Tailoring MWD of Bimodal Polyethylene in the Presence of Ziegler-Natta Catalyst

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Summary: Linear poly (ethylene-co-1-butene) was produced through two-step polymerization in one reactor using a Ziegler-Natta catalyst, where in the first step, low molecular weight homopolymer of ethylene in the presence of hydrogen and in the next step, high molecular weight copolymer of ethylene with 1-butene in the absence of hydrogen were produced. Molecular weight distribution of bimodal polyethylene was tailored through adjustment of polymerization time of each stage and hydrogen concentration of the first stage. Increasing hydrogen concentration shifted the molecular weight distribution curve to the lower molecular weights and broadened molecular weight distribution while interestingly increased high molecular weight incorporation of copolymer produced in the second stage due to increasing of reaction rate in the second step. To achieve bimodal molecular weight distribution, the polymerization times of the first and the second steps, which are highly dependent on the amount of hydrogen, were adjusted properly. The effects of the mentioned parameters on the processability as well as rheological properties of some samples were investigated. The rheological results showed shear thinning behavior of all specimens and confirmed the changes in molecular weight and molecular weight distribution. It was also demonstrated that the melt miscibility between low molecular weight and high molecular weight fractions improved with increasing of chains having very low molecular weight.

Keywords: bimodal distribution; polyethylene; ziegler natta catalyst

Introduction

Polyolefins with bimodal molecular weight distribution have advantages over typical polyolefins with narrow molecular weight distribution.[1,2] Ziegler-Natta catalysts generally create broad distributions of molecular weight and chemical distribution (CCD). This has been attributed to the presence of different types of active sites on these catalysts.[3] Each site type produces polymer populations with specific average molecular weight and chemical composition. Molecular weight (MW) and molecular weight distribution (MWD) play an important role in determining mechanical and rheological properties of polymers. Resins with bimodal MWD have high molecular weight fractions which provide strength and toughness and segments with lower molecular weights which improve their flow and extrudability.[1–6] Controlling the Mw and MWD of polyethylene is needed to optimize both the mechanical and rheological properties. Various approaches have been examined for production of polyethylene with tailored properties such as physical blending of polyethylene resins with different molecular weight,[7,8] direct synthesis using hybrid or mixed catalysts [9–12] and multi-stage polymerization which involves different staging of variables, usually in multi reactor setups.[13]

Cascade type process including reactors in series order is usually used to produce

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polyolefins with bimodal distribution, where catalyst passes through two or more reactor zones and polymer fractions are produced one after another. Instead of cascade process, bimodal polyethylene resins can be synthesized in multisteps in one reactor by changing the reaction conditions.[14–16] Some authors reported multi-step polymerization of ethylene in one reactor to produce bimodal polyethylene,[14–16] but the manner that final properties change under various polymerization conditions has not been discussed.[14]

In this article, the aim is to demonstrate the importance of controlling molecular characteristics of polyethylene and regulation of molecular weight and molecular weight distribution by careful tuning of effective parameters. The effect of polymerization parameters in the two steps on processability and the rheological properties was discussed.

Experimental Part

Materials

Ziegler-Natta type catalyst (industrial grade) with the atomic ratio of elements (Ti:Mg:Cl = 0.797: 1: 2.4) was utilized. Polymerization grade ethylene provided by Isfahan petrochemical complex and hydrogen of extra pure grade (99.999%) was used. Triethylaluminum (Aldrich) and 1-butene (industrial grade from Arak Petrochemical Complex) were taken as a cocatalyst and comonomer respectively. Also, n-hexane (industrial grade from Isfahan Petrochemical Complex), dried overnight in the presence of sodium wire and molecular sieves, was used as the reaction media.

Polymerization

To prepare polyethylene with bimodal distribution, polymerization was conducted in a 5 liter Buchi reactor. The polymerization setup comprised of purification columns to adsorb humidity, sulfur compounds as well as carbon oxides and a mass flow meter (Brooks, type 5816) to measure the rate of ethylene consumption and cumulative amount of produced polymer. The polymerization was performed in two steps. In the first step, the required amount of hydrogen was injected to the reactor through Buchi press-flow gas controller (type bpc 9901) then polymerization started at constant temperature and pressure of 84 °C and 9 bar respectively. At the end of the first stage the unreacted gas was vented and the reactor purged slightly with ethylene so that the atmosphere became free from hydrogen. In the second step, 0.7 bar 1-butene was injected, then ethylene was introduced and polymerization continued at 3.5 bar and 80 °C. The average rate of polymerization in each stage was calculated using the total amount of production dividing by the elapsed time.

Homo-polymerization and copolymerization of ethylene were conducted individually in two stages to investigate the changes of molecular weight and molecular weight distribution at each condition. Homo-polymerization was performed under total pressure of 9 bar and two different hydrogen concentrations, while copolymerization was performed under total pressure of 3.5 bar and 82 °C in the presence of 1-butene.

To produce polyethylene with bimodal distribution, some experiments were performed considering constant and variable polymerization times for the first and second stages respectively.

Polymer Characterization

The molecular weight (MW) and molecular weight distribution (MWD) were analyzed by gel permeation chromatography (GPC), (Waters 2000) at 135 °C with 1,2,4-trichlorobenzene as a solvent. Melt flow rate was measured at 190 °C under 2.16 Kg weight according to ASTM D1238. Impact test was performed on nutched specimens with 2.7 thichness under 23 °C and 50% humidity. Tensile was performed by Tensile Tester (Instron-6025) with the rate of 50 mm/mm according to ASTM D638. Melting temperature was measured by differential scanning calorimetry (DSC-PL) under

Table 1.
molecular weight characteristics of homopolymers and pure copolymer.

Sample	Hydrogen	Comonomer	Mw	Mn	PDI	MFR
	mol	bar[a)]				g/10 min
A	0.66	0	18840	1168.4	16.1	>300
B	0.4	0	58793	14054	4.18	7.6
C	0	0.6	430406	74336	5.79	–

[a)] Measured pressure is at 80 °C.

nitrogen atmosphere and the heating cooling rates were 10 °C/min according to ASTM 3418-03.

Results and Discussion

Table 1 and Figure 1 show molecular weight, molecular weight distribution, polydispersity index and also MFR of two pure homo-polymers and a pure copolymer. Obviously, in the pure homopolymerization, addition of hydrogen amount by 0.26 mol (from 0.4 mol (specimen b) to 0.66 mol (specimen a)), caused much broader MWD, considerable decrease of molecular weight and increase of MFR from 7.6 to about 300. On the other hand, pure copolymerization of ethylene in the absence of hydrogen (specimen c) resulted in higher molecular weights. From a two-step polymerization a bimodal molecular weight distribution should be resulted with MWD lying within corresponding distributions of each step.

Figure 2 shows the GPC graph of specimens produced through the two step polymerization. The polymerization conditions consisted of constant first step polymerization time of 30 minutes under 0.4 mol hydrogen and the second step polymerization times of 30, 60 and 120 min under 0.7 bar 1-butene. According to Figure 2 and Table 2, increasing the time of polymerization resulted in higher molecular weight which means higher incorporation of copolymer. The first stage incorporation (P1) was higher than that of the next stage (P2), P1 > P2, which means higher rate of polymerization in the first stage than the second one despite lower polymerization time in the first stage.

In the case of H1-30-30 and H1-30-60, the molecular weight distribution was not wide enough and high molecular weight especially in the case of H1-30-120, could make processability difficult.

Figure 3 shows two step polymerization of ethylene in the presence of 0.66 mol hydrogen with various times of polymerization in each step. In these runs the first step polymerization carried out in 30 and 60 min. Contrary to the previous set of experiments, in this condition, the rate of

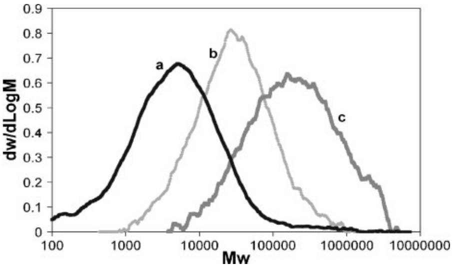

Figure 1.
Molecular weight distribution of samples prepared by pure homopolymerization under a) 0.66 mol hydrogen, b) 0.4 mol hydrogen and c) copolymerization.

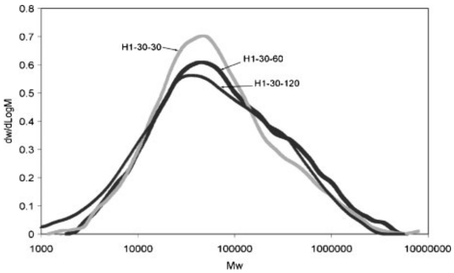

Figure 2.
Effect of polymerization time on molecular weight distribution in the presence of 0.4mol hydrogen. The sample codes are defined in Table 2.

Table 2.
physical and molecular properties of specimens under 0.4 bar hydrogen.

Sample a)	Mw	Mn	Density	PDI	MFR	P1/P2	
			(g/cm^3)		g/10 min	%/%	g/g
H1-30-30	178201	26666	0.962	6.68	0.13	69/31	49/22
H1-30-60	227151	28544	0.9616	7.95	–b)	59/41	48/33
H1-30-120	–c)	–c)	0.95	–	–b)	49/59	52/53

The amount of comonomer is 0.7 bar in 80 °C in all samples. a)The first and second numbers represent the first and second polymerization times (min) respectively. b)Polymer melt did not come out of the die of the MFR instrument. c)Data did not obtain from GPC because of high molecular weight.

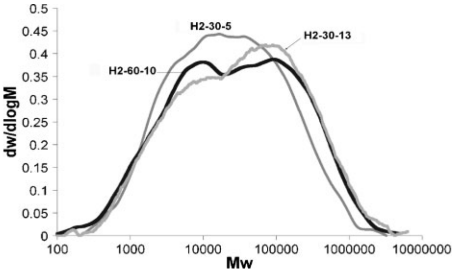

Figure 3.
Effect of polymerization time on molecular weight distribution in the presence of 0.66 moles hydrogen, the sample codes are defined in Table 3.

polymerization in the first step became lower than the rate of polymerization in the second step because of higher hydrogen utilized in the first step. For this reason the considered polymerization times for the second step were considered significantly lower than the first step to achieve bimodal distribution.

Considering Table 3, increasing the hydrogen amount from 0.4 to 0.66 mol not only decreased molecular weight and rate of polymerization in the first step, but also increased the high molecular weight incorporation in the second step. In the case of polymerization under 0.66 mol hydrogen, high molecular weight incorporation within the second polymerization time of 13 min was 76% (in H2-30-13), while in the case of polymerization under 0.4 mol hydrogen, this figure was about 41% (in H1-30-60) during copolymerization time of 60 min. The relevant molecular weights are presented in Table 2 and Table 3. It is seen that despite the higher incorporation of copolymer in the second stage as shown in Table 3, average molecular weight of the specimens are considerably lower representing very wide molecular weight distribution.

The narrowest molecular weight distribution belonged to the H2-30-5 specimen with quite low average molecular weights (Table 3). Increasing of the second polymerization time to 13 min, increased molecular weight and molecular weight distribution significantly according to the Table 3. Physical properties of the specimens are also given in this table.

Comparing these results with the previous ones, and Figure 3 with Figure 2, it was figured out that average molecular weights of the specimens were reduced as it was expected, but, the molecular weight distribution broadened considerably, meaning better processability and lower mechanical properties.

Table 3.
Physical and molecular properties of bimodal specimens under 0.66 mol hydrogen.

Sample a)	Mw	Mn	PDI	Density	MFR	P1/P2	
				(g/cm^3)	g/10 min	%/%	g/g
H2-30-5	86000	5536	15.4	$>$0.968	0.5	38/62	7/11.5
H2-60-10	131519	4594	28.6	$>$0.968	0.17	37/63	14/24
H2-30-13	158103	5922	26.7	0.953	0.08	24/76	9.5/30

The measured amount of comonomer is 0.7 bar at 80 °C in all samples. a)The first and second numbers represent the first and second polymerization times (min) respectively.

Rheological Study

Figure 4 and Figure 5 illustrate the complex viscosity versus frequency of the specimens produced under 0.4 and 0.66 mol hydrogen respectively. Obviously increasing the time of polymerization in the second step increased the complex viscosity as a consequence of higher average molecular weight in each system. From Cox-Merz relation, $\eta(\dot{\gamma}) = \eta^*(\omega)|_{\dot{\gamma}=\omega}$ the viscosity as a function of shear rate can be approximated. As it is demonstrated in Figure 4 and Figure 5, the viscosity obeys power law relationship in non-Newtonian region. The transition from Newtonian to non-Newtonian (pseudo plastic) region is sharper and shifts to lower frequencies or shear rates for specimens with narrow molecular weight distribution (Figure 4). Zero shear viscosity was estimated from the curves at very low shear rate where the viscosity is independent of shear rate. As shown in Table 4 with increasing molecular weight in each series zero shear viscosity increases correspondingly.

For investigating the melt miscibility of high molecular weight and low molecular weight fractions cole-cole plots were prepared (Figures 6, 7). Figure 6 shows a deviation in lower frequencies from a linear relationship of G′ and G″ in case of polymerization under 0.4 bar hydrogen for all specimens except for H1-30-30 specimen. Figure 7 shows cole-cole plots of specimens produced under 0.66 mol hydrogen. The figure represents relatively linear relationships indicating improved melt miscibility in comparison with the previous one. Considering the high measured density in both sets of experiment, it can be concluded that the branching content is quite low and it seems that the difference between molecular weights of each step plays a role.

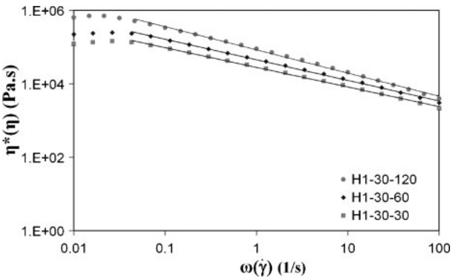

Figure 4.
Complex viscosity of samples prepared in a two-step polymerization with different time of polymerization under 0.4 mol hydrogen.

Table 4.
Zero shear viscosity and power-law parameters of different specimens.

Sample	η_o (Pa.s)	K (Pa.s^n)	n	Mw
H1-30-30	146552	28204	0.47	178201
H1-30-60	250790	45078	0.44	227151
H1-30-120	704893	84117	0.369	-----
H2-30-13	235971	53149	0.395	158103
H2-60-10	154149	38036	0.398	131519
H2-30-5	83944	23154	0.438	85199

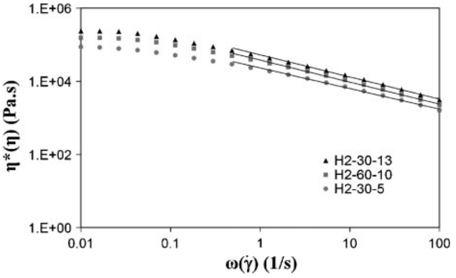

Figure 5.
Complex viscosity of samples prepared in a two-step polymerization with different time of polymerization under 0.66 mol hydrogen.

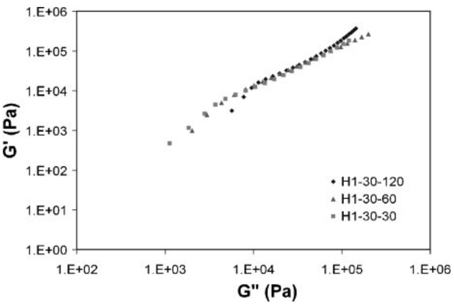

Figure 6.
Cole-Cole plots G'' vs G' for samples prepared in a two-step polymerization with different time of polymerization under 0.4 mol hydrogen.

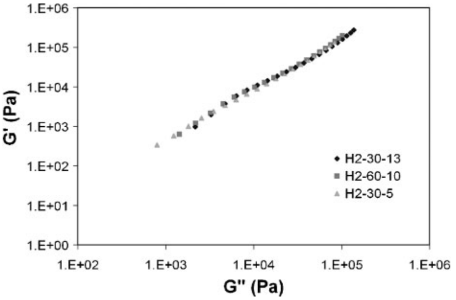

Figure 7.
Cole-Cole plots G“ vs G’, for samples prepared in a two-step polymerization with different time of polymerization under 0.66 mol hydrogen.

Figures 8 and 9 illustrate G″/G′ (tanδ) versus frequency of specimens produced under 0.4 and 0.66 mol hydrogen respectively. It is demonstrated that the specimens produced under first series conditions have higher melt elasticity than specimens produced under the second series conditions. This is due to the higher average molecular weight of the specimens in the first series than the second one, however, the productivity ratio (first stage/second stage) of the latter is lower. This is due to the presence of chains with very low molecular weight in specimens from the second series.

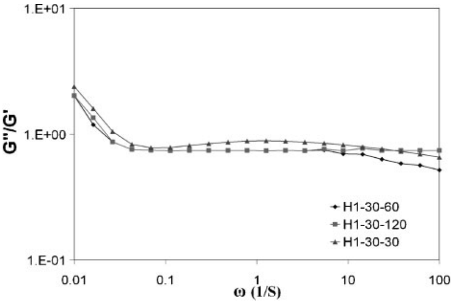

Figure 8.
Comparison of tanδ (G″/G′) of three samples prepared in the two-step polymerization with different time of polymerization under 0.4 mol hydrogen.

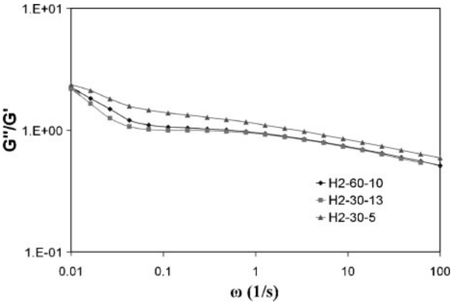

Figure 9.
Comparison of tanδ (G″/G′) of three samples prepared in the two-step polymerization with different time of polymerization under 0.66 mol hydrogen.

Conclusion

Using two-step polymerization, regulation of molecular weight and molecular weight distribution was performed by manipulating the hydrogen concentration added in the first stage and the time of polymerization, which all considerably affect molecular weight and its distribution. Increasing hydrogen concentration results in lower polymerization rate and lower molecular weight in the first stage, but higher polymerization rate in the second stage. So, molecular weight can be regulated by variation of polymerization times of both steps especially the second step. The more hydrogen amount in the first stage causes the lower needed time of polymerization in the second stage compared with the first stage to achieve bimodal distribution. The rheological results show shear thinning behavior of all specimens and confirm the changes in molecular weight and molecular weight distribution. Increasing the amount of chains with very low molecular weight improves melt miscibility between low molecular weight and high molecular weight fractions and decreases the melt elasticity.

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