

Effect of Dimethyl Formamide in the Synthesis of Linear Low Density Polyethylene on Branched and Molecular Structure

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Received 9 November 2010; accepted 1 April 2011

DOI 10.1002/app.34619

Published online 15 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this research work, effect of dimethyl formamide (DMF) as an external electron donor in gas phase ethylene/1-butene copolymerization process in the presence of Ziegler–Natta catalyst has been investigated. Different experiments were performed using $\text{TiCl}_4/\text{MgCl}_2$ as catalyst, triethyl aluminum as cocatalyst and in the presence of various amounts of DMF as an external electron donor. Then, effect of DMF on various parameters such as catalyst activity, molecular weight, and short chain branching content of the samples has been studied. The results showed that the more the ratio of DMF/Ti, the

lower the catalyst activity. Moreover, the curves relating molecular weight and short chain branching content of the samples to the ratio of DMF/Ti passed through an extremum point at about DMF/Ti = 0.25. A justification for the occurrence of the extremum point has been proposed in this research work, and some analysis methods are adopted to confirm the suggested justification. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1267–1272, 2012

Key words: Ziegler–Natta polymerization; polyethylene; branched; dimethyl formamide

INTRODUCTION

Despite the considerable academic and industrial interests in homogeneous, single site metallocene catalysts, the fact remains that the vast majority of polyolefins are commercially produced from heterogeneous Ziegler–Natta (Z–N) catalysts.¹ Z–N catalysts are mostly recognized by multiple active sites.² Improvements in catalyst design are due to new and better electron donors used to modify the active sites of Z–N catalysts.³

Among all polyethylene (PE) production processes, gas phase polymerization is the most versatile and developed one because of its economical and technological advantages.⁴ British Petroleum Chemical has used prepolymerization step before gas phase polymerization to improve the functionality and activity of the catalysts.^{5–8} In this method, the prepolymerization process is done in a semibatch reactor, and the produced prepolymer is dried by hot nitrogen gas at the end of the process. Then, the dried prepolymer powder is fed to the main gas phase polymerization reactor under nitrogen blanketing. In gas phase polymerization step, catalyst activity is controlled by activity retarding agents. Electron donor compounds such as amines, amides,

phosphines, esters, and ethers are activity retarders capable of producing complex with catalysts and reducing the polymerization rate. Because of various effects of electron donor on quality and properties of the final polymer, such as molecular weight, MWD, stereo-specificity of polymer, melt flow index, and so forth, the extent of electron donor should be exactly controlled.⁹

Several research works have focused on the effect of different external electron donors on the yield of olefin polymerization. Karol et al. have studied the effect of ether type external electron donors on activity of vanadium and titanium catalysts.¹⁰ Their results showed that the presence of external electron donor would lead to decrease in catalyst activity; however, this reduction was related to ether type.¹⁰ Lim et al. focused on the effect of *para*-ethoxy ethylbenzoate (PEEB) on the catalyst activity and isotacticity of produced polypropylene in the gas phase polymerization.¹¹ Their results indicated that with increase in PEEB amount, the catalyst activity would be reduced, but polymer isotacticity would be increased. In another study, Chen et al. demonstrated that the presence of diphenyl dimethoxyl silane (DDS) in high ratio (DDS/Ti = 5) would lead to decrease in catalyst activity, increase in molecular weight of polyethylene, and decrease in polydispersity index.¹²

In this work, the influence of dimethyl formamide (DMF) as an external electron donor in gas phase ethylene/1-butene copolymerization process with $\text{TiCl}_4/\text{MgCl}_2$ catalyst and triethyl aluminum

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TABLE I
Yielded Polymer for Different Experiments at 80°C and 20 bar Pressure

Sample	Al/Ti	DMF/Ti	Yielded PE (g)
1	10	0.0	250
2	10	0.05	239
3	10	0.1	215
4	10	0.15	205
5	10	0.25	194
6	10	0.5	75

cocatalyst is investigated. At first different experiments were performed using various amounts of DMF as external electron donor. Then, effect of DMF on various parameters such as catalyst activity, molecular weight, and short chain branching (SCB) content of the products has been studied.

EXPERIMENTAL

Materials

The solution of supported $\text{TiCl}_4/\text{MgCl}_2$ catalyst in *n*-hexane (200 mmol Ti/L) supplied from Tabriz Petrochemical was used as received. The solution of triethyl aluminum (TEAL) cocatalyst in *n*-hexane (1000 mmol Al/L) was purchased from Aldrich. Ethylene and hydrogen gases (99.999%) were supplied from Air product. Nitrogen gas was provided from Technical gas services. All gases were further purified by passing through the columns packed by molecular sieves that were able to absorb humidity, CO_2 , and sulfur compounds.

Polymerization

The prepolymerization procedure used in this research work was based on conventional industrial process of British Petroleum Chemical.⁶⁻⁹ The slurry prepolymerization reactions of ethylene were performed in a 1-L jacketed round bottom stainless steel reactor equipped with a mechanical spiral stirrer and oil circulating temperature control system. After purging the reactor by nitrogen for 2 h at 80°C, the reactor was cooled up to 60°C and 200 mL of *n*-hexane was transferred to the reactor under nitrogen blanketing. Then, 1.5 mmol of cocatalyst, 0.15 mmol of catalyst and appropriate amount of DMF external electron donor were injected to the reactor by gas tight syringe under nitrogen atmosphere. At 60°C ethylene was continuously fed to the reactor with a constant flow rate for about 120 min until prepolymer with 40 g PE/mmol Ti was obtained. The prepared prepolymer was dried by the nitrogen flow at 60°C. Then, to disperse the prepolymer particles inside the reactor, the speed of the stirrer was increased to 1000 rpm and gas phase polymerization was started by introducing the reactants to that

same reactor of prepolymerization step. The partial pressure of reactants in the gas phase polymerization was as follows: 2 bar hydrogen, 3 bar 1-butene, 8 bar nitrogen, and ethylene with 7 bar pressure was continuously fed to the reactor, so that the polymerization was conducted under total pressure of 20 bar at 80°C for 120 min. It should be noted that the repeatability of the experiments (done with and without DMF) was checked by characterizing of the samples that were synthesized twice.

Measurements

MWD measurements were carried out in Waters 2000 ALLIQNCE gel permeation chromatography apparatus equipped with a differential refractive index detector at 135°C. 1,2,4-Trichlorobenzene was used as the solvent.

Differential scanning calorimetry (DSC) apparatus used in this research work was Mettler Toledo Stare system 822 Module, interfaced to a digital computer equipped with Star^e software.

Short chain branching contents of the samples were determined by the use of DSC thermo-grams in a way, which has been reported recently.¹³

RESULTS AND DISCUSSION

Different experiments were performed using $\text{TiCl}_4/\text{MgCl}_2$ as catalyst and TEAL as cocatalyst in the presence of various amounts of DMF as an external electron donor in the way described in "Experimental" section. The results are summarized in Table I.

Catalyst activity is calculated by the following equation:

$$E = \frac{Y}{\text{Ti} \times t} \quad (1)$$

where Y is the yielded polymer in grams, Ti is the used titanium in mmol, t is the duration of

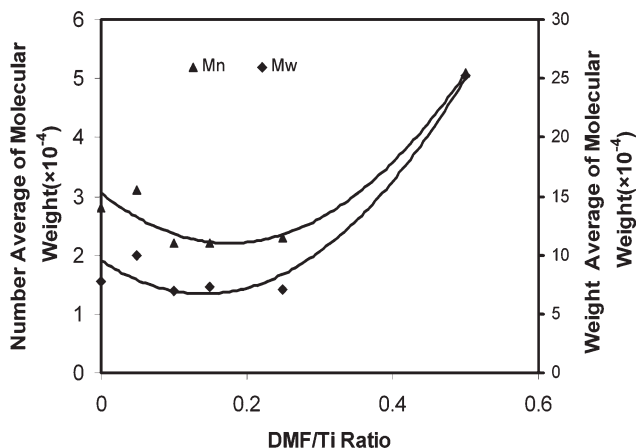


Figure 1 Effect of DMF/Ti ratio on molecular weight.

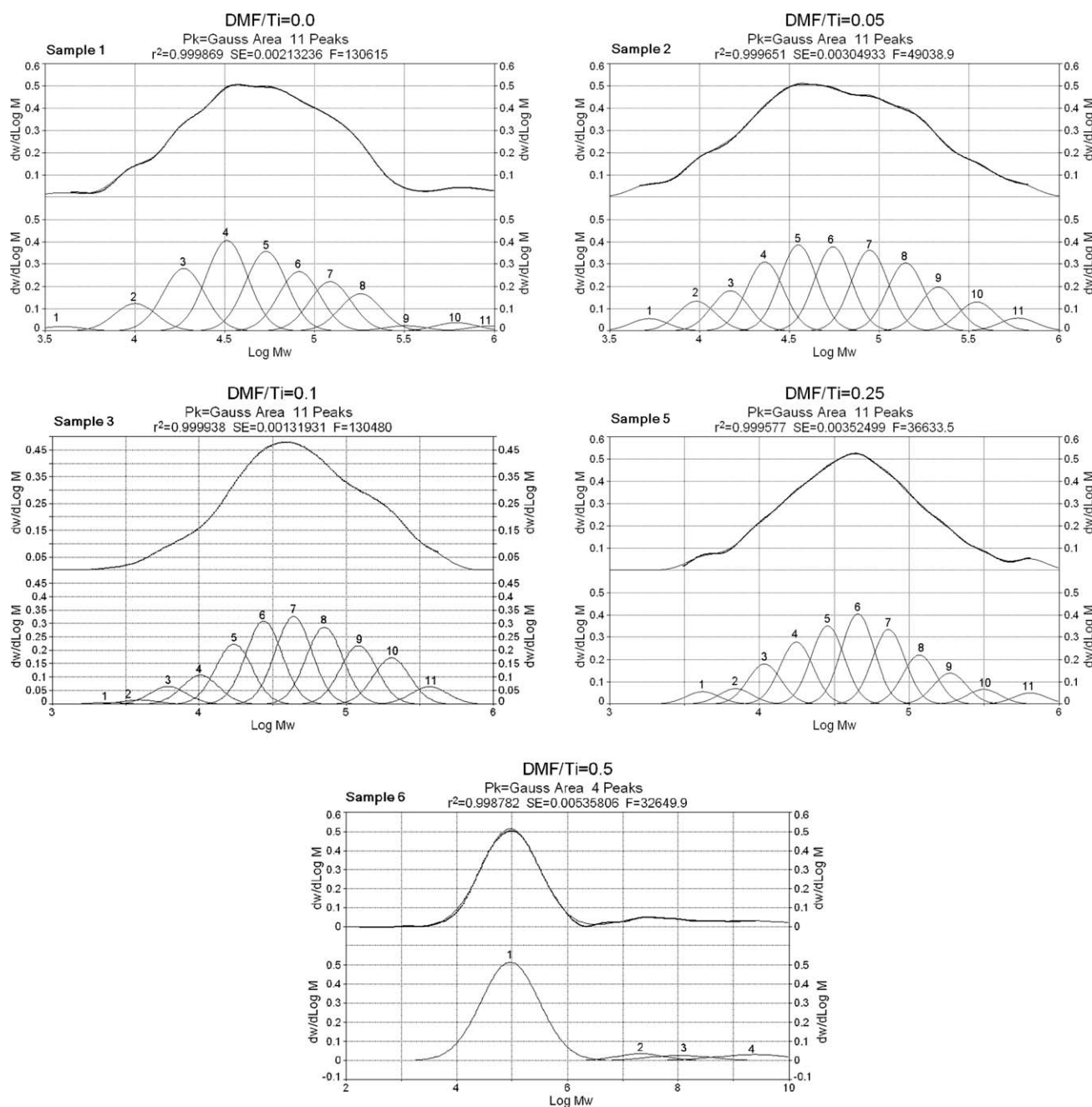


Figure 2 MWD curves and deconvoluted peaks of the samples.

polymerization in hour, and E is the catalyst activity in g/mmol Ti h.

As it can be seen, the increase of DMF/Ti ratio reduces the catalyst activity, but the intensity of reduction is more profound after DMF/Ti = 0.25. This is due to the mechanism of the performance of an external electron donor. The external electron donor is able to both, transfer (convert) active sites and/or annihilate them selectively.¹⁴ According to the obtained results it seems that, up to the ratio of about DMF/Ti = 0.25 the external electron donor tends to transfer (convert) some active sites which are able to produce linear chains (with higher molecular weights) to the

ones capable of producing branched chains (with lower molecular weights). As these new sites are less active than the originals, the catalyst activity will be reduced. At DMF/Ti ratio more than 0.25, in addition to the mentioned mechanism, a fraction of external electron donors will annihilate some of the active sites. Therefore, the activity of the catalyst will reduce intensively over the ratio of DMF/Ti = 0.25. This suggestion has been confirmed in other parts of this article.

Molecular weight

The effect of DMF electron donor on number average molecular weight (M_n) and weight average

TABLE II
Relative Area Under Deconvoluted Peaks of MWD Curves of the Samples

Mw of deconvoluted peaks	Sample 1	Sample 2	Sample 3	Sample 5	Sample 6
2000–4000	–	–	% 0.1	–	–
4000–6000	% 1	% 2	% 1	% 3	–
6000–7000	–	–	% 4	% 3	–
9000–12,000	% 6	% 5	% 6	% 8	–
14,000–20,000	% 15	% 7	% 12	% 13	–
20,000–30,000	–	% 12	% 17	% 16	–
30,000–40,000	% 21	% 15	–	–	–
40,000–60,000	% 19	% 15	% 18	% 19	–
65,000–75,000	–	–	% 16	% 16	–
80,000–90,000	% 14	% 15	–	–	–
90,000–100,000	–	–	–	–	% 84
115,000–125,000	% 12	–	% 12	% 1	–
135,000–180,000	% 9	% 12	–	–	–
180,000–210,000	–	–	% 1	% 6	–
210,000–250,000	–	% 8	–	–	–
250,000–400,000	% 1	% 5	% 4	% 3	–
400,000–600,000	–	% 2	–	–	–
600,000–700,000	% 2	–	–	% 2	–
700,000–1,000,000	% 1	–	–	–	–
1,000,000–1,500,000	–	–	–	–	–
1,500,000–2,000,000	–	–	–	–	–
$20 \times 10^6 - 50 \times 10^6$	–	–	–	–	% 5
$100 \times 10^6 - 200 \times 10^6$	–	–	–	–	% 4
Over 200×10^6	–	–	–	–	% 7
Total number of deconvoluted peaks	11	11	11	11	4

molecular weight (Mw) of the samples has been shown in Figure 1. According to this figure, there is a slight reduction in Mn and Mw up to the ratio of about DMF/Ti = 0.25, but more increase in electron donor content will increase both of them intensively. As it was suggested before, up to the ratio of DMF/Ti = 0.25, some active sites, which are able to produce linear high molecular weight chains, are converted to the sites capable of producing branched low molecular weight chains. Because of this, there is a reduction in Mw and Mn. At the ratios of DMF/Ti higher than 0.25, some active sites will be annihilated by DMF. Therefore, the number of active sites is decreased, which is synonymous to increment of chain length and their molecular weights.

Deconvolution of molecular weight distribution curves

It has been proved that deconvolution of molecular weight distribution (MWD) curve of a polymer by multiple Gaussian functions is an effective method to study the distribution of active sites of the catalyst.¹² It is believed that each Gaussian component belongs to the distribution curve of a group of polymer chains which are produced by one type of active center.

In this research work, deconvolution of size exclusion chromatography (SEC) diagrams was performed by Peakfit software (Version 4.06). The results are shown in Figure 2 and summarized quan-

titatively in Table II. The numbers in Table II denote the relative area under each Gaussian peak. As it can be seen, increasing of DMF/Ti ratio up to 0.25 has no effect on the total number of deconvoluted peaks (all of these samples have been deconvoluted to 11 peaks). As each Gaussian peak is related to a type of active sites, it can be concluded that increasing of DMF/Ti ratio up to 0.25 does not annihilate the active sites but converts some of them to other kind of active centers. As it was suggested before, the active sites which are able to produce linear high molecular weight chains are converted to the sites capable of producing branched low molecular chains. Because of this, up to DMF/Ti = 0.25, the peaks with higher Mw are disappeared (follow the arrows in Table II). According to Table II, for DMF/Ti = 0.5 the number of peaks has been diminished to four peaks, which confirms the annihilation of some of the active centers. Obviously, the reduction in number of active sites will cause increment of chain length and their molecular weight.

Short chain branching content

The number average short chain branching content (C_n) and weight average short chain branching content (C_w) of the samples were measured from DSC thermograms with the use of a new method reported previously.¹³ The variation of C_n and C_w versus DMF/Ti is illustrated in Figure 3. Again a

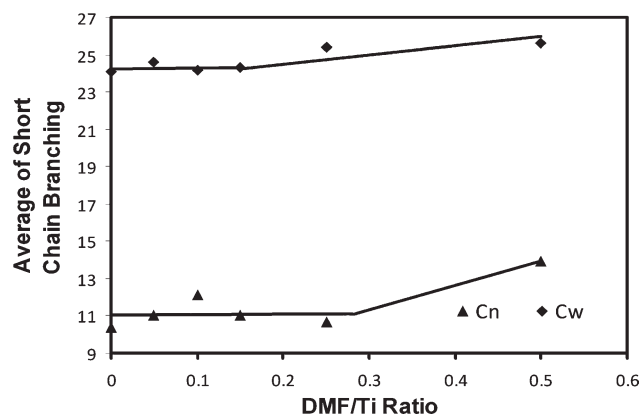


Figure 3 Effect of DMF/Ti ratio on SCB content.

slight increase in C_n and C_w up to DMF/Ti ratio of about 0.25 confirms the conversion of some active sites which are able to produce linear chains (with high Mw) to the ones capable of producing branched chains (with low Mw). At higher ratios of DMF/Ti, in addition to the mentioned mechanism, the external electron donor (DMF) starts to annihilate some of the active sites especially the ones, which are able to produce linear chains. Therefore, the number and weight average of short chain branching content will increase more intensively.

Fractionation of the samples by DSC

To confirm the suggested justification, all of the samples were fractionated by multiple step isothermal crystallization method with the use of differential scanning calorimetry technique.¹⁵ The annealing steps were performed as follows: First, the sample was heated to 160°C at a rate of 10°C/min and maintained at this temperature for 10 min (to eliminate thermal history of the sample). Then, the sample was cooled rapidly to the first isothermal crystallization temperature at a rate of 200°C/min and the isothermal crystallization step was lasted for 45 min.

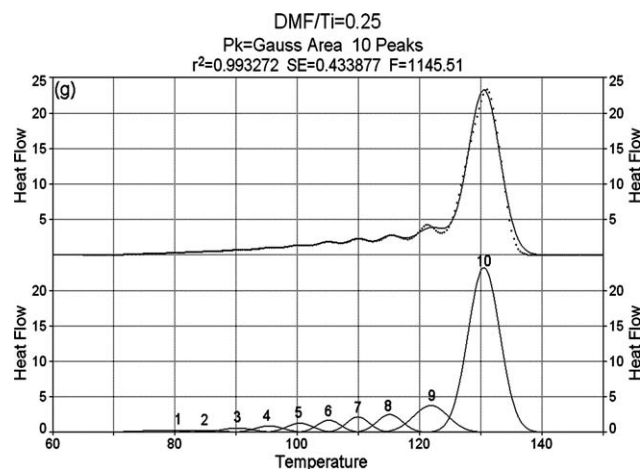


Figure 4 DSC thermogram and deconvoluted peaks of sample 5.

The temperature decrement of steps was 5°C in the range of 135–70°C. The annealed sample was thereafter heated by 10°C/min, and melting endotherms were recorded. Figure 4 shows DSC thermogram for one of the samples after fractionation as an example. Each peak belongs to a family of lamellas with specified thickness corresponding to the chains with specific SCB content.¹⁶ With the use of Peakfit software (Version 4.06) the thermogram of the fractionated sample was deconvoluted to several Gaussian peaks (see Fig. 4). The maximum temperature of each peak is simply related to a defined SCB content.¹⁶ The relative area under each peak denotes the amount of chains of the sample having this SCB content. The results for all of the samples are summarized in Table III. The numbers in this table denote the relative area under each peak with a specific SCB/1000C. For better comparison, the percentage of linear chains (chains with less than 9 SCB/1000C) and high-branched chains (chains with more than 27 SCB/1000C) are plotted against DMF/Ti ratio in Figure 5. According to this figure, up to the ratio of

TABLE III
Relative Area Under Deconvoluted Peaks of DSC Thermograms of Fractionated Samples

SCB/1000C	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
35	1.45	1.28	1.61	1.76	2.32	3.25
31	1.10	1.40	1.66	1.35	0.93	1.94
28	1.12	1.39	1.41	1.07	1.10	2.11
25.5	2.02	1.62	1.77	1.63	1.93	3.12
22.5	2.63	3.00	3.67	2.48	3.06	4.70
19	3.05	3.35	2.78	2.78	2.87	5.43
16	4.25	3.95	6.28	4.67	5.88	8.86
13	2.84	7.26	4.95	4.82	4.40	8.82
8.75	20.03	6.54	10.46	6.95	9.80	19.64
3.75	61.52	70.21	65.41	72.48	67.71	42.13
Less than 9	81.55	76.75	75.87	79.43	77.5	61.77
More than 27	3.67	4.07	4.68	4.18	4.35	7.3
Between 9 and 27	14.79	19.18	19.45	16.38	18.14	30.93

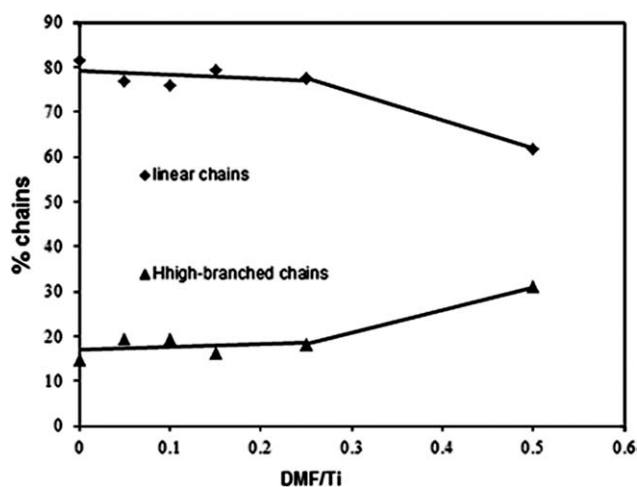


Figure 5 Effect of DMF/Ti ratio on the percentage of linear and branched chains.

DMF/Ti = 0.25 a slight increase in high-branched chains and slight reduction in linear chains are observed which is due to the conversion of active sites, which are able to produce linear chains (with high Mw) to the ones capable of producing branched chains (with low Mw). As it was suggested before, at ratios of DMF/Ti higher than 0.25 some of active centers which are responsible to produce linear chains will be annihilated. Because of this, the intensity of reduction in percentage of linear chains (and obviously increase in percentage of branched chains) in this region has been increased.

CONCLUSIONS

In this research work, the effect of DMF as an external electron donor in gas phase ethylene/1-butene copolymerization process in the presence of Ziegler-Natta catalyst has been investigated. Different experiments were performed using $\text{TiCl}_4/\text{MgCl}_2$ as catalyst, triethyl aluminum as cocatalyst, and in the presence of various amounts of DMF as an external electron donor. It has been concluded that up to the ratio of DMF/Ti about 0.25 the external electron donor tends to transfer (convert) some active sites, which are able to produce linear higher Mw chains to the ones capable of producing branched lower

Mw chains. At higher ratios of DMF/Ti, in addition to the mentioned mechanism, the external electron donor (DMF) starts to annihilate some of the active sites especially the ones which are able to produce linear chains. According to the suggested mechanism, the following obtained results were justified:

1. Increase of DMF/Ti ratio reduces the catalyst activity, but the intensity of reduction is more profound after DMF/Ti = 0.25
2. There is a slight reduction in Mn and Mw up to the ratio of DMF/Ti = 0.25, but more increase in electron donor content will increase both of them intensively.
3. There is a slight increase in the number and weight average of short chain branching content up to DMF/Ti ratio of about 0.25, but more increase in electron donor content will increase C_n and C_w more intensively.

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