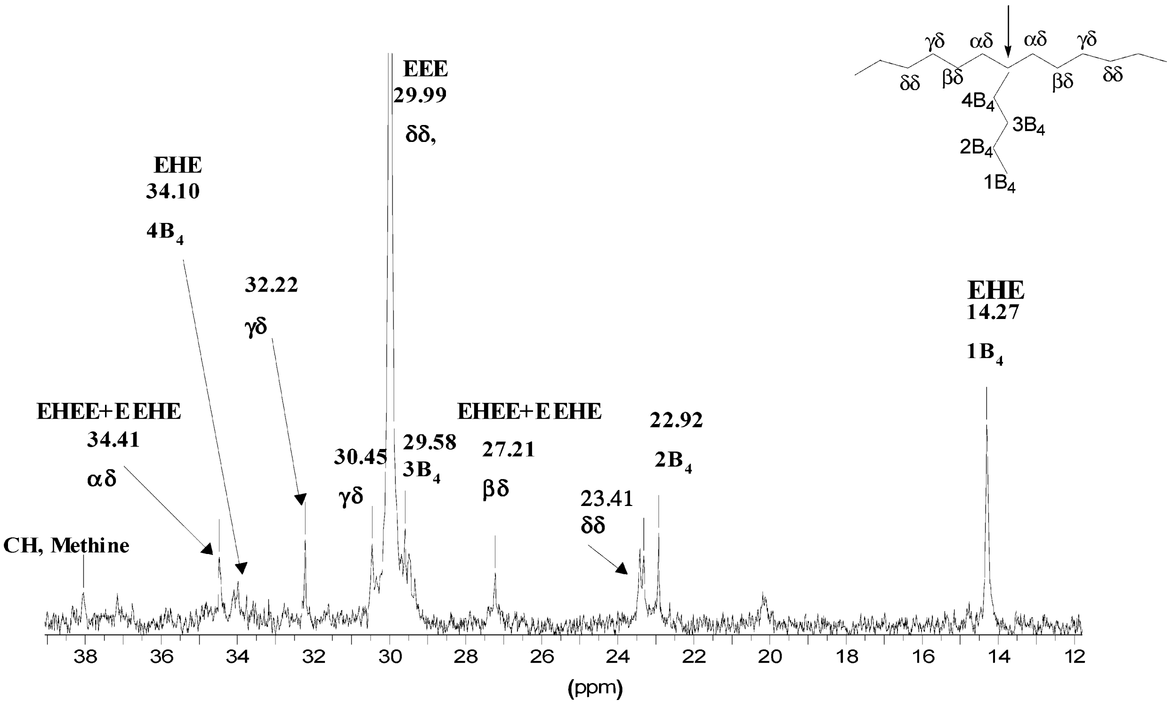


Figure 2. Polyethylene with SCBs from complex **5**/MAO.

branches has been described. For catalyst **5** the presence of the macroligand is apparently necessary for the production of SCBs during ethylene homopolymerization.

To determine the effect of leaching, which could be a consequence of the abstraction of titanium fragments from the supported catalyst upon treatment with MAO, control polymerizations were performed. It has been observed that the concentration of leached species increases with longer reaction time with MAO.[19] In this system, leaching is minimized by allowing the polymerization to proceed for short reaction intervals (10 min). Precontacting the supported catalyst with MAO followed by filtration and use of the filtrate for ethylene polymerization indicated low activity, 10−15% relative to the activity of the supported catalyst.

During olefin polymerizations involving group 4 metal catalyst, the activated metal is present as a cation and is counterbalanced by a noncoordinating anion. The interactions between this contact ion pair have a great deal of influence on the catalytic activity, lifetime of the active species, chain-termination, and chain-transfer processes.[15] Hence, there is a need to study the polymerization properties of the macroligated metal cation−anion pair. To explore the effect of the counterion, ethylene polymerizations were performed using **5**, **6**, **7**, and **8** with MAO as the alkylating agent and $B(C_6F_5)_3$ (**I**) as the cocatalyst. Under comparable Ti:B ratio, **6** and **7** showed similar activities for the production of polyethylene, and these catalysts are more active than **5**, with **8** being the least active. The molecular weights of the polyethylenes produced range from high for those prepared using **7** to moderate for those prepared by **5**, **6**, and **8**. Under the experimental conditions for ethylene polymerization **5**, **6**, and **8** afforded HDPE as determined by the polymer melting point. However, **7** (Table 3, entries 5 and 6) afforded polyethylene with a melting point of 121.4 °C and were attributed to the presence of short chain branches. To establish the type of branches formed, ^{13}C NMR of the polymer was performed. The observed resonances were attributed to presence of butyl branches and were assigned as 14.17 (1B$_4$, CH$_3$, EHE), 22.98 (2B$_4$), 23.48 ($\delta\delta$), 27.17 ($\beta\delta$, EHEE+EEHE), 29.40 (3B$_4$, EHE), 29.99 ($\delta\delta$, EEE), 30.47 ($\gamma\delta$, HEEE+EEEH), 32.22 ($\gamma\delta$), 34.10 (4B$_4$, EHE), 34.41 (αδ, EHEE+EEHE), and 38.00 (methine, EHE). The presence of butyl branches is attributed to the coproduction of 1-hexene during polymerization of ethylene. From ^{13}C NMR, 1-hexene incorporated was determined to be 1.5 mol %. The absence of ethyl and hexyl branches was also noted. The molecular weight and extent of branching in PE do not change with an increase in the B:Ti ratio (1:1 to 10:1).

In branched polyolefins, the content and the identity of the branch can be a function of proximity between the cationic metal center and anionic (borate) counterion. To further explore the interactions between the metal cation and other borate counterions for the production of SCBs, ethylene polymerizations was performed using **7** with MAO as the alkylating agent with

Table 3. Ethylene Homopolymerization Using Different Cocatalysts Using Complex 7 with MAO as the Alkylating Agent

entry	catalyst **7** (μmol)	Al:Ti	B^f (mg)	activity (kg/(mol of Ti h atm))[e]	T_m[a] (°C)	ΔH_f (J/g)[a]	% crystallinity[b]	crystal size[d] (Å)	M_w[c] (polymer)	PDI[c]
5	5.5	805	**I** (2.8)	64	124.4	7.2	2.4	126	216 200	bimodal
6	8.0	496	**I** (30.2)	60	121.4	6.2	2.1	120	242 300	bimodal
7	6.0	745	**II** (4.3)	146	118.4	7.2	2.4	116	217 900	2.6
8	8.2	513	**II** (45.8)	301	123.5	11.6	3.9	120	227 200	bimodal
9	5.0	726	**III** (5.5)	275	130.4	28.8	9.8	138	97 600	2.05
10	7.5	596	**III** (51.8)	108	131.4	36.7	12.5	140	84 600	1.87

[a] DSC first scan. [b] Calculated with respect to polyethylene single crystal, $\Delta H_f = 293$ J/g. [c] Determined through GPC at 135 °C in TCB using light scattering detectors calibrated with PS standards. [d] Determined from WAXS using the Scherrer equation. [e] Ethylene pressure of 4 atm, reaction for 5−10 min. [f] (**I**) $B(C_6F_5)_3$, (**II**) $(C_6H_5)N(CH_3)_2H(B(C_6F_5)_4)$, (**III**) $(C_6H_5)C(B(C_6F_5)_4)$.

two different borate cocatalysts $(C_6H_5)N(Me)_2H(B(C_6F_5)_4)$ (**II**) and $(C_6H_5)_3CB(C_6F_5)_4$ (**III**). Interestingly, ethylene polymerization using **7**/MAO with **II** affords polyethylene with SCBs as seen from DSC and ^{13}C NMR studies (Table 3, entries 7 and 8). In sharp contrast, ethylene polymerization using **7**/MAO with **III** affords HDPE. With cocatalysts **II** and **III**, the metal cation is counterbalanced by the $B(C_6F_5)_4^-$ ion. The SCBs observed using complex **7**/MAO/ **II** can be attributed to the coordination of the dimethylaniline coproduct to the cationic titanium center. On the other hand, the 1,1,2-triphenylethane formed during the metal activation protocol **7**/MAO/**III** (entries 9 and 10, Table 3) does not interact with the metal center.

Various SSCs have been supported on organic, typically polymeric (soluble polymer or cross-linked bead), and inorganic materials (alumina, silica). Interestingly, polyolefins of ultrahigh molecular weight and varied degrees of crystallinity have been observed.[16−18] Polyolefins produced from constrained geometry catalysts (CGCs) supported on cross-linked polystyrene beads have lower crystallinity compared to polyolefins obtained from homogeneous analogues.[19] To correlate the influence of the macroligand on the apparent crystal size and the resulting degree of crystallinity of the polyethylene synthesized, wide-angle X-ray diffraction (WAXD) analysis was performed. The reflections used for analysis were *d*(110) and *d*(200), where the broadening of the *d*(110) is affected by distortions of the *a* and *b* axes of the polyethylene orthorhombic unit cell. To compare the polyethylenes obtained from homogeneous catalysts and the macroligated catalysts, WAXD analysis of polyethylene produced from **3** (homogeneous catalyst) in conjunction with MAO was performed, and the *d*(110) and *d*(200) reflections were observed to be relatively sharp. The apparent crystal size of the polyethylene was determined to be of 180 Å using the Scherrer equation.[20] In contrast, polyethylene produced from **7** (macroligated catalyst, solvent swollen) in conjunction with MAO shows broadened *d*(110) and *d*(200) reflections. The broadening of peaks can be attributed to the reduction in apparent crystal size of the polyethylene and increase in amorphous content of the polymer. The polyethylene produced from **7**/MAO has an apparent crystal size of 150 Å. It was noted that the amorphous halo was much more pronounced in polyethylenes with smaller apparent crystal sizes and lower degree of crystallinity. DSC measurements showed that the enthalpy of fusion and degree of crystallinity of the polyethylenes were considerably reduced (Table 2, entry 3). The WAXD data (apparent crystal size, broadening of *d*(110) and *d*(200)) together with the DSC results (lower enthalpy of fusion, lower degree of crystallinity) show that the macroligated catalysts result in less ordered polyethylene crystals with a corresponding increase in amorphous and intermediate component content, i.e., the formation of less stable crystalline lamellae.

Summary

The reaction of titanium−piano stool complexes with poly(styrene-*r*-4-hydroxystyrene) afforded immobilized aryloxycyclopentadienyl macroligated catalysts. A novel method for the production of short chain branches (SCBs) in polyethylene by the use of the macroligated catalysts in conjunction with various cocatalysts during ethylene homopolymerization has been demonstrated. The exclusive formation of butyl short chain branched polyethylene has been attributed to the production of 1-hexene by an ethylene trimerization process and subsequent copolymerization with ethylene. From control experiments it has been established that the presence of macroligated catalyst is vital for the production of butyl SCBs in polyethylene. The formation of SCBs was found to be dependent on the cyclopentadienyl substituents, the influence exerted by the polystyrene macroligand, and the nature of the cocatalysts.

Experimental Section

Methods and Materials. All reactions were performed under nitrogen in Schlenk glassware or in an inert atmosphere drybox. All solvents used were obtained from a solvent purification manifold.[23] Titanium tetrachloride, bis(trimethylsilyl)cyclopentadiene, 2,5,5-tris(trimethylsilyl)-1,3-cyclopentadiene, cyclopentadienyltitanium trichloride, pentamethylcylocpentadienyltitanium trichloride, AIBN, styrene, acetoxystyrene, and hydrazine hydrate were obtained from Aldrich and used as received. The complexes trimethylsilylcyclopentadienyltitanium trichloride and bis(trimethylsilyl)cyclopentadienyltitanium trichloride were synthesized according to literature procedures.[24,25] Polymerization was performed using a gas manifold and thick-walled reactors.[26]

Instrumentation. ^{1}H NMR spectra were obtained at 300 MHz using a Bruker DPX 300, ^{13}C NMR spectra were recorded at 75 MHz using a Bruker DPX 300 in the continuously proton-decoupled (CPD) mode, and ^{13}C NMR (high temperature, HT) spectra were recorded at 150 MHz on an Avance DPX 600 using a quantitative pulse program for solution NMR at 135 °C. Elemental analysis was performed using three Exeter Analytical Inc. 240XA CHN analyzers and a Leeman Labs Inc. dual view-DRE-sequential-ICP was used to analyze the Ti and Si loadings in the samples. Gel permeation chromatography was performed with Polymer Laboratories PL-220 high-temperature GPC equipped with a Wyatt MiniDawn (620 nm diode laser) high-temperature light scattering detector and refractive index detector at 135 °C using 1,2,4-trichlorobenzene as solvent and calibrated using polystyrene standards. The d*n*/d*c* value for polyethylene used was −0.11. Thermal analysis was performed using TA DSC 2910 equipped with liquid nitrogen cooling accessory unit under a continuous nitrogen purge (50 mL/min) with a heating and cooling scan of 10 °C/min. Infrared analyses were performed using a Perkin-Elmer 2000 FTIR on samples prepared as KBr pellets. Scanning electron microscopy was performed using a JEOL 35 CF SEM using low accelerating voltage imaging of gold-coated polymers and for ultrahigh magnification using a field emission gun scanning electron microscope (FEG SEM, JEOL JSM 6320F). The wide-angle X-ray diffractograms of the polymer powder taken in a capillary were performed using Cu Kα radiation (wavelength of 1.54 Å) with a nickel filter, and the X-rays were collimated into a fine beam of circular cross section using a pinhole collimator. A HDPE standard was used to calibrate the *d*(110) and *d*(200) peak positions.

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Supporting Information Available: The synthesis of the macroligand (HPS) and the macroligated catalysts (**5**−**8**), representative ethylene homopolymerizations using macroligated catalysts, ethylene polymerization control experiments using **3** and **4** with MAO, ethylene polymerization using **5**−**7** with MAO/B(C_6F_5)$_3$, ^{13}C NMR plot of polyethylene with SCBs, WAXS plots of polyethylene, and SEM micrographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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