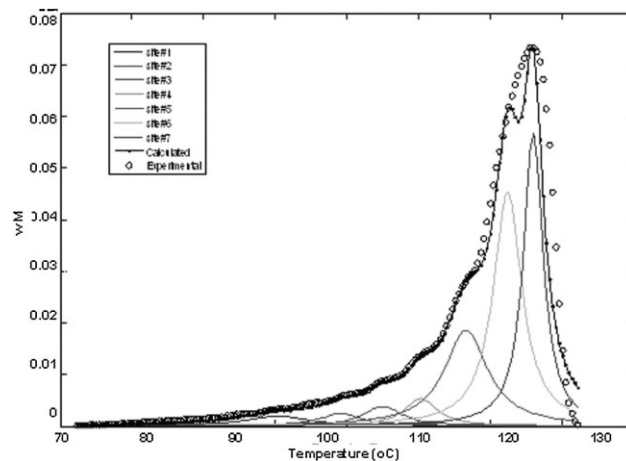


Ethylene Homo- and Copolymerization Using a Bis-IndZrCl₂ Metallocene Catalyst: Structural Composition Distribution of the Copolymer

Mohammadmehdi Mortazavi, Hassan Arabi,* Gholam Hossein Zohuri,* Saeid Ahmadjo, Mehdi Nekoomanesh, Mostafa Ahmadi

A bis-IndZrCl₂ catalyst was synthesized and used for ethylene homo- and copolymerization. The activity of the catalyst increases with increasing Al/Zr ratio; optimum activity was reached at 60 °C. \overline{M}_v of the polymer decreased as the polymerization temperature increased; increasing reaction pressure increased both \overline{M}_v and catalyst activity. The copolymerization of ethylene with different α -olefins was studied using the same catalyst system. The results indicate that under identical conditions there was a general decrease in the rate of polymerization as compared to the homopolymerization. The CCD and the lamellar thickness were investigated using DSC. The heterogeneity of the CCD increased with increasing comonomer content and molar mass.



Introduction

In the past decades, metallocene catalysts have been the center of olefin polymerization and now their importance has increased as new catalysts to produce polymers with unique properties.^[1–4] These attentions are due to their high catalytic activity and excellent ability of comonomer incorporation in olefin polymerization for catalyst named ansa-metallocene.^[5] Also these catalysts are able to tailor the composition of polymers and produce polymers with

narrow molecular weight distribution and uniform comonomer distribution. These interesting features have efficiently led extensive efforts to utilize metallocene catalysts. In comparison with Ziegler-Natta catalysts, metallocene catalysts can control the polymer properties excellently. Also incorporation of α -olefin in ethylene copolymerization using metallocene catalysts is better and they have higher activity.^[6–8] Particularly, the ansa-metallocene catalyst showed even better stereospecificity.^[5,8–14]

It is well known that polyethylene is one of the world's largest volume thermoplastics. The share of polyethylene based on metallocene catalysts market will reach about 20% until 2010.^[15] Copolymerization of ethylene with α -olefins produces important commercial products which have the main share of this market. There have been many efforts toward finding suitable catalysts for copolymerization of α -olefins,^[9,10,16,17] studying the kinetic behavior^[18,19] and microstructure of copolymer.^[20–24] The density of copolymer which is one of the critical parameters

M. Mortazavi, H. Arabi, S. Ahmadjo, M. Nekoomanesh, M. Ahmadi
Department of Catalyst, Iran Polymer and Petrochemical
Institute, P.O. Box 14965/115, Tehran, Iran

E-mail: h.arabi@ippi.ac.ir

G. H. Zohuri

Department of Chemistry, Faculty of Science, Ferdowsi University
of Mashhad, P.O. Box 1436, Mashhad, Iran

E-mail: g.zohuri@ippi.ac.ir

influencing its properties can be controlled by the extent and distribution of branching. The thermal and mechanical properties of ethylene copolymers are depend upon the structural characteristics of the polymer chains such as molecular weight (\overline{M}_w), molecular weight distribution (MWD), comonomer content, and short chain branching distribution (SCBD).^[24–26] Therefore, finding the relationship between structural properties of polyethylene and final properties of the sample is one of the great interests.^[27–29] The incorporation of comonomer can be controlled easily by careful selection of reactor conditions using these new catalysts, leading the reaction to achieve new grades of polyethylene.

In the present work, bis-IndZrCl₂ metallocene catalyst was synthesized. Homopolymerization of ethylene and its copolymerization with higher α -olefins (1-hexene and 1-octene) at a moderate condition were carried out. The effects of different reaction parameters such as temperature, cocatalyst concentration, and monomer pressure on polymerization kinetics were investigated. New DSC techniques such as the stepwise crystallization (SC) and self-successive nucleation/annealing (SSA) method which are recently used for the determination of the chemical composition distribution (CCD) and the lamellar thickness were utilized for investigation of the heterogeneity of intermolecular composition distribution and characteristic of lamellar structure.

Experimental Part

Indene (90%), 1-hexene, 1-octene, and MeLi solution in Et₂O were purchased from Merck (Germany), MAO (10 wt.-% in toluene) and the molecular sieve was provided by Aldrich (Germany). Toluene, Et₂O, pentane, and CH₂Cl₂ were provided by Luba (India) and all of them were refluxed and distilled over drying agent before use and kept over type 4Å/13X activated molecular sieves. All the manipulation involving air and/or water sensitive compounds were performed under atmosphere of dried N₂ in a glove box.

Catalyst Synthesis

The bis-IndZrCl₂ catalyst was synthesized by modifying the method described in ref.^[30] MeLi (20 mmol) was added dropwise to a solution of indene (2.4 g in 30 mL Et₂O). The mixture was stirred for 40 min at room temperature. The resulting solution was added to ZrCl₄ (10 mmol in 30 mL pentane) immediately. The prepared suspension was stirred for further 2 h at room temperature. The final product was filtered and the residue was refluxed for 6 h in CH₂Cl₂ (100 mL). The solvent was removed from the filtrate. The obtained solid was washed several times using dried Et₂O to purify as much as possible and then dried.

¹H NMR: δ = 6.17 [d, 4H, Cp-H(1,3)], 6.49 [t, 2H, Cp-H(2)], 7.25–7.32 (m, 4H, Ar), 7.60–7.64 (m, 4H, Ar).

Polymerization

Ethylene homopolymerization and its copolymerization with 1-hexene and 1-octene was carried out in a 1 L Buchi reactor (Buchiglauster bmd300) containing fully controlled system of temperature, stirring speed, and reaction pressure. Toluene was introduced into the reactor (450 mL) and saturated with ethylene (1 atm pressure) at the reaction temperature. MAO and the catalyst solutions were added, respectively. Sufficient amount of comonomer was added to the reactor just before introduction of the catalyst system in copolymerization experiments. At the end of the polymerization (mainly 1 h) the content of the reactor was poured into an excess amount of methanol, followed by filtering and drying 12 h.

Characterization

All the DSC results were obtained using Mettler-Toledo apparatus 823^e Module, interfaced to a digital computer equipped with Star E 9.01 software (sensor FR55). The sample was heated from room temperature to 160 °C at 10 °C · min⁻¹ rate and remained for 10 min; followed by cooling to 0 °C at the same rate. Finally the polymer was reheated to 160 °C using the same rate. The melting point and crystallinity was determined according to the results at the final step. The intrinsic viscosity was determined in Decahydronaphthalin at 135 ± 1 °C using a SOFICA-CINEVISCO viscometer serial V04/1CE. The catalyst structure was characterized using H NMR (400 MHz, AVANCE 400 BRUKER).

Thermal Fractionation Method

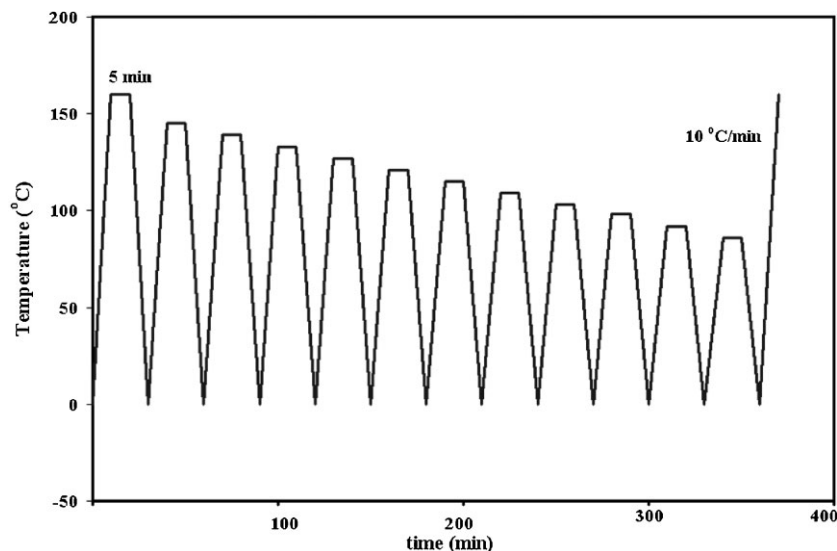
Self-successive nucleation/annealing method was used to analyze the CCD of copolymers using the following procedure:

The sample was heated to 160 °C at 10 °C · min⁻¹ rate and maintained at this temperature for 10 min. The sample was then cooled to ambient temperature at the same rate, immediately heated to 145 °C and maintained at the temperature for 5 min. The temperature stages were speared from each other by 6 °C. The annealing temperatures covered the range of 85–145 °C. Finally the cooled sample was heated at 10 °C · min⁻¹ and melting endotherms were recorded (Figure 1).^[31]

Results and Discussion

Homopolymerization

Generally, the role of MAO in the polymerization reaction includes alkylation, generation of cationic active species, and stabilization of these species by coordinative contact with its counterion.^[32] Table 1 shows catalytic activity against [Al]/[Zr] molar ratio. As can be seen, by increasing the [Al]/[Zr] ratio up to 5 000 the activity of the catalyst increases significantly; however, further increase in the ratio decreases activity of the catalyst. The behavior might be attributed to excessive complexation of MAO with active



■ Figure 1. Schematic method of SSA.

above 60 °C could be attributed to low propagation rate and deactivation of active site probably by changing its structure.^[32,34] The \bar{M}_v of the polymer linearly decreased with the increase in temperature (Figure 3). This behavior could be due to more chain transfer reaction which occurred at higher temperature.^[4,32,36,37]

Table 2 illustrates the influence of monomer pressure on activity and molecular weight of the polymer obtained. Higher activity obtained at higher monomer pressure. By increasing the polymerization pressure the monomer concentration increases which leads to rise in productivity and the molecular weight of the polymer as well.^[38–41]

centers. Therefore, the vacant coordination positions at these active centers become unavailable for monomer complexation.^[33] Very high concentration of MAO could change the structure of active centers via changing the ligand group, i.e., replacing chlorine with alkyl group for each active center that will change the electronic atmosphere of the active center to less active one.^[34] Similar behavior was observed for variation of \bar{M}_v against MAO concentration. The increasing of \bar{M}_v at low concentration of the MAO could be due to the elimination of chain transfer agent generated from impurities. However, chain transfer to the cocatalyst will be dominated at high concentration.^[35]

The influence of reaction temperature on polymerization behavior is shown in Figure 2. The optimum activity was obtained at 60 °C. Thus the reduced activity in temperatures

Table 1. Effect of Al concentration on activity of the catalyst. Conditions: monomer pressure 2 bar, temperature 60 °C, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

[Al]/[Zr]	Activity (kg polymer) · (mol Zr) ⁻¹ · h ⁻¹	\bar{M}_v
1 250	4.1×10^3	4.2×10^5
2 500	1.7×10^4	–
3 750	1.8×10^4	4.7×10^5
4 250	1.9×10^4	–
5 000	2.6×10^4	5.0×10^5
6 250	2.1×10^4	4.5×10^5
7 500	1.7×10^4	3.7×10^5

Copolymerization

Copolymerization of ethylene with various amounts of 1-hexene and 1-octene was carried out. Table 3 and 4 show the catalytic behavior of (Ind)₂ZrCl₂ and physical properties of the copolymers. Figure 4 and 5 show the rate/time profiles for the copolymerization. The profiles are of decay types for both homopolymerization and copolymerization. In metallocene type catalysts, usually a low enhancement factor has been reported for small molecule α -olefins such as 1-butene, whereas rate depression has been reported for longer α -olefins such as 1-hexene and 1-octene.^[42] The term comonomer effect factor (CEF) is defined as the ratio of average polymerization of copolymer to homopolymerization and decay index (DI) is the ratio of maximum catalytic activity to its minimum value ($R_{p, \max}/R_{p, \min}$) which is an indication of the extent of decrease in catalyst activity at the end of the polymerization run. The corresponding results are listed in Table 3 and 4. The observed results of CEF < 1 and DI \gg 1 indicate that a rate depression effect has happened in this homogeneous catalytic system. The negative trend observed for CEF in copolymerization can be attributed to a competitive coordination of the comonomer to the active center resulting in a possible deactivation of some catalytic centers.^[42] The CEF also decreased with the increase in the molar mass of the comonomer used.

Effect of Comonomer on Chemical Composition Distribution and Lamellar Thickness

Nowadays many researchers study the influence of metallocene catalyst on comonomer incorporation, mole-

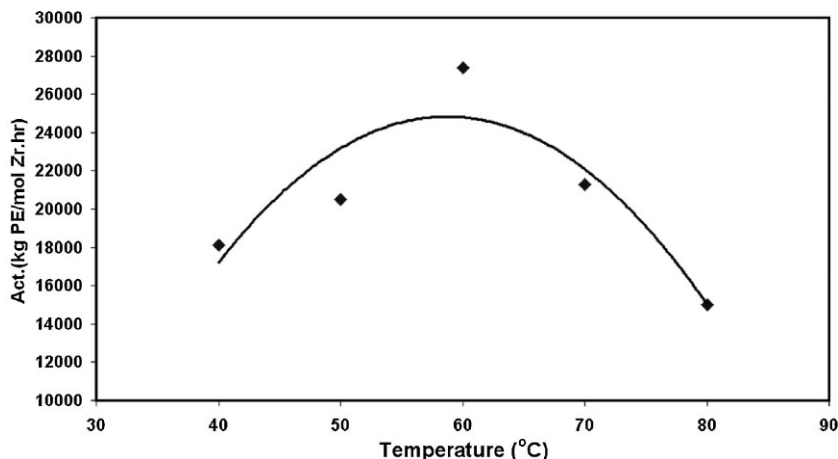


Figure 2. The effect of temperature on catalyst activity. Conditions: monomer pressure, 2 bar; [Al]/[Zr], 5 000:1; toluene, 450 mL; [Cat], 1.0×10^{-6} mol Zr.

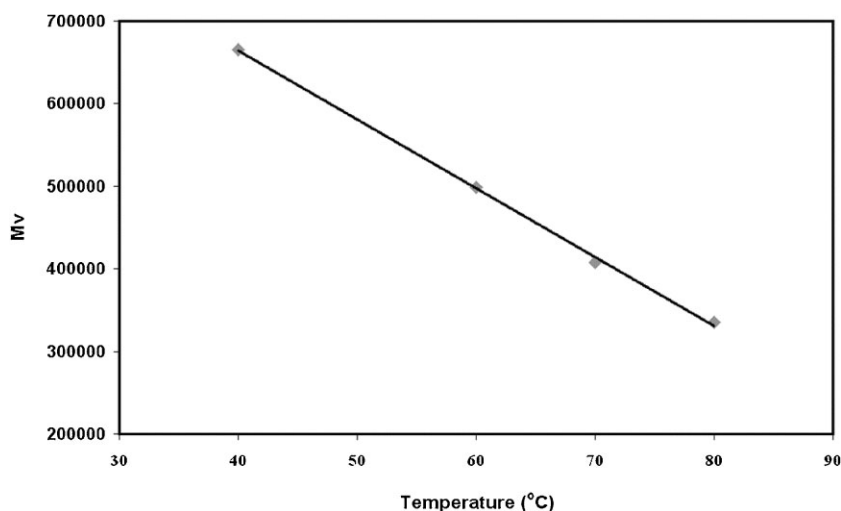


Figure 3. The effect of temperature on the viscosity average molecular weight. Conditions: monomer pressure, 2 bar; [Al]/[Zr], 5 000:1; toluene, 450 mL; [Cat], 1.0×10^{-6} mol Zr.

Table 2. Effect of pressure on ethylene polymerization. Conditions: temperature 60 °C, [Al]/[Zr] = 5 000:1, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

Pressure	Activity	\bar{M}_v
bar	(kg polymer) · (mol Zr) ⁻¹ · h ⁻¹	
2	2.6×10^4	5.0×10^5
3	3.4×10^4	5.2×10^5
4.5	3.8×10^4	–
6	4.0×10^4	6.6×10^5

cular weight of the copolymer and its distribution.^[6,31,42–44] Primary characteristics of the copolymer such as melting temperature and crystallinity are listed in Table 3 and 4. As expected by increase of the comonomer concentration in copolymerization media, crystallinity and melting temperature of the copolymer was decreased. To obtain some information about structure of the copolymer, new DSC characterization methods called SSA or SC were employed.^[31]

During the isothermal crystallization steps, the separation of the crystalline material into groups of lamellae of different thickness depending on the amount and distribution of the α -olefin units in the macromolecular chain, takes place.^[44] Introduction of α -olefin in backbone of the polymer increases the heterogeneity of the polymer and decreases the lamellar thickness.^[45,46] The lower temperature endotherm peaks corresponds to the greater number of short chain branches in the polymer backbone. As can be seen in Figure 6, the multiplicity of the endotherm peak is related to different lamellar thicknesses of the sample used. The DSC Index (DSCI) is often used for the determination of the heterogeneity of the copolymer.^[6,44] This value can be obtained from the ratio of the each peak height to the height of the biggest peak or the Δ_{melt} for each peak related to the Δ_{melt} of the biggest peak. The latter definition is more accurate and was employed in this work. By using the DSCI concept, it was possible to make semi-quantitative estimation for the heterogeneity of the

copolymer. Similar DSCI values close to one indicated relatively homogeneous incorporation of the comonomer in the polymer chain. For each sample, the results of DSCI value are listed in Table 5 and 6. It was observed that increase of the comonomer content increased the heterogeneity of the copolymer. This trend was also seen when the molar mass of the comonomer was increased.

The multiplicity of the melting peaks observed in DSC heating curves arises from the segregation of the crystallizable sequence length. The longer segment rather crystallization to thicker lamellar crystals, which melt at higher temperatures. Thus, the number of peaks is related to CCD.^[44–46]

Table 3. Catalytic behavior and physical properties of ethylene/1-hexene copolymer. Conditions: temperature 60 °C, monomer pressure 4 bar, [Al]/[Zr] = 4 000:1, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

1-Hexene concentration mmol · L ⁻¹	Activity (kg polymer) · (mol Zr) ⁻¹ · h ⁻¹	T _m	Crystallinity %	CEF	DI ^{a)}
0	3.3×10^4	139.3	58.9	1.00	8.6
26	2.5×10^4	134.9	52.6	0.78	25.9
52	2.0×10^4	134.3	51.3	0.61	32.2
106	0.7×10^4	133.5	49.4	0.22	25.4

^{a)}DI = $R_{p, \max}/R_{p, 60\text{min}}$.

Table 4. Catalytic behavior and physical properties of ethylene/1-octene copolymer. Conditions: temperature 60 °C, monomer pressure 4 bar, [Al]/[Zr] = 4 000:1, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

1-Octene concentration mmol · L ⁻¹	Activity (kg polymer) · (mol Zr) ⁻¹ · h ⁻¹	T _m	Crystallinity %	CEF	DI ^{a)}
0	3.3×10^4	139.3	58.9	1.00	8.6
20	1.9×10^4	136.4	52.5	0.59	22.1
40	0.7×10^4	–	50.5	0.20	33.0
80	0.1×10^4	133.9	42.6	0.03	–

^{a)}DI = $R_{p, \max}/R_{p, 60\text{min}}$.

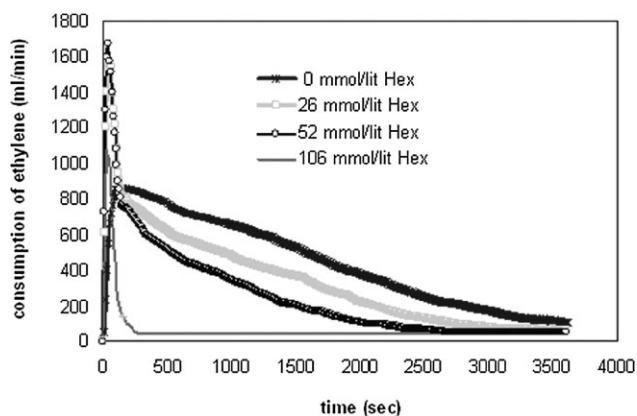


Figure 4. Profile of rate versus time for copolymerization ethylene/1-hexene. Conditions: temperature, 60 °C; monomer pressure, 4 bar; [Al]/[Zr], 4 000:1; toluene, 450 mL; [Cat], 1.0×10^{-6} mol Zr.

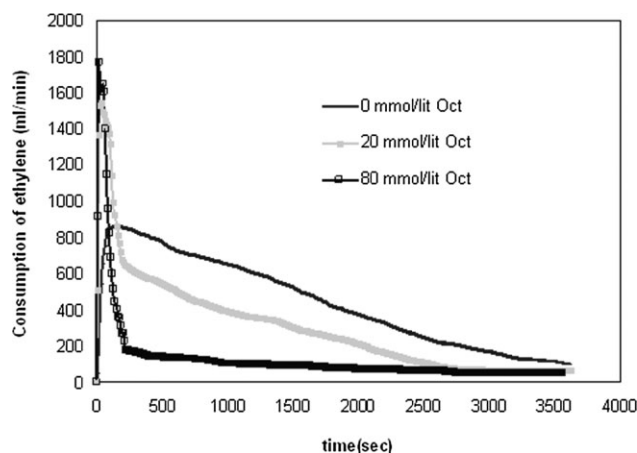


Figure 5. Profile of rate versus time for copolymerization ethylene/1-octene. Conditions: temperature, 60 °C; monomer pressure, 4 bar; [Al]/[Zr], 4 000:1; toluene, 450 mL; [Cat], 1.0×10^{-6} mol Zr.

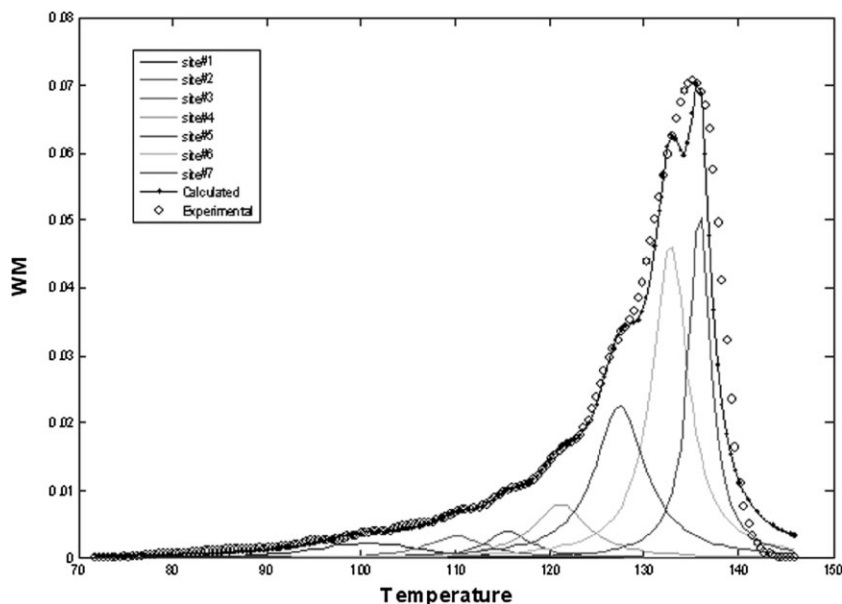


Figure 6. DSC thermogram of ethylene/1-hexene copolymer.

Table 5. Lamellar thickness and DSCI of the fractionated ethylene/1-hexene copolymer and its distribution. Conditions: temperature 60 °C, monomer pressure 4 bar, [Al]/[Zr] = 4000:1, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

1-Hexene concentration mmol · L ⁻¹	Peak no.	T_m	I_c (Å)	W	DSCI
106	1	136.0	36.5	29.6	0.86
	2	132.4	22.1	34.4	1.00
	3	126.6	13.5	21.4	0.62
	4	120.3	9.5	4.7	0.14
	5	115.0	7.6	3.9	0.11
	6	109.1	6.2	2.7	0.08
	7	100.3	4.9	3.3	0.10
52	1	136.7	42.1	26.9	0.75
	2	133.3	24.5	36.1	1
	3	127.7	14.6	21.1	0.59
	4	121.5	10.1	7.7	0.21
	5	115.9	7.9	3.7	0.10
	6	110.6	6.5	2.5	0.07
	7	104.8	5.5	2.1	0.06
26	1	139.0	79.7	34.9	0.91
	2	134.7	29.5	38.3	1.00
	3	128.7	15.7	16.9	0.44
	4	121.9	10.3	5.2	0.14
	5	116.0	7.9	2.4	0.06
	6	110.7	6.5	1.1	0.03
	7	105.3	5.6	1.1	0.03

The thickness of different lamellae can be calculated from the Thomson-Gibbs' Equation^[26]

$$T_m = T_m^\circ (1 - 2\delta_e / \Delta H l_c) \quad (1)$$

where T_m is the observed melting point (K), T_m° the equilibrium melting point of an infinite polyethylene crystal (414.5 K), δ_e the surface energy of a polyethylene crystal ($70 \times 10^{-3} \text{ J} \cdot \text{m}^{-2}$), ΔH the enthalpy of fusion of 100% crystalline polyethylene per unit volume ($288 \times 10^6 \text{ J} \cdot \text{m}^{-3}$), and l_c (m) is the thickness of the lamellae with melting point T_m .

The relative amount of lamellae of different thicknesses was calculated based on the area of the thermogram peaks. The results are listed in Table 5 and 6. The lamellar thickness distribution

in the samples obtained over homogeneous catalyst for 1-hexene and 1-octene comonomers are presented in Figure 7 and 8, respectively. As can be observed, the lamellae thickness varies from 5 to 80 Å and from 5 to 50 Å for copolymers obtained by 1-hexene and 1-octene comonomers, respectively.

Table 6. Lamellar thickness and DSCI of fractionated ethylene/1-octene copolymer and its distribution. Conditions: temperature 60 °C, monomer pressure 4 bar, [Al]/[Zr] = 4000:1, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

1-Octene concentration mmol · L ⁻¹	Peak no.	T_m	I_c (Å)	W	DSCI
80	1	137.2	47.1	53.0	1.00
	2	132.2	21.6	27.0	0.51
	3	126.0	13.0	10.4	0.20
	4	119.9	9.3	3.4	0.06
	5	114.7	7.5	1.8	0.04
	6	108.8	6.2	2.5	0.05
	7	100.1	4.9	2.0	0.04
20	1	137.3	48.2	30.0	0.83
	2	133.6	25.4	36.1	1.00
	3	127.6	14.5	21.1	0.59
	4	121.2	9.9	5.5	0.15
	5	115.8	7.8	3.1	0.09
	6	110.7	6.5	1.6	0.04
	7	105.0	5.5	2.6	0.07

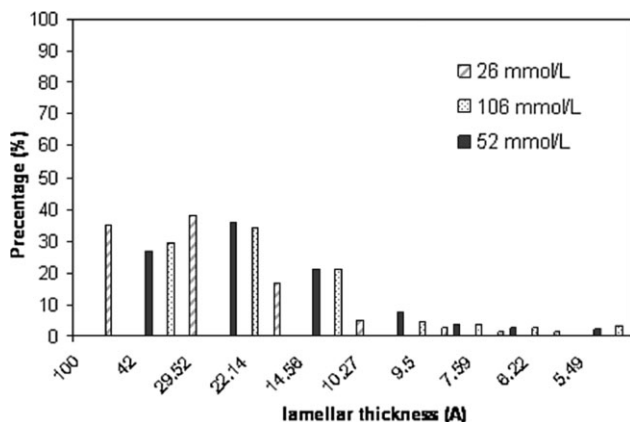


Figure 7. Effect of 1-hexene concentration on lamellae thickness distribution. Conditions: temperature, 60 °C; monomer pressure, 4 bar; [Al]/[Zr], 4 000:1; toluene, 450 mL; [Cat], 1.0×10^{-6} mol Zr.

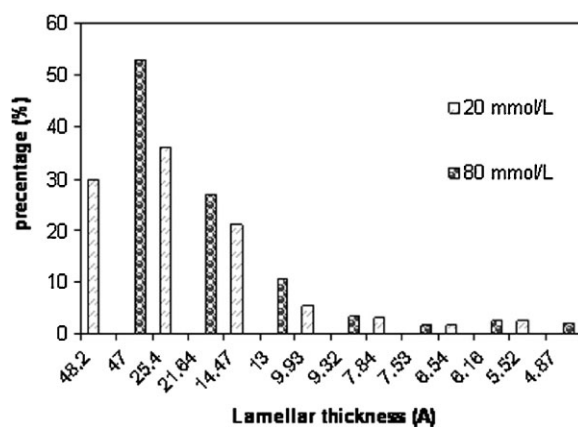


Figure 8. Effect of 1-octene concentration on lamellae thickness distribution. Conditions: temperature 60 °C, monomer pressure 4 bar, [Al]/[Zr] = 4 000:1, toluene 450 mL, [Cat] = 1.0×10^{-6} mol Zr.

Conclusion

The comparative activity of bis-IndZrCl₂ catalyst in polymerization of ethylene and its copolymerization with 1-hexene and 1-octene was investigated. The effects of [Al]/[Zr] molar ratio, temperature and monomer pressure on the activity, and molecular weight of the polymer was investigated. Also the effect of comonomer concentrations on the copolymerization behavior and characteristics of the copolymer obtained were studied. The following conclusions can be drawn:

The activity of the catalyst increased with the increase in MAO, the cocatalyst, concentration to an optimum value of 2.6×10^4 (kg polymer) · (mol Zr)⁻¹ · h⁻¹. The \bar{M}_v of the polymer obtained also increased to an optimum value of 5×10^5 at a [MAO]/[Zr] molar ratio of 5 000:1, however,

further increase of the concentration resulted in decrease the molecular weight of the polymer.

The maximum activity was obtained at polymerization temperature of 60 °C, while, the \bar{M}_v of the polyethylene was decreased with the reaction temperature. \bar{M}_v of the polymer as well as the catalyst productivity increased by the monomer pressure.

Addition of comonomers 1-hexene and 1-octene decreased the polymerization activity, crystallinity, and the melting point of the copolymer obtained. The behavior could be due to branching of the polymer chain. The CEF and DI both were decreased with addition of the comonomers. The higher the concentration of the comonomers, the lower the lamellar thickness and the smaller the size of crystals. The lower value of CEF indicates that negative comonomer effect was prevailing in copolymerization. Heterogeneity of the copolymer distribution for copolymer of ethylene/1-octene was higher than the copolymer of ethylene/1-hexene.

Acknowledgements: The authors would like to thank the National Iranian Petrochemical Company-Research and Technology (NIPC-RT) for the financial support of this work.

Received: January 17, 2009; Revised: April 15, 2009; Accepted: April 16, 2009; DOI: 10.1002/mren.200900003

Keywords: comonomer composition distribution; ethylene/ α -olefin copolymerization; metallocene catalyst; polyethylene; structural analysis

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