Dual Site Ethene/1-Hexene Copolymerization with MAO Activated $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ and $(Me_5Cp)_2ZrCl_2$ Catalysts. Possible Transfer of Polymer Chains between the Sites

Ingvild Bruaseth[†] **and Erling Rytter***[†,‡]

Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway, and Statoil Research Centre, N-7005 Trondheim, Norway

Received November 14, 2002; Revised Manuscript Received March 4, 2003

ABSTRACT: Ethene homopolymerization and copolymerization in toluene solution with varying amounts of 1-hexene were catalyzed by the methylaluminoxane (MAO) activated zirconocene catalysts $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ and $(Me_5Cp)_2ZrCl_2$ and a mixture of these two in a 1:1 molar ratio. The dual site catalyst (1:1 mixture) has a homo- and copolymerization activity intermediate between the individual catalysts. Deviations from the expected average behavior taking into account the ca. 6-fold higher 1 h yield of $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ are observed. The dual site system results in a copolymer with ca. 30% too low comonomer incorporation. The melting endotherm attributed to $(Me_5Cp)_2ZrCl_2$ is found to be ca. 30−70% too high, and the observed molecular weights for the copolymers are higher than expected and even higher than for the two individual catalysts. Chain transfer to trimethylaluminum (TMA) is found to become less important at high comonomer concentrations concurrent with an increase of the concentration of vinyl and *trans*-vinylene unsaturations. Further, it is noteworthy that with the dual site system it is possible to produce ethene/1-hexene copolymers with narrow molecular weight distribution as a mixture of chains containing low and high comonomer contents. The observed discrepancies in the mixed system from the average of the $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ and $(Me_5Cp)_2ZrCl_2$ catalysts are provisionally explained by chain transfer between the sites coupled with an activity increase of the latter of these sites.

1. Introduction

Linear polyethylene with short chain branches is produced when ethene is copolymerized with an α-olefin like 1-hexene. Because of the short chain branches from incorporated 1-hexene, the copolymers show a lower melting point, lower crystallinity, and lower density than the corresponding homopolymers.[1] Simultaneously, the molecular weight is reduced, probably because termination after comonomer insertion is facilitated. Metallocenes are single site catalysts and known to produce polymers with a narrow molecular weight distribution (MWD) and copolymers with more narrow distribution of short chain branches (SCBD) than conventional heterogeneous Ziegler−Natta catalysts. Both MWD and SCBD play an important role with respect to the processing behavior of the copolymer.[2]

Mixing of two metallocenes with known polymerization behavior can be used to control polymer microstructure. Several studies have been performed of ethene polymerization by mixing two metallocenes.[3−8] Common observations were that, by combining catalysts which separately give polyethene with different M_w, polyethene with broader and in some cases bimodal MWD can be obtained. When it concerns copolymerization by combined catalysts, there is to our knowledge only a few reports in the literature. Soares and Kim developed a criterion in order to test the MWD bimodality of polymers made by dual single-site catalysts,[9−11] as exemplified by ethene/1-hexene copolymerization of the mixtures $Et(Ind)_2ZrCl_2/Cp_2HfCl_2$ and $Et(Ind)_2ZrCl_2$/CGC (constrained geometry catalyst) supported on silica. Heiland and Kaminsky[6] studied a mixture of $Et(Ind)_2ZrCl_2$ and the hafnium analogue in copolymerization of ethene and 1-butene.

These studies do not contain any indication of interaction between the two different sites, e.g., by readsorption of a terminated chain at the alternative site. Such reports have been issued, however, for polymerization of propene. Chien et al.[12,13] studied propene polymerization by homogeneous binary zirconocene catalysts. A blend of isotactic polypropylene (i-PP), atactic polypropylene (a-PP), and a stereoblock fraction (i-PP-*b*-a-PP) was obtained with a binary system comprising an isospecific and an aspecific precursor with a borate and TIBA as cocatalyst.[13] By using a binary mixture of isospecific and syndiospecific zirconocenes, a blend of isotactic polypropylene (i-PP), syndiotactic polypropylene (s-PP), and a stereoblock fraction (i-PP-*b*-s-PP) was obtained.[12] The mechanism for formation of the stereoblock fraction was proposed to involve the exchange of propagating chains between the two different catalytic sites. Przybyla and Fink[14] used two different types of metallocenes (isospecific and syndiospecific) supported on the same silica for propene polymerization. They reported that, with a certain type of silica support, chain transfer between the active species in the catalyst system occurred, and stereoblock PP was obtained. Lieber and Brintzinger[15] have proposed a more detailed explanation of how the transfer of a growing polymer chain from one type of metallocene to another occurs. They studied propene polymerization by catalyst mixtures of two different *ansa*-zirconocenes. The different catalysts were first studied individually with regard to their tendency toward alkyl−polymeryl exchange with the alkylaluminum activator and then pairwise with respect to their capability to produce polymers with a stereoblock structure. They reported that formation of stereoblock polymers by a mixture of zirconocene catalysts with different stereoselectivities is contingent upon an efficient polymeryl exchange between the Zr catalyst centers and the Al centers of the cocatalyst.

[†] Norwegian University of Science and Technology.
[‡] Statoil Research Centre.

10.1021/ma025832r CCC: \$25.00

In a previous study of ethene/1-hexene copolymerization with all seven different $(Me_nCp)_2ZrCl_2$ catalysts, we found the general trend that the more congested the active site, the less comonomer is incorporated.[16] The catalysts $(1,3\text{-}Me_2Cp)_2ZrCl_2$ and $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$, in particular the last one, showed a surprisingly high comonomer incorporation, coupled with a high activity and an unexpected high molecular weight. Evidently, the vacant space in the substitution pattern allows the comonomer to be incorporated but prevents deactivation and latent site formation. One possible explanation is that β-agostic sites, assumed to be the precursor for termination, become less energetically attractive, as also substantiated by DFT quantum-chemical calculations.

The objective of this work is to investigate ethene homo- and copolymerization with varying amounts of 1-hexene using the two different unbridged zirconocene catalysts $(Me_5Cp)_2ZrCl_2$ and $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ and a mixture of these two. The former site, $(Me_5Cp)_2ZrCl_2$, incorporates only a minimum amount of 1-hexene. The influence of the dual site catalyst on polymerization activity, incorporation of comonomer, and polymer microstructure has been studied and compared with the individual catalysts at corresponding polymerization conditions. The polymers were analyzed by DSC, GPC, and FTIR. In addition, three polymer samples were analyzed by TREF and CRYSTAF.

2. Experimental Details

2.1. Chemicals. Bis(1,2,4-trimethylcyclopentadienyl)zirconium dichloride (abbreviated 1,2,4-Me_3Cp) and bis(pentamethylcyclopentadienyl)zirconium dichloride (abbreviated Cp*) from Boulder Scientific Co., 10 wt % methylaluminoxane (4.56 wt % Al) in toluene from Albemarle S.A., nitrogen (99.999%) from Hydrogas, and ethene (polymerization grade) and 1-hexene from Borealis were all used as received. Toluene (p.a.) from Merck was refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere before use. Standard Schlenk and glovebox techniques were used during all manipulations.

2.2. Polymerization. The reactor was mounted after drying for at least 1.5 h at 150 °C. Then the reactor was repeatedly evacuated and purged with nitrogen and finally with ethene. The reactor temperature was set (80 °C), and toluene (200 mL) was introduced into the reactor. For the copolymerization runs, the desired amount of 1-hexene was added immediately after the toluene. The stirring rate was set (2000 rpm) to minimize gas/liquid transport limitations. The reactor was pressured with ethene to the wanted total pressure (2 bar). Ethene was then equilibrated before the MAO solution was added. After 7 min the catalyst dissolved in toluene was injected. The total amount of catalyst was 0.23 μmol, and the Al/Zr ratio was 3000 except for six of the polymerizations where the ratio was 3600. The total pressure was held constant during the reaction, and the instantaneous consumption of ethene was measured. The polymerization was stopped after 1 h by closing the feed of ethene. The polymer product was poured into a mixture of methanol (300 mL) and hydrochloric acid (30 mL) and stirred overnight. After filtration, the polymer was washed with methanol and dried in open air. The polymer was stored without additives in a refrigerator.

2.3. Polymer Characterization. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer 7 series thermal analyzer. The polymer (2.0 ± 1.0 mg) was heated to 180 °C (50 °C/min), held at 180 °C for 1 min, cooled to 40 °C (10 °C/min), and held at 40 °C for 3 min. Finally, the polymer was heated to 160 °C (10 °C/min). The reported melting point is the peak value from the last heating. The fractionation method based on successive self-nucleation/annealing (SSA) was performed with the DSC according to a previously reported procedure.[16]

Gel permeation chromatography (GPC) was performed with a Polymer Laboratories PL-210 GPC instrument equipped with three columns and operated at a flow rate of 1.0 mL/min and a temperature of 160 °C. The polymer was dissolved in 1,2,4-trichlorobenzene (0.7 ± 0.3 mg/mL) stabilized with 0.125 wt % BHT and heated at 150 °C for 1 h before the run was started. The instrument was calibrated against narrow polystyrene samples. Molecular weights were obtained by universal calibration.

Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS66V spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector. Homopolymers and copolymers were pressed into disks approximately 500 μm thick, and 200 scans were utilized. The difference before and after bromination was used to find the absorbance of selected peaks. Contents of unsaturations (vinyl, *trans*-vinylene, and vinylidene) were estimated according to previously reported procedures.[16] The incorporation of 1-hexene in the copolymers was estimated from the absorption at 1378 cm^{-1} measured after subtraction of a spectrum for ethene homopolymer. A calibration curve with mol % against absorbance per film thickness was found from standards with known 1-hexene content (determined by ^{13}C NMR) kindly supplied from Borealis, Norway, and Hanne Wigum, Department of Chemical Engineering, NTNU.

3. Results and Discussion

3.1. Catalytic Activity. Ethene was homopolymerized and copolymerized with 1-hexene under the same conditions. From Tables 1 and 3 it is clear that 1,2,4-Me_3Cp and the 1:1 mixture showed a significant increase in activity up to a fairly steady level when at least 0.1 mol/L comonomer was added. On the other hand, no such increase was apparent for Cp* (see Table 2). Further, the activity of 1,2,4-Me_3Cp is well above the one for Cp*, by a factor of about 6. These observations agree with results obtained by Wigum et al.[16] As might be expected, the achieved activity per zirconium for the mixture is lying between the activities for the individual catalysts at comparable additions of 1-hexene, thus reflecting the half concentration of the more active 1,2,4-Me_3Cp catalyst.

In the literature, there has been presented experimental evidence that each metallocene in a mixture behaves as if present alone in the reactor.[5,6] Therefore, it should be possible to predict the activities for such mixtures from observed activities and mole fractions of the individual catalysts.[17] The correspondence between predicted (10.5 t PE/(mol Zr h)) and observed (11.0 t PE/(mol Zr h)) homopolymerization activity is good in the present study. For copolymerization with addition of 0.16 mol/L 1-hexene, the predicted activity is 25, in fair agreement with the observation of 28. As indicated in Tables 1−3, several polymerizations were reproduced. It can be seen that the polymerization activity is less reproducible than polymer characteristics like melting point and amount of incorporated 1-hexene. Huang and Rempel[18] have proposed that this common observation is due to residual oxygen that reacts with trimethylaluminum (TMA) present in the MAO cocatalyst. Small fluctuations in the oxygen concentration can result in changes in the concentration and chemistry of MAO, which then may give rise to the high variance in catalytic activity for metallocenes.

Examples of activity profiles for ethene/1-hexene copolymerization using the three different catalyst systems with the same initial concentration of 1-hexene (0.72 mol/L) are given in Figure 1. This figure clearly illustrates the difference between the activities for 1,2,4-Me_3Cp and Cp*. Note also that copolymerization with Cp* deactivates more rapidly. Because of the large

Table 1. Experimentally Obtained Activity and Polymer Characteristics from the Homopolymerization and Copolymerization of Ethene and 1-Hexene with 1,2,4-Me$_3$Cp/MAO[a]

run	1-hexene added (mL)	[H]$_{\mathrm{initial}}$[c] (mol/L)	[H][d] in polymer (mol %)	activity[e]	T_m (°C)[f]	*trans*-vinylene/ vinyl/vinylidene[g]	M_n FTIR (g/mol) × 10^{-3}	M_n GPC (g/mol) × 10^{-3}	M_w GPC (g/mol) × 10^{-3}	MWD[h]
35	0	0	0	17	134.0	0.016/0.016/0	446	186	446	2.4
106	1	0.04	0.5	9	128.4	nd	nd	nd	nd	nd
38	3	0.12	2.9	44	117.7	0.033/0.036/0.217	49	49	166	3.4
31	4	0.16	3.4	45	115.4	0.024/0.027/0.192	58	47	183	3.9
50	6	0.23	3.8	53	111.9	0.022/0.028/0.181	61	43	115	2.6
76	6	0.23	nd	43	112.5	nd	nd	49[i]	112[i]	2.3
77	6	0.23	2.7	19	114.7	0.013/0.028/0.069	127	62[i]	141[i]	2.3
82	6	0.23	3.0	38	113.9	0.013/0.026/0.119	88	59[i]	137[i]	2.3
36	8	0.31	4.8	66	109.9	0.021/0.030/0.265	44	37	98	2.6
37	10	0.38	4.6	65	107.2	0.019/0.022/0.174	65	nd	nd	nd
39	10	0.38	5.0	62	107.9	0.017/0.029/0.213	54	46	104	2.3
40	10	0.38	5.5	64	107.4	0.019/0.037/0.272	43	46	109	2.4
44[b]	10	0.38	4.7	41	108.5	0.013/0.031/0.176	64	nd	nd	nd
70	10	0.38	5.4	nd	106.7	0.025/0.031/0.238	48	41	104	2.5
48	15	0.55	6.0	55	103.7	0.012/0.032/0.199	58	45	101	2.2
49	20	0.72	6.2	67	96.7	0.018/0.029/0.255	46	47	94	2.0
57	25	0.88	7.9	42	92.7	0.018/0.024/0.361	35	32	65	2.0

[a] $T = 80$ °C; $P_{\mathrm{total}} = 2$ bar; [Al]/[Zr] = 3000 (except run 31 where [Al]/[Zr] = 3600), $n_{\mathrm{Zr}} = 0.23$ μmol; solvent = toluene; polymerization time = 1 h. [b] Polymerization time: 15 min. [c] Initial concentration of 1-hexene in the reactor (mol/L). [d] Incorporated 1-hexene, determined by FTIR. [e] Calculated from the yields (t PE/(mol Zr h). Run 44: t PE/(mol Zr 15 min). [f] Determined by DSC. [g] Determined by FTIR per 1000 C in the polymer backbone. [h] Determined by GPC. [i] Average of values given in Table 4.

Table 2. Experimentally Obtained Activity and Polymer Characteristics from the Homopolymerization and Copolymerization of Ethene and 1-Hexene with Cp*/MAO[a]

run	1-hexene added (mL)	[H]$_{\mathrm{initial}}$[b] (mol/L)	[H][c] in polymer (mol %)	activity[d]	T_m (°C)[e]	*trans*-vinylene/ vinyl/vinylidene[f]	M_n FTIR (g/mol) × 10^{-3}	M_n GPC (g/mol) × 10^{-3}	M_w GPC (g/mol) × 10^{-3}	MWD[g]
51	0	0	0	4.0	134.2	0.068/0.065/0	105	38	134	3.5
52	3	0.12	0.3	5.6	131.9	0.103/0.085/0.005	72	45	148	3.3
32	4	0.16	0.4	5.0	131.0	0.102/0.097/0.007	68	40	121	3.0
cp14	6	0.23	0.5	nd	129.7	0.095/0.077/0.014	75	50	131	2.6
75	6	0.23	nd	3.3	128.5	nd	nd	44[h]	99[h]	2.3
81	6	0.23	0.5	2.8	128.7	0.072/0.042/0.009	114	41[h]	97[h]	2.4
83	6	0.23	0.5	5.9	129.7	0.091/0.078/0.014	76	39[h]	98[h]	2.5
21	10	0.38	0.7	5.5	128.5	0.101/0.081/0.015	71	43	116	2.7
20	10	0.38	0.7	7.1	128.4	0.100/0.084/0.015	70	45	106	2.4
69	10	0.38	0.7	6.3	127.9	0.115/0.078/0.015	67	53	140	2.6
cp13	15	0.55	1.0	nd	126.4	0.092/0.075/0.023	74	76	156	2.1
53	20	0.72	1.0	13	124.4	0.099/0.084/0.024	68	34	87	2.6

[a] $T = 80$ °C; $P_{\mathrm{total}} = 2$ bar; [Al]/[Zr] = 3000 (except runs 20, 21, and 32 where [Al]/[Zr] = 3600), $n_{\mathrm{Zr}} = 0{,}23$ μmol; solvent = toluene; polarization time = 1 h. [b] Initial concentration of 1-hexene in the reactor (mol/L). [c] Incorporated 1-hexene, determined by FTIR. [d] Calculated from the yields (t PE/(mol Zr h). [e] Determined by DSC. [f] Determined by FTIR per 1000 C in the polymer backbone. [g] Determined by GPC. [h] Average of values given in Table 4.

difference between the activities of the individual catalysts, it might be expected that the polymer properties resulting from the mixed catalyst system are close to the polymer found for 1,2,4-Me$_3$Cp.

3.2. Comonomer Incorporation. In Figure 2 the amount of 1-hexene in the copolymers is plotted against the amount of 1-hexene added initially for each of the three catalyst systems. 1,2,4-Me$_3$Cp incorporates significantly more 1-hexene than Cp*, as also obtained by Wigum et al.[16] The data are in line with the study by Rudolph et al.[19] for Cp*/MAO as they found only up to 1.4 mol % incorporation with a molar ratio of ethene to 1-hexene of 1/20 in the monomer feed. Again, the mixed system results in properties intermediate between the two individual catalysts, but the 1-hexene content in the polymer certainly is lower than expected from the 6-fold larger activity for the neat 1,2,4-Me$_3$Cp catalyst. It might very well be that it is this lower comonomer incorporation that causes some of the anomalous polymer properties described below.

3.3. Thermal Characterization. The melting points of the copolymers made by 1,2,4-Me$_3$Cp and Cp* are decreasing almost linearly as the 1-hexene incorporation increases, as displayed in Figure 3. It is well-known that due to short chain branches, copolymers have a lower melting point than the homopolymer of ethene.[1,20] When the amount of short chain branches increases, the melting point decreases because the crystallite size in the polymer becomes smaller as the side chains probably are excluded from the crystals. Crystallization of such a polymer is determined to a major extent, if not completely, by the comonomer distribution along and among the chains.[21]

The melting behavior can be analyzed in more detail by studying the endotherms compared in Figure 4a. What might seem astonishing is the position of the main melting point for the mixed catalyst system, first rather sharply decreasing and then increasing and becoming almost constant with the comonomer content. The mixed catalyst system with addition of 0.23−0.72 mol/L 1-hexene yielded copolymers with two melting endotherms, in accordance with a copolymer with two different fractions of comonomer/short chain branches (SCB). The high-temperature peak results from incorporation of few comonomer units (Cp*), whereas the low-temperature broad peak corresponds to incorporation of a high

Table 3. Experimentally Obtained Activity and Polymer Characteristics from the Homopolymerization and Copolymerization of Ethene and 1-Hexene with a 1:1 Mixture of 1,2,4-Me$_3$Cp and Cp*; the Cocatalyst Is MAO[a]

run	1-hexene added (mL)	[H]$_{\mathrm{initial}}$[b] (mol/L)	[H][c] in polymer (mol %)	activity[d]	T_m (°C)[e]	*trans*-vinylene/ vinyl/vinylidene[f]	M_n FTIR (g/mol) × 10^{-3}	M_n GPC (g/mol) × 10^{-3}	M_w GPC (g/mol) × 10^{-3}	MWD[g]
73	0	0	0	11	134.4	0.042/0.026/0	204	73	311	4.3
105	1	0.04	0.4	12	126.2	nd	nd	nd	nd	nd
23	4	0.16	1.6	28	118.0	0.029/0.023/0.047	141	67	206	3.1
26	4	0.16	1.9	32	120.5	0.032/0.032/0.063	111	70	213	3.1
74	4	0.16	1.2	25	117.0	0.037/0.036/0.046	118	80	260	3.3
64	6	0.23	2.3	25	120.9 (111.1)	0.040/0.035/0.059	104	61	184	3.0
67	6	0.23	2.2	33	120.9 (111.1)	0.035/0.036/0.053	113	59	202	3.4
78	6	0.23	nd	24	122.0 (113.4)	nd	nd	57[h]	142[h]	2.5
80	6	0.23	2.0	23	121.2 (113.1)	0.033/0.035/0.048	121	57[h]	165[h]	2.9
88	6	0.23	1.9	11	121.5 (113.1)	0.040/0.038/0.052	109	52[h]	150[h]	2.9
60	7	0.27	2.4	7.6	123.4 (111.4)	0.039/0.028/0.059	112	57	170	3.0
72	10	0.38	3.1	24	120.9 (105.4)	0.049/0.043/0.070	86	69	185	2.7
61	13	0.48	3.6	32	122.2 (102.0)	0.047/0.045/0.094	75	49	126	2.6
65	15	0.55	4.1	26	122.2 (100.0)	0.060/0.048/0.137	57	51	121	2.4
62	16	0.59	nd	21	121.9 (96.2)	nd	nd	58	155	2.7
63	20	0.72	4.7	25	122.9 (94.5)	0.068/0.051/0.169	49	46	97	2.1
66	20	0.72	4.6	29	124.4 (95.5)	0.068/0.062/0.154	49	46	101	2.2

[a] $T = 80$ °C; $P_{\mathrm{total}} = 2$ bar; $[\mathrm{Al}]/[\mathrm{Zr_{tot}}] = 3000$ (except runs 23 and 26 where $[\mathrm{Al}]/[\mathrm{Zr_{tot}}] = 3600$), $n_{\mathrm{Zr_{tot}}} = 0.23$ μmol; solvent = toluene; polarization time = 1 h; $[\mathrm{Zr_{tot}}] = [\mathrm{Zr_{Cp*}}] + [\mathrm{Zr_{1,2,4-Cp}}]$. [b] Initial concentration of 1-hexene in the reactor (mol/L). [c] Incorporated 1-hexene, determined by FTIR. [d] Calculated from the yields (t PE/(mol Zr h). [e] Determined by DSC. [f] Determined by FTIR per 1000 C in the polymer backbone. [g] Determined by GPC. [h] Average of values given in Table 4.

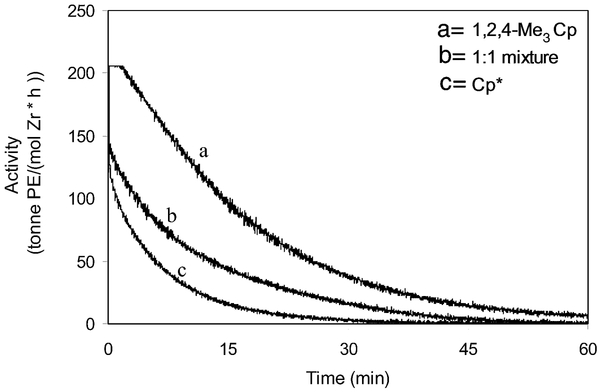

Figure 1. Polymerization rate as a function of reaction time for ethene/1-hexene copolymers made by 1,2,4-Me$_3$Cp, Cp*, and 1:1 mixture of these two catalysts. Cocatalyst = MAO; initial concentration of 1-hexene = 0.72 mol/L; $T = 80$ °C; $P_{\mathrm{total}} = 2$ bar(a, run 49; b, run 63; c, run 53).

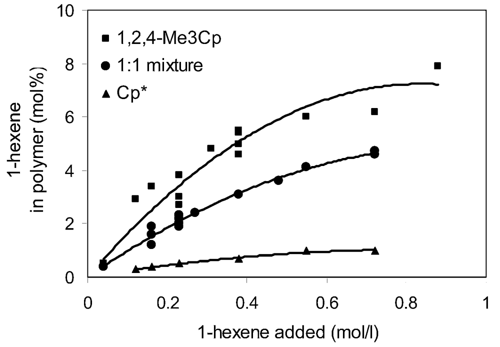

Figure 2. Incorporation of 1-hexene (mol %) in ethene/1-hexene copolymers as a function of amount of 1-hexene added to the reactor (mol/L). Catalysts = 1,2,4-Me$_3$Cp, Cp*, and a 1:1 mixture of these two; cocatalyst = MAO; $T = 80$ °C; $P_{\mathrm{total}} = 2$ bar.

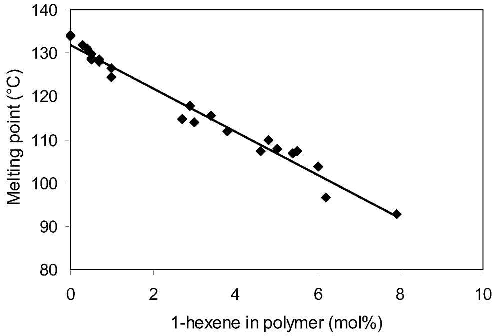

Figure 3. Melting point as a function of incorporated 1-hexene (mol %) of ethene homopolymers and ethene/1-hexene copolymers. Catalysts = 1,2,4-Me$_3$Cp and Cp*; cocatalyst = MAO; $T = 80$ °C; $P_{\mathrm{total}} = 2$ bar.

amount of comonomer units (1,2,4-Me$_3$Cp). When low amounts of 1-hexene were used (0.04 or 0.16 mol/L), the copolymers had only one melting peak. The reason might be that the melting of the two fractions now occurs so close in temperature that they do not separate into two peaks.[21] It follows that the high-temperature peak in Figure 4a is approximately constant, or even moved to slightly higher temperatures, when larger initial amounts of 1-hexene are used in the polymerization and cross-crystallization is faded out. From Tables 2 and 3 it can be seen that the melting point of the high-temperature fraction is lower than the melting point of the copolymer made by Cp* at analogues conditions, except for addition of 0.72 mol/L 1-hexene where the melting points merge. It appears reasonable that high comonomer concentration leads to polymer fractions originating from the two sites with larger differences in their comonomer content and thereby easier separation in the crystallization process.

The interpretation above is supported by successive self-nucleation/annealing (SSA), a DSC technique designed to fractionate ethylene/α-olefin copolymers.[22] The procedure allows melt/melt and melt/solid segregation to occur during thermal cycles that promote self-nucleation, crystallization, and annealing processes. This technique can give information about the distribution of short chain branching (SCBD).[23] SSA was performed on polymers made by the 1:1 mixture, in addition to one of the polymers made by the individual catalysts, to qualitatively examine the comonomer distribution (Figure 4b). As expected, no fractionation occurs for the homopolymer. For each of the copolymers, however, a clear fractionation was obtained after ap-

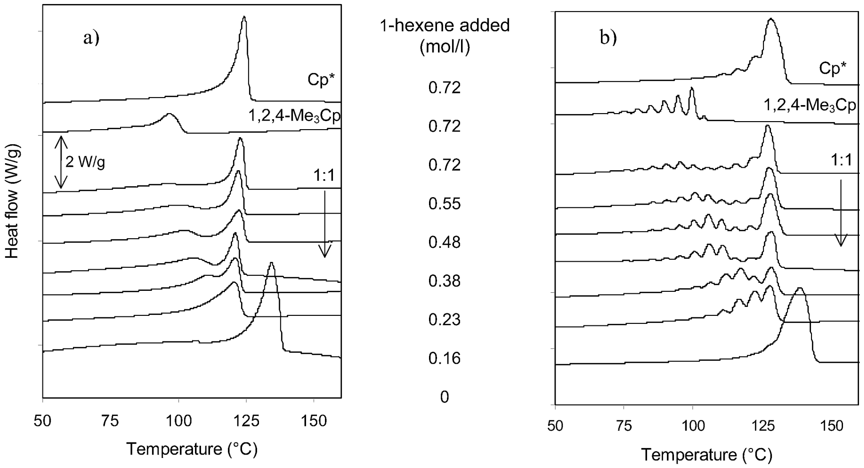

Figure 4. Melting curves for ethene homopolymer and ethene/1-hexene copolymers made by 1:1 mixture of 1,2,4-Me_3Cp and Cp* and melting curves for ethene/1-hexene copolymer made by Cp* and 1,2,4-Cp for comparison with mixture (a) before and (b) after application of SSA. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar (runs 53, 49, 63, 65, 61, 72, 64, 26, and 73).

plication of SSA since a series of melting peaks appeared in the melting curves. When 0.23 mol/L 1-hexene or more was used in the polymerization, the resulting copolymers had a clear bimodal trend in the distribution of melting peaks. The results are in accordance with a bimodal distribution of the SCB in copolymers made by the dual site catalyst, clearly identifying the lower melting point fractions to 1,2,4-Me_3Cp and the higher to Cp*. As displayed by the two upper curves in Figure 4b, the copolymer from 1,2,4-Me_3Cp is better fractionated than the one from Cp*. The distribution of SCB is unimodal in copolymer from individual catalysts. By comparison of SSA curves for copolymers made by the individual catalysts and the mixture, with high and equal initial amounts of 1-hexene (Figure 4b: three upper curves), it can be seen that the SSA curve resulting from the mixture includes all the peaks in the curves for the two individual catalysts. Obviously, the dual site catalyst will produce a copolymer with broader SCBD than copolymers made by the individual catalysts, as also obtained by others.[17]

A closer look at the melting endotherms, however, shows that the picture is not as simple as described above. Again, the influence of the Cp*-based polymer fraction is much stronger than expected from the individual activities, clearly pointing to an in situ *enhancement of the activity of the Cp* site.* To check this effect further, polymers made by the two catalysts individually were blended by dissolution in hot xylene and subsequent coprecipitation with cold methanol. The polymers were blended in accordance with the individual activity ratio and in addition in a 50/50 wt % mixture. The melting curves presented in Figure 5 show that the behavior of the polymer from the mixed catalyst is between what is expected from the activity ratio and a 50/50 wt % precipitated mixture and rather closer to the latter.

Crystallization analysis fractionation (CRYSTAF) and temperature rising elution fractionation (TREF) were performed for runs 49, 53, and 63, and an activity enhancement of the Cp* site was confirmed. The work with CRYSTAF is continued, and in addition preparative CRYSTAF is performed on copolymers made by the mixture. Further analysis of fractions by differential scanning calorimetry (DSC) indicates the formation of block copolymers. This work will be reported in more detail shortly.

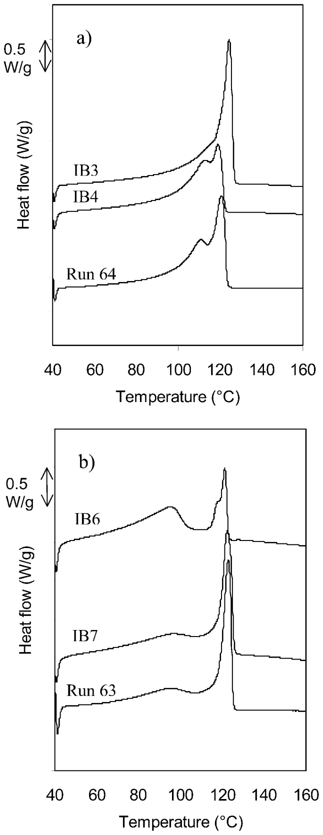

Figure 5. Comparison of melting curves for ethene/1-hexene copolymers made by 1:1 mixture of 1,2,4-Me_3Cp and Cp* and melting curves for blended copolymers prepared by 1,2,4-Me_3-Cp and Cp* individually. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar. (a) 0.23 mol/L 1-hexene added initially in the copolymerizations. IB3 = 50/50 wt % blend of run 82 and run 83. IB4 = activity ratio blend of run 82 and run 83. (b) 0.72 mol/L 1-hexene added initially in the copolymerizations. IB7 = 50/50 wt % blend of run 49 and run 53. IB6 = activity ratio blend of run 49 and run 53.

3.4. Molecular Weight and Molecular Weight Distribution.

The weight-average molecular weights (M_w) for the homo- and copolymers of 1,2,4-Me_3Cp and Cp* are plotted against the amount of 1-hexene incorporated in Figure 6. There is a significant reduction in M_w for copolymers made by 1,2,4-Me_3Cp compared with the homopolymer analogue. For the copolymer with lowest determined incorporation (2.9 mol %), the reduc-

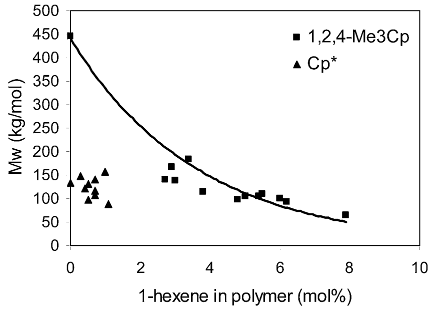

Figure 6. Weight-average molecular weight (M_w) for ethene homopolymers and ethene/1-hexene copolymers made by 1,2,4-Me_3Cp and Cp*. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar.

Table 4. Reproducibility of GPC Results for Ethene/1-Hexene Copolymers Made by Cp*, 1,2,4-Me_3Cp, and a 1:1 Mixture of These Two[a]

run	catalyst	M_w (kg/mol)	M_n (kg/mol)	MWD
75	Cp*	102	39	2.6
		96	39	2.5
		97	45	2.2
		94	45	2.1
		105	50	2.1
81	Cp*	107	38	2.8
		89	43	2.1
		94	41	2.3
83	Cp*	105	38	2.8
		110	43	2.6
		90	41	2.2
		88	33	2.7
avg	Cp*	98	41	2.4
$S(y)$		8	4	0.3
$S(y_{av})$		2	1	0.1
76	1,2,4-Me_3Cp	114	53	2.2
		112	52	2.2
		109	41	2.7
		112	48	2.3
77	1,2,4-Me_3Cp	144	61	2.4
		136	64	2.1
		143	67	2.1
		140	55	2.6
82	1,2,4-Me_3Cp	151	61	2.5
		148	65	2.3
		113	50	2.3
		134	60	2.2
avg	1,2,4-Me_3Cp	130	56	2.3
$S(y)$		16	8	0.2
$S(y_{av})$		5	2	0.1
78	1:1 mixture	150	61	2.5
		156	60	2.6
		109	49	2.2
		133	52	2.6
		128	53	2.4
80	1:1 mixture	161	61	2.6
		179	57	3.1
		165	50	3.3
		160	58	2.8
		161	59	2.8
88	1:1 mixture	165	59	2.8
		155	54	2.9
		141	45	3.1
		137	50	2.7
avg	1:1 mixture	150	55	2.7
$S(y)$		18	5	0.3
$S(y_{av})$		5	1	0.1

[a] Cocatalyst = MAO; initial concentration of 1-hexene = 0.23 mol/L; T = 80 °C; P_{total} = 2 bar.

tion of M_w was as high as 280 kg/mol. As more 1-hexene was incorporated, the M_w is reduced gradually by a further 101 kg/mol, but still the M_w is high for the comonomer content. In contrast, Cp* showed no significant reduction in M_w as comonomer was incorporated. If we study the data in Tables 1−3 in more detail for a given 1-hexene addition, *it is remarkable that* M_w for the copolymers produced by the mixed catalyst system consistently, with only one exception, *is higher than for any of the individual catalysts*. This novel effect is studied in more detail below.

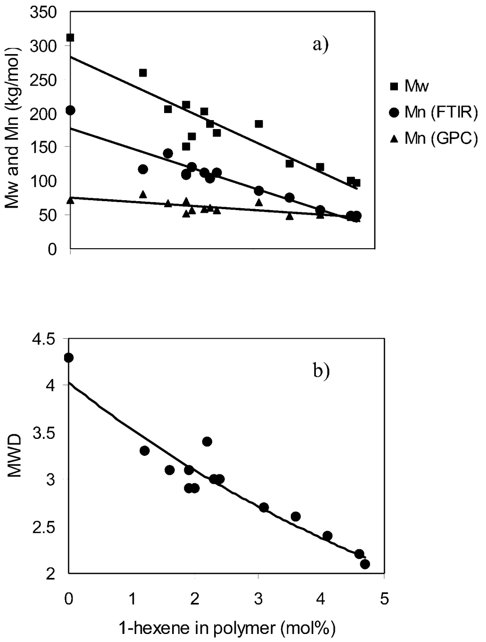

Figure 7. Weight- and number-average molecular weight (a) and molecular weight distribution (b) for ethene homopolymer and ethene/1-hexene copolymers made by 1:1 mixture of 1,2,4-Me_3Cp and Cp* as a function of the amount of 1-hexene in the polymer. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar.

The observation of highest M_w for the copolymer made by the mixed catalyst system was highly unexpected since, as mentioned earlier, previous experimental evidence indicates that each metallocene in a mixture behaves as if present alone in the reactor.[5,6] Indeed, the *homopolymer* made by the mixture has an M_w (311 kg/mol) between the M_w's for the two individual catalysts (446 and 134 kg/mol). Prediction from activity and mole fraction of the two individual catalysts in the mixture[17] gives an M_w for the homopolymer of 387 kg/mol, in fair agreement with the observation.

Three *copolymerizations* at the same conditions were performed for each of the three catalyst systems to study the reproducibility of the molecular weights determined by GPC. The data in Table 4 confirm that the average M_w obtained for the 1:1 mixture lies above the average M_w's for the copolymers made by the two individual catalysts. A t-test shows that this statement is accurate at the 99+% confidence level. One possible explanation for the observed high M_w's can be deduced from previous reports stating that chain transfer to TMA is important for Cp*.[24,25] The chains originating at Cp* contain minimal comonomer but terminate frequently with TMA. Thus, these chains can fairly easy be incorporated into the more open 1,2,4-Me_3Cp catalytic site and continue to polymerize.

Weight-average molecular weight and number-average molecular weight (M_n), the latter from both GPC and FTIR, are plotted in Figure 7a as a function of 1-hexene incorporation for the 1:1 mixed catalyst system. The M_w follows the normal decreasing trend as the amount of incorporated comonomer increases, whereas M_n(GPC) is more constant. This implies, as displayed in Figure 7b, that the broadest molecular weight

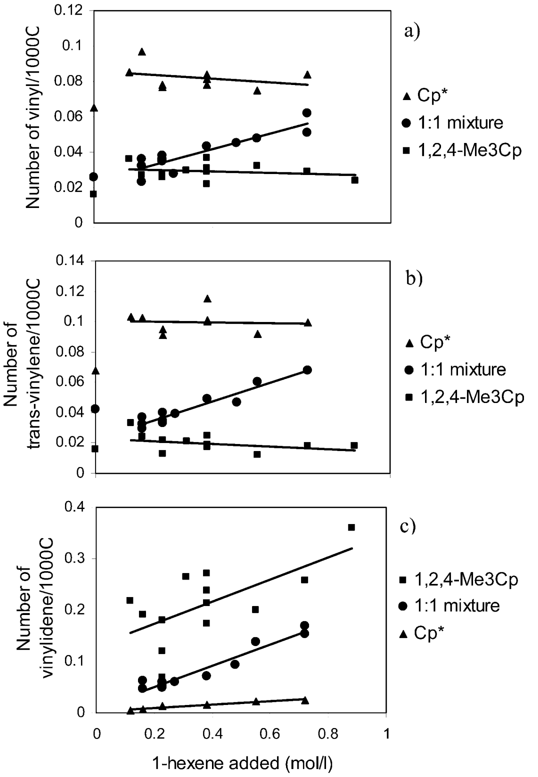

Figure 8. Number of vinyl (a), *trans*-vinylene (b), and vinylidene (c) unsaturations per 1000 C in the polymer backbone as a function of initial amount of 1-hexene. Catalysts = 1,2,4-Me$_3$Cp, Cp*, and 1:1 mixture of these two; cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar.

distribution was found for the homopolymer. In fact, the MWD decreases toward the theoretical value 2.0 as the incorporation of comonomer increases. The MWD's of the mixture are reasonably consistent with the molecular weights in Figure 6 for the individual catalysts. Nevertheless, it is noteworthy that by mixing two catalysts a very narrow MWD can be obtained from polymer chains that differ dramatically in their comonomer content. Comparing with the MWDs of the individual catalysts, we observe a similar trend, a narrower molecular weight distribution at high 1-hexene concentrations. Possibly the comonomer is able to stabilize one rotational conformer of the catalysts.

By comparing M_n(GPC) and M_n(FTIR) in Figure 7a, it can be seen that M_n(FTIR) $\gg$ M_n(GPC) for the homopolymer which indicates that chain transfer to TMA is an important termination mechanism. The difference between M_n(GPC) and M_n(FTIR) is getting smaller as more 1-hexene is incorporated, to become equal for the highest incorporations. Chain transfer to TMA probably is getting less important as these chains may continue to polymerize on the other site; alternatively, TMA has to compete with the comonomer for access to the active site. However, Cp* evidently terminate with TMA over the whole comonomer concentration range (see Table 2). An alternative explanation in terms of formation of additional internal double bonds, thereby reducing M_n(FTIR), cannot entirely be ruled out. Note also that part of the reduction ΔM_n(FTIR−GPC) is due to the enhanced termination after comonomer insertion.

3.5. Unsaturations and Chain Termination. FTIR spectroscopy was used to determine the content of polymer unsaturations in the polymers. Vinyl and *trans*-vinylene unsaturations are present in the homopolymers, whereas the copolymers in addition contain vinylidene. Wigum et al.[16] summarized the most relevant termination reactions during homo- and copolymerization. Formation of vinyl unsaturation is a result of transfer of a β-hydrogen atom on the growing chain to the metal center or to a coordinating monomer with ethene as the last inserted monomer. When 1-hexene is the last inserted monomer, these termination mechanisms will produce vinylidene unsaturations after 1,2-insertion and *trans*-vinylene after 2,1-insertion. When ethene is the last inserted monomer, formation of *trans*-vinylene can be explained in terms of an isomerization reaction followed by termination.[26] Chain transfer to TMA is an important termination mechanism for some catalysts, including Cp*.[24] In addition, trisubstituted end groups have been detected in ethene/1-hexene copolymers.[27] The formation of this end group arise when 1-hexene is the last inserted monomer followed by isomerization and β-H transfer to the metal center.[27] However, there is no indication of trisubstituted end groups in the copolymers in this work. No band in the FTIR spectrum is observed within the range 840−790 cm^{-1}, which is the absorption range for trisubstituted alkene.[28]

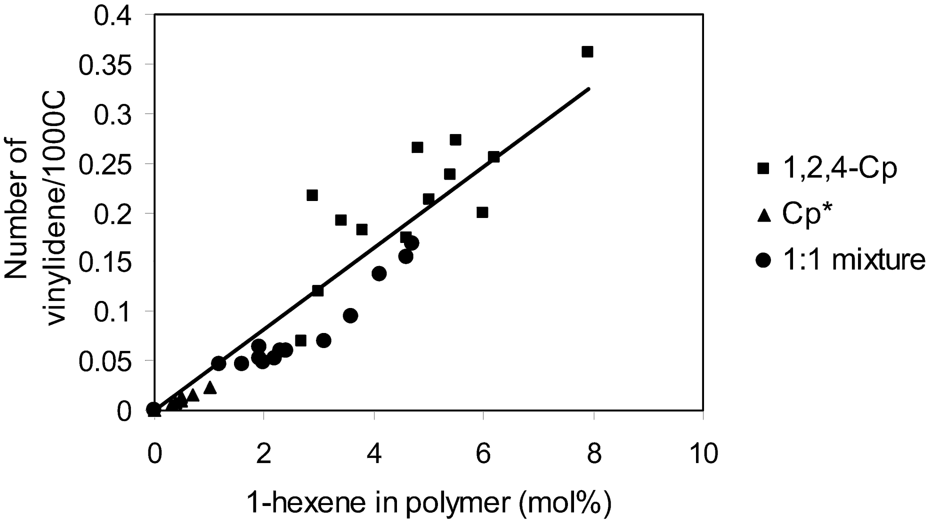

Figure 9. Number of vinylidene unsaturations per 1000 C in the polymer backbone as a function of 1-hexene incorporated for copolymers made by 1,2,4-Me$_3$Cp, Cp*, and 1:1 mixture of these two. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar.

The number of unsaturations per 1000 C in the polymer backbone against the amount of 1-hexene added is displayed in Figure 8. From Figure 8c it can be seen that copolymers made by the mixed catalyst system have vinylidene unsaturations that are lying between the two individual catalysts. As more 1-hexene is added, there is an increase in the amount of vinylidene. In a plot of vinylidene content against the amount of 1-hexene in the polymer (Figure 9), a near linear dependence confirms that termination takes place after comonomer insertion.

It is evident from Figure 8 that vinylidene is the major unsaturation for 1,2,4-Me_3Cp, in contrast to Cp* where *trans*-vinylene and vinyl are dominating, as also obtained by Wigum et al.[16] For these individual catalysts, *trans*-vinylene and vinyl decrease with comonomer content, indicating both a slight suppression of termination after ethene insertion and that 2,1-insertion of 1-hexene does not take place. For the dual site catalyst, it is astonishing that the concentration of these unsaturations approaches the Cp* values for high comonomer additions, an additional indication of activity enhancement of a Cp* or Cp*-like site. However, as mentioned earlier, chain transfer to TMA is reduced in the mixed system for high comonomer concentrations, possibly offering more room for standard termination mechanisms. In any case, vinylidene unsaturations dominate at these concentrations.

3.6. Dual Site Interaction Mechanisms. *Catalyst Ligand Exchange.* One possibility that would lead to unexpected results is ligand exchange between the two catalysts, giving a certain amount of (1,2,4-Me_3Cp)-Cp^*ZrCl_2. If this catalyst behaves like Cp* concerning comonomer incorporation, but deactivates more slowly and terminate less frequently with TMA, most of the data can be explained. Ligand exchange can possibly be facilitated by the comonomer, causing additional stress at the active site. If (1,2,4-Me_3Cp)Cp^*ZrCl_2 dominates, this would explain why MWD equals 2.0, but not the large spread in comonomer content in a given polymer. However, in a recent investigation of ethene/1-hexene copolymerization with the dual catalyst system $Me_4Si_2(Me_4Cp)_2ZrCl_2$ and (1,2,4-$Me_3Cp)_2ZrCl_2$, similar effects as described in the present investigation were detected. This system is very similar to the present one, except that one methyl group of the Cp* ligand is exchanged for a bridge to the second ligand. Therefore, the hypothesis of ligand exchange is more or less ruled out.[29]

Chain Transfer from Site to Site. If chains terminated at Cp* with TMA coordinate to 1,2,4-Me_3Cp and continue to polymerize there, the molecular weight increases. Further, it may look as if the Cp* catalyst becomes more dominating if the “dangling” comonomer-rich part of the resulting chain crystallizes poorly, although this argument cannot be confirmed at the present stage. Nevertheless, the model seems to explain most of the observations for the mixed catalyst system, including reduction in chain transfer to TMA, as these chains simply disappear by coordination to the more open site. Why the vinyl and *trans*-vinylene end groups typical for the Cp* catalyst increase in concentration with the 1-hexene content is at first sight more difficult to explain and points to a relative activity enhancement of the Cp* site.

The site-to-site transfer mechanism may follow an analogy to the model discussed by Lieber and Brintzinger[15] for propene polymerization by a mixture of the highly substituted isospecific catalyst Me_2Si(2-Me-4-tBu-$Cp)_2ZrCl_2$ with more open metallocene structures. Chain transfer to TMA, or polymeryl, Po, exchange if one likes, most likely takes place via an alkyl double-bridged intermediate between zirconium and aluminum, the alkyls in this case being one methyl and one polymeryl group. Because of the congested nature of the active site for the specified catalyst, and for Cp* in our case, it is easy to comprehend that the bridged complex can open up at the Zr−polymeryl bonds and subsequently terminate to give Me_2AlPo.[30] The heterobimetallic cation, $L_2ZrMePoAlMe_2^+$, also probably can be formed with TMA for the more open catalysts, like L = 1,2,4-Me_3Cp, with resulting deactivation or latent site formation. However, this complex evidently does not result in termination but probably can be reactivated by expelling a TMA monomer. In order for chain transfer from the Cp* to the 1,2,4-Me_3Cp site to take place, the nature of the cationic species depends on the state of the receiving site; is it polymerizing, or has the propagation been terminated by chain transfer to ethylene or by β-hydrogen elimination? Since the observed anomalous effects essentially depend on a high comonomer level, and that termination after 1-hexene insertion dominates, it seems probable that the bimetallic cation at the receiving site will be of the type $L_2ZrHPoAlMe_2^+$ or $L_2ZrEtPoAlMe_2^+$. Now, the polymeryl can also be situated at the terminal positions on aluminum, but this is less interesting as no chain transfer then can occur. This mechanism does contain fine energetic and thermodynamic balances that need to be explored, e.g., by DFT modeling.

Although we believe that chain transfer from Cp* to 1,2,4-Me_3Cp is important, the model needs to be extended somewhat to rationalize all the information satisfactorily. For polymerization with the Cp* catalyst alone, Me_2AlPo accumulates in the reaction vessel. We also know that this catalyst deactivates unusually rapidly during polymerization. It therefore very well might be that Me_2AlPo is the key component in the deactivation mechanism by equilibrium coordination to the active site cation. But for the dual site system, the second catalytic site removes Me_2AlPo continuously, and the deactivation thus can be reduced significantly. This scavenger effect of (1,2,4-$Me_3Cp)_2ZrR^+$ then explains the dominating role of the Cp* catalyst seen in the polymer properties.

Work is in progress to further develop the model for the investigated system, including CRYSTAF polymer analysis, DFT modeling, and sensitivities toward process parameters. In any case, a model should incorporate the following features: (i) The two sites interact with each other during polymerization. (ii) TMA plays a role in the mechanism. (iii) The observations depend on the comonomer content.

4. Conclusions

By mixing the catalysts (1,2,4-$Me_3Cp)_2ZrCl_2$ and (Me_5-$Cp)_2ZrCl_2$, the latter abbreviated $Cp^*{}_2ZrCl_2$ or simply Cp* and the former 1,2,4-Me_3Cp, in a 1:1 molar ratio, the overall activity for copolymerization of ethene and 1-hexene is intermediate between the individual catalysts. However, a number of surprising deviations from the expected average behavior, taking into account the ca. 6-fold higher 1 h yield of 1,2,4-Me_3Cp, include (i) ca. 30% too low comonomer incorporation in the polymer,

(ii) a melting endotherm attributed to Cp* that is ca. 40−70% too high, (iii) a higher M_w than expected, even higher than for the two individual catalysts, (iv) a chain transfer to TMA that becomes less important at high comonomer concentrations, and (v) a concentration of vinyl and *trans*-vinylene unsaturations that increases with the 1-hexene content. However, 2,1-insertion of 1-hexene probably does not take place.

Further, it is noteworthy that it is possible to produce polymers with narrow molecular weight distributions as a mixture of chains containing low and high comonomer contents. We have proposed that a possible mechanism for formation of the unique copolymers may be chain transfer from Cp* to 1,2,4-Me_3Cp through coordination of $PoAlMe_2$ to the latter site, combined with a scavenger effect that enhances the Cp* site activity.

Acknowledgment. We are grateful to Borealis AS for financial support. TREF measurements by Arja Lethinen at Borealis-Porvoo, Finland, and CRYSTAF measurements by Deborah Sarzotti at Department of Chemical Engineering, University of Waterloo, Canada, are acknowledged. We also thank Arild Follestad, Espen Ommundsen, and Kjell-Arne Solli at Borealis-Rønningen for interesting discussions.

References and Notes

(1) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143−187.
(2) Gabriel, C.; Lilge, D. *Polymer* **2001**, *42*, 297−303.
(3) Ahlers, A.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 457−461.
(4) D'Agnillo, L.; Soares, J. B. P.; Penlidis, A. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 831−840.
(5) Han, T. K.; Choi, H. K.; Jeung, D. W.; Ko, Y. S.; Woo, S. I. *Macromol. Chem. Phys.* **1995**, *196*, 2637−2647.
(6) Heiland, K.; Kaminsky, W. *Makromol. Chem.* **1992**, *193*, 601−610.
(7) Kim, J. D.; Soares, J. B. P.; Rempel, G. L. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 331−339.
(8) Liu, J.; Rytter, E. *Macromol. Rapid Commun.* **2001**, *22*, 952−956.
(9) Soares, J. B. P.; Kim, J. D. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1408−1416.
(10) Kim, J. D.; Soares, J. B. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1417−1426.
(11) Kim, J. D.; Soares, J. B. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1427−1432.
(12) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2439−2445.
(13) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447−3458.
(14) Przybyla, C.; Fink, G. *Acta Polym.* **1999**, *50*, 77−83.
(15) Lieber, S.; Brintzinger, H. H. *Macromolecules* **2000**, *33*, 9192−9199.
(16) Wigum, H.; Tangen, L.; Støvneng, J. A.; Rytter, E. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3161−3172.
(17) Chu, K. J.; Soares, J. B. P.; Penlidis, A. *Macromol. Chem. Phys.* **2000**, *201*, 340−348.
(18) Huang, J.; Rempel, G. L. *Polym. React. Eng.* **1997**, *5*, 125−139.
(19) Rudolph, S.; Giesemann, J.; Kressler, J.; Menke, T. J.; Menge, H.; Arends, P. *J. Appl. Polym. Sci.* **1999**, *74*, 439−447.
(20) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.
(21) Mathot, V. B. F. In *Calorimetry and Thermal Analysis of Polymers*; Mathot, V. B. F., Ed.; Hanser: Munchen, 1994; pp 232−298.
(22) Müller, A. J.; Hernández, Z. H.; Arnal, M. L.; Sánchez, J. J. *Polym. Bull. (Berlin)* **1997**, *39*, 465−472.
(23) Arnal, M. L.; Balsamo, V.; Ronca, G.; Sánchez, A.; Müller, A. J.; Cañizales, E.; Urbina de Navarro, C. *J. Therm. Anal. Calorim.* **2000**, *59*, 451−470.
(24) Thorshaug, K.; Støvneng, J. A.; Rytter, E.; Ystenes, M. *Macromolecules* **1998**, *31*, 7149−7165.
(25) Ystenes, M.; Eilertsen, J. L.; Liu, J.; Ott, M.; Rytter, E.; Støvneng, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3106−3127.
(26) Thorshaug, K.; Rytter, E.; Ystenes, M. *Macromol. Rapid Commun.* **1997**, *18*, 715−722.
(27) Yano, A.; Sone, M.; Hasegawa, S.; Sato, M.; Akimoto, A. *Macromol. Chem. Phys.* **1999**, *200*, 933−941.
(28) Silverstein, R. M.; Webster, F. X. In *Spectrometic Identification of Organic Compounds*; Silverstein, R. M., Webster, F. X., Eds.; John Wiley & Sons: New York, 1998; p 141.
(29) Bruaseth, I.; Rytter, E. To be published.
(30) Liu, J.; Støvneng, J. A.; Rytter, E. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3566−3577.

MA025832R