9200 *Macromolecules* **2000,** *33,* 9200−9204

meso- and *rac*-Diastereomers of 1- and 2-*tert*-Butyldimethylsiloxy-Substituted Ethylenebis(indenyl)zirconium Dichlorides for Formation of Short- and Long-Chain Branched Polyethene

Esa Kokko,[†] Petri Lehmus,[†] Reko Leino,[‡] Hendrik J. G. Luttikhedde,[‡] Peter Ekholm,[‡] Jan H. Näsman,[‡,§] and Jukka V. Seppälä*,[†]

Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FIN-02015 HUT, Finland, and Laboratory of Polymer Technology, Åbo Akademi University, FIN-20500 Åbo, Finland

Received May 19, 2000; Revised Manuscript Received September 6, 2000

ABSTRACT: Ethene was homo- and copolymerized over the methylaluminoxane (MAO) activated *meso*- and *rac*-diastereomers of 1- and 2-*tert*-butyldimethylsiloxy-substituted ethylenebis(indenyl)zirconium dichlorides (*meso*-**1**, *rac*-**1**, *meso*-**2**, *rac*-**2**) at 40 °C in toluene. Homopolyethenes produced at low ethene concentration under slurry conditions revealed significantly modified melt rheological properties resulting from long-chain branching (LCB). In addition, a small amount of ethyl branching was found in polyethenes produced with *meso*-**1**, *rac*-**1**, and *meso*-**2**. The *meso*-catalysts were found to have an excellent comonomer response; in the copolymerization of ethene with 1-hexene r_E(*meso*-**1**) = 10 ± 1 and r_E(*meso*-**2**) = 11 ± 1. Comonomer reactivity ratios indicate a strong preference toward formation of isolated comonomer units in the polymer chain. Chain termination occurs preferentially after regular 1,2-insertion of the comonomer, although irregular 2,1-insertions also inflict some chain terminations with the racemic catalysts but not with the *meso*-catalysts. In ethene homopolymerization, chain transfer to monomer is the prevailing chain transfer mechanism for all studied catalysts and results in a high vinyl end group selectivity.

Introduction

Rational design of novel organometallic catalysts has enabled the tailoring of polyethene and polypropene microstructures.[1−3] Siloxy-substituted group 4 bis(indenyl) complexes are an example of both electronically and sterically modified metallocene catalyst precursors[4−6] and form a class of highly active and efficient copolymerization catalysts.[7,8]

Achiral *meso*-diastereomers of bis(indenyl) *ansa*-metallocenes are often considered as undesired side products of their racemic congeners, and their olefin polymerization behavior is seldomly reported. Obviously, one reason for this has been the dominance of research on propene polymerization catalysts; lack of stereocontrolling elements in *meso*-metallocenes results in atactic homopolymers from prochiral monomers.[9−13] However, the presence of two diastereotopic and thus unequivalent coordination sites can potentially be utilized to differentiate between olefins of different sizes. C_1 symmetric metallocenes containing two diastereotopic active sites have been successfully employed in alternating copolymerization of ethene and propene.[14−16] Uozumi et al.[17] have reported the alternating copolymerization of ethene and 1-octene with the *meso*-$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/MAO catalyst system. Moreover, in ethene homopolymerization Izzo et al. have recently employed *meso*-$Et(Ind)_2ZrCl_2$ to obtain ethyl branched polyethene.[18]

In this paper we report the homo- and copolymerization behavior of *meso*-diastereomers of 1- and 2-*tert*-butyldimethylsiloxy-substituted ethylenebis(indenyl)zirconium dichlorides and make a comparison with their racemic congeners. Figure 1 shows the studied catalysts. The effect of catalyst selection and monomer concentration on the molecular weight, end group composition, comonomer content, and branching of the produced polyethenes is discussed.

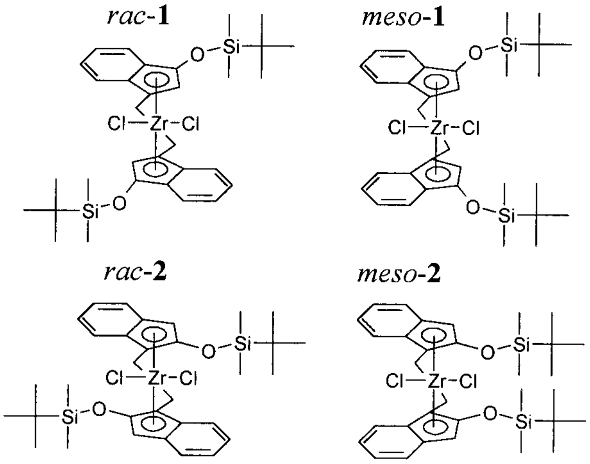

Figure 1. The studied catalysts.

Experimental Section

General Considerations. All reactions with organometallic reagents were carried out in an argon atmosphere using standard Schlenk, vacuum, or glovebox techniques. Solvents were dried and distilled under argon prior to use. Bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane,[4] *meso*-**1**,[6] *rac*-**1**,[6] and *rac*-**2**[4] were prepared as described previously. $ZrCl_4$ (ABCR GmbH & Co., 99.9%) and *n*-BuLi (Aldrich, 2.5 M in hexanes) were used as received. The ^1H and ^{13}C NMR spectra of *meso*-**2** were recorded using a JEOL JNM-LA 400 NMR spectrometer and referenced against the residual protons of the deuterated solvent (CD_2Cl_2 = 5.36 ppm). Direct inlet ionization mass spectra (EIMS) were obtained at 70 eV on a Varian-8000 mass spectrometer.

[†] Helsinki University of Technology.
[‡] Åbo Akademi University.
[§] Deceased.

10.1021/ma000872l CCC: $19.00

Table 1. Ethene Polymerization Results[a]

		mol wt[b]			end-group analysis[c]		
catalyst	$p(C_2H_4)$ [bar]	M_w [kg/mol]	M_n [kg/mol]	M_w/M_n	*trans*-vinylene	vinyl	vinylidene[d]
meso-**1**	2.0	118	53	2.2	0.03	0.94	0.03
	1.0	137	59	2.3	0.07	0.87	0.06
	0.5	185	64	2.9	0.14	0.82	0.05
rac-**1**	2.0	190	81	2.3	0.01	0.97	0.02
	1.0	218	95	2.3	0.05	0.91	0.04
	0.5	214	83	2.6	0.07	0.83	0.09
meso-**2**	2.0	62	31	2.0	0.00	0.92	0.08
	1.0	77	32	2.4	0.00	0.92	0.08
	1.0	87	38	2.3	0.00	0.88	0.12
	0.5	115	40	2.9	0.00	0.82	0.18
rac-**2**	2.0	127	60	2.1	0.00	0.98	0.02
	1.0	155	68	2.3	0.00	0.97	0.03
	0.5	188	74	2.5	0.00	0.96	0.04

[a] Polymerization conditions: $T = 40$ °C; $t = 10-30$ min; volume (toluene) = 320 mL; [metallocene] = 0.90 μM ([*rac*-**2**] = 0.15 μM); $[Al]_{MAO} = 1.5$ mM (*meso*-**1** $[Al]_{TIBA} = 0.6$ mM, $[Al]_{MAO} = 0.24$ mM). [b] By RI detector GPC. [c] By FT IR: *trans*-vinylene 965 cm^{-1}; vinyl 908 cm^{-1}; vinylidene 888 cm^{-1}. The total number of unsaturations is assumed to be one per chain. [d] Vinylidene bond content is possibly overestimated due to overlapping peaks.

***meso*-[Ethylenebis(2-*tert*-butyldimethylsiloxy)indenyl)]zirconium Dichloride (*meso*-2).** To an ice-cooled solution of bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane (114.4 g, 220 mmol) in THF (450 mL) was added dropwise *n*-BuLi (177.5 mL of a 2.5 M solution in hexanes, 444 mmol), and the reaction mixture was stirred for 3 h at room temperature. The resulting solution was cooled to −80 °C, and $ZrCl_4$ (51.4 g, 220 mmol) was added portionwise. The reaction mixture was gradually allowed to warm to room temperature and stirred overnight. Evaporation of the solvents left a yellow solid that was extracted with CH_2Cl_2 (1000 mL) and filtered through Celite to remove lithium chloride. The resulting clear solution was evaporated to dryness, extracted with Et_2O (1000 mL), and filtered through Celite. Concentration and subsequent crystallization at room temperature gave 51.2 g (34.2%) of a 10:1 mixture of *rac*-**2** and *meso*-**2** as determined by ^1H NMR analysis. Recrystallization from CH_2Cl_2 at −15 °C gave 39.3 g (26.2%) of pure *rac*-**2** as yellow crystals. Concentration of the mother liquor gave after repeated recrystallizations at −30 °C a small sample of pure *meso*-**2** as a dark yellow microcrystalline solid. In the EIMS mass spectrum of *meso*-**2**, parent ions of composition $C_{32}H_{44}Si_2O_2ZrCl_2^+$ were observed at m/e = 676−684 in the appropriate isotope ratios. The base peak at $m/e = 73$ corresponds to $[CH_3Si(CH_2)O]^+$. ^1H NMR (CD_2Cl_2, δ): 7.59 (dq, $J = 8.5$ Hz, 0.8 Hz, 2H); 7.23 (dt, $J = 8.5$ Hz, 1.0 Hz, 2H); 7.06−7.02 (m, 2H); 6.92−6.88 (m, 2H); 5.96 (dq, $J = 8.5$ Hz, 0.9 Hz, 2H); 3.92−3.82 (m, AA′, 2H); 3.73−3.62 (m, BB′, 2H); 1.00 (s, 18H); 0.35 (s, 6H); 0.33 (s, 6H). ^{13}C NMR (CD_2Cl_2, δ): 152.29; 125.89; 125.23; 124.83; 124.25; 123.25; 118.30; 109.40; 98.40; 26.52; 26.02; 18.87; −3.57; −3.68.

Polymerizations. Methylaluminoxane (MAO) and triisobutylaluminum (TIBA) were obtained from Witco. Ethene (grade 3.5), hydrogen (grade 5.0), and nitrogen (grade 5.0) were supplied by AGA. Toluene (pro analysi) and 1-hexene (99%) were obtained from Aldrich. Ethene and toluene were purified by passing through columns containing molecular sieves, Al_2O_3, and CuO. MAO, hydrogen, and nitrogen were used without further purification. Polymerization[8,19] and characterization[8,19,28] of the polymers were carried out as reported elsewhere.

Results and Discussion

Catalyst Synthesis and Characterization. *meso*-[Ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (*meso*-**2**) was isolated as the minor product from a large-scale preparation of the corresponding racemic metallocene. The crude *rac*/*meso*-**2** mixture was prepared by addition of $ZrCl_4$ to a suspension of dilithiated bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane in THF at −80 °C.[4] Subsequent workup and crystallization from Et_2O gave a 10:1 mixture of the two diastereomers from which pure *rac*-**2** was separated by recrystallization from methylene chloride. A small sample of *meso*-**2** was obtained as a yellow microcrystalline solid after repeated recrystallizations of the mother liquor at −30 °C. The highly symmetric ^1H NMR spectrum of *meso*-**2** is consistent with rapid conformational interconversion between the two equienergetic staggered mirror image forms.[4,11,20,21] The bridge protons give the characteristic AA′BB′ spin pattern at 3.92−3.82 (AA′) and 3.73−3.62 (BB′), respectively. The ^1H NMR chemical shift of the H_β-proton of *meso*-**2** (5.96 ppm) is comparable to that of *meso*-[ethylenebis(2-(dimethylamino)indenyl)]zirconium dichloride (5.85 ppm)[21] and shielded considerably compared to the corresponding value for *meso*-[ethylenebis(indenyl)]zirconium dichloride (6.70 ppm).[20] The strong shielding effect indicates increased electron density in the five-membered ring.

Homopolymerization. All polymerizations were carried out under 0.5−2.0 bar ethene pressure at 40 °C. *meso*-**1** exhibited similar sensitivity toward MAO concentration as *rac*-**1**,[8] and the highest polymerization activity was obtained by reducing MAO concentration and replacing most of the MAO with triisobutylaluminum (TIBA). Polymerization activities of the 2-siloxy-substituted catalysts *meso*-**2** and *rac*-**2** were not sensitive to MAO concentration. At low MAO concentration *rac*-**2** had the highest activity, 3.4×10^6 [kg(PE) $mol_{cat.}^{-1}$ $(mol/L)^{-1}$ h^{-1}]. The polymerization activities of *meso*-**1**, *rac*-**1**, and *meso*-**2** were somewhat lower; 1.3×10^6, 1.1×10^6, and 0.7×10^6 [kg(PE) $mol_{cat.}^{-1}$ $(mol/L)^{-1}$ h^{-1}], respectively.

Each catalyst produced polyethene with distinctive characteristics as shown in Table 1. The 1-siloxy-substituted catalysts produced polyethenes with higher number-average molecular weight (M_n) than their 2-substituted congeners, whereas both racemic catalysts produced higher M_n compared with their *meso*-isomers. *trans*-Vinylene double bonds were not detected in any of the polymer samples produced with the 2-siloxy-substituted catalysts *meso*-**2** and *rac*-**2**. Of the 1-siloxy-substituted catalysts *meso*-**1** produced polyethene with higher *trans*-vinylene content than its racemic congener *rac*-**1**.

For all catalysts, M_n of the obtained polyethenes were independent of ethene concentration (C_E), indicating predominant chain termination via transfer to mono-

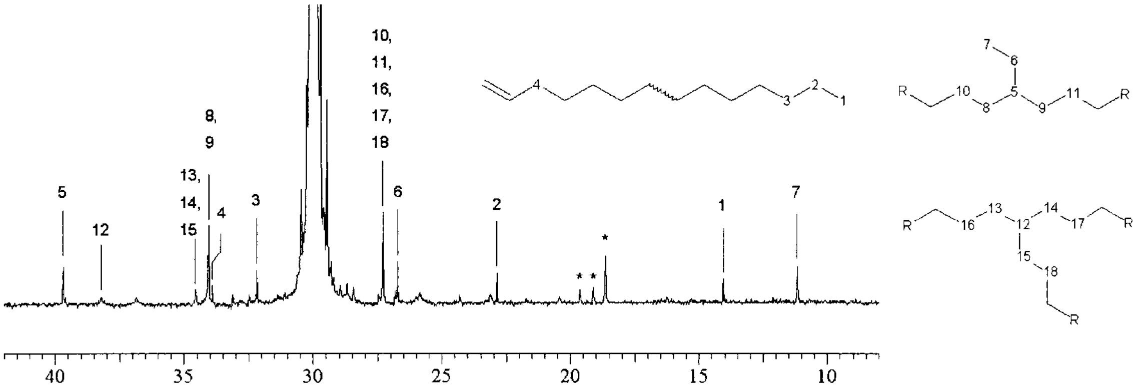

Figure 2. ^{13}C NMR spectrum (10 mm tube, 12 500 transients) of a homopolyethene obtained with *meso*-**1** (p_E = 2.0 bar). Ethyl branch content is approximately 0.4 branches/1000 C atoms and long-chain branch content 0.06 branches/1000 C atoms. * = solvent/impurity.

mer. In addition, vinyl content of the polyethenes produced with the 1-siloxy-substituted catalysts decreased and *trans*-vinylene content increased with decreasing monomer concentration. This is consistent with monomer assisted chain transfer processes.[19,22] Due to the low *trans*-vinylene content and high M_n, the exact position of *trans*-vinylenes could not be determined. The vinylenes should, however, be located at the vicinity of chain end if they were formed via chain transfer reaction.

Indeed, formation of *trans*-vinylene double bonds in polyethenes produced with metallocene catalysts has been proposed to result from an isomerization reaction related to chain transfer. The isomerization may proceed via rotation[22] or allylic[23] mechanisms. Internal *trans*-vinylenes found in ethene copolymers produced with $Ph_2C[CpFlu]ZrCl_2$/MAO (Cp = cyclopentadienyl; Flu = fluorenyl) have been proposed to form via an allylic activation route.[24,25] This results in hydrogen generation and excess unsaturation in the polymer backbone. Hydrogen formation in ethene homopolymerization has, however, not been reported.[25]

Branching of Homopolymers. ^{13}C NMR analysis of the polyethenes revealed two microstructural details: (1) all homopolyethenes except those obtained with *rac*-**2** contained a small amount of ethyl branches; (2) several samples were found to contain branches longer than six-carbon atoms. Figure 2 shows a ^{13}C NMR spectrum of a polymer sample obtained with *meso*-**1**. Assignment of the signals was made according to prior studies.[26,27]

Izzo et al. proposed recently that the ethyl branches of polyethenes obtained with the nonstereoselective C_s symmetric *meso*-$Et(Ind)_2ZrCl_2$ are formed via a bimolecular mechanism with monomer assisted β-H abstraction.[18] All three catalysts of the present study that produced ethyl branches are likewise nonstereoselective, including the C_2 symmetric *rac*-**1**.[6] Both *meso*-**1** and *meso*-**2** have a similar C_s symmetry as *meso*-$Et(Ind)_2ZrCl_2$, although due to the influence of the siloxy groups their coordination sites are sterically more hindered. Assuming that a similar bimolecular mechanism is responsible for the branching observed here for *rac*-**1**, *meso*-**1**, and *meso*-**2**, the lower level of ethyl branching obtained with these catalysts could be explained by steric arguments. The absence of ethyl branching with *rac*-**2** may be related to the stereoselectivity; the catalyst produces isotactic polypropene.[4,7] Also, the insertion of a coordinated olefin may be more difficult due to very high ethene polymerization rate and lower copolymerization ability of *rac*-**2** (Tables 3 and 4).

Table 2. Rheological Properties of Polyethenes Produced at 2.0 bar Ethene Pressure at 40 °C

	M_w [kg/mol]	M_w/M_n	$\eta_0{}^a$ calcd	$\eta^*(\omega_{ref})^b$ [Pa s]	$G'(G''_{ref})^c$ [Pa]
meso-**1**	118	2.3	6200	662000	10600
rac-**1**	190	2.3	34000	1 220000	12500
meso-**2**	62	2.0	600	18700	5960
rac-**2**	127	2.1	8000	526000	9520
ref-1[d]	183	2.0	30000	28900	1200
ref-2[d]	69	1.9	900	1200	1200

[a] The η_0 for a linear polymer has been calculated using an equation $\eta_0 = 3.4 \times 10^{-15} M_w{}^{3.6}$ by Raju et al.[35] [b] ω_{ref} = 0.02 rad/s. [c] G''_{ref} = 10 000 Pa. [d] Data from ref 19.

The long branches detected by ^{13}C NMR are presumably formed by incorporation of a vinyl-terminated polyethene macromonomer into a growing polyethene chain.[19,28,29] Long-chain branching is expected to affect heavily the rheological properties[30−33] of the polymer samples. Table 2 shows a summary of the measured rheological properties. The details of rheological analysis have been given elsewhere.[19] In addition to the present samples, two reference samples with different weight-average molecular weight (M_w) and narrow molecular weight distribution (M_w/M_n) are included. Structures of the reference samples are concluded to be highly linear as a consequence of the employed polymerization method and observed rheological properties.

A comparison of the rheological properties of the examined samples with the references indicated a complex rheological behavior. The complex viscosity (η^*) was increased considerably at low oscillating frequency (η^*(0.02 rad/s)); likewise, the storage modulus (G') value was enhanced at low loss modulus values ($G'(G''$ = 10 kPa)). The observed η^* at low oscillating frequency[34] for the polyethene sample produced with *meso*-**1** was more than 2 orders of magnitude higher than the expected zero-shear viscosity value (η_0) for linear polymer.[35]

Despite that all catalysts of the present study had detectable differences in their copolymerization ability, as will be discussed below, significant variations in the rheological behavior of the produced polyethenes were not observed.[36] The *meso*-**2**-catalyzed homopolyethene appeared to have less complex rheological behavior. This is at least partly due to the lower M_w that also contributes to the observed rheological properties. The employed slurry conditions may have diminished the differences in copolymerization ability, and the mobility

Table 3. Ethene−1-Hexene Copolymerization Results[a]

catalyst	C6/C2 feed ratio	mol wt[b]			comonomer content[c] [mol %]	end-group analysis[d]		
		M_w [kg/mol]	M_n [kg/mol]	M_w/M_n		*trans*-vinylene	vinyl	vinylidene
meso-**1**	0.5	35	20	1.8	5.4	0.00	0.52	0.48
	1.6	22	11	2.0	13	0.00	0.24	0.76
rac-**1**	2.5	44	23	1.9	11	0.05	0.21	0.74
meso-**2**	0.8	16	9	1.8	5.9	0.00	0.36	0.64
	1.6	11	6	1.8	10	0.00	0.24	0.76
	2.5	9	5	1.8	13	0.00	0.19	0.81
rac-**2**	0.8	111	48	2.3	2.3	0.06	0.77	0.17
	1.6	99	42	2.4	4.0	0.06	0.69	0.25
	2.5	68	34	2.0	5.6	0.06	0.60	0.34

[a] Polymerization conditions: $p(C_2H_4) = 1.0$ bar ($[C_2H_4] = 0.12$ M); $T = 40$ °C; $t = 15-30$ min; [metallocene] $= 0.30-1.0$ μM; $[Al]_{MAO} = 1.2-3.0$ mM; volume(toluene) = 320 mL. [b] By RI detector GPC. [c] By ^{13}C NMR. [d] By FT IR: *trans*-vinylene 965 cm^{-1}; vinyl 908 cm^{-1}; vinylidene 895 cm^{-1}. The total number of unsaturations is assumed to be one per chain.

Table 4. Comonomer Reactivity Ratios at 40 °C

	meso-**1**	*rac*-**1**	*meso*-**2**	*rac*-**2**
r_{ethene}	10 ± 1	16 ± 1	11 ± 1	36 ± 3
$r_{1-\text{hexene}}$	0.001	0.005	0.005	0.003

of olefinic macromomomers at the vicinity of the active sites has been the decisive factor for LCB frequency.[19,37−39] Thus, both the employed polymerization method and the choice of proper catalyst appear to be critical factors for LCB formation. More work is, however, required to conclude the importance of the polymerization process.

Copolymerization. The introduction of comonomer increased the activity of *meso*-**2** while the activity of *meso*-**1** decreased. The characterization results of ethene and 1-hexene copolymerizations are shown in Table 3. The decreasing M_n and increasing amount of vinylidene bonds with increasing comonomer content indicate a strong tendency toward chain termination after 1,2-insertion of 1-hexene. Of the studied catalysts, *meso*-**2** was the most prone to inflict a chain transfer after 1,2-insertion of comonomer and *rac*-**2** the least prone, as seen from the reduction of M_n and changes in the end group composition of the copolymers in comparison with the corresponding homopolyethenes. Although chain transfer after 1,2-insertion of the comonomer dominated, a small fraction of chain terminations occurred after 2,1-insertions with *rac*-**2** and probably with *rac*-**1**,[40] as seen from the small content of *trans*-vinylene unsaturations in copolymers. The absence of *trans*-vinylenes in the copolymers prepared with *meso*-catalysts suggested inhibition of chain transfer after 2,1-insertion of comonomer. 2,1-Insertions are expected to occur due to a low regioselectivity of *meso*-catalysts.

Both *meso*-catalysts had better comonomer responses than their racemic congeners. The reactivity ratios are collected in Table 4. The products of the reactivity ratios ($r_E r_H$) for each catalyst approached zero. This indicates that 1-hexene had a tendency toward isolated monomer insertion along polymer chains. A comparison with literature values reveals that the comonomer reactivites of *meso*-**1** and *meso*-**2** are comparable to that of *rac*-dimethylsilylenebis(benz[*e*]indenyl)zirconium dichloride,[41] which is considered to be a highly efficient copolymerization catalyst. The improved copolymerization ability of the *meso*-catalysts over their racemic congeners is probably steric in origin, although difficult to rationalize due to the additional steric hindrance induced by the siloxy substituents. The crystal structure determination of *meso*-**1** revealed an unusually large angle of 64.6° between the cyclopentadienyl planes,[6] which should enhance the accessibility of the metal atom toward olefin coordination. The corresponding angle for *rac*-**2** is 61.0°,[4] whereas for *rac*-**1** and *meso*-**2** these data are only available for their tetrahydroindenyl analogues *rac*-$[Et(1\text{-}t\text{-}BuMe_2SiO)IndH_4]_2ZrCl_2$ (63.6°)[6] and *meso*-$[Et(2\text{-}t\text{-}BuMe_2SiO)IndH_4]_2ZrCl_2$ (57.9°).[42]

It should be pointed out that in the 2-siloxy-substituted catalysts the bulky substituents are nearly equatorial and directed away from the active site, whereas in the 1-substituted systems the siloxy groups are directed toward the front of the metallocene wedge. In solid state, both *meso*-**1** and the hydrogenated congener of *rac*-**1** displayed very short intramolecular Cl−O distances which were, in fact, shorter than the sum of the relevant van der Waals radii (3.20 Å). The close proximity of a growing polymer chain to the oxygen atom may affect the space available for monomer insertion and chain orientation, thereby influencing both polymerization activity and hindering repetitive comonomer incorporation.

Summary and Conclusions

We have shown that the *meso*-diastereomers of 1- and 2-*tert*-butyldimethylsiloxy-substituted ethylenebis(indenyl)zirconium dichlorides are good catalyst precursors for ethene−1-olefin copolymerization. For all studied catalysts, chain transfer to monomer is the predominant termination mechanism at 40 °C even at low ethene concentrations, indicating that the stereochemistry of the catalyst precursor (*rac* vs *meso*) does not significantly influence the chain transfer mechanism in homopolymerization of ethene. In copolymerization reactions, the *meso*-catalysts are prone to undergo chain transfer after 1,2-insertion of comonomer but not after 2,1-insertion. A small amount of ethyl branching was found in polyethenes produced with the nonstereoselective *meso*-metallocenes, and all studied catalysts produced long-chain branched polyethene under slurry conditions. The employed conditions may have contributed to the incorporation of olefinic macromonomers. The *meso*-catalysts produce fairly low molecular weight homopolyethenes, making them excellent candidates for production of LCB model polyethenes.

Acknowledgment. The authors thank National Technology Agency (TEKES) and Neste Foundation for financial support.

References and Notes

(1) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428−447.
(2) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1204.

(3) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1346.
(4) Leino, R.; Luttikhedde, H.; Wilén, C.-E.; Sillanpää, R.; Näsman, J. H. *Organometallics* **1996**, *15*, 2450−2453.
(5) Luttikhedde, H. J. G.; Leino, R.; Lehtonen, A.; Näsman, J. H. *J. Organomet. Chem.* **1998**, *555*, 127−134.
(6) Leino, R.; Luttikhedde, H. J. G.; Lehtonen, A.; Ekholm, P.; Näsman, J. H. *J. Organomet. Chem.* **1998**, *558*, 181−188.
(7) Leino, R.; Luttikhedde, H. J. G.; Lehmus, P.; Wilén, C.-E.; Sjöholm, R.; Lehtonen, A.; Seppälä, J. V.; Näsman, J. H. *Macromolecules* **1997**, *30*, 3477−3483.
(8) Lehmus, P.; Kokko, E.; Härkki, O.; Leino, R.; Luttikhedde, H.; Näsman, J. H.; Seppälä, J. V. *Macromolecules* **1999**, *32*, 3547−3552.
(9) Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061−2068.
(10) Spaleck, W.; Aulbach, M.; Bachmann, B.; Küber, F.; Winter, A. *Macromol. Symp.* **1995**, *89*, 237−247.
(11) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046−5059.
(12) Maciejewski Petoff, J. L.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316−11322.
(13) Vathauer, M.; Kaminsky, W. *Macromolecules* **2000**, *33*, 1955−1959.
(14) Leclerc, M. K.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 922−925.
(15) Arndt, M.; Kaminsky, W.; Schauwienold, A.-M.; Weingarten, U. *Macromol. Chem. Phys.* **1998**, *199*, 1135−1152.
(16) Jin, J.; Uozumi, T.; Sano, T.; Teranishi, T.; Soga, K.; Shiono, T. *Macromol. Rapid Commun.* **1998**, *19*, 337−339.
(17) Uozumi, T.; Miyazawa, K.; Sano, T.; Soga, K. *Macromol. Rapid Commun.* **1997**, *18*, 883−889.
(18) Izzo, L.; Caporaso, L.; Senatore, G.; Oliva, L. *Macromolecules* **1999**, *32*, 6913−6916.
(19) Kokko, E.; Malmberg, A.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 376−388.
(20) Piemontesi, F.; Camurati, I.; Resconi, L.; Balboni, D.; Sironi, A.; Moret, M.; Zeigler, R.; Piccolrovazzi, N. *Organometallics* **1995**, *14*, 1256−1266.
(21) Luttikhedde, H. J. G.; Leino, R.; Ahlgrén, M. J.; Pakkanen, T. A.; Näsman, J. H. *J. Organomet. Chem.* **1998**, *558*, 227−230.
(22) Thorshaug, K.; Støvneng, J. A.; Rytter, E.; Ystenes, M. *Macromolecules* **1998**, *31*, 7149−7165.
(23) Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Schroepfer, J. N. *J. Mol. Catal. A: Chem.* **1998**, *128*, 257−271.
(24) Karol, F. J.; Kao, S.-C.; Wasserman, E. P.; Brady, R. C. *New J. Chem.* **1997**, *21*, 797−805.
(25) Wasserman, E.; Hsi, E.; Young, W.-T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39* (2), 425−426.
(26) Randall, J. C. Characterization of Long-Chain Branching in Polyethylenes Using High-Field Carbon-13 NMR. In *Polymer Characterization by ESR and NMR*; ACS Symp. Ser. Vol. 142; Woodward, A. E., Bovey, F. A., Eds.; American Chemical Society: Washington, DC, 1980; pp 93−118.
(27) De Pooter, M.; Smith, P. B.; Dohrer, K. K.; Bennett, K. F.; Meadows, M. D.; Smith, C. G.; Schouwenaars, H. P.; Geerards, R. A. *J. Appl. Polym. Sci.* **1991**, *42*, 399−408.
(28) Malmberg, A.; Kokko, E.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *Macromolecules* **1998**, *31*, 8448−8454.
(29) Wang, W.-J.; Yan, D.; Zhu, S.; Hamielec, A. E. *Macromolecules* **1998**, *31*, 8677−8683.
(30) Harrell, E. R.; Nakajima, N. *J. Appl. Polym. Sci.* **1984**, *29*, 995−1010.
(31) Bersted, B. H. *J. Appl. Polym. Sci.* **1985**, *30*, 3751−3765.
(32) Carella, J. M.; Gotro, J. T.; Graessley, W. W. *Macromolecules* **1986**, *19*, 659−667.
(33) Vega, J. F.; Santamaría, A.; Muñoz-Escalona, A.; Lafuente, P. *Macromolecules* **1998**, *31*, 3639−3647.
(34) Apparently, the η_0 of four examined samples was even higher at still lower frequency ($\eta^* < 0.02$ rad/s) since the Newtonian viscosity range was not yet reached.
(35) Raju, V. R.; Smith, G. G.; Marin, G.; Knox, J. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1183−1195.
(36) An increase in the ethene concentration in polymerization medium decreased branching in the obtained polymer.
(37) Soares, J. B. P.; Hamielec, A. E. *Macromol. Theory Simul.* **1996**, *5*, 547−572.
(38) Malmberg, A.; Liimatta, J.; Lehtinen, A.; Löfgren, B. *Macromolecules* **1999**, *32*, 6687−6696.
(39) Kolodka, E.; Wang, W.-J.; Charpentier, P. A.; Zhu, S.; Hamielec, A. E. *Polymer* **2000**, *41*, 3985−3991.
(40) The ratio of *trans*-vinylene vs vinyl unsaturations in the homopolyethene produced with *rac*-**1** catalyst at $[C_2H_4] = 0.12$ M was 1:18. In the corresponding copolymer the ratio was 1:4, suggesting that the increased amount of *trans*-vinylenes was caused by comonomer 2,1-insertion.
(41) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal. A: Chem.* **1998**, *128*, 215−227.
(42) Leino, R.; Luttikhedde, H. J. G. In *Olefin Polymerization: Emerging Frontiers*; ACS Symp. Ser. Vol. 749; Arjunan, P., McGrath, J. E., Hanlon, T. L., Eds.; American Chemical Society: Washington, DC, 2000; pp 31−47.

MA000872L