

A practical criterion for synthesizing ethylene-1-butene copolymer in powder form in slurry polymerization with a Ziegler-Natta catalyst and predicting its incorporated 1-butene

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ABSTRACT

The concentration of ethylene and 1-butene in *n*-hexane as polymerization media was calculated at five different pressure levels (4, 6, 8, 10, and 12 bar) and four different 1-butene concentrations (0.13, 0.26, 0.39, and 0.52 mol/L) in *n*-hexane at $T = 80^{\circ}\text{C}$ using the Peng-Robinson thermodynamic equation of state. Some combinations of conditions were selected to perform the copolymerization reaction in the presence of an industrial $\text{TiCl}_4/\text{MgCl}_2$ Ziegler-Natta catalyst. The forms of the synthesized products were visually and qualitatively classified as either powder or sticky. The percentage of incorporated 1-butene comonomer into the polyethylene chains was analyzed using calibrated FTIR tests. It was shown that for ethylene/1-butene concentration ratios (β) in *n*-hexane above approximately 1.80, the product forms as a powder. For values below 1.30 threshold, the product was sticky. Thus, this ratio could be used as a criterion for selecting the proper combination of copolymerization pressure and 1-butene concentration when aiming to achieve a powdered form of the product. It was shown that β has a strong correlation with the weight percentage of 1-butene in the final LLDPE polymer. Therefore it can be used as an accurate prediction for wt.% of incorporated 1-butene into the LLDPE chain within the studied concentration ranges with the specific catalyst system utilized. **Polyolefins J (2023) 10: 243-251**

Keywords: Ziegler-Natta catalyst; LLDPE; ethylene-1-butene copolymerization; 1-butene incorporation; Peng-Robinson equation of state.

INTRODUCTION

Linear low-density polyethylene (LLDPE) is an important polymer belonging to the α -olefin family, primarily used in packaging film applications [1-7]. In recent years, linear low-density polyethylene consumption has continued to grow globally. The report published by Express Wire claims that the global market size will reach 48610 million USD by 2026 [8]. Its structure consists of a linear chain of repeating units of ethylene with higher α -olefin comonomers such as 1-butene, 1-hexene, 1-octene or longer comonomers

incorporated into the backbone of the LLDPE chain [9,10]. However, the most common comonomers used in the industry for synthesizing LLDPE are 1-butene, 1-hexene and 1-octene [10]. Normally, the synthesis of LLDPE occurs within gas phase reactors in the industry [10]. However, in the lab, when it is not a primary concern to strictly synthesize LLDPE in the gas phase, it is much easier to synthesize LLDPE in the slurry phase, where the final incorporation of 1-butene into the chain is not in high ranges, because

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of the difficulties associated with the proper and consistent fluidization of polymer particles in gas phase laboratory reactors, as well as the need for precise control of reaction media temperature and its uniformity. However, synthesizing LLDPE in the slurry phase using 1-butene as a comonomer in high percentages of incorporated 1-butene leads to the formation of a sticky product composed of polymer particles that are stuck together. However, in certain researches, achieving a desirable morphology for the final polymer, especially in powder form, is one of the objectives. Investigating the changes in particle size distribution (PSD) and morphology may also be one of the primary parameters to be studied. In such cases, when copolymerization reactions need to be conducted under different pressures or concentrations of 1-butene, it is impossible to predict the final form of the product in order to prevent it from becoming sticky before the polymerization reaction is carried out. So, the only option is to conduct the polymerization reaction, which will be time-consuming and increase costs.

As is known, ethylene is a much more reactive monomer towards ZN-type catalysts compared to 1-butene in the copolymerization of ethylene with 1-butene [11]. Despite this difference in reactivity, it is important to note that ethylene is in a gaseous state under normal reaction conditions. However, in slurry polymerization, it needs to be dissolved in the media to reach the active centers. Therefore, the relative concentration of ethylene to 1-butene in the media becomes crucial in determining the microstructure and characteristics of the final product. It has been observed that under reaction conditions with low concentrations of 1-butene in the media or high pressures of ethylene, the product is in powder form. However, as the concentration of 1-butene in the media increases or the pressure of ethylene in the reaction decreases, resulting in a decrease in the relative concentration of ethylene to 1-butene, the product tends to form powders that are suspended in a sticky media. After drying, these powders form a continuous rigid mass instead of distinct separated particles. So, it was assumed that there must be a turning point in the ethylene/1-butene concentration ratio in the media, as well as the amount of incorporated 1-butene, beyond which the final product would be non-sticky and in powder form and below that point, the product tends to be sticky. This study aimed to determine this relative concentration value and its corresponding 1-butene incorporation into the polyethylene chain. Because

of the increase in the incorporation of 1-butene into the LLDPE chains, the chains with higher levels of incorporated 1-butene will dissolve in *n*-hexane as media and form a sticky product.

To do this, there was a need to find an efficient and accurate equation of state (EoS) for the participants involved in the polymerization reactor (*n*-hexane as media, ethylene and 1-butene). Using such an EoS, one can accurately calculate the concentration of each monomer in a media under different reaction conditions, such as pressure and temperature. On the other hand, cubic equations of state (cubic EoS) play a fundamental role in the chemical industry, especially in the petrochemical industry [12]. The two most popular cubic EoS are the Redlich-Kwong (RK) [12] and the Peng-Robinson (PR) [13,14] EoS. The preference for this type of model is mainly due to its simplicity and accuracy, particularly in relation to hydrocarbon processing [15]. The advantages of these two methods include accurate behavior prediction, easy adaptation to improve accuracy in volumetric and thermodynamic properties calculations, and easy extension to mixtures, among others [12]. However, the Peng-Robinson model EoS has been proven to be very effective in modeling the behavior of hydrocarbons, including ethylene, 1-butene and *n*-hexane [16-21]. So, to investigate the mentioned hypothesis, the Peng-Robinson EoS was used to calculate the concentration of the two monomers (ethylene and 1-butene) in both the vapor and liquid phases in the reactor. The reactor was filled with *n*-hexane as the reaction media, and the experiments were conducted at a constant temperature with varying reaction pressures. Some of the reaction conditions and the intervals between them were selected to carry out the copolymerization reactions. Then, the final product was visually inspected to assess its morphology as being in powder or sticky form and analyzed using a calibrated FTIR test to determine the amount of 1-butene incorporated into the synthesized LLDPE copolymer. This was done in order to determine the assumed concentration ratio of ethylene to 1-butene in the reaction media. This ratio would determine whether the product would be in powder form or sticky form, as well as the corresponding amount of incorporated 1-butene.

EXPERIMENTAL

Materials

The catalyst used for polymerizations was an

industrial fourth-generation Ziegler-Natta catalyst based on $\text{TiCl}_4/\text{MgCl}_2$ as the catalyst and TEA as the cocatalyst. Triethylaluminium (TEA, 25% w/w in hexane) was supplied by Sigma-Aldrich. C-donor was supplied Chemtura (99.8% purity). Liquid *n*-hexane was supplied from a functioning polyethylene plant (Arak Petrochemical Company). Ultra-pure nitrogen (99.999% purity), propylene (99.95% purity), and ethylene (99.95% purity) gases were supplied by Roham Gas Company and used in the polymerization reaction without any additional handling or treatment. 1-Butene (99.95% purity) was supplied by Amirkabir Petrochemicals.

Polymerization procedure

Polymerization was carried out in a 1-L steel reactor equipped with a mechanical agitator and a high-pressure catalyst/co-catalyst/external donor injection apparatus. The polymerization temperature was automatically controlled around the set point by circulating oil between the inner and outer walls of the reactor. Ethylene consumption during the polymerization reaction was compensated for by regulating the flow of ethylene gas through a mass flow controller, which maintained the reactor pressure at the desired level. Before each polymerization reaction, the reactor was first filled with nitrogen gas up to 5 bar and then vented suddenly for 10 times to ensure purging of all the dead corners. After that, the reactor was purged at 115°C for about one hour with a flow of nitrogen to ensure the absence of moisture and oxygen. In the polymerization batches, 550 mL of *n*-hexane was poured into the reactor while a nitrogen stream was passed through the same valve at 40°C which prevented the outer atmosphere coming inside. Afterward, an 8 mmol solution of triethylaluminium (TEA) in *n*-hexane was injected into the reactor while purging with nitrogen using a syringe. Next, 5 g of propylene was transferred into the reactor at 40°C and 300 RPM agitation speed using a bomb mounted on a balance to control the amount transferred. Then the pressure of the reactor was set to about 12 bar using nitrogen. Utilizing 20 mL of high-pressure *n*-hexane through the injection port of the polymerization setup, 180 mg of C-donor was inserted into the reactor. Finally, the pre-polymerization reaction started with a 20 mg catalyst injection, 5 minutes after adding external donor, using the same high-pressure injection apparatus. High-pressure injection apparatus consisted of a piston of 20 mL volume filled with *n*-hexane and recharged after each injection. The piston was

connected from the bottom to a 5 mL volume tube line with a cap on the top. Catalyst and donor were injected by removing the cap of the tube while purging it with nitrogen from a point connected to a joint located near to the top of the tube. After insertion, the cap was closed and a high pressure of nitrogen (about 40 bar) was conducted to the top of the piston. By opening the connection valve between the bottom of the piston and the tube line and then opening the valve of the reactor inlet port, all the ingredients of the tube line were injected into the reactor abruptly and washed by 20 mL of high pressure *n*-hexane, ensuring no catalyst particle or donor remained in the tube. Pre-polymerization reaction takes 30 minutes. After pre-polymerization, the reactor was purged with nitrogen for 20 minutes to ensure the removal of any unreacted monomers. The reactor was then heated up to 80°C with an agitation speed of 300 RPM. At $T=80^\circ\text{C}$, the vapor pressure of *n*-hexane was approximately 0.4 bar. Additionally, 0.6 bar of nitrogen gas was injected into the reactor to reach a total pressure of 1 bar. The total pressure of the reaction was determined by adding the ethylene pressure to 1, which was contributed by *n*-hexane and nitrogen.

Weighted 1-butene was injected into the reactor simultaneously with ethylene at the beginning of the reaction, and the reactor pressure was abruptly increased by introducing ethylene gas until it reached the predetermined reaction pressure. After 60 minutes of polymerization, the reactor gases were vented. The reactor was then cooled down to 40°C under mild agitation, and finally, the agitator was switched off. Finally, the polyethylene powder was dried at 80°C and 400mm Hg overnight.

Eight polymerization batches were conducted at various reaction pressures and different concentrations of 1-butene, as indicated in Table 3. The pre-polymerization reactions were consistent across all batches. The only differences between the batches were the total reaction pressure, which was supplied by ethylene gas, and the concentration of 1-butene in the reaction media. After the completion of the reaction and verifying the product morphology, in terms of whether it is in powder or sticky form (Figure 1), was analyzed through FTIR testing for samples of each batch product.

FTIR tests

FTIR tests were conducted using the Bruker Tensor 27 FTIR Spectrometer, which was calibrated with standard samples of LLDPE containing a known

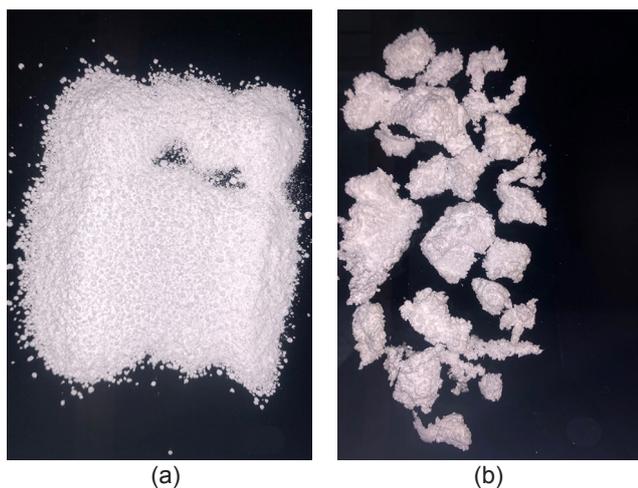


Figure 1. (a) Powder form product, (b) Sticky form product.

1-butene content. The tests were done according to Montell Test Method (MTM) 15873E, the standard test method of Lyondell Basell Company. The amount of 1-butene incorporated into each sample was reported in weight percent (wt.%). The peak used to calculate the weight percent of incorporated 1-butene into LLDPE chains is located at 769-772 cm^{-1} . Measuring the area under the peak and using a calibration curve for absorbance vs. weight percent of 1-butene, the weight percent of 1-butene in LLDPE products was calculated. The standard samples themselves had been characterized by ^{13}C -NMR.

Thermodynamic calculations

Thermodynamic calculations were based on Peng-Robinson Equation of State for a system consisting of *n*-hexane, ethylene, and 1-butene at $T=80^\circ\text{C}$ (nitrogen was excluded from the calculations due to its small quantity). These calculations were performed for the main co-polymerization process. Ethylene concentration in *n*-hexane as a liquid phase and reaction media was calculated for four different 1-butene concentrations in *n*-hexane (0.13, 0.26, 0.39,

Table 1. Ethylene concentration in *n*-hexane (mol/L) calculated at different pressures in *n*-hexane at $T=80^\circ\text{C}$ using Peng-Robinson EoS.

1-butene concentration in <i>n</i> -hexane (mol/L)	Ethylene concentration in <i>n</i> -hexane (mol/L) at different pressures				
	P= 4 bar	P= 6 bar	P= 8 bar	P= 10 bar	P= 12 bar
0.13	0.30	0.48	0.66	0.84	1.02
0.26	0.29	0.47	0.64	0.82	1.00
0.39	0.28	0.45	0.63	0.81	0.99
0.52	0.26	0.44	0.62	0.80	0.98

and 0.52 mol/L) and at pressures of 4, 6, 8, 10, and 12 bar. The results are shown in Table 1.

RESULTS AND DISCUSSION

The results of thermodynamic calculations for ethylene concentration in the reaction media (*n*-hexane) at different pressures at 80°C and in different concentrations of 1-butene in the media are presented in Table 1. Calculations show that 1-butene is almost totally soluble in *n*-hexane under all selected conditions, regardless of pressure values. Only a negligible amount of 1-butene will be present in the vapor phase. On the other hand, the concentration of ethylene is completely dependent on the pressure value. Using the data in Table 1, the β factor, which is defined here as the relative molar concentration of ethylene/1-butene, is calculated in Table 2 using Equation (1).

$$\beta = [\text{Ethylene}] / [1\text{-Butene}] \quad (1)$$

Data from Tables 1 and 2 is presented in Figures 2, 3, and 4. It is evident that there is a linear relationship between the concentration of ethylene in *n*-hexane and the reaction pressure at various reaction pressures, as well as the concentration of 1-butene in the reaction media (Figure 2). This relationship also holds true for β (Figure 3). Equations of linear fitted lines for β vs. reaction total pressure at different 1-butene concentrations in the media are presented in Figure 3. The fitted line and its equation in Figure 2 correspond to a 1-butene concentration of 0.26 mol/L, demonstrating a strong linear correlation.

As shown in Table 1 and Figure 2, there are slight changes in the ethylene concentration in *n*-hexane when the concentration of 1-butene in the media is varied within the ranges studied in this work. Therefore, it would be a reliable estimate to use Equation (2), which represents the line fitted to the

Table 2. β Factor, relative molar concentration of ethylene/1-butene in *n*-hexane, calculated at different pressures and 1-butene concentrations in *n*-hexane at $T=80^\circ\text{C}$.

1-butene concentration in <i>n</i> -hexane (mol/L)	P= 4 bar	P= 6 bar	P= 8 bar	P= 10 bar	P= 12 bar
0.13	2.32	3.68	5.05	6.43	7.81
0.26	1.11	1.81	2.48	3.17	3.86
0.39	0.71	1.16	1.62	2.08	2.55
0.52	0.51	0.85	1.19	1.54	1.89

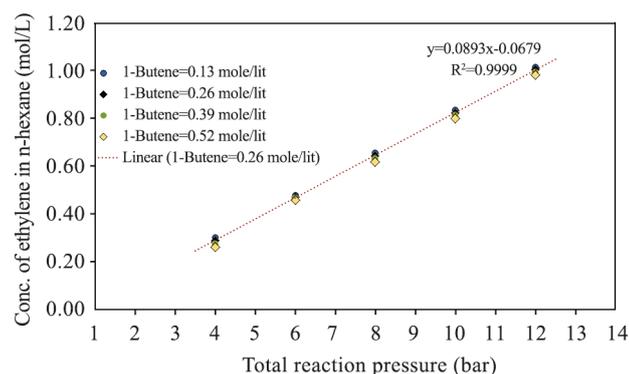


Figure 2. Ethylene concentration in *n*-hexane as a function of reaction pressure at different 1-butene concentrations in *n*-hexane.

mean ethylene concentrations in *n*-hexane at four different 1-butene concentrations against pressure, to calculate the ethylene concentration in *n*-hexane in the presence of 1-butene within the range of 0.13 to 0.52 mol/L:

$$[\text{Ethylene}] = 0.0894 \times P - 0.0760 \quad (2)$$

The concentration of ethylene in *n*-hexane is given in mol/L, and P represents the total pressure in bar. Considering Equation (2), with the concentration of 1-butene in mol/L, β can be calculated using Equation (1).

Based on our primary assumption that the production of powder or sticky product of LLDPE depends on the relative molar concentration (β) of ethylene/1-butene in the reaction media, we aimed to determine the critical value of β over which leads to powder formation. Conversely, values below this critical point result in sticky product formation. To investigate this, we conducted copolymerization experiments under various conditions with different β values, and the resulting products were analyzed (see Table 3). β values for batch numbers 1, 3, and 4 were calculated using fitted lines. These batches were conducted

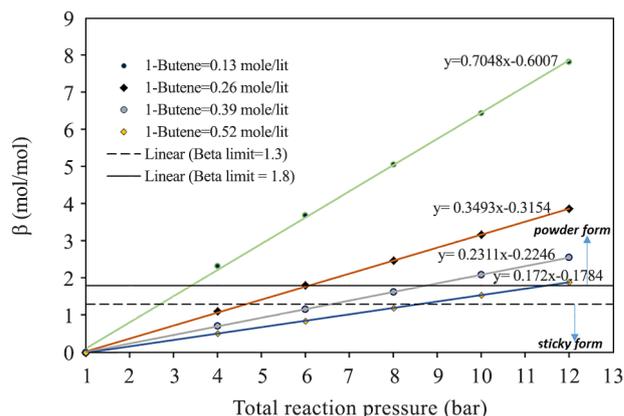


Figure 3. β factor as a function of reaction pressure at different 1-butene concentrations in *n*-hexane.

before the design of this study, but their results were not excluded. Batch numbers 5-7 were used to check the reproducibility of the results.

Reviewing the results presented in Table 3, it can be observed that under polymerization conditions where the calculated β factor exceeds the approximate value of 1.8, the final product is in powder form and the weight percentage of 1-butene in the product is less than approximately 4.3%. On the other hand, when the β factor decreases to approximately 1.3 or below, the product becomes sticky and contains a higher percentage of 1-butene and in the final LLDPE product, the weight percentage of 1-butene exceeds 5.2%. So, it seems reasonable to use a β factor value above 1.8 and below 1.3 as a criterion for predicting the final form of the polymer. It must be noticed that the lower limit of β , below which the polymer forms a sticky product, is not exactly 1.8. It falls somewhere between 1.3 and 1.8 (Table 3, batches 5-7 and 3 for comparison). However, the lowest value was not determined in this study.

The experimental value of β , over which resulted in the formation of powder, was approximately 1.8. So, the lines $\beta=1.3$ and $\beta=1.8$ were depicted in Figures 3 and 4, respectively, to indicate that all points above the

Table 3. Copolymerization conditions, calculated β and final polymer characteristics.

Batch no.	Reaction pressure (bar)	1-butene concentration in <i>n</i> -hexane (mol/L)	β	Incorporated 1-butene (wt.%)	Physical form
1	7	0.650	0.85	10.57	sticky
2	8	0.520	1.19	6.70	sticky
3	10	0.624	1.32	5.19	sticky
4	5	0.130	2.92	1.92	powder
5	6	0.260	1.81	3.90	powder
6	6	0.260	1.81	4.32	powder
7	6	0.260	1.81	4.13	powder
8	12	0.260	3.86	1.58	powder

line $\beta=1.8$ and below the line $\beta=1.3$ result in powder and sticky form products, respectively. The same observations hold true for a 1-butene content of 4.3%, which leads to the formation of a powdered product. In this study, it was found that the maximum 1-butene content that did not result in stickiness in the LLDPE product was 4.3%. However, when the content of 1-butene reached 5.2%, the product became sticky. Therefore, the turning point is somewhere between 4.3% and 5.2% wt.% of 1-butene in LLDPE.

As is well known, there is a distribution of comonomers, such as 1-butene, in polyethylene chains during copolymerization reactions with Ziegler-Natta catalysts. Between the chains, shorter chains are richer in comonomers than longer chains [22]. By increasing the relative concentration of 1-butene to ethylene in the reaction media, the likelihood of incorporating 1-butene monomers into the growing polyethylene chains also increases. As a result, the 1-butene rich tail of the distribution grows alongside with a shift in their 1-butene incorporated values into higher numbers. So, in a specific region, which falls within the range of $1.3 < \beta < 1.8$, there are significant fractions of 1-butene rich chains that contain a sufficient weight percentage of incorporated 1-butene which make those polymer chains to be soluble in the reaction media in polymerization temperature, resulting in a sticky product. So, it seems that the stickiness of the product requires two prerequisites. First, a sufficiently high incorporation of 1-butene values, and second, a large enough fraction of these chains to make the product sticky after dissolving in the reaction media.

Of course, for values of $1.3 < \beta < 1.8$, it is not possible to predict the final form of the product due to a lack of experimentation and data in this range. Therefore, further analysis is needed.

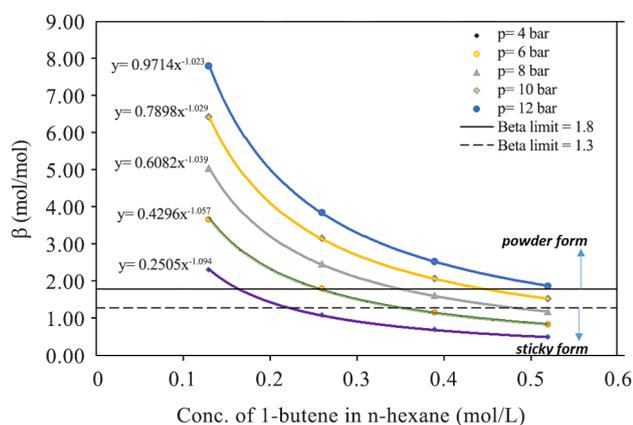


Figure 4. β factor as a function of 1-butene concentrations in *n*-hexane at different reaction pressures.

Figure 4 depicts the relationship between β and the concentration of 1-butene in media at various pressures. As can be seen, there is a strong power type correlation between the points at each pressure. Therefore, the fitted lines can be used to calculate β for concentrations of 1-butene other than the values used in this study.

In Figure 5, three overall FTIR spectra belonging to batch numbers 5, 6, and 7 are presented. These experiments were conducted under the identical fixed conditions to assess the reproducibility of the results. These spectra are presented as a representative.

As can be seen from Table 3, there is an acceptable deviation between the results (3.9, 4.32, and 4.13 wt.%

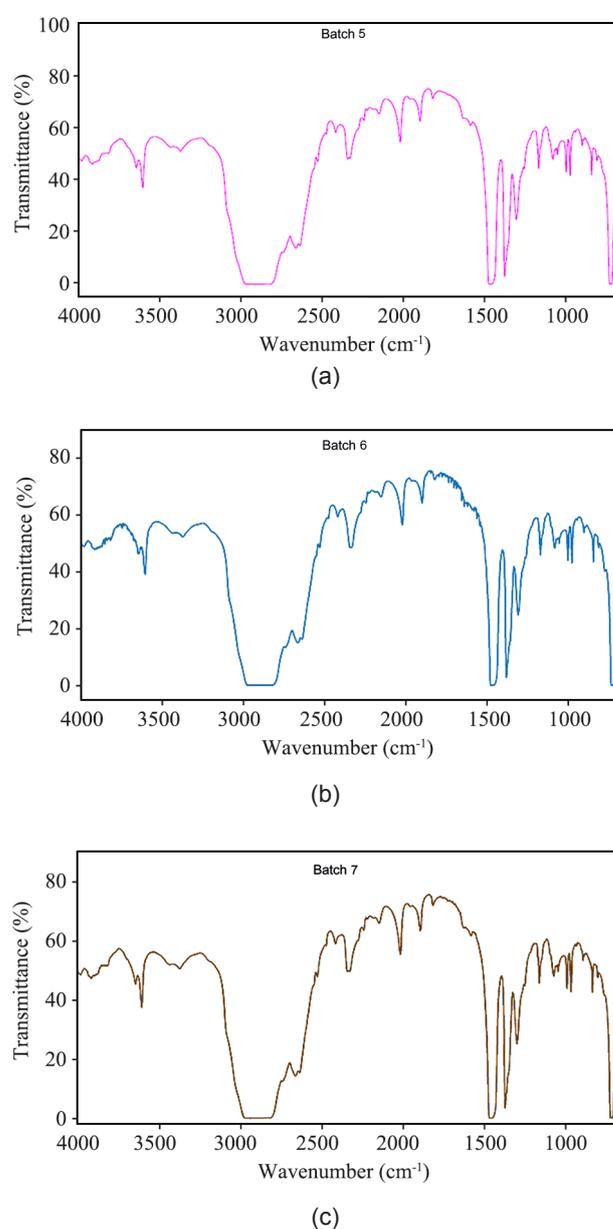


Figure 5. FTIR spectrum of three polymerization batches.

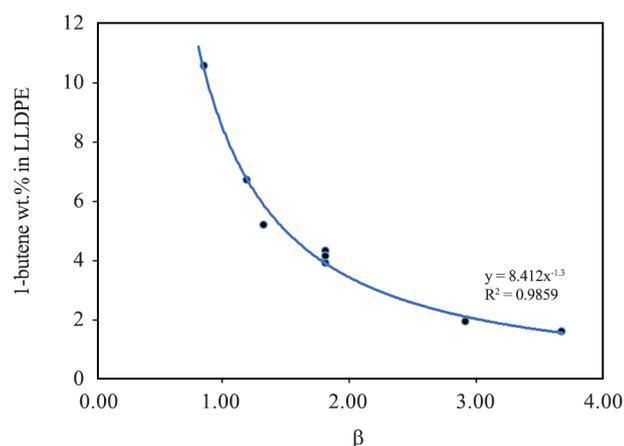


Figure 6. Correlation between β factor and incorporated 1-butene into LLDPE chain.

of incorporated 1-butene), considering the sensitive nature of polymerization with Z-N catalysts.

Depicting the weight percentage of 1-butene in the final LLDPE versus β values shows a strong correlation (Figure 6 and Equation (3)):

$$1\text{-Butene wt. \% in LLDPE} = 8.412 \times \beta^{-1.3} \quad (3)$$

So, for the conditions investigated in this study and the points in between, one can use Equation (3) as a good guess for wt.% of incorporated 1-butene into LLDPE chain prior to polymerization, simply by calculating β and putting it in Equation (3).

However, results presented here for the critical limits of β holds true just for the catalyst system used in this study. As many characteristics of the synthesized polymer chains depend on the nature of the catalyst system implemented, recalibrating of β will be necessary for other catalyst systems. But, the guidelines given here for connecting ethylene to 1-butene relative concentration in media to the final LLDPE characteristics is beneficial for those too. Besides, the critical range of β found in this work may be a good initial guess for the other catalyst systems to find their own limits.

In this work, the comonomer used was 1-butene, but the presented idea can be applicable for other copolymerization reactions of ethylene with the different alpha olefins as comonomers.

CONCLUSION

Ethylene concentration in *n*-hexane in the presence of 1-butene with 0.13, 0.26, 0.39 and 0.52 mol/L

concentrations was calculated using Peng-Robinson thermodynamic Equation of State for pressures of 4, 6, 8, 10 and 12 bar as reaction total pressure and at $T=80^\circ\text{C}$. β factor was defined as the relative molar concentration of ethylene/1-butene in *n*-hexane, shown to be a reliable criterion for judging the final form of the synthesized product in the sense of being sticky or in powder form for polymerization with a commercial fourth generation $\text{TiCl}_4/\text{MgCl}_2/\text{Donor-C}/\text{TEA}$ Ziegler-Natta catalyst system at $T=80^\circ\text{C}$. Polymerization reactions showed acceptable reproducibility results. Ethylene concentration in *n*-hexane had small changes with change in 1-butene concentration in media in the range studied. Almost all of 1-butene was present in liquid phase in all pressures studied. Correlations with good accuracy are proposed for calculating β for pressures and 1-butene concentrations within the range of studied values. It was shown that for polymerization reactions with β values over 1.8 the final LLDPE product is in powder form and has 1-butene wt.% lower than 4.3%. On the contrary, for β values under 1.3 the final LLDPE product will be sticky and 1-butene wt.% in final product exceeds 5.2%. The polymers with 1-butene wt.% up to 4.3% were in powder form, while polymers with 1-butene wt.% of 5.2% and higher were sticky. Therefore, the transition point occurs between 4.3% and 5.2% of incorporated 1-butene. So, a practical criterion ($\beta > 1.8$) was developed to be met for reaching powder form of product which would be possible in the direction of decreasing 1-butene concentration in media or increasing reaction pressure. For the range of $1.3 < \beta < 1.8$ none of the polymerizations done here had β in this range and so is still unknown and needs further evaluation. For next studies setting reactions with β in this range are proposed for more accurate determination of the turning point. It was demonstrated that 1-butene wt.% in the final LLDPE product has a good correlation with β value and the Equation $1\text{-Butene wt.\% in LLDPE} = 8.412 \times \beta^{-1.3}$ was proposed as a good estimate of 1-butene wt.% in the final LLDPE product before running the polymerization reaction.

Results reported here were drawn using a definite Ziegler-Natta type catalyst system, so extending the findings needs testing of different catalyst systems which will be under the scope of further studies and the values found here for β and related equations may not be accurate for other situations, but might be a good guess as starting point for surveying other unknown catalyst systems and make sense about the

sensitive range of β as a key factor for determining the final LLDPE product characteristics.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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