Chemical Composition Distribution Study in Ethylene/1-Hexene Copolymerization to Produce LLDPE Material using MgCl$_2$-TiCl$_4$-Based Ziegler-Natta Catalysts

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ABSTRACT: The characteristic features of LLDPE polymerization with ZN catalyst are the time drift effect during polymerization and the bending effect when trying to decrease density of the copolymer by adding more comonomer to the polymerization. The time drift in LLDPE polymerization is revealed by a constant decrease of comonomer incorporation during polymerization time. The bending is revealed by difficulties in lowering the density of LLDPE material below the density of 920 kg/m^3. With increasing comonomer content during polymerization, the density does not decrease, but the soluble fraction increases. To try to observe if these phenomena are connected, two types of catalysts, SiO$_2$ supported and precipitated MgCl$_2$ ZN catalysts, were studied. A short time (10 min) and an extended time (60 min) copolymerization test series where the polymerizations were performed in the presence of a gradually increasing comonomer amount. Both catalysts show a strong bending when density is presented as a function of 1-hexene both in 10- and 60-min polymerization, indicating no connection between time drift and bending. The density, melting point, and crystallinity results all indicate that both catalysts are making similar copolymer material with identical chemical composition distribution. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 826–836, 2010

Key words: Ziegler-Natta catalyst; CCD; copolymerization; LLDPE; 1-hexene comonomer

INTRODUCTION

In a typical ZN copolymerization a drop in density together with a drop in melting point and the crystalline fraction is seen when the comonomer is incorporated. At lower copolymer amounts, the incorporation of the comonomer is even, but when higher amounts of comonomer are incorporated the chemical composition distribution (CCD) becomes uneven. If this is due to a change in the reactivity ratio of the monomers in the active polymerizing sites or due to a change in the setup of active polymerizing sites is not fully understood. The drop in melting temperature is due to the disturbing effect of the comonomer in the PE chain when it tries to crystallize by folding its molecule chain. The comonomer causes the chain to fold more often and creates these thinner lamellas which show a lower melting point with a corresponding decrease in crystallinity. A drop in molecular weight is also seen while there is normally an increase in activity following an increase in comonomer incorporation.[1–4] A bending of the density and melting point curves in a comonomer test polymerization series is also witnessed.[5–8] At the start there is a harmonic drop in density and melting point of the copolymer with an increasing amount of incorporated comonomer. This continues with up to 3–4 mol % of comonomer. When even higher amounts of comonomer are incorporated there is no similar drop in the density and melting point. Several times it is difficult to come down to a density <920 kg/m^3, and to a melting point below 120°C even if the comonomer content is significantly increased. Contrary to this, the soluble fraction starts to increase when going to a higher comonomer percent, (i.e., higher than 3–4 mol %). The fact that the soluble fraction starts to increase when exceeding the turning point, corresponding to about 3–4 mol % of comonomer, has earlier limited the production of LLDPE to grades with a density >920 kg/m^3. This bending or obstruction to decrease in density can be explained by the uneven CCD in ZN PE copolymers.

When using a typical ZN catalyst in LLDPE polymerization a drop in M_w is very often observed when an increasing amount of comonomer is incorporated. This is especially the case with higher amounts of incorporated comonomer, reflecting the increase in the soluble fraction.

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Another phenomenon seen in copolymerization with a ZN PE catalyst is the time drift.[9–15] This time drift has not only been observed in ZN PE polymerization but also in ZN PP polymerization.[16,17] The time drift when using a ZN PE catalyst in a copolymerization shows up as a continuous decrease in comonomer incorporation during the time the polymerization is proceeding. This means that a ZN PE catalyst can incorporate during the first 10 min of the polymerization for instance 10 mol % of comonomer, but loses this ability to incorporate comonomers rapidly. Subsequently, after 1 h of polymerization the incorporation of comonomer has fallen to only 3 mol %. A corresponding increase in molecular weight, molecular weight distribution and density, together with a decrease in the soluble fraction is noticed in the material from a 1-h polymerization compared to material from a 10-min polymerization. The time drift phenomenon has been explained by a gradual change in the oxidation state of Ti in the catalyst caused by the cocatalyst, or by the sterical hindrance caused by the growing polymer particle. This could explain the broad chemical composition distribution (CCD) seen in LLDPE produced with ZN catalysts. The bending of the density/comonomer weight fraction curve has been explained by a gradually lower molecular weight in the copolymer caused by the chain transfer of the comonomer, (i.e., the higher the comonomer weight fraction the more chain transfer, the lower molecular weight which hinders density from dropping).

The bending has also been explained by the change in the Ti oxidation stage in the catalyst. Then the loss of the comonomer sensitivity of the reduced Ti would explain the difficulty in reaching lower densities especially in long-term polymerizations. The polymerization would then start with a high portion of comonomer sensitive Ti(IV) and Ti(III) that would gradually reduce to comonomer insensitive Ti(II). As more comonomer would be added to the polymerization to bring down density, it would mainly be consumed in the commencement of the polymerization when Ti has a higher oxidation state producing very low molecular weight comonomer rich material that would appear in the soluble fraction, and subsequently mainly homopolymer would be produced preventing the density to fall. If this is the case, a short-term polymerization would show less bending in comparison to a long-term polymerization.

In this investigation we attempt to clarify if there is a connection between these two well-known phenomena. To try to bring additional understanding to the correctness of the different explanations we have performed a short-term (10 min) copolymerization testing and a long-term (60 min) copolymerization testing where the polymerization has been performed in the presence of a gradually increasing comonomer amount. The results from this investigation should give an answers which of the two options are valid, namely if the bending of the resulting density/comonomer fraction curve would appear in only the 60-min polymerization series, then the time drift and the bending are representing the same phenomenon. Again if the bending of the density/comonomer fraction curve is to be found in both the 10- and the 60-min test series, then the time drift and the bending are representing separate independent phenomena. It is of uppermost importance to create an answers to these questions when further developing Ziegler-Natta catalysts to produce higher quality LLDPE material, as the bending phenomena is one of the main problems hindering the development of going into lower densities in LLDPE materials that are known to offer attractive material properties. If the bending shows to be a function of the time drift phenomena, the catalyst development can try to solve the bending phenomena by eliminating the time drift. Again, if these phenomena show to be independent the bending problem has to be over come trough other arrangements.

EXPERIMENTAL

Materials

In this study we have chosen to test two typical commercial ZN PE catalysts. One is a SiO_2-based catalyst (Cat-A)[18–21] containing $MgCl_2$-$TiCl_4$-$Al(OR)_3$ with a Ti content of 2 wt %, and the other is a high yield precipitated $MgCl_2$-$TiCl_4$-based catalyst (Cat-B)[5,9,22–27] with a Ti content of 7 wt %. These catalysts are extensively used in the commercial production of LLDPE in both unimodal and multi modal slurry and gas phase processes.

Polymerization

1-hexene was used as the comonomer in the copolymerization. One thousand eight hundred milliliter (987 g, 17.0 mol) of i-butane was introduced into a 3 L autoclave reactor as the reaction medium. Subsequently, the temperature of the reactor system was set to 85°C. The catalyst and the cocatalyst were fed into the reactor by means of two feeder vessels that were connected in line to the reactor lid. Cat-A was added in dry form to the feeder vessel. Between 80 and 100 mg of Cat-A was used in each polymerization. Cat-B was added as an oil slurry (6 g in 25 g of oil). About 250 mg of the catalyst oil slurry (0.3 mL, 10 mg catalyst) was used from this catalyst in each polymerization. The catalyst was added into the upper feeder vessel together with 10 mL (6.3 g,

TABLE I
The Polymerization Results from the Bexene-*co*-Polymerizations with Cat-A in 10 min Polymerizations

Polymerization code	A10	B10	C10	D10	E10	F10	G10	H10
Comonomer, mL	0	20	40	60	80	100	120	140
Activity/wet (kg PO/g cat, h^{-1})	0.7	1.3	1.9	2.7	3.4	2.6	3.3	2.3
MFR 2 (g/10 min)		2.4		4.3	4.6		4.9	
MFR 21 (g/10 min)	28.9	88.4	134.1	136.1	168	200.2	185.3	214
Comonomer content (wt %)	0	2.7	3.3	4.3	5.5	6.1	7.2	7.2
Density (kg/m^3)	970	950.8	944.5	938.8	935.8	933.6	928.7	931
M_w (GPC)	137,000	107,000	92,300	85,400	93,300	75,200	85,100	75,600
M_n	15,800	17,800	14,900	16,900	13,200	10,900	12,400	11,200
MWD	8.7	6	6.2	5	7.1	6.9	6.9	6.7
XS wt %	0	2.3	2.3	3.6	4.7	7.3	8.7	8.3
T-Vinyline (wt %)	0	0.02	0.02	0.01	0.03	0.02	0.04	0.03
Vinyl (wt %)	0.09	0.15	0.17	0.19	0.21	0.22	0.22	0.22
Vinylidene (wt %)	0.04	0.06	0.08	0.08	0.1	0.12	0.12	0.13
T_m (°C)	133.9	129.6	127.8	125.9	124.8	124.3	124.4	123.8
X_c (%)	75.7	61.4	60.4	50.7	51.8	49.9	46	50

87 mmol) of pentane. A 20 wt % heptane solution of triethylaluminium (TEA) was used as the cocatalyst. An Al/Ti molar ratio of 40 was used in all copolymerizations. The cocatalyst was first introduced into the reactor and the catalyst was subsequently introduced by pressurising the upper feeder vessel to 30 bar with N$_2$ and thereafter allowing the excess pressure push in the catalyst in to the reactor. Two additional feeder vessels were connected in series between the lid of the reactor and the ethylene monomer feed line. 1-hexene comonomer (0–140 mL) was introduced into the lower feeder vessel. H$_2$ pressure (1.8–2.0 bar) was added to the upper 500 mL feeder vessel (22.3 mmol). The polymerization was started by opening the monomer feed line and thereby introducing both the comonomer and the H$_2$ together with the ethylene monomer. The partial pressure of the added ethylene was varied depending on the amount of hydrogen added to maintain a constant H$_2$/ethylene molar ratio of 35.0–35.8 mol/kmol. A total pressure of 19.2–19.5 bar was maintained by the ethylene feed throughout the test polymerization. The co polymerization was performed at 85°C. The copolymerization was continued for 10 or for 60 min. The polymerization was halted by venting off the monomer and the *i*-butane. The polymerization arrangement was semiconstant in respect of H$_2$ and 1-hexene as these components were added batch wise but the maximum consumption of these components were only 10–13% and therefore the experimental conditions could be regarded to be relatively constant. Activity is defined as the amount of polymer produced during 1 h in the said conditions per gram of catalyst. The unit for activity used in this work was kg PO/g cat, h^{-1}. So regardless the polymerization time, i.e., 10 or 60 min, the activity has been normalized to a 60-min polymerization.

Characterization of the polymers

The melt flow index (MFR) using weights of 2.16, 5.0, and 21.6 kg were measured from the copolymers

TABLE II
The Polymerization Results from the Hexene-*co*-Polymerizations Cat-A in 60 min Polymerizations

Polymerization code	A60	B60	C60	D60	E60	F60	G60	H60
Comonomer, mL	0	20	40	60	80	100	120	140
Activity/wet (kg PO/g cat, h^{-1})	0.8	1.5	2.1	2.7	3.1	3.0	3.7	3.7
MFR 2 (g/10 min)	0.6	1.9	2.9	1.5		1.4		
MFR 21 (g/10 min)	16.6	47.7	71.5	54	46	39	34.3	37.7
Comonomer content (wt %)	0	0.6	1.8	1.9	2.2	2.7	3	3.6
Density (kg/m^3)	961.2	950.4	945.5	941.2	939.9	937.4	935.8	935
M_w (GPC)	172,000	123,000	116,000	122,000	118,000	131,000	129,000	130,000
M_n	30,900	27,900	21,700	26,300	25,900	27,500	30,400	27,100
MWD	5.6	4.4	5.4	4.6	4.5	4.8	4.2	4.8
XS wt %	0.1	0.3	0.8	0.9	1	1.1	1.5	1.6
T-Vinyline (wt %)	0	0	0.01	0.01	0.01	0.01	0.01	0.01
Vinyl (wt %)	0.11	0.13	0.16	0.16	0.16	0.15	0.17	0.17
Vinylidene (wt %)	0.04	0.04	0.06	0.05	0.05	0.05	0.06	0.06
T_m (°C)	137.1	130.9	131.4	128.2	126.9	129.04	126.4	126.81
X_c (%)	67.8	68.1	63.7	59.7	55.5	51.43	57	55.24

TABLE III
The Polymerization Results from the Hexene-*co*-Polymerizations with Cat-B in 10 min Polymerizations

Polymerization code	I10	J10	K10	L10	M10	N10	O10
Comonomer, mL	0	20	40	60	80	100	120
Activity/wet (kg PO/g cat, h^{-1})	21.1	21.3	47.1	32.5	50.4	50.1	49.5
MFR 21 (g/10 min)	1.8	10.2	7.6	13.7	10.8	11.7	14.4
Comonomer content (wt %)	0.0	1.8	2.6	3.5	4.7	5.6	5.7
Density (kg/m^3)	955.3	941.6	936.4	936	929	926	927
M_w (GPC)	274,000	203,000	208,000	157,000	176,000	170,000	173,000
M_n	52,800	41,300	38,600	39,000	33,000	34,000	12,000
MWD	5.2	4.9	5.4	4.0	5.3	4.9	15.0
XS wt %		1	0.9	2.2	4.4	4.8	5.8
T-Vinyline (wt %)	0.01	0	0	0	0.01	0.01	0.01
Vinyl (wt %)	0.11	0.14	0.14	0.15	0.18	0.19	0.19
Vinylidene (wt %)	0.02	0.04	0.05	0.06	0.08	0.09	0.1
T_m (°C)	135	129.1	127.4	126.5	125.4	125.7	124.8
X_c (%)	69.2	56.8	53.2	52.7	50.9	46.1	48

according to the ISO-1133 standard. The densities of the copolymers were measured by first pressing a plate of the polymer at 175°C and then cutting a sample from this plate. The density of the copolymer was calculated from the weight difference when immersing the sample into isododecane. The melting point (T_m) and crystallinity (X_c) were measured by DSC. X-ray diffraction that would have given a more detailed picture of the crystallinity of the copolymers was not used in this investigation. Weight average molecular weight (M_w), number average molecular weight (M_n) and the M_w/M_n ratio (MWD) were measured by GPC and the hexene content in the copolymer was measured by Fourier transform infrared spectroscopy (TFIR). A round plate is pressed out of the copolymer at 160°C with the thickness of about 250 μm. After accurate measurement of the thickness of the plate the absorbance is measured by TFIR at 1377 cm^{-1} after which the hexene content is calculated. TFIR was also used to

measure the amount of double bonds in the polymers. In addition the xylene soluble fraction (XS %) was measured from all the copolymers. The polymerization results are listed in Tables I–IV.

Temperature Rising Elution Fractionation (TREF) curves of the copolymers were measured using a column filled with Cromosorb P silica and immersed in a temperature programmable oil bath to reveal the chemical composition distribution (CCD) of the comonomer in the copolymer. About 7.5–12.5 mg of polymer was placed in a 4 mL glass vessel. Xylene solvent (2.5 mL) was then added to the sample vessel, and the sample was dissolved in this solution at 140°C. The dissolving process took 2–4 h. This solution was then added by syringe into the packed column at 135°C. The dissolved polymer was then allowed to subsequently crystallize by cooling down the column to 15°C at a cooling rate of 1.5°C/min. The elution was then started by pumping pure 1,2,4-trichlorobenzene (TCB) through the column. The

TABLE IV
The Polymerization Results from the Hexene-*co*-Polymerizations with Cat-B in 60 min Polymerizations

| Polymerization code	I60	J60	K60	L60	M60	N60	O60	P60
Comonomer, mL	0	20	40	60	80	100	120	140
Activity/wet (kg PO/g cat, h^{-1})	22.0	33.0	23.6	28.5	29.6	27.5	24.4	23.1
MFR 21 (g/10 min)	0.9	2.4	5.1	4.9	2.9	3.1	3.6	3.8
Comonomer content (wt %)	0.0	0.4	1	1.6	2.2	2.8	3.1	3.7
Density (kg/m^3)	952.3	943.9	942.3	939.4	935.5	933.4	931.9	930.9
M_w (GPC)	343,000	268,000	215,000	222,000	243,000	241,000	240,000	242,000
M_n	68,500	54,000	44,400	46,700	48,000	48,700	47,500	51,600
MWD	5	5	4.8	4.8	5.1	4.9	5	4.7
xs wt %	0.1	0	0.2	0.5	0.9	1.1	1.6	2.5
T-Vinyline (wt %)	0	0	0	0	0.01	0	0.01	0
Vinyl (wt %)	0.1	0.11	0.11	0.12	0.12	0.14	0.15	0.14
Vinylidene (wt %)	0.02	0.02	0.04	0.03	0.03	0.05	0.06	0.06
T_m (°C)	136	132.3	130	128.8	128.1	127.5	128	127.1
X_c (%)	70.7	63.4	61.4	61.2	54.4	50.5	55	51.8
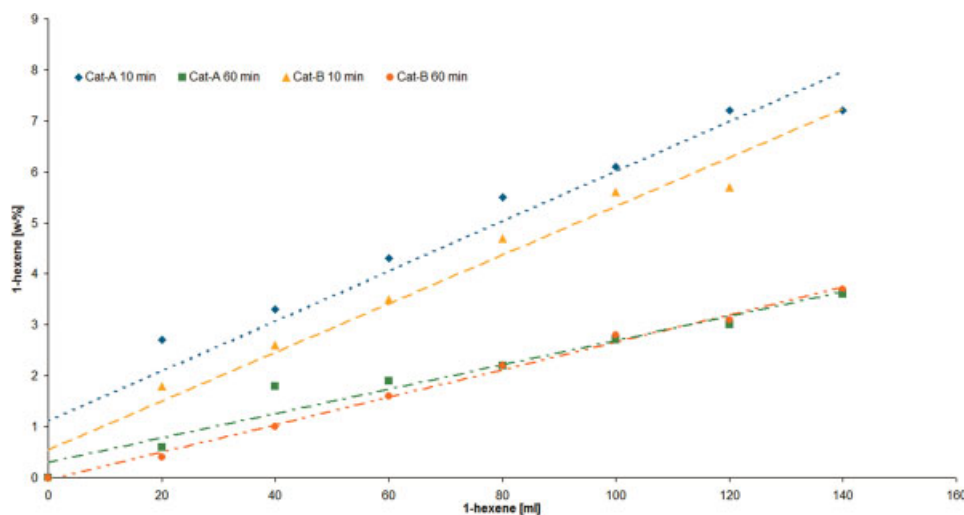
Figure 1 Incorporation of 1-hexene-*co*-monomer in ethylene polymerization when using Cat-A and Cat-B catalyst in 10- and 60-min polymerizations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature of the TCB was gradually increased from 20 to 130°C. The effluent from the column passes through a heated line to a infrared (IR) detector which was used to measure the absorbance of the effluent stream. The absorbance of the polymer carbon-hydrogen stretching bands at about 2925 cm^{-1} served as a continuous measure of the relative concentration of the polymer in the effluent. A solubility distribution curve, (i.e., a plot of weight fraction of polymer dissolving as a function of temperature), was thus obtained.

RESULTS AND DISCUSSION

Activity

The activity results indicate that in all cases there is an activating effect resulting from the addition of 1-hexene to the polymerization (Tables I–IV). This has earlier been one of the arguments backing the diffusion theory of Busico et al.[12,13,28–32] which states that polymerization of ethylene is diffusion limited and that comonomers create a looser structure in the polymer. This enables easier diffusion of the monomer into the growing polymer particles which results in higher activity in the polymerization. However, the situation seems to be more complicated as according to the results there is an increase in activity only to a certain point, whereafter activity starts to dissipate or clearly drop. In the case of Cat-A the 10-min polymerization activities reaches a maximum of about 3.5 kg PO/g cat, h^{-1} and at 50 kg PO/g cat, h^{-1} for Cat-B with a 1-hexene/ethylene monomer ratio of 1 : 1. At higher monomer ratios there is a clear decrease in the 10-min poly-

merization activities. The corresponding 60-min results with Cat-A and Cat-B show a fading out of the activity starting from the same 1-hexene/ethylene monomer ratio of 1 : 1. The results seen in this investigation can therefore not essentially support the diffusion theory.

Comonomer incorporation

Figure 1 shows the incorporation of 1-hexene when using Cat-A and Cat-B in the 10- and 60-min polymerizations. The results showed that in a 10-min polymerization Cat-A has a slightly higher incorporation of hexane compared to Cat-B, and that they showed an identical incorporation in a 60-min polymerization. The fact that both catalysts are showing the same incorporation of comonomer was noteworthy as Cat-B has traditionally been considered to have a much higher comonomer incorporation compared to Cat-A. The reason for this misunderstanding might be due to the fact that the precipitated MgCl$_2$-TiCl$_4$-based catalyst (Cat-B) generally show a much higher activity compared to a silica-based catalyst, and because of this the polymerization time has been shorter (<30 min) automatically giving a higher comonomer incorporation and thereby a misleading impression of being highly comonomer sensitive. The silica-based catalyst (Cat-A) generally shows lower activity which often results in longer polymerization time (60 min) which in turn shows up in lower comonomer incorporation, because of the time drift giving a misleading impression of a lower comonomer sensitivity.

The comonomer incorporation results further showed that the incorporation of comonomer is a
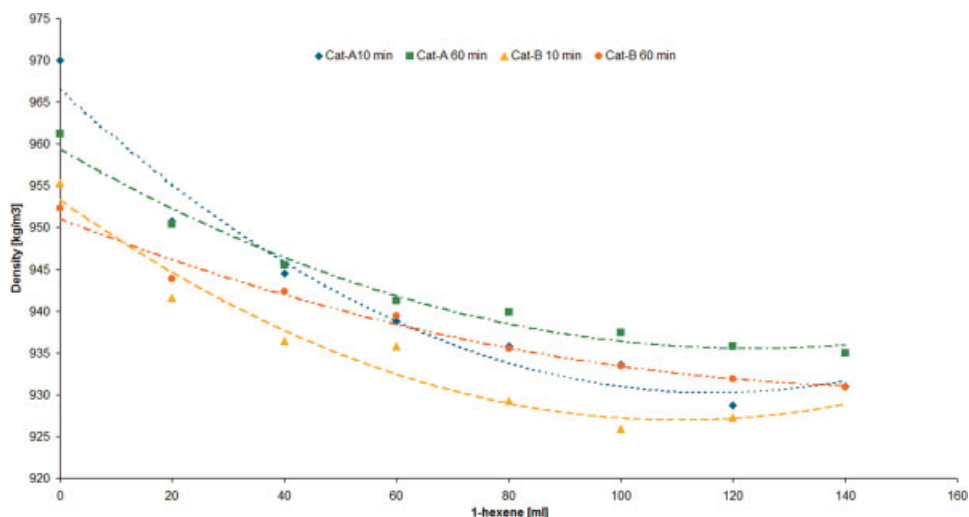
Figure 2 Density as a function of the added amount of 1-hexene in ethylene polymerization when using Cat-A and Cat-B in 10- and 60-min polymerizations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

linear function of the 1-hexene/ethylene monomer ratio, indicating a first order reaction (Fig. 1). The results also showed that the incorporation of comonomer is about twice as high in a 10-min polymerization compared with a 60-min polymerization, so confirming the time drift observations.

Bending of the density/comonomer curve

Figure 2 shows the density of the copolymers as a function of the added amount of comonomer for Cat-A and Cat-B in the 10- and 60-min polymerizations. All the curves show the same trend, (i.e., quite a harmonic decrease in density with increasing addition of comonomer down to a 1-hexene/ethylene monomer ratio of about 1 : 1 and then a strong bending in the density decrease curve). This phenomenon was observed in both 10- and 60-min polymerizations indicating that the bending cannot be explained with the oxidation state theory and the time drift theory as these theories should predict bending only in the 60-min polymerizations, and no bending or a significantly smaller bending in the 10-min polymerizations. This indicates that the time drift phenomenon and the bending phenomenon are two independent features connected to the use of typical ZN catalysts in LLD PE polymerization.

Bending of the melting point values as a function of the comonomer feed

Figure 3 shows a typical example of a DSC curve achieved of the copolymers (10-min polymerization with Cat A with 120 mL of hexene) and Figure 4 shows the melting point values (T_m) of the copolymers as a function of the added amount of 1-hexene in the polymerizations. The results are in agreement

with the results shown in Figures 1 and 2. Two groups of curves are achieved according to the two different levels of incorporated 1-hexene, namely the higher level of 1-hexene coming from the 10-min polymerizations giving the two lower curves and the lower level of incorporation originating from the 60-min polymerizations giving the upper curves in Figure 4. The split up of the curves in these two pairs on the basis of the 1-hexene occurs due to the fact that M_w does not have as much influence on the T_m values as M_w influences density. All four curves show initially a steady decrease in T_m and then the same bending of the T_m values, especially at 1-hexene/ethylene monomer ratio above 1 : 1 as seen in Figure 2. This indicates the same as was stated in connection with the density results. The results also
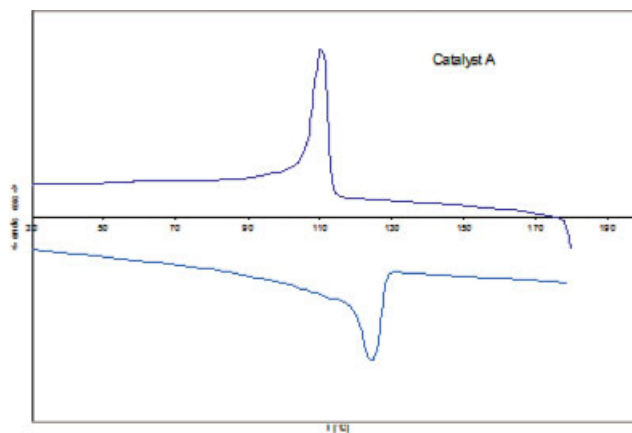

Figure 3 A typical example of a DSC curve achieved of the copolymers (10-min polymerization with Cat A with 120 mL of hexene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
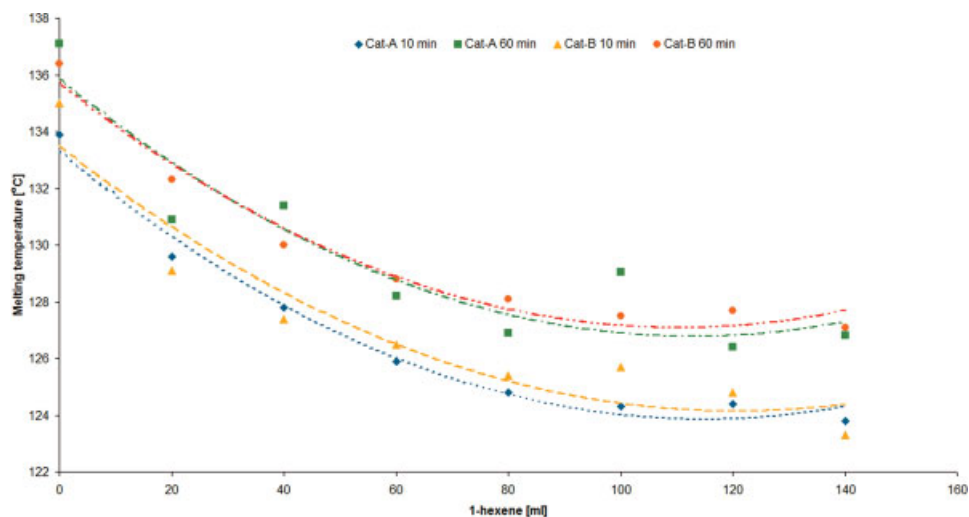
Figure 4 Melting point (T_m) of the copolymers as a function of the added amount of hexene in ethylene polymerization when using Cat-A and Cat-B in 10- and 60-min polymerizations. A typical example of a DSC curve achieved of the copolymers (10-min polymerization with Cat A with 120 mL of 1-hexene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

showed that both catalysts make similar material at the same 1-hexene/ethylene monomer feed.

Bending of the crystallinity values with increased amount of comonomer

Figure 5 shows the amount of crystalline material (X_c) in the copolymers as a function of the added amount of 1-hexene. The resulting curves are in positive agreement with the density values shown in Figure 2. First there is a steady decrease of the fraction of crystalline material (X_c) starting from 70 to 75% down to 50–55%, but at 1-hexene/ethylene monomer ratio above 1 : 1, a clear bending of the curves can be noticed. To some extent a grouping into 10- and the 60-min results can be distinguished

in the resulting group of curves. The results also indicate that there is no connection between the time drift phenomenon and the bending phenomenon, but these phenomena are separate features connected to the use of ZN catalysts in LLD PE polymerization.

Density as a function of the 1-hexene fraction

Figure 6 shows the density of the copolymers as a function of the incorporated amount of comonomer. The curves resemble much of what is shown in Figure 2, but both the resulting curves that had been obtained with Cat-B are located beneath the curves obtained with Cat-A due to the higher M_w produced
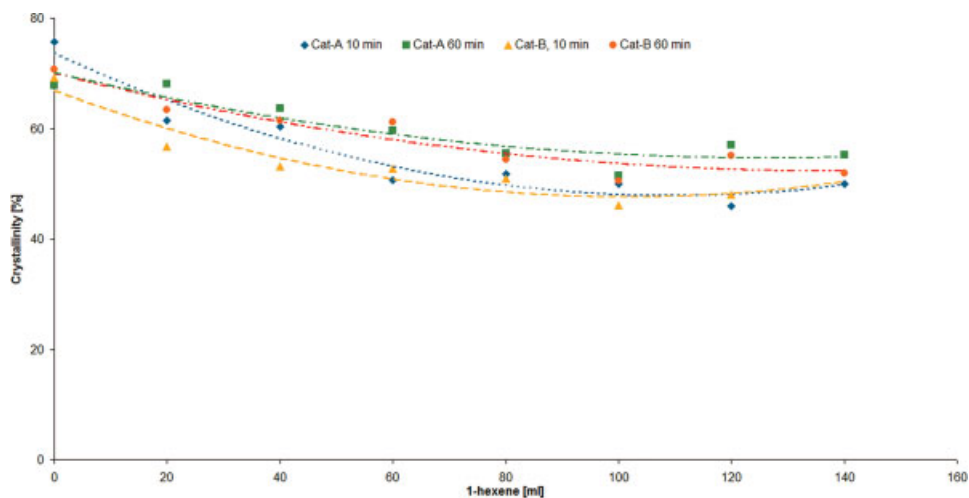

Figure 5 The DSC crystalline fraction (X_c) of the copolymers as a function of the added amount of hexene in ethylene polymerization when using Cat-A and Cat-B in 10- and 60-min polymerizations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
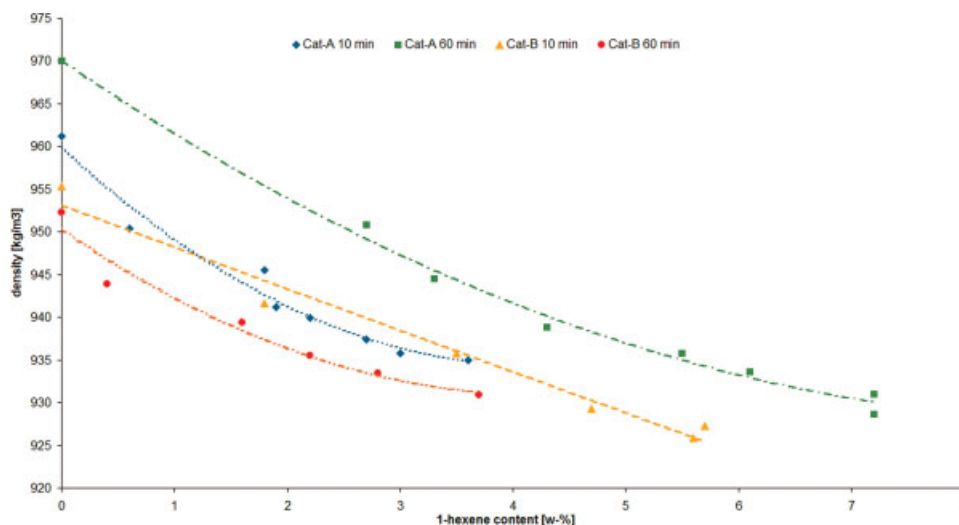
Figure 6 Density as the function of the incorporated amount of hexene in ethylene polymerization when using Cat-A and Cat-B in 10- and 60-min polymerizations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with the precipitated catalyst. M_w and comonomer equally affects the density. The same bending as seen in Figure 2 can also be seen in these curves. In some cases almost the same polymerization result has been achieved with Cat-B in the 10-min polymerizations, as was achieved with Cat-A in the 60-min polymerizations. As an example, copolymer L10 was produced with Cat-B in a 10-min polymerization giving a M_w of 157,000 g/mol with a 1-hexene content of 3.5 wt % which is comparable to the copolymer G60 obtained with Cat-A in a 60-min polymerization, giving a M_w of 129,000 g/mol and a comonomer content of 3.0 wt %. The first polymer had a density of 936.0 kg/m^3 and the second a density of 935.6 kg/m^3. These results indicate that identical material is produced by both catalysts and there is no fundamental difference in CCD in poly-

mers regardless of which catalyst has been used, and regardless of how long the polymerization had proceeded.

M_w and MFR as a function of the amount of comonomer added

As stated above the bending of the density/1-hexene % curve has been explained by a gradually lower M_w in the copolymer caused by the chain transfer of the comonomer, (i.e., the higher the comonomer weight fraction, the more chain transfer, the lower the M_w which hinders density from dropping). The results in Tables I–IV show that there is a change in M_w due to the addition of comonomer. This clearly shows in Figure 7 that are the MFR(21) values of the copolymers achieved with Cat-A in 10- and the
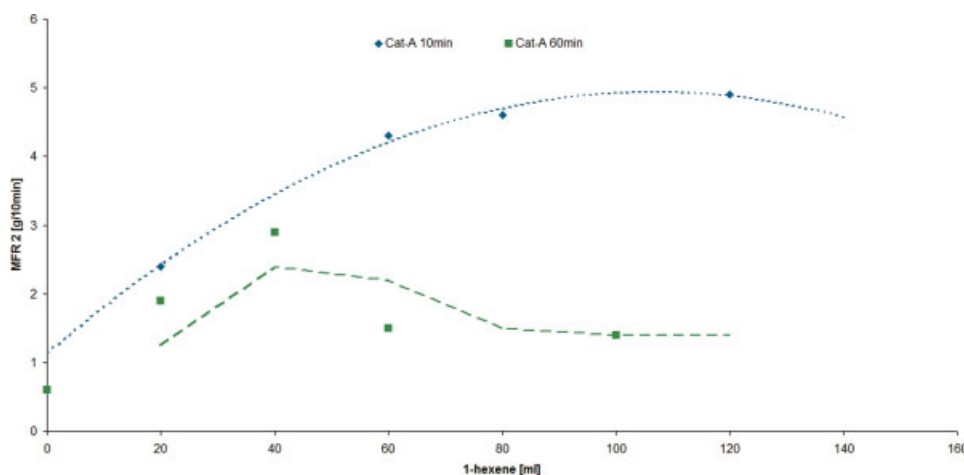

Figure 7 MFR[21] values of the hexene-*co*-polymers achieved with Cat-A in 10- and 60-min polymerizations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
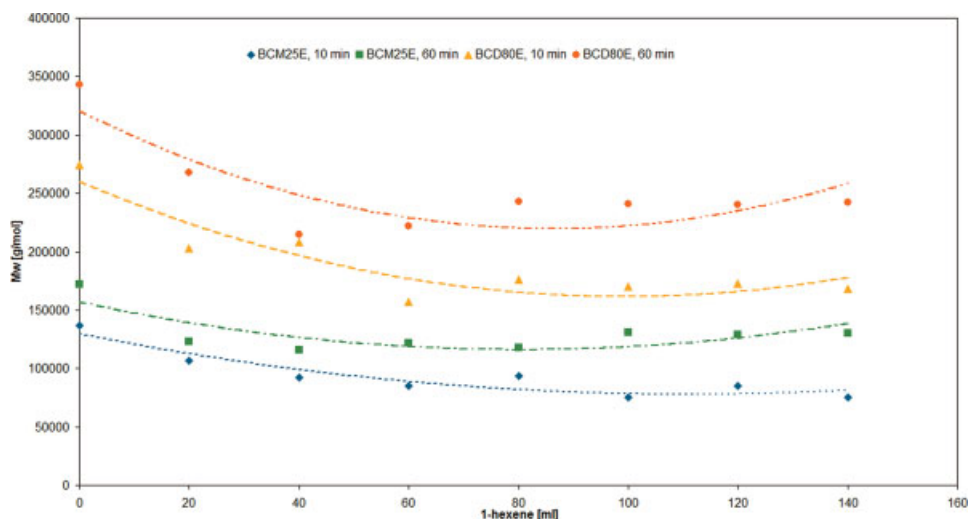
Figure 8 Molecular weight values (M_w) of the 1-hexene-comonomer in ethylene polymerization when using Cat-A and Cat-B in 10- and 60-min polymerizations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

60-min polymerizations. All the MFR curves had about the same outlook. The resulting curves showed that in the 10-min polymerizations there was a steady increase in MFR throughout the test series indicating a decrease in M_w. Contrary to this, the results from the 60-min polymerization showed an increase at the very beginning but that a maximum in the MFR value was already reached for a 1-hexene/ethylene monomer ratio of 0.5 after which MFR is rapidly decreasing to somewhere between the MFR value of the homopolymer and the maximum value. All the MFR curves from the 60-min polymerizations displayed the same behavior. The GPC curves showing the M_w and M_n values were in total agreement with the MFR curves. Figure 8 shows M_w of the copolymers as a function of the amount of comonomer added. The results from the 10-min polymerizations show a quite steady decrease, but with a pronounced decrease at the very beginning after which M_w is fading out and becoming almost constant at the very end of the test series. The change in M_w is much more dramatic in the results obtained in the 60-min runs. The 60-min polymerization results with Cat-B is a good example (Fig. 8). When polymerising in homopolymer conditions, a M_w of about 350,000 g/mol is obtained. When adding comonomer to the polymerization up to a 1-hexene/ethylene monomer ratio of 0.25 M_w drops to about 270,000 g/mol and when the 1-hexene/ethylene monomer ratio is increased to 0.5 a M_w of approximately 220,000 g/mol is obtained. This is also the lowest point on the curve. If still more comonomer is added, there is an increase in M_w to between 240,000 and 250,000 g/mol. A relatively stable plateau is seen here as no further changes in M_w can be seen at even higher 1-hexene/ethylene monomer ratios. The M_w results

therefore describe a mirror image to what was seen in the MFR results in Figure 7. Both M_w and M_n described this kind of a curve in both 10- and in the 60-min polymerization regardless of which catalyst had been used. This indicates that the same polymerization behavior takes place both in short and in long-term polymerization, and once again, that there is no link between the time drift and the bending.

These results are not in agreement with the former assumption, that the difficulty in bringing down the density values of LLDPE when using a ZN catalyst would be connected to a decrease in M_w that would counter balance the drop in density caused by an increased comonomer content. There is a decrease in Mw, indeed, but this happens at the very beginning of the test series and in the area where there is also a fastest drop in density. The situation is therefore opposite to what has previously been assumed. The reason why we see a rapid drop in M_w at the very beginning, and why this is not causing a counter balancing effect in the drop of the density is not totally clear. A possible explanation would be a dominating effect from incorporated comonomer in lowering the density in the 0–1 mol-% region.

The effect of added comonomer on MWD

It was expected that the 60-min polymerizations would show a broader MWD as it could be assumed that in these polymerizations there is first a period of high comonomer incorporation giving lower M_w during the first 10 min. After that there is a successively lower incorporation the longer the polymerization proceeds, with less degradation in M_w giving a combined M_w with a correspondingly broader MWD. In a 10-min polymerization, a more narrow

set up of M_w would form the MWD that therefore should be narrower.

The results in Tables I–IV showed that the situation was close to the opposite to what could have been anticipated. All the MWD results from the 60-min runs turned out to have a MWD of about five. The MWD results from the 10-min polymerizations were in the case of Cat-A clearly higher, being between six and eight. In the case of Cat-B, the MWD values were in the beginning of the test series also around 5, but dramatically increased at the end of the test series. So also in this case the situation resulted in being more complex and can only to partially be explained by the instable run conditions in the 10-min polymerizations.

TREF curves from the 10- and 60-min copolymers

According to the oxidation state theory Ti(II) is gradually formed during polymerization because of the reductive power of the cocatalyst. Ti(II) is known not to polymerize comonomers but only ethylene giving rise to the distinct HD peak in the TREF curves. The longer the polymerization, the more Ti(II) is formed and the higher the high density peak in the TREF diagram. This would also explain the polarization seen when trying to force down density when using a ZN catalyst by increasing the comonomer to extreme values. This would only result in obtaining a very high XS % but an almost unchanged high density fraction. Here the comonomer wouldbe extensively incorporated at the beginning of the polymerization when Ti(IV) and Ti(III) are still available and at the end of the polymerization the high density peak would be formed by Ti(II). If this theory holds, then a much lower HD peak would be seen in a TREF curve from a 10-min
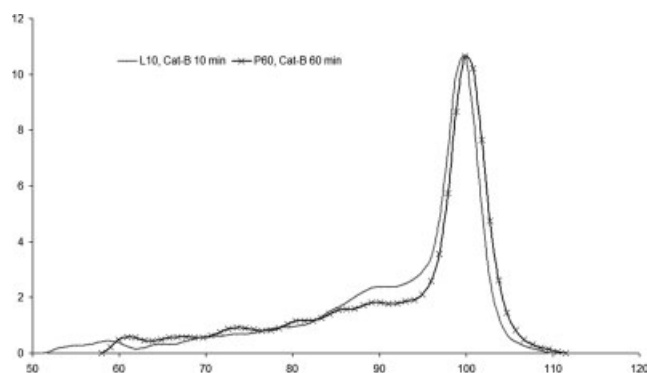

Figure 9 TREF curve of the L10 hexene-*co*-polymer achieved with Cat-B in a 10-min polymerization having 3.5 wt % of hexene-comonomer compared with the TREF curve of the P60 hexene-*co*-polymer achieved Cat-B in a 60-min polymerization having 3.7 wt % of hexene-comonomer. X-axis in TREF curve is elution temperature, Y-axis in TREF curve is eluted weight fraction.

Figure 10 TREF curves of the G60 and H60 hexene-copolymers obtained with Cat-A in 60-min polymerizations having 3.0 and 3.6 wt % of hexene-comonomer in comparison with the TREF curve of the C10 hexene-copolymer achieved with Cat-A in a 10-min polymerization having 3.3 wt % of hexene-comonomer. X-axis in TREF curve is elution temperature, y-axi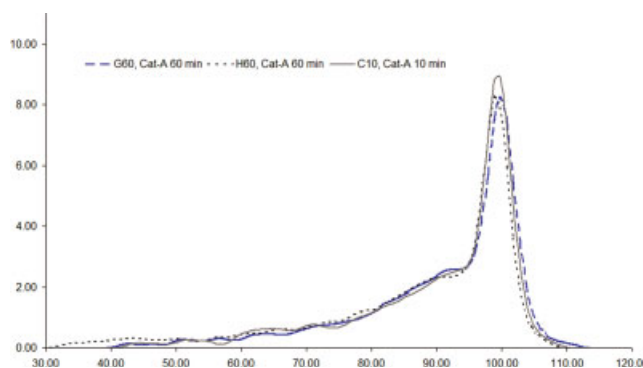s in TREF curve is eluted weight fraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymerization compared with a TREF curve from a 60-min polymerization.

As TREF curves are not so much dependent on M_w but far more on the comonomer set up, three comparable copolymers could be found in the Cat-A test series, namely G60 and H60 from the 60-min test series and C10 from the 10-min test series, having hexane contents of 3.0, 3.6, and 3.3%. The TREF curves of these three copolymers are shown in Figure 9. Two comparable copolymers were found in the Cat-B test series, namely L10 from the 10-min test series and P60 from the 60-min test series. The TREF curves of these two copolymers are shown in Figure 10. In both cases, when comparing the resulting TREF curves, no significant difference could be seen when comparing the TREF curves originating from the 10-min polymerization with the TREF curves originating from the 60-min polymerization, as almost identical TREF curves were obtained. This result showed that exactly the same type of material with the same CCD is produced at the beginning of the polymerization and at the end of a long-term polymerization. The results further showed that the time drift phenomenon and the bending phenomenon are two independent features of the polymerization when using ZN catalysts. The time drift is independently changing the comonomer sensitivity of the catalyst by time and the bending being dependent on the 1-hexene/ethylene monomer ratio only.

CONCLUSIONS

1-Hexene activates SiO_2 and $MgCl_2$-based ZN catalysts (Cat-A and -B) up to 1-hexene/ethylene

monomer ratio of about 1 : 1 after which activity dissipates or decreases. Cat-A and Cat-B have the same ability to incorporate 1-hexene, but twice as much 1-hexene is incorporated in a 10- compared with a 60-min polymerization due to the time drift phenomena.

Both catalysts show a strong bending when density is presented as a function of 1-hexene both in a 10- and in a 60-min polymerization indicating no connection between time drift and bending. The melting point results display the same as the density results, indicating no connection between time drift and bending. The crystallinity results also support the previous findings by indicating no connection between time drift and bending.

The density, melting point and crystallinity results all indicate that both Cat-A and Cat-B are producing a similar kind of copolymer material. Density plotted as a function of 1-hexene amount of polymer curve indicates that both Cat-B and Cat-A produces the same 1-hexene copolymer with the same CCD. The TREF curves indicated that the same type of copolymer was produced regardless of polymerization time. Identical chemical composition distribution was achieved in 10- and 60-min polymerizations, indicating no connection between time drift and bending.

There is a rapid drop in molecular weight and M_n for small additions of comonomer in the polymerization. However for 1-hexene/ethylene monomer ratios above 0.5 M_w and M_n slightly increases and then stabilizes showing no further change even if the 1-hexene/ethylene monomer ratio is significantly increased. Ten minutes polymerization gives, for some reason, a broader molecular weight distribution compared with 60-min polymerizations.

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