Molecular Weight Bimodality of Ethylene/1-Butene in A Two-step Polymerization Process: Effects of Polymerization Conditions

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A B S T R A C T

The molecular weight and molecular weight distribution were adjusted by controlling polymerization process to meet bimodal poly(ethylene-*co*-1-butene) using Ziegler-Natta catalyst. The process was carried out through two-step polymerization in a semi-batch reactor where in the first step, a low molecular weight homopolymer of ethylene was produced in the presence of hydrogen and in the next step, the high molecular weight copolymer of ethylene with 1-butene was produced after the hydrogen was removed from the reactor. The effects of hydrogen and comonomer concentrations and the polymerization time for the first and second steps were investigated. Although, the second step was run in the absence of hydrogen, the results indicate that shifting the reaction from the first step to the second step leaves potentially some effects on the active centres. The higher hydrogen concentration decreased the rate of polymerization and molecular weight in the first step while, it indirectly raised the rate of polymerization and consequently the yield of reaction at the second step considerably. Increased comonomer concentration in the second step reduced the average molecular weight and increased the melt flow rate while slightly increased the rate of polymerization. It is found that the effect of comonomer concentration on the rate of copolymerization in the second step is lowered by the increase of hydrogen concentration at the first step.

INTRODUCTION

Molecular weight (MW) and molecular weight distribution (MWD) play important roles in determining the mechanical and rheological properties of polymers. Polyolefins with bimodal molecular weight distribution have advantages over unimodal with narrow molecular weight distributions [1].

Polyolefins with bimodal distribution have a fraction of high molecular weight which provides strength and toughness and a part with lower molecular weight which facilitates polymer flow and extrusion processing. These polymers exhibit a reduced melt flow perturbation, preferred in applications such as high strength films [1,2].

Controlling the MW and MWD of polyethylene is essential to optimize both the mechanical and rheological properties. There are several ways to regulate molecular weight distribution and manufacture

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polyethylene with tailored properties. One of the techniques is melt blending of polyethylene resins with different molecular weights [3,4]. In spite of the ease of processing, there is limited product homogeneity. The other method involves using mixed or hybrid catalysts [2,5,6] having the capability of producing molecules with different molecular weights. Controlling polymerization conditions is another method to manufacture bimodal polyethylene [1]. The usual industrial process is a cascade type process. The process includes reactors arranged in series where, catalyst passes through two or more reactor zones and polymer fractions are produced in sequence.

The aim of this work was to achieve a method of molecular weight regularization with bimodal molecular weight distribution in a two step polymerization of ethylene using an industrial catalyst. Since the technique requires at least two reactors in series, there is no considerable experimental data available under such polymerization conditions in the literature. There are only few reports on polymerization in a single reactor by changing the reaction conditions [7-9].

Shan et al. synthesized bimodal polyethylene in a two-step polymerization process using metallocene catalyst. They have investigated the rheological and mechanical properties of the resin products but the effects of polymerization parameters are not discussed [8]. Recently, Chen et al. used a method to produce bimodal polyethylene using Ziegler Natta catalyst by multiple switching of H_2 concentration in a multi-step polymerization and investigated the effect of hydrogen concentration multiple switching on the bimodality of polyethylene [10]. The polymerization conditions of a two-step polymerization with respect to processability and the rheological properties of bimodal MWD polyethylene were discussed in our previous paper [11].

In the present work, while we investigate exactly the effect of polymerization conditions on active sites productivity of the first step, the copolymerization of ethylene/1-butene was carried out in the next step. The influence of polymerization time and hydrogen concentration in the first step and the effect of comonomer concentration and polymerization time in the next step were examined. To our knowledge, this

extended report has not been published elsewhere.

EXPERIMENTAL

Materials
The Ziegler-Natta type catalyst (industrial grade) with an elemental atomic ratio of Ti/Mg/Cl: 0.797/1/4.2 was utilized. Polymerization grade ethylene (99.99%) was provided by Pars Gas Co., Isfahan, Iran, and hydrogen of extra pure grade (99.999%) from Roham Gas, Iran was used. Triethylaluminium (Aldrich, USA) and 1-butene (industrial grade from Arak Petrochemical Complex, Iran) were used as a cocatalyst and comonomer, respectively. Also, *n*-hexane (polymerization grade by Pars Cylinder Co., Isfahan, Iran) dried overnight in the presence of sodium wire and molecular sieves were used as the reaction media.

Polymerization
To prepare a bimodal polyethylene, polymerization was conducted in a 5 L Buchi reactor (Buchi Glas Uster, Switzerland). The polymerization setup was comprised of purification columns to adsorb humidity, sulphur compounds and carbon oxides besides a mass flow- meter (Brooks, type 5816, USA) to measure the rate of ethylene consumption and cumulative amounts of polymer products.

The polymerization was performed in two steps. In the first step, the required amount of hydrogen was injected into the reactor through press-flow gas controller (Buchi, type bpc 9901, Switzerland) and polymerization was performed at constant temperature and pressure of 84°C and 9 bar, respectively. At the end of the first step the unreacted gas was vented off and the reactor was purged slightly by ethylene so that the reaction atmosphere became free from hydrogen. In the second step, a desired amount of 1-butene was injected into the reactor which was followed by ethylene feed and the polymerization was performed at 3.5 bar and 80°C. The polymerization conditions, productivity ratios and physical properties of the products are given in Table 1. The average rate of polymerization in each step was calculated using the total amount of production divided by the elapsed time.

Table 1. Polymerization conditions and physical properties of products.

Sample No.	Sample [a] code	H_2 (mol)	Productivity ratio [b] step 1/step 2	1-Butene [c] (bar)	MW (g/mol)	PDI	T_m (°C)
1	C1H1-30-30	0.40	45 / 22	0.70	178201	6.68	135.0
2	C1H1-30-60	0.40	44 / 30	0.70	227151	7.95	134.7
3	C1H1-20-30	0.40	40 / 28	0.70	145673	6.93	134.5
4	C1H1-20-60	0.40	41 / 43	0.70	156216	6.30	134.1
5	C1H2-30-5	0.66	7 / 11	0.70	85199	15.40	131.1
6	C1H2-30-10	0.66	6 / 20	0.70	157772	22.80	130.8
7	C1H2-60-5	0.66	11 / 10	0.70	122969	14.50	130.7
8	C1H2-60-10	0.66	10 / 22	0.70	131519	28.60	131.5
9	C2H2-60-10	0.66	10 / 20	0.30	145118	14.50	132.3
10	C3H2-60-10	0.66	10 / 19	0.10	218406	25.80	133.6
11	C4H2-60-10	0.66	10 /16	0.00	260420	30.60	136.2
12	C1H3-60-60	0.58	50 / 40	0.70	189891	24.14	134.8
13	C1H4-60-60	0.50	76 / 35	0.70	124524	15.50	135.3
14	C4H1-30-120	0.40	59 / 21	0.00	239463	17.30	133.9
15	C5H1-30-120	0.40	55 / 46	0.25	208729	14.30	134.6
16	C6H1-30-120	0.40	52 / 53	0.50	167125	13.40	135.6

[a] H stands for hydrogen; H1: 0.4 mol, H2: 0.66 mol and C is the symbol of co-monomer; C1: 0.7 bar, C2: 0.3 bar C3: 0.1 bar, C4: 0 bar, C5: 0.25 bar, C6: 0.5 bar, the first and second numbers are the polymerization times at the first and second steps, respectively. [b] g/g; [c] measured pressure at 80°C.

Characterization

Molecular Weight and Molecular Weight Distribution
The average molecular weight (MW) and molecular weight distribution (MWD) were obtained using a Waters gel permeation chromatography (2000, USA) at 135°C with 1,2,4-trichlorobenzene as a solvent.

Thermal Analysis
Melting temperature was measured by differential scanning calorimetry (Netzsch DSC 200 F3, Germany) under nitrogen atmosphere. The heating and cooling rates were 10°C/min according to ASTM D3418-03.

The thermal fractionation by DSC was performed using a successive self-nucleation annealing (SSA) procedure prior to DSC final analysis. This is a technique, by which polyethylene molecules are segregated based on recrystallization and reorganiza-tion from the melt according to methylene sequence lengths (MSL) and annealing, thus, each peak of SSA-DSC endotherm represents a group of chain

segments having similar MSL. The technique has been applied by several authors [12-14] and good agreement between NMR and SSA results has been reported [14].

The first step was to erase previous thermal history, therefore the samples were heated to 160°C and heated for 3 min and then cooled with the rate of 10°C/min to room temperature. In the second step, the polymer samples were heated at 5°C/min to the first selected annealing and/or self nucleation temperature and were kept at that temperature for about 10 min. The crystallization was achieved by subsequent cooling of the samples to room temperature at a cooling rate of 5°C/min. Then, the temperature was raised to a second annealing and/or self nucleation temperature at the rate of 5°C/min and kept for 10 min.

The heating-annealing-cooling cycle was repeated at a temperature interval of 5°C from 135 to 60°C. Finally, the treated samples were heated from 0°C to 160°C at a heating rate of 10°C/min. The SSA-DSC

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Table 2. Effect of hydrogen concentration on polymerization rate of both steps and subsequent productivity ratios.

Sample code	H_2 (mol)	Polymerization rate (g/min)		Productivity ratio (g/g)
		Step 1	Step 2	Step 1/Step 2
Homopolymer	0.00	7.00	-	-
C1H1-30-60 (No.2)	0.40	1.47	0.5	44 / 30
C1H2-30-10 (No.6)	0.66	0.20	2.0	6 / 20

endotherms were deconvoluted using peakfit software and SCB content was determined using calibration curve and calculation technique described by Zhang et al. [13].

Melt Flow Rate
Melt flow rate was measured at 190°C and 2.16 kg weight according to ASTM D1238 using Zwick, 4100 made in Germany.

**RESULTS AND DISCUSSION**

Hydrogen Effect
Table 2 shows explicitly the effect of hydrogen concentration on polymerization rates and subsequent productivity ratio. The rates of polymerization and subsequent productivity in the first step dropped considerably in the presence of hydrogen as explained by several authors [15, 16]. While, in the second step its absence increases the polymerization rate. As it is shown in Table 2, by increasing hydrogen from 0.26 mol to 0.4 mol in the first step, the rate of polymerization of the next step increased approximately 5 times.

It seems that with increase in hydrogen feed concentration, the activity of catalyst sites would be preserved more and thus, in the second step where there is no hydrogen, the catalyst productivity would be enhanced. This observation is in accordance with Garoff's claim, stating that there is a growing delay in active sites reaching their maximum activity with increased hydrogen concentration [15].

As a decay type catalyst was used in this work, higher delay time preserved the activity of active sites for the second polymerization step in the absence of

hydrogen. This noticeable effect has improved productivity in both steps. Although in the case of specimen C1H2-30-10 (No. 6) (polymerized under 0.66 mol hydrogen) the polymerization time of the second step is only 10 min, the related productivity is 4 times higher than that of the first step, while in the case of the specimen C1H1-30-60 (No. 4) (polymerized under 0.4 mol hydrogen) this productivity value is only 2.3 despite the higher polymerization time of the second step.

Generally, hydrogen plays the role of chain transfer agent in the polymerization of olefins. Moreover, it is well accepted that because of transfer reactions, molecular weight distribution becomes broader at higher hydrogen concentration. Figure 1 compares the effect of increased mole of hydrogen in the first step. Increasing hydrogen amount by 0.26 mol, the polydispersity index was raised from 8 to about 22.8 and fractions were produced with very low molecular weights.
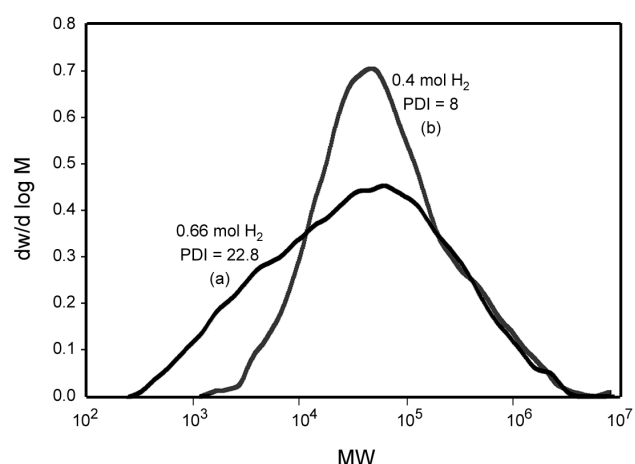
Figure 1. Effect of hydrogen amount added in the first step on MW and MWD: (a) 0.66 mol H_2 (sample No. 6), and (b) 0.4 mol H_2 (sample No. 2).
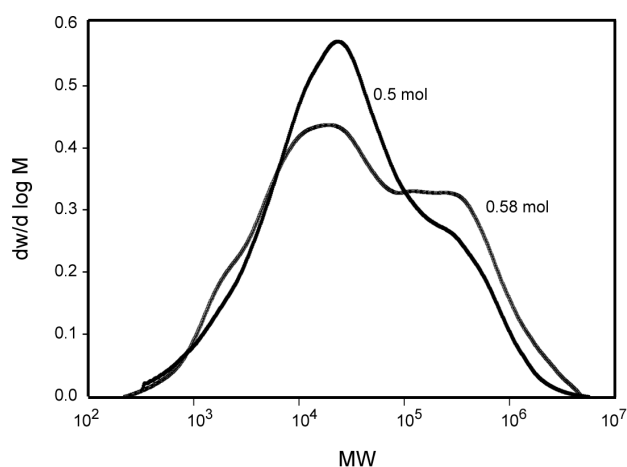
Table 3. Effect of added hydrogen concentration on polymerization and melt flow rates of the first step.

Sample code	H$_2$ (mol)	Polymerization rate (g/min)		MFR (g/10 min)
		Step 1	Step 2	
C1H3-60-60 (No.12)	0.58	0.83	0.67	0.07
C1H4-60-60 (No.13)	0.50	1.27	0.58	0.21

Even very small changes in hydrogen partial pressure might have considerable effect on productivity and average molecular weight according to Tables 1 and 3. Although the amount of hydrogen in the specimen C1H3-60-60 (No. 12) was slightly higher (0.08 mol) than that of the specimen C1H4-60-60 (No. 13), the productivity ratio (step 1/step 2) of the C1H4-60-60 sample was considerably higher and subsequently its average molecular weight was lower.

Figure 2 shows the GPC graphs of the two specimens. The small increase in hydrogen concentration in the first step led to higher incorporation of high molecular weight polymer in the second step that decreased the melt flow rate of the product according to Table 3.

The small changes in hydrogen concentration did not change the position of lower molecular weight fraction peak, considerably. Although, in case of specimens produced under much higher amount o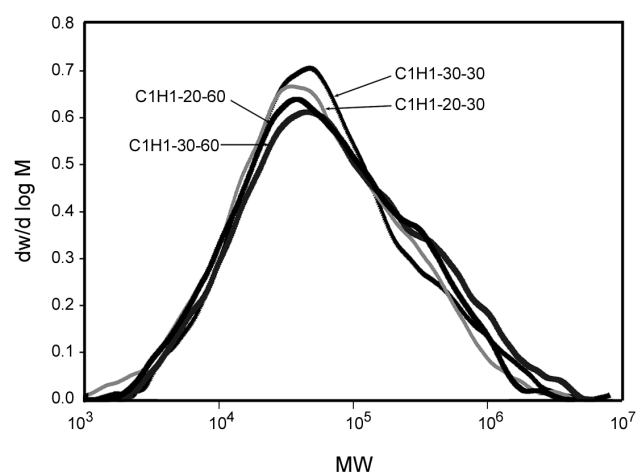f hydrogen (0.66 mol) the low molecular weight fraction peak shifted to lower molecular weights and overall molecular weight decreased significantly [11].

Considering Table 1, it is evident that melting temperature of specimens polymerized under 0.66 mol hydrogen is lower (2-3 degrees) than melting temperature of those polymerized under 0.4 mol hydrogen and constant comonomer concentrations. The overall reduction of molecular weight due to formation of a high amount of very low molecular weight fractions resulted in production of thinner crystals with lower melting temperature.

Time Effect

According to Table 1, to investigate the effect of time, two series of experiments were carried out at various polymerization times for each step and two different hydrogen partial pressures confined to the first step. The GPC graphs of samples produced in the presence of 0.4 and 0.66 mol hydrogen concentrations are presented in Figures 3 and 4, respectively.

Figure 2. Effect of hydrogen amount added in the first step on MW and MWD with equal polymerization time of 60 min in each step.

Figure 3. Effect of polymerization time of both steps on MW and MWD in the presence of 0.4 mol H$_2$.
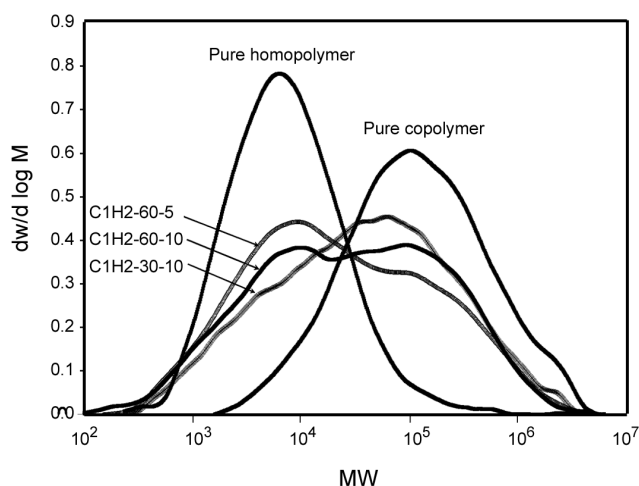
Figure 4. Effect of polymerization time of both steps on MW and MWD in the presence of 0.66 mol H_2.

By comparing Figures 3 and 4, one can find the dependency of polymerization time on hydrogen concentration, to obtain different forms of bimodal polyethylene [11]. Changing the polymerization time of the first step and/or the second step in the presence of 0.66 mol hydrogen sharply affected the molecular weight distribution curve. This diversity of MWD cannot be obtained in the presence of 0.4 mol hydrogen as it is evident in Figure 3.

Considering Figure 4, in the case of $(t_1,t_2) = (60,10)$, it seems as if there is a relative equilibrium between two fractions, with the product ratio (step 1/step 2) being 38/62. Decreasing polymerization time of the second step by 5 min led to lower polymer fractions to about 14-15%. Interestingly, the same reduction (15%) was nearly achieved in step 1 when polymerization time of the first step was lowered by 30 min. This is an indication of the extent to which

polymerization time can be varied in each step.

Table 4 shows the selected polymerization times and their corresponding polymerization rates for 0.4 and 0.66 mol hydrogen concentrations used in the first step. The rate of polymerization of the second step was about 6-10 times higher than that of the first step in the presence of 0.66 mol hydrogen. While, in the case of 0.4 mol hydrogen, the related rate of polymerization of the first step was higher. This result shows that management of the polymerization time is dependent on hydrogen concentration in the first step. In other words, with higher hydrogen concentration in the first step, a lower polymerization time should then be envisaged for the second step.
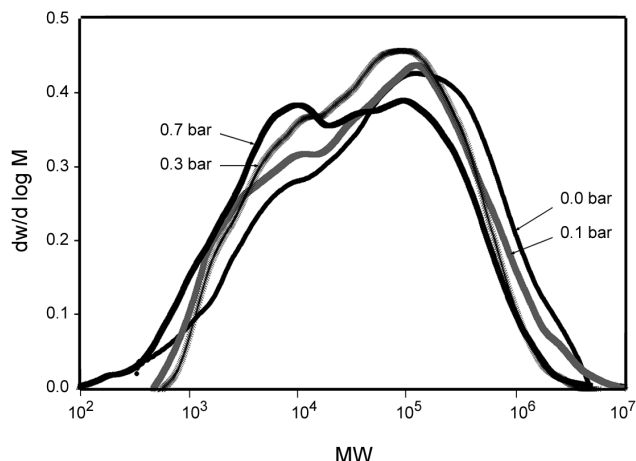
Comonomer Effect
For investigating the effect of comonomer, specimens were produced under similar polymerization conditions with different comonomer contents.
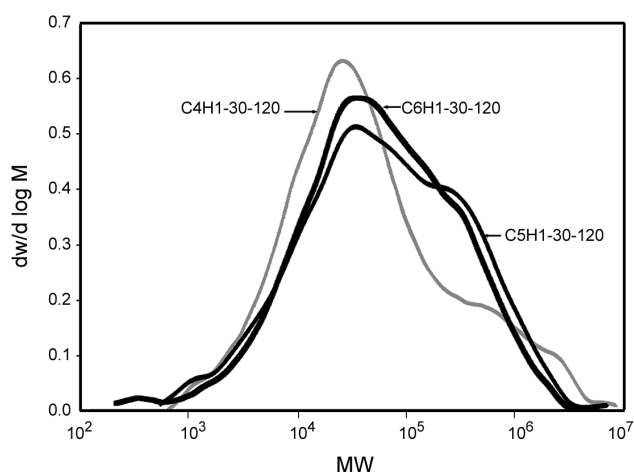
**Figure 5.** Effect of comonomer amount added in the second step on MW and MWD in the presence of 0.4 mol H_2.

Table 4. Effect of added hydrogen concentration in the first step and management of polymerization time on polymerization rate.

Sample No.	H_2 (mol)	Polymerization time (min)		Polymerization rate (g/min)	
		Step 1	Step 2	Step 1	Step 2
1	0.40	30	30	1.64	0.773
2	0.40	30	60	1.60	0.550
5	0.66	30	5	0.23	1.600
6	0.66	30	10	0.23	2.040

Figure 6. Effect of comonomer amount added in the second step on MW and MWD in the presence of 0.66 mol H_2.

Figures 5 and 6 depict the effect of comonomer on molecular weight and molecular weight distribution in the presence of 0.4 and 0.66 mol hydrogen, respectively. As it was expected, increasing the comonomer concentration, shifted the molecular weight distribution to lower levels because of transfer to comonomer reaction mechanism. According to Table 5, in a polymerization process under 0.4 mol hydrogen concentration, there was a marked contrast in polymerization rate from zero to 0.25 bar co-monomer partial pressure (at 80°C) whereas, in a process with comonomer partial pressure of lower than 0.66 mol the rate of polymerization was not
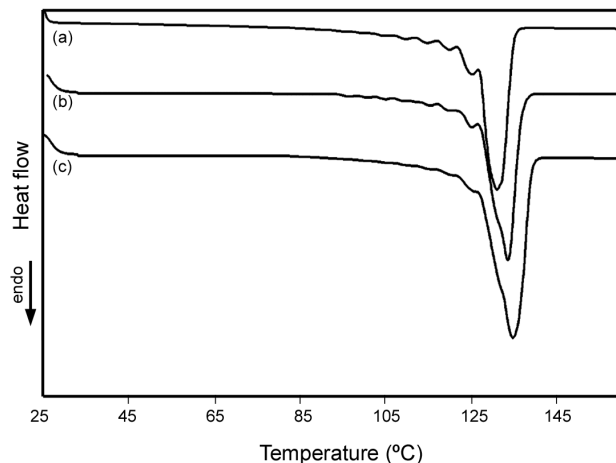
Figure 7. DSC-SSA Endotherms of specimens synthesized under different comonomer partial pressures of 0.7, 0.3, 0.1 bar added in the second step for: (a) C1H2-60-10 (No. 8), (b) C2H2-60-10 (No. 9) and (c) C3H2-60-10 (No. 10), respectively.

enhanced considerably.

It is suggested that in the first step, the effect of comonomer concentration on the rate of copoly-merization is decreased with increase in hydrogen concentration. However, further increase in co-monomer partial pressure (i.e., from 0.25 to 0.5 bar, as in polymerization under 0.4 mol hydrogen) does not change the rate of polymerization. This effect is in accordance with some observations on the the effectiveness of comonomer addition at low con-centrations [16].

Table 5. Effect of added comonomer in the second step on polymerization rate and physical properties of the final copolymer.

Sample No.	H_2 (mol)	1-Butene [a] (bar)	Polymerization rate (g/min)	T_m (°C)	SCB (br/1000 carbon atoms)	MFR (g/10 min)
16	0.40	0.50	0.44	133.9	-	- [b]
15	0.40	0.25	0.45	134.6	-	- [b]
14	0.40	0.00	0.24	135.6	0.0	- [b]
8	0.66	0.70	2.20	131.5	6.2	0.17
9	0.66	0.30	2.00	132.3	4.5	0.13
10	0.66	0.10	1.90	133.6	4.4	0.09
11	0.66	0.00	1.60	136.2	0.0	0.03

[a] Measured partial pressure at 80°C; [b] the melt did not leave the MFR die.

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For investigating the effect of comonomer feed concentration on copolymer products, the chain branching was studied using SSA technique. Figure 7 shows the SSA-DSC endotherms of specimens prepared under 0.66 mol hydrogen and different comonomer feed partial pressures. It is evident that, at higher comonomer concentration, the crystal segregation becomes more distinct and the peaks would shift to lower temperatures.

Table 5 shows the corresponding SCB numbers, melting temperatures and melt flow rate. The SCB is increased from 4.4 to 6.5 with increase in co-monomer feed from 0.1 bar to 0.7 bar (at 80°C). It is clear that, with increased comonomer concentration, the melting temperature is lowered due to increased SCB, while, the melt flow rate is increased slightly due to lowered average molecular weight.

CONCLUSION

In this work, to regulate molecular weight of poly-ethylene, the polymerization process was divided into two steps. In the first step, polymerization was performed in the presence of hydrogen, while in the second step, after removing the hydrogen, the process was continued in the presence of 1-butene as a comonomer.

Among different parameters affecting molecular weight and molecular weight distribution of poly-ethylene, hydrogen content is the most critical parameter. Although hydrogen reduces the polymer-ization rate in the first step, its higher amount in this step results in higher polymerization rate at the second step where the hydrogen is totally absent. At constant polymerization time for each step, slightly higher amount of hydrogen in the first step may result in considerably higher molecular weight of the copolymer due to lower productivity in the first step and at the same time higher productivity in the second step.

Rising comonomer content lowers the average molecular weight and as a result melting temperatures due to increased transfer reactions. The rate of poly-merization slightly increases with increased amount of comonomer. It seems that the increase in the rate of polymerization is more significant in the case where

lower amount of hydrogen is used in the first step. Using the conditions acquired to synthesize poly-ethylene copolymer, it is estimated from SSA technique that the number of short chain branches is about 4-6.5/1000 of carbon atoms depending on the comonomer concentration of the second step.

SYMBOLS AND ABBREVIATION

MW   : Molecular weight (weight average)
MWD : Molecular weight distribution
Ti   : Titanium
Mg   : Magnesium
Cl   : Chlorine
GPC   : Gel permeation chromatography
DSC   : Differential scanning calorimetry
SSA   : Successive self-nucleation annealing
MSL   : Methylene sequence lengths
SCB   : Short chain branching
NMR   : Nuclear magnetic resonance

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