Macromolecules

Volume 32, Number 11 June 1, 1999

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Homo- and Copolymerization of Ethylene and α-Olefins over 1- and 2-Siloxy-Substituted Ethylenebis(indenyl)zirconium and Ethylenebis(tetrahydroindenyl)zirconium Dichlorides

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Received November 13, 1998; Revised Manuscript Received March 16, 1999

ABSTRACT: The influence of siloxy substitution of ethylene-bridged bis(indenyl)- and bis(tetrahydroindenyl)zirconium dichlorides on ethylene/α-olefin copolymerization and ethylene homopolymerization performance was investigated. Ethylene was copolymerized with 1-hexene and 1-hexadecene over *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-3-indenyl)]zirconium dichloride (**1**), *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydro-3-indenyl)]zirconium dichloride (**H1**), *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)-1-indenyl)]zirconium dichloride (**2**), and *rac*-ethylenebis(1-indenyl)zirconium dichloride (**EBI**) using methylaluminoxane (MAO) as cocatalyst. 1-Siloxy substitution was found to remarkably improve the copolymerization ability and 2-siloxy substitution to enhance the polymerization activity of ethylenebis(indenyl)zirconium dichlorides. Optimum homo- and copolymerization performance was observed at a very low Al(MAO) concentration, which for **2** could be reduced to a level of 0.2 mmol/dm^3 by using a small amount of triisobutylaluminum. The 1-siloxy-substituted metallocene catalysts **1** and **H1** (hydrogenated **1**) revealed decreasing comonomer incorporation and increasing induction times with increasing Al(MAO) concentration, which indicates the presence of unfavorable interactions between these metallocenes and MAO. Chain termination occurred mainly by chain transfer to the monomer and β-hydrogen transfer to the metal for catalysts with indenyl and tetrahydroindenyl ligands, respectively.

Introduction

Even distribution and high comonomer content in ethylene−α-olefin copolymers together with narrow molecular weight distribution are benefits brought about by single-site metallocene catalysts compared to conventional Ziegler−Natta catalysts.[1,2] Metallocenes with improved copolymerization ability are of great interest, because they enable, for example, the use of bulky comonomers and under certain conditions the in situ production of low-pressure long-chain branched polyethylene.[1,3,4] Further improvement of the copolymerization performance of metallocene catalysts by modification of the ligand substitution pattern has been the objective of recent studies.[2,5] For example, benzannelation of indenyl ligands has been found to enhance copolymerization ability, while 2-methyl substitution enhances molecular weight but reduces activity.[2] DOW's dimethylsilylene-bridged amidocyclopentadienyltitanium complexes, i.e., the constrained geometry catalysts, are exceptionally good copolymerization catalysts and enable the production of long-chain branched polyethylene by in situ incorporation of vinyl-terminated macromonomers into the growing chain.[1,3,6] The best copolymerization performance reported so far as a result of rational catalyst design has been achieved by combination of these beneficial contributions of the catalyst structures. Xu and Ruckenstein[5] reported recently the improved copolymerization properties of a benzannelated 2-methyl-substituted constrained geometry catalyst. A prerequisite for such rational catalyst design is the knowledge of the influence of different structural patterns on the polymerization performance.

We have previously introduced a new class of ethylene-bridged siloxy-substituted metallocenes, which are

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10.1021/ma981764q CCC: $18.00 © 1999 American Chemical Society
Published on Web 05/13/1999

Table 1. Ethylene/1-Hexene Copolymerization Results at 80 °C[a]

cat.	[Zr] (μmol/dm^3)	C_6/C_2	[Al(MAO] (mmol/dm^3)	Al(MAO)/ Zr	time (min)	yield (g)	M_w[b] (kg/mol)	M_w/M_n[b]	C_6 conv (%)	C_6 content (mol %)	r_E[c]	r_H[c]
1	0.9	3.6	1.5	1700	10	8.4	28	1.9	33	13.7	15	0.007
1	0.3	3.6	1.5	5000	15	2.6	28	2.0	10	14.1	17	0.007
1	0.3	3.6	2.3	7500	20	1.4	29	1.8	6	14.1	18	0.005
1	0.9	3.6	4.6	5000	20	1.6	28	1.9	6	12.4	21	0.007
1	0.3	3.6	4.6	15000	20	0.3	27	1.9	1	11.7	23	0.006
1	0.9	2.4	1.5	1700	10	15.2	36	1.9	46	10.0	14	0.005
1	0.3	2.4	2.3	7500	10	1.9	36	1.9	6	9.7	19	0.005
1	0.3	2.4	4.6	15000	15	0.3	36	1.9	1	8.8	22	0.006
H1	0.9	3.6	1.5	1700	10	2.0	57	2.0	6	10.1	27	0.002
H1	0.3	3.6	1.5	5000	20	0.9	64	2.0	3	10.7	26	0.005
H1	0.3	3.6	2.3	7500	20	0.4	75	2.0	1	9.1	31	0.003
H1	0.9	3.6	4.6	5000	20	0.5	66	1.9	1	7.8	36	
2	0.3	7.1	2.3	7500	30	1.0	38	1.9	4	12.1	43	0.004
2	0.3	7.1	4.6	15000	30	1.2	35	1.8	4	12.5	42	0.006
2	0.3	7.1	30.5	100000	30	1.2	26	2.0	4	11.5	46	0.005
2	0.3	3.6	2.3	7500	10	1.7	49	1.9	3	5.5	56	
2	0.3	3.6	4.6	15000	10	1.5	47	1.8	3	6.2	52	
2	0.3	3.6	30.5	100000	10	1.3	41	1.8	3	5.6	57	

[a] $[C_2] = 0.042$, 0.084, or 0.126 mol/dm^3; [1-hexene] = 0.30 mol/dm^3. [b] By GPC. [c] Calculated according to refs 11 and 19.

highly active in ethylene and propylene polymerizations and reveal optimum polymerization behavior at low Al/Zr ratios.[7] The key objective of this study was to examine the influence of the siloxy substituents and their position on the ligand on the ethylene/α-olefin copolymerization performance. Additionally the potential of siloxy-substituted catalysts in ethylene homopolymerizations at low Al(MAO) concentrations was studied. Polymerization parameters of interest were the cocatalyst concentration, monomer concentration, and polymerization temperature.

Experimental Section

Materials. The catalyst precursors *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-3-indenyl)]zirconium dichloride (**1**), the hydrogenated congener *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydro-3-indenyl)]zirconium dichloride (**H1**), and *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)-1-indenyl)]zirconium dichloride (**2**) were prepared at Åbo Akademi University according to literature procedures.[8a,b] *rac*-[Ethylenebis(1-indenyl)]zirconium dichloride (**EBI**) and *rac*-[ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**EBTHI**) were supplied by Witco. Ethylene (AGA, grade 3.5), toluene (Merck, GR grade), and comonomers 1-hexene (Aldrich, 99%) and 1-hexadecene (Merck, 95%) were purified by passage through a series of columns containing molecular sieves (not for 1-hexene), CuO, and Al_2O_3. Methylaluminoxane (10% w/w) and triisobutylaluminum (TIBA) were supplied by Witco. *N*,*N*-Dimethylanilinium tetra(perfluorophenyl)borate was supplied by AKZO and used in a solution of toluene and TIBA. All operations with these materials were carried out in nitrogen atmosphere using standard vacuum or glovebox techniques.

Polymerization and Characterization. All polymerizations were carried out in a 0.5 dm^3 stainless steel autoclave. The polymerization medium toluene (270 g) and cocatalyst methylaluminoxane (MAO) were fed first to the evacuated and N_2-purged reactor, after which the comonomer was added batchwise followed by the feeding of ethylene after 10 min. When TIBA was used, it was fed together with the medium toluene, and the cation-forming agent MAO or borate was introduced after the 10 min contact time. To start the polymerization, the metallocene catalyst precursor dissolved in toluene was pumped with a highly accurate dosing pump into the reactor. The ethylene pressure (±25 mbar) and reactor temperature (±0.2 °C) were maintained constant. Particular care was given to examine the catalysts under conditions in which the chemical reaction rate was smaller than the ethylene absorption rate. The sufficiency of agitation was assured by the observation that increasing stirring speed had no influence on the ethylene consumption rate.[9] At the end of the polymerization the reactor was degassed, the reaction mixture poured into a solution of hydrochloric acid in ethanol, and the polymer product washed first with a HCl/EtOH solution and then with ethanol. Ethylene−1-hexadecene copolymers were further washed with acetone, and all copolymers were dried in a vacuum at 60 °C.

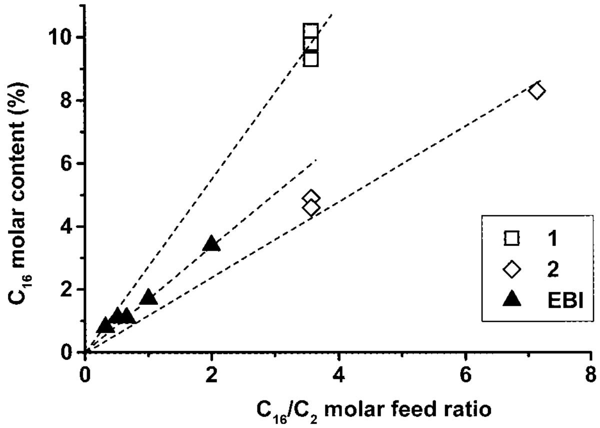

Figure 1. Effect of siloxy substituent and its position on 1-hexadecene incorporation at 80 °C with Al(MAO)/Zr ratios 1700, 5000, and 10 000 for **1**/MAO, 7500 and 38 000 for **2**/MAO, and 7500 for **EBI**/MAO. Decreasing the Al(MAO) concentration leads to increasing comonomer content values for **1**/MAO.

^{13}C NMR spectra of the copolymers were recorded at 125 °C on a Varian GEMINI 2000 NMR spectrometer operating at 75 MHz, with a 45° pulse angle, 6 s delay, and typically 3000 scans. The carbon signals were assigned according to Randall[10] and the reactivity ratios calculated according to Uozumi and Soga.[11] Molecular weights and molecular weight distributions (MWD) were determined on a Waters 150-C ALC GPC instrument operated at 140 °C with 1,2,4-trichlorobenzene as solvent. Analysis of unsaturated end groups was based on IR spectra which were recorded from melt-pressed polymer sample films using a Nicolet Magna FT-IR spectrometer and evaluated by the method of Haslam et al.[12]

Results and Discussion

Copolymerization of Ethylene and 1-Hexene or 1-Hexadecene. *Influence of the Position of the Siloxy Substituent.* To evaluate the influence of the position of the siloxy substituent on the copolymerization performance, we have studied the comonomer incorporations of the siloxy-substituted and the unsubstituted bis(indenyl)zirconium dichlorides at different comono-

Table 2. Ethylene/1-Hexene Copolymerization Results at 40 °C[a]

cat.	[Zr] (μmol/dm^3)	C$_6$/C$_2$	[Al(MAO] (mmol/dm^3)	Al(MAO)/ Zr	time (min)	yield (g)	M_w[b] (kg/mol)	M_w/M_n[b]	C$_6$ conv (%)	C$_6$ content (mol %)	r_E[c]	r_H[c]
1	3.0	2.5	1.5	500	20	3.9	46	1.9	14	12.2	14	0.004
1	1.8	2.5	1.5	850	20	2.8	46	1.7	10	11.5	15	0.005
1	0.9	2.5	1.5	1700	20	1.3	44	1.9	4	11.2	16	0.003
1	0.9	2.5	4.6	5000	40	0.3	41	1.9	1	11.3	16	0.004
H1	3.0	2.5	1.5	500	6	6.7	200	2.6	26	13.5	11	0.003
H1	1.8	2.5	1.5	850	15	5.9	220	2.3	20	12.0	14	0.006
H1	0.9	2.5	1.5	1700	25	4.2	280	2.3	13	10.3	18	0.005
H1	0.9	2.5	4.6	5000	60	0.01	230	2.4				

[a] [C$_2$] = 0.12 mol/dm^3, [1-hexene] = 0.30 mol/dm^3. [b] By GPC. [c] Calculated according to refs 11 and 19.

Table 3. Reactivity Ratios Determined for the Siloxy-Substituted Catalyst Systems 1/MAO, H1/MAO, and 2/MAO from ^{13}C NMR Data

	1[a]	**H1**[a]	**2**[b]
T = 80 °C, 1-hexene			
r_E	19 ± 4	30 ± 5	55 ± 3
r_H	0.006 ± 0.001	0.004 ± 0.002	0.005 ± 0.001[c]
T = 80 °C, 1-hexadecene			
r_E	25 ± 1		63 ± 2
r_{HD}			0.002 ± 0.001[c]
T = 40 °C, 1-hexene			
r_E	15 ± 1	14 ± 4	
r_H	0.004 ± 0.001	0.004 ± 0.002	

[a] [C$_2$]$_{80°C}$ = 0.084 mol/dm^3, [C$_2$]$_{40°C}$ = 0.12 mol/dm^3, [comonomer] = 0.30 mol/dm^3, [Al(MAO)] = 1.5−4.6 mmol/dm^3. [b] [Al(MAO)] = 2.3−30.5 mmol/dm^3. [c] [C$_2$] = 0.042 mol/dm^3.

mer/monomer feed ratios for ethylene/1-hexadecene copolymerizations at 80 °C (Figure 1). It can clearly be observed that 1-siloxy-substitution enhances comonomer incorporation compared to 2-siloxy substitution.

A partial explanation for the higher comonomer incorporation obtained with the 1-siloxy-substituted catalysts may be their larger angles between the cyclopentadienyl planes, as observed in the molecular structures of **H1** (Cp−Cp = 63.6°) and the meso diastereomer of **1** (Cp−Cp = 64.6°),[8a] as compared to that of **2** (Cp−Cp = 61.0°).[8b] It should be noted, however, that for **EBI** a Cp−Cp angle of 63.47° has been observed,[13] which is close to that of **H1**. Dimethylsilylene-bridged bis(indenyl)zirconium dichlorides, which are generally known to be good copolymerization catalysts, have interplanar Cp−Cp angles ranging from 59.2° to 61.9°.[14] The molecular structure of **1** has not been elucidated yet. However, based on earlier observations for 2-siloxy-substituted complexes, these bis(indenyl)zirconocenes tend to have larger Cp−Cp angles and larger Cl−Zr−Cl angles than their hydrogenated congeners.[7,8b,c] The position of the siloxy substituent may also affect the space available for long-chain α-olefin coordination. Molecular modeling studies are in progress to clarify the possible influence of these steric effects.[15]

In addition, electronic effects may arise from variations in the position of the siloxy substituent, influencing the stabilization of the cationic active site, the formation of the olefin separated ion pair, and the actual chain propagation reaction. As will be seen from the ethylene homopolymerization results, 2-siloxy substitution leads to a drastic improvement in the overall activity, which should be more pronounced in the case of the mobile and sterically less hindered ethylene monomer. This could also be a reason for the lower comonomer incorporation of **2** compared to **1** and **EBI**.

Influence of Methylaluminoxane. Table 1 contains results of the influence of Al(MAO) concentration on the copolymerization ability of the siloxy-substituted metallocene catalysts in ethylene/1-hexene copolymerizations. The comonomer incorporation of the 1-siloxy-substituted catalysts **1**/MAO and **H1**/MAO clearly depends on the applied Al(MAO) concentration, increasing with decreasing Al(MAO) concentration. On the other hand, the copolymerization ability of the 2-siloxy-substituted catalyst **2**/MAO seems to be insensitive toward the applied Al(MAO) concentration. Assuming that the 1-siloxy-substituted complexes have a more open coordination sphere, they may be more subjected toward coordination of MAO or the free trimethylaluminum of MAO to the donor substituents. The activities of **1**/MAO and **H1**/MAO decrease strongly with increasing Al(MAO) concentration, and both catalyst systems show increasing induction times with increasing Al(MAO) concentration.[16] Induction times of several hours have been observed earlier by Brintzinger and coworkers[17] for the 2-(dimethylamino)-substituted bis(indenyl) *ansa*-zirconocene/MAO catalyst system in polymerization of propylene. Such induction periods are unusual for metallocene-based olefin polymerization catalysts and indicate that the reaction generating the active species may be inhibited by yet unknown equilibria between the Lewis basic donor substituents and the aluminoxane cocatalyst. Simultaneous coordination of an aluminum-based anion to the cationic zirconium atom and the electron-deficient oxygen atom could also induce the formation of dormant sites. Replacement of the *tert*-butyldimethylsiloxy groups with the bulkier triisopropylsiloxy groups was earlier found to increase the comonomer incorporation of both MAO-activated catalyst systems **1** and **2**.[18] This could be understood as a consequence of better shielding of the siloxy groups.

Influence of Polymerization Temperature. For the best copolymerization catalysts **1**/MAO followed by its hydrogenated congener **H1**/MAO, the influence of temperature on copolymerization behavior was examined in more detail. At 80 °C comonomer incorporation was higher for **1** at all applied Al(MAO) concentrations (Table 1). From Tables 1 and 2 it can be seen that decreasing the temperature to 40 °C did not remarkably influence the copolymerization ability of **1**/MAO, while for **H1**/MAO a clear improvement in copolymerization ability was observed. Actually, from Table 2 it can be seen that at 40 °C and low Al/Zr ratios (e.g., Al/Zr = 500), **H1**/MAO was even a better copolymerization catalyst than its non-hydrogenated congener **1**/MAO, producing higher molecular weight and higher comonomer content copolymers. Steric effects may contribute to the observed temperature dependence. Fluctuation between the indenyl-backward and the indenyl-forward conformations[20] in combination with the fluctuation of the hydrogenated six-rings of **H1** may be enhanced at

Table 4. Use of TIBA for Reduction of Al(MAO) Concentration for Catalyst 2/MAO[a]

[Al(TIBA)] (mmol/dm^3)	[Al(MAO)] (mmol/dm^3)	Al(MAO)/Zr (mol/mol)	time (min)	yield (g)	productivity (ton (PE)/mol (Zr) h)	M_w[b] (kg/mol)	M_w/M_n[b]
0	30.5	200000	10	0.4	48	154	2.2
0	3.8	25000	10	1.7	204	147	2.3
0	1.5	10000	10	3.4	408	155	2.3
0	0.75	5000	10	3.4	408	162	2.6
2	0.75[c]	12500	15	2.0	400	124	2.1
2	0.75	5000	10	4.8	576	172	2.4
2	0.37	2500	10	4.2	504	150	2.3
2	0.22	1500	10	4.5	540	155	2.5
1	0.22	1500	10	5.4	648	177	2.5
0.5	0.22	1500	10	5.7	684	215	2.8
2	0.11	750	10	2.7	324	141	2.4
2	0[d]		5	3.8	912	222	4.2

[a] $T = 40$ °C, $[C_2] = 0.12$ mol/dm^3, $[Zr] = 0.15$ μmol/dm^3. [b] By GPC. [c] $[Zr] = 0.06$ μmol/dm^3. [d] $2^+B(C_6F_5)_4^-$, metallocene/borate ratio 1:2.

elevated polymerization temperatures and possibly interfere with the monomer coordination. The copolymerization behavior of **1**, which has essentially planar indenyl moieties, is considerably less influenced by the polymerization temperature.

Reporting reactivity ratios obtained under one set of polymerization conditions is obviously not sufficiently informative when evaluating the copolymerization performance of metallocenes with more complex ligand substituents as a whole. To roughly summarize the copolymerization characteristics of siloxy-substituted catalysts, we have presented in Table 3 reactivity ratios covering a wide range of operating conditions. We want to emphasize the influence of the Al(MAO) concentration on the range of r_E values reported for the 1-siloxy-substituted catalysts, for which copolymerizations at low Al(MAO) concentrations led to considerably lower r_E values than copolymerizations at higher Al(MAO) concentrations.[21] The variation in the r_H values is within experimental error due to the rather low comonomer content.

Influence of Comonomer. For both catalysts **1**/MAO and **2**/MAO the incorporation of 1-hexadecene was 15–40% lower than the incorporation of 1-hexene, which is reflected in the respective r_E values in Table 3. The reason for lower 1-hexadecene incorporation is probably due to the steric bulk and lower rate of diffusion. Under the applied copolymerization conditions, enhancement in the ethylene consumption rate due to addition of comonomer, the so-called comonomer effect,[1] was not observed. The observations of this study together with the previously[7a] “observed” comonomer effect for catalyst **2**/MAO under conditions of limiting ethylene absorption rate can be seen as an example for the physical nature of the comonomer effect.[22]

Ethylene Homopolymerization Studies. In ethylene homopolymerizations the concentration of the siloxy-substituted catalysts had to be decreased to a very low level[23] before the ethylene absorption rate in spite of efficient stirring was not rate determining. In the case of siloxy substitution at the 2-position, catalyst concentrations had to be exceptionally low, in homopolymerizations at 1 bar ethylene pressure as low as 0.15 and 0.06 μmol/dm^3 at 40 and 80 °C, respectively. At a temperature of 80 °C experiments with the 1-siloxy-substituted **1** and **H1** and the unsubstituted **EBI** could be performed with 0.3 μmol/dm^3 catalyst concentration without ethylene absorption being the limiting factor. This is one indication of the activating effect of siloxy substitution in the 2-position of the indenyl ligand.

Reduction of the Amount of Methylaluminoxane. Reducing the amount of Al(MAO) was found to increase the productivity of siloxy-substituted catalysts as expected from earlier studies.[7] However, we could not reduce the amount of Al(MAO) below a level of 1 mmol/dm^3 without loss in productivity and assume this to be mainly due to impurities that remained in our system after the contact time of MAO. At low Al(MAO) concentrations a rapid decay in the ethylene consumption was, in fact, observed. To extend the range of applied Al(MAO) concentrations to even lower values, we made a series using TIBA, which is an impurity scavenger and good alkylating agent.[24] The results of this series are shown for the 2-siloxy-substituted **2** in Table 4. It can be seen that productivities could be increased further by using 2 mmol/dm^3 TIBA and reducing Al(MAO) concentrations down to 0.2 mmol/dm^3. Reducing the amount of TIBA by 75% to 0.5 mmol/dm^3 increased productivity further by 25%, which indicates that excess TIBA has also a retarding effect on overall activity similar to excess MAO. Maximum initial activity at 1 bar ethylene pressure (≈500 kg (PE)/(mol (Zr) s)) was observed when using borate as a cation-forming agent. This high initial activity gives an idea of the potential of the 2-siloxy substitution, since it is probably free of rate reducing interactions between the ligand substituents and the cocatalyst, which seem to be present in the case of MAO as cocatalyst.

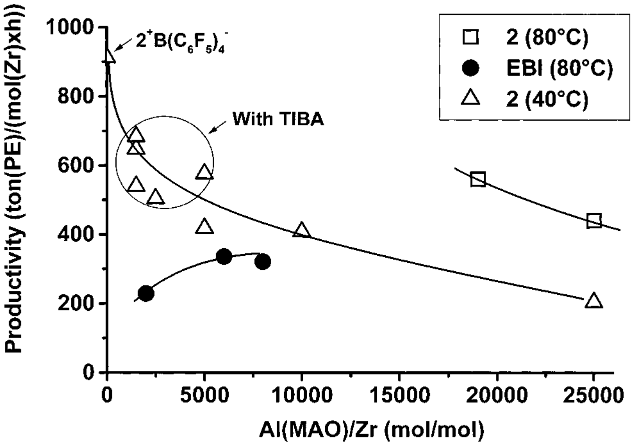

Figure 2. Productivity of **2**/MAO and **EBI**/MAO as a function of Al(MAO)/Zr ratio ($p_{C_2} = 1$ bar).

In Figure 2 the productivity of the 2-siloxy-substituted catalyst precursor **2**/MAO is compared to the productivity of **EBI**/MAO. It should be emphasized that the Al(MAO) concentrations used in this study were exceptionally low, and in this respect the productivity of the 2-siloxy-substituted catalyst was extremely high already at 40 °C. The electron-donating nature of the siloxy

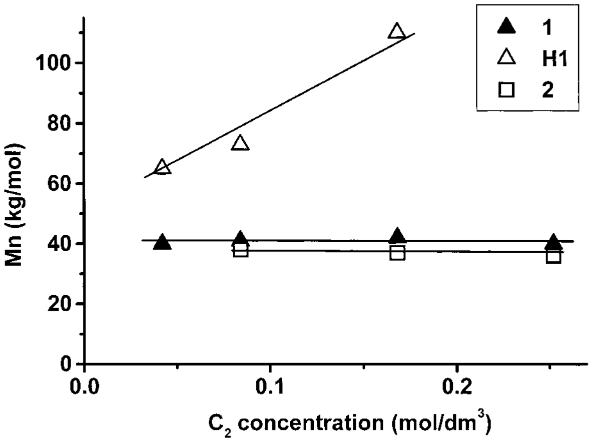

Figure 3. Influence of ethylene concentration on molecular weight of polyethylene obtained with the siloxy-substituted catalysts at 80 °C ([Al(MAO)] = 1.5 mmol/dm^3).

substituent is likely to have a stabilizing effect on the cationic active site,[7] which could explain the enhancement in overall activity of **2**/MAO compared to **EBI**/MAO. In addition, weaker binding of the counterion to the cationic metallocene alkyl may increase the rate of monomer insertion to the metal−alkyl bond and thus the chain propagation rate. The decrease in activity with increasing Al(MAO) concentration is likely to result from enhanced unfavorable interactions between the cocatalyst and metallocene. As observed earlier by Piccolrovazzi et al.[25a] and Collins and co-workers,[25b] the tentative coordination of aluminum to donor substituents of the catalyst may enhance the inductive electron-withdrawing effect at the expense of the electron-donating resonance effect, resulting in decreased polymerization activities. For the 1-siloxy-substituted catalysts **1**/MAO and **H1**/MAO excess MAO did not only decrease the polymerization activity but also retarded the start of polymerization,[16] which renders comparison of productivities difficult.

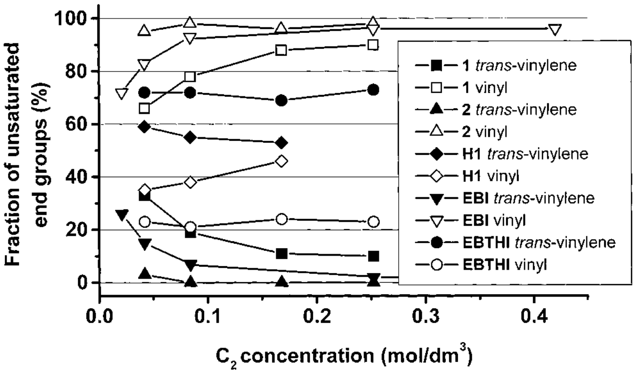

Figure 4. Unsaturated end group pattern of polyethylene obtained with the siloxy-substituted catalysts (**1**/MAO, **H1**/MAO, **2**/MAO) and **EBI**/MAO and **EBTHI**/MAO at 80 °C.

Molecular Weight and Unsaturated End Group Analysis. End group analysis together with examination of the influence of monomer concentration on molecular weight gives insight into the termination mechanisms of the polymerization. Figure 3 shows that the molecular weight of the polymer produced with **H1**/MAO increases with ethylene concentration, which is indicative for termination occurring by β-hydrogen transfer to the metal.[26a,b] For **1** and **2**, having indenyl ligands, the molecular weight of the polymer is independent of monomer concentration which is consistent with termination occurring due to β-hydrogen transfer to a coordinated monomer[1,26b,c] or due to alkene C−H activation.[27] The siloxy substituent and its position do not seem to have any significant influence on the molecular weight of the formed polymer at 80 °C,[28] but hydrogenation of the ligand increases the molecular weight. At 40 °C the number-average weights of the polymers obtained at 1 bar ethylene pressure and 1.5 mmol/dm^3 Al(MAO) concentration were 90, 220, and 70 kg/mol for **1**, **H1**, and **2**, respectively. Unsaturated end groups as a function of monomer concentration are shown in Figure 4 for polyethylene obtained with the siloxy-substituted catalysts, and for comparison also **EBI** and its hydrogenated congener **EBTHI** are included. The type of ligand, indenyl (**1**,**2**, and **EBI**) or hydrogenated indenyl (**H1** and **EBTHI**), strongly influences the unsaturated end group pattern of the polymers (Figure 4). Thorshaug et al.[29] have proposed that the formation of *trans*-vinylene end groups in ethylene homopolymerizations at low pressures results after isomerization and termination from a double β-agostic state. The increasing amount of *trans*-vinylene end groups with decreasing monomer concentration could be understood as resulting from an increasing amount of isomerizations due to a decreasing rate of propagation and termination. This is also consistent with the smallest influence of monomer concentration on the end group pattern of polyethylene produced by the catalyst system **2**/MAO, which would thus have the fastest propagation and termination reaction compared to the other catalysts.

For 2-siloxy-substituted catalysts we have earlier found that a high molecular weight shoulder is formed in ethylene polymerizations at decreasing temperature and Al(MAO) concentration, resulting in high polydispersities between 3 and 5.[7] We suggested that this might be a consequence of different types of active centers due to the different conformers of **2**. In our previous study[7] the high amount of catalyst and low Al(MAO) concentration led to high ethylene consumption with consequent limited mass transfer from the gas to liquid phase, resulting in a low ethylene concentration. In this study we observed that decreasing the monomer

Table 5. Influence of Ethylene Concentration on Molecular Weight and Unsaturated End Group Pattern of Polymers Made over Catalysts 1/MAO and 2/MAO at 40 °C

cat.	[C$_2$] (mol/dm^3)	yield (g)	M_w[a] (kg/mol)	M_n[a] (kg/mol)	M_w/M_n[a]	*trans*-vinylene[b] (%)	vinyl[b] (%)	vinylidene[b] (%)
1[c]	0.06	0.4	214	83	2.6	7	84	9
1[c]	0.12	3	213	93	2.3	5	91	4
1[c]	0.24	2.3	187	85	2.2	1	97	2
2[d]	0.06	1.6	188	74	2.5	0	96	4
2[d]	0.12	3.4	155	68	2.3	0	97	3
2[d]	0.24	6.3	127	60	2.1	0	98	2

[a] By GPC. [b] By FT-IR. [c] [Zr] = 0.90 μmol/dm^3, [Al(MAO)] = 1.5 mmol/dm^3, polymerization time 25−50 min. [d] [Zr] = 0.15 μmol/dm^3, [Al(MAO)] = 1.5 mmol/dm^3, polymerization time 10 min.

concentration at a temperature of 40 °C led to broadening of the MWD as shown in Table 5 for polyethylene obtained with **1**/MAO and **2**/MAO. We could now give one further explanation for our previous observations. The broadening of the MWD could be understood to result from insertion of a vinyl-ended macromolecule into the growing chain, which in the case of subsequent termination would lead to a vinylidene bond. The amount of vinylidene bonds increased, in fact, with decreasing pressure (Table 5). On the other hand, we want to point out that incorporation of vinyl-terminated macromonomers without subsequent termination would lead to the formation of long-chain branched polyethylene, as observed previously at low ethylene concentrations for the unsubstituted **EBI**.[4]

Summary and Conclusions

The position of the *tert*-butyldimethylsiloxy substituent has a major influence on polymerization performance of the ethylene-bridged bis(indenyl)zirconium dichlorides. Siloxy substitution at the 1-position of the indenyl ligand remarkably improves the copolymerization ability, while substitution at the 2-position slightly reduces copolymerization ability as compared to the unsubstituted **EBI**. On the other hand, 1-siloxy substitution increases sensitivity toward excess MAO, which is observed as a decreased comonomer incorporation and an increased induction time with increasing Al(MAO) concentration. The reason for this behavior could be due to unfavorable interactions between MAO and the widely spaced donor substituents. Siloxy substitution in the 2-position of the indenyl ligand results in immediate and extremely high polymerization activity at very low Al(MAO) concentrations. Hydrogenation of the 1-siloxy-substituted indenyl ligand decreased the comonomer incorporation at elevated temperatures and caused chain termination to occur by β-hydrogen transfer to the zirconium metal instead of chain transfer to monomer. Catalysts with indenyl ligands were found to produce preferentially vinyl-terminated polymers at increasing ethylene concentrations, which was not the case for catalysts with hydrogenated indenyl ligands.

In conclusion, siloxy substitution has clearly been demonstrated to be a tool to improve the polymerization behavior of the family of ethylene-bridged bis(indenyl)zirconium dichlorides. Combination of the benefits of siloxy substitution by rational catalyst design, for example by providing better shielding of the siloxy groups, may introduce highly active 1-siloxy-substituted bis(indenyl)zirconium dichlorides with very good copolymerization ability as potential catalysts for the production of polyethylene polymers containing low amounts of long-chain branching.

Acknowledgment. Financial support from the Neste Foundation, the Academy of Finland, and the Finnish Technology Development Center (TEKES) is gratefully acknowledged.

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MA981764Q