

# Copolymerization of ethylene/ $\alpha$ -olefins using bis(2-phenylindenyl)zirconium dichloride metallocene catalyst: structural study of comonomer distribution

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## Abstract

Catalysts have a major role in the polymerization of olefins and exert their influence in three ways: (1) polymerization behaviour, including polymerization activity and kinetics; (2) polymer particle morphology, including bulk density, particle size, particle size distribution and particle shape; and (3) polymer microstructure, including molecular weight regulation, chemical composition distribution and short- and long-chain branching. By tailoring the catalyst structure, such as the creation of a bridge or introducing a substituent on the ligand, metallocene catalysts can play a major role in the achievement of desirable properties. Kinetic profiles of the metallocene catalyst used in this study showed decay-type behaviour for copolymerization of ethylene/ $\alpha$ -olefins. It was observed that increasing the comonomer ratio in the feedstock affected physical properties such as reducing the melting temperature, crystallinity, density and molecular weight of the copolymers. It was also observed that the heterogeneity of the chemical composition distribution and the physical properties were enhanced as the comonomer molecular weight was increased. In particular, 2-phenyl substitution on the indenyl ring reduced somewhat the melting point of the copolymers. In addition, the copolymer produced using bis(2-phenylindenyl)zirconium dichloride (bis(2-PhInd)ZrCl<sub>2</sub>) catalyst exhibited a narrower distribution of lamellae (0.3–0.9 nm) than the polymer produced using bisindenylzirconium dichloride catalyst (0.5–3.6 nm). The results obtained indicate that the bis(2-PhInd)ZrCl<sub>2</sub> catalyst showed a good comonomer incorporation ability. The heterogeneity of the chemical composition distribution and the physical properties were influenced by the type of comonomer and type of substituent in the catalyst.

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**Keywords:** metallocene catalyst; copolymerization; copolymer composition distribution; differential scanning calorimetry (DSC); crystallinity

## INTRODUCTION

Polyethylene is one of the world's largest volume polymers. The market share of polyethylene produced using metallocene catalysts reached about 20% in 2010, and these catalysts are considered as one of the most important developments in polyolefin technology.<sup>1,2</sup> Polyethylene copolymers of higher  $\alpha$ -olefins such as propylene, 1-butene, 1-hexene and 1-octene are important commercial products which have the main share of this market.<sup>3</sup>

A greater extent of short-chain branches in the backbone of these polymers results in lower melting point, crystallinity and density, therefore making them more flexible and processable. The physical properties such as melting point, crystallinity and density of ethylene copolymers are dependent upon the structural characteristics of the copolymer chains, such as molecular weight, molecular weight distribution, comonomer content and short-chain branching distribution.<sup>4–6</sup>

The type of catalyst is one of the most influential factors determining the characteristics of the resulting polymers. Metallocene catalysts have several advantages over conventional Ziegler–Natta catalysts: higher activity, narrow molecular weight

distribution, high comonomer incorporation and narrow chemical composition distribution (CCD).<sup>7–9</sup> There has been much effort made towards finding suitable catalysts for copolymerization of  $\alpha$ -olefins,<sup>10–13</sup> and studying the kinetic behaviour<sup>14–16</sup> and microstructure of copolymers.<sup>3,16–23</sup> Using new metallocene catalysts, incorporation of comonomer can easily be controlled, and by careful selection of operating conditions it is possible to achieve new grades of polyethylene. Ansa metallocene catalysts that favour comonomer incorporation were developed based on

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this interest.<sup>24–26</sup> The ansa catalysts show higher comonomer incorporation than non-bridged catalysts.<sup>10,27–30</sup> Since the discovery of bridged catalysts, much research has been focused on catalyst design and the role of the bridges in catalytic performance.<sup>30–36</sup> In recent research it has been found that addition of substituents to ligands can improve catalyst activity and comonomer incorporation ability.<sup>3,37–43</sup> This observation is believed to be due to the steric and electronic effects of the substituent on the ligand.<sup>44,45</sup>

In the work reported in the present study, bis(2-phenylindenyl)zirconium dichloride (bis(2-PhInd)ZrCl<sub>2</sub>) metallocene catalyst was synthesized using an indirect method which has the advantage of allowing the preparation of the catalyst at room temperature instead of at  $-78^{\circ}\text{C}$ . The performance of the catalyst in the copolymerization of ethylene with propylene, 1-hexene and 1-octene was investigated. The kinetic behaviour of the catalyst during the copolymerization was studied. The comonomer composition distribution was determined using the new technique of self-successive nucleation/annealing (SSA) differential scanning calorimetry.

## EXPERIMENTAL

### Materials

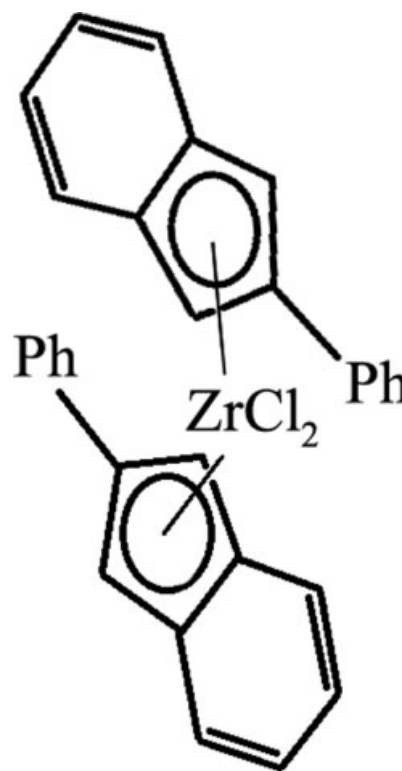
Methylaluminoxane (MAO; 10 wt% solution in toluene) was obtained from Aldrich Chemical Co. (Munich, Germany). Toluene was purchased from Luba (India). 1-Hexene and 1-octene were provided by Merck Chemical Co. (Munich, Germany) and were refluxed and distilled over a drying agent before use and kept over 4A/13X activated molecular sieves. Ethylene and propylene were obtained from Arak Petrochemical Company (Arak, Iran). All the manipulations involving air- and/or water-sensitive compounds were performed under an atmosphere of dried nitrogen in a glove box.

### Preparation of catalyst

The bis(2-PhInd)ZrCl<sub>2</sub> (scheme 1) was synthesized using indirect method. At first MeLi (20 mmol) was added to 2-Phenylindene (10 mmol) dissolved in Et<sub>2</sub>O (30 mL) over a period of about 5 min at room temperature. The mixture was stirred for 40 min following to addition of ZrCl<sub>4</sub> (5 mmol) dispersed in toluene (30 ml) at once. The suspension was stirred for 90 min at room temperature. The product was filtered. The filtrate was treated at room temperature with HCl (10 mmol) and stirred for 60 min. The final product was obtained by removing the solvent under reduced pressure. It was characterized by HNMR:  $\delta$  7.59 (d,4H), 7.39(m,4H), 7.27(m,2H), 7.19(dd,4H), 7.02(dd,4H), 6.55 (s,4H).

### Copolymerization

Ethylene copolymerizations with propylene, 1-hexene and 1-octene were carried out in a 1 L Buchi reactor (Buchiglauster bmd300) containing systems for full control of temperature, stirring speed and reaction pressure. Toluene (450 mL) was introduced into the reactor and saturated with ethylene (101 kPa pressure) at the reaction temperature. MAO and catalyst solutions were then added. Sufficient amount of comonomer was added to the reactor just before the introduction of the catalyst itself. For copolymerization of ethylene with 1-hexene the comonomer was introduced at  $40^{\circ}\text{C}$  and then the temperature increased up to the reaction temperature. At the end of the polymerization (usually 1 h) the content of the reactor was poured into an excess of methanol, filtered and dried at  $70^{\circ}\text{C}$ .



**Scheme 1.** Structure of bis(2-PhInd)ZrCl<sub>2</sub> catalyst.

### Polymer characterization

DSC was carried out using a Mettler-Toledo model 823<sup>o</sup> instrument, interfaced to a digital computer equipped with Star E 9.01 software (Sencor FRS5). Samples were heated from room temperature to  $160^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C min}^{-1}$  and held there for 10 min, followed by cooling to  $0^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C min}^{-1}$ . Finally the samples were reheated to  $160^{\circ}\text{C}$  using the same heating rate. The melting point and crystallinity were determined according to the results obtained from the final step.<sup>46</sup>

The intrinsic viscosity was determined in decahydronaphthalene at  $135 \pm 1^{\circ}\text{C}$  with a SOFICA-CINEVISCO viscosimeter (V04/1CE) and using the Mark–Houwink equation.<sup>47</sup> The number of branches in the copolymers was calculated using the Fourier transform infrared method, being calibrated using <sup>13</sup>C NMR evaluated standard. Densities of the copolymers were calculated using an Ohaus Voyager Pro VP64C balance with densitometer facility.

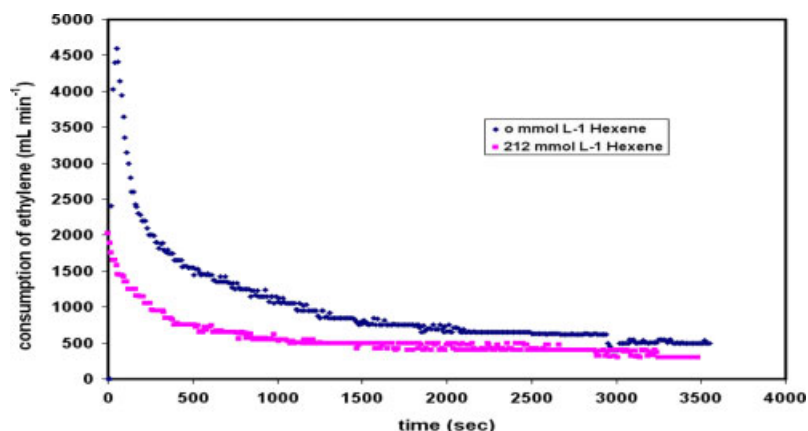
### Thermal fractionation

The SSA method was used to analyse the CCD of the copolymers, as described in previous work.<sup>16</sup>

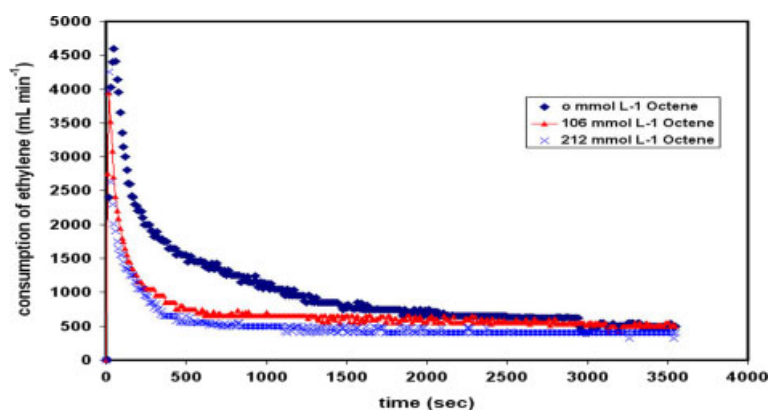
## RESULTS AND DISCUSSION

### Kinetic study

Ethylene copolymers were produced using various amounts of propylene, 1-hexene and 1-octene. The decay-type rate–time profiles of the copolymerizations are shown in Figs 1–3. The term “comonomer effect factor” (CEF) and decay index (DI) are defined as  $R_{p,av}(co)/R_{p,av}(hom)$  and  $R_{p(max)}/R_{p(min)}$ , ( $R_{p,av}$  is the average rate of polymerization,  $R_{p(max)}$  is the maximum rate



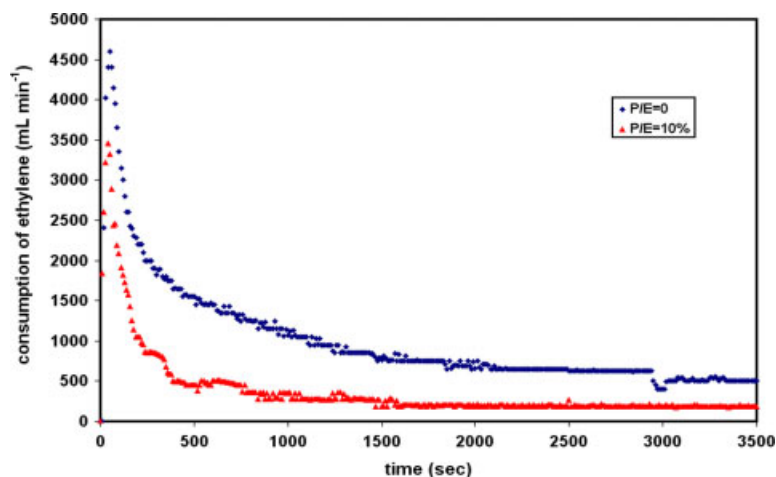
**Figure 1.** Profile of rate versus time for copolymerization of ethylene/1-hexene (temperature = 60 °C, monomer pressure = 404 kPa, [Al]/[Zr] = 700 : 1, toluene = 450 mL, [catalyst] = 1.0 × 10<sup>-5</sup> mol Zr).



**Figure 2.** Profile of rate versus time for copolymerization of ethylene/1-octene (temperature = 60 °C, monomer pressure = 404 kPa, [Al]/[Zr] = 700 : 1, toluene = 450 mL, [catalyst] = 1.0 × 10<sup>-5</sup> mol Zr).

of polymerization and  $R_{p(\min)}$  is the rate of polymerization at 60 min) respectively, which were used to follow the kinetic behavior of the catalyst. The kinetic results are listed in Table 1. The observed results of  $CEF < 1$  and  $DI \gg 1$  indicate that a depression effect occurs for the CEF and DI for homogenous polymerization of the catalyst with increasing monomer concen-

tration in the feed. The decreasing trend observed for CEF in the copolymerizations may be attributed to a competitive coordination of the comonomer to the active centre resulting in a possible deactivation of some catalytic centres.<sup>16,48</sup> The CEF also decreased with increasing molecular weight of the comonomer used.



**Figure 3.** Profile of rate versus time for copolymerization of ethylene/propylene (temperature = 60 °C, monomer pressure = 404 kPa, [Al]/[Zr] = 700 : 1, toluene = 450 mL, [catalyst] = 1.0 × 10<sup>-5</sup> mol Zr).

**Table 1.** Kinetic parameters of ethylene copolymers

	Homopolymer	Propylene	Hexene	Octene	Hexene	Octene	Hexene	Octene
Comonomer concentration in feed (mmol L <sup>-1</sup> )	0	P/E = 10% <sup>a</sup>	35	35	106	106	212	212
Activity <sup>b</sup>	8070	7578	6700	5900	6500	5700	5100	4600
CEF	1.00	0.94	0.83	0.73	0.79	0.71	0.63	0.57
DI	9.5	15.4	–	7.2	8.6	6.2	6.0	5.6

Conditions: temperature = 60 °C, monomer pressure = 404 kPa, [Al]/[Zr] = 700 : 1, toluene = 450 mL, [catalyst] = 1.0 × 10<sup>-5</sup> mol Zr.  
<sup>a</sup> Propylene in feed/ethylene in feed.  
<sup>b</sup> In kg polymer (mol Zr h)<sup>-1</sup>.

**Table 2.** Physical properties of copolymers

	Homopolymer	Propylene	Hexene	Octene	Hexene	Octene	Hexene	Octene
Comonomer concentration in feed (mmol L <sup>-1</sup> )	0	P/E = 10% <sup>a</sup>	35	35	106	106	212	212
T <sub>m</sub> (°C)	140.7	126.1	124.6	130.0	117.4	123.2	107.8	114.4
Crystallinity (%)	67.1	30.6	40.8	56.9	33.2	45.5	23.4	30.1
Density (kg m <sup>-3</sup> )	0.955	0.918	0.926	0.930	0.914	0.928	0.914	0.920
Br/1000 C <sup>b</sup>	–	13.3	4.7	3.7	6.8	5.7	11.9	10.0
M <sub>v</sub>	235 000	94 400	219 000	68 200	–	34 456	92 000	–

<sup>a</sup> Propylene in feed/ethylene in feed.  
<sup>b</sup> Branches per 1000 carbon atoms in chain.

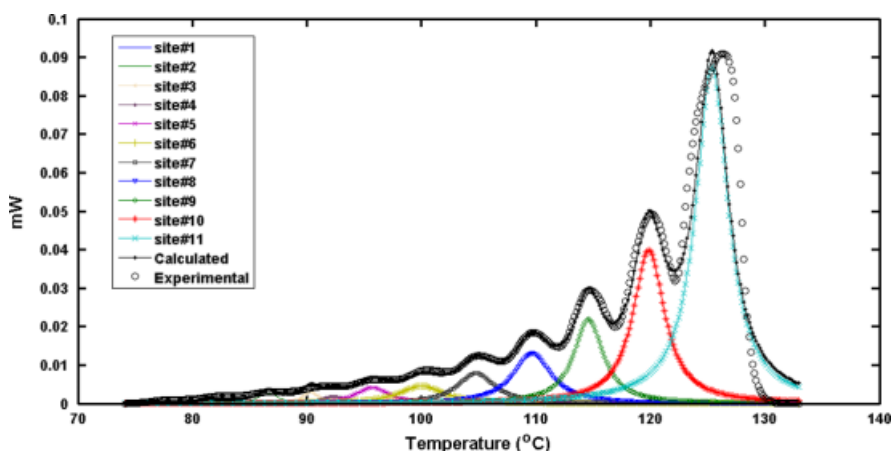
### Effect of comonomer type on copolymer properties

Table 2 gives a selection of copolymer properties: melting temperature, crystallinity, molecular weight, density and number of branches per 1000 carbon atoms of the backbone chain. As can be seen, on increasing the comonomer content in the feed, melting temperature, crystallinity and molecular weight of the copolymers decrease. As expected, by increasing the comonomer concentration in the polymerization medium and by decreasing the molecular weight of comonomer, the comonomer content and therefore the number of branches in the copolymers increase. The lower the molecular weight of comonomer the higher the activity of the monomer to incorporate into the polymer chains. Also a higher concentration of comonomer increases the possibility of its incorporation into the polymer chains. Addition

of branches in the copolymers causes the density and crystallinity to decrease.<sup>49–52</sup> The molecular weight of the copolymers also decreases with increasing comonomer ratio in the feed, which could be interpreted as a result of an increase in chain transfer reaction by  $\beta$ -hydride elimination.<sup>53–55</sup>

### Effect of comonomer type on CCD of copolymers

The influences of metallocene catalysts on comonomer incorporation and on copolymer molecular weight and its distribution are interesting subjects in the field of polymerization.<sup>7,56–59</sup> Some traditional methods such as temperature rising elution fractionation, <sup>13</sup>C NMR and crystallization analysis fractionation are widely used for studying the structures of copolymers. Recently researchers have used several new methods based on stepwise DSC, namely

**Figure 4.** DSC thermogram of copolymer (106 mmol L<sup>-1</sup> 1-octene) deconvoluted to weighted summation of standard Lorentzian distribution functions.

**Table 3.** Lamellar thickness ( $l_c$ ) and DSCI value of ethylene/1-hexene copolymer and their distribution

1-Hexene concentration (mmol L <sup>-1</sup> )	Peak no.	$T_m$ (°C)	$l_c$ (nm)	Weight %	DSCI
35	1	69.4	0.28	0.91	0.04
	2	78.3	0.32	2.97	0.06
	3	86.0	0.36	2.92	0.07
	4	90.8	0.40	1.58	0.08
	5	95.4	0.44	3.19	0.10
	6	100.2	0.49	3.66	0.13
	7	104.9	0.55	4.38	0.17
	8	109.9	0.64	7.10	0.24
	9	114.8	0.75	8.39	0.35
	10	120.6	0.96	24.88	0.61
	11	126.1	1.31	40.02	1.00
106	1	77.7	0.32	0.49	0.04
	2	81.7	0.34	1.40	0.07
	3	86.4	0.37	3.45	0.10
	4	91.0	0.40	3.50	0.14
	5	95.5	0.44	5.55	0.19
	6	100.2	0.49	8.53	0.27
	7	105.0	0.55	11.05	0.41
	8	110.2	0.64	22.16	0.74
	9	115.3	0.77	29.92	1.00
212	1	77.7	0.32	0.85	0.02
	2	81.8	0.34	2.15	0.10
	3	86.2	0.36	4.15	0.85
	4	90.9	0.40	7.03	1.00
	5	95.5	0.44	11.61	0.67
	6	100.4	0.49	20.24	0.38
	7	105.4	0.56	33.63	0.24
	8	109.5	0.63	18.68	0.16
	9	116.6	0.81	1.66	0.06

Conditions: temperature = 60 °C, monomer pressure = 404 kPa, [Al]/[Zr] = 700 : 1, toluene = 450 mL, [catalyst] =  $1.0 \times 10^{-5}$  mol Zr.

**Table 4.** Lamellar thickness ( $l_c$ ) and DSCI value of ethylene/1-octene copolymer and their distribution

1-Octene concentration (mmol L <sup>-1</sup> )	Peak no.	$T_m$ (°C)	$l_c$ (nm)	Weight %	DSCI	
35	1	102.1	0.51	4.51	0.04	
	2	111.4	0.67	6.70	0.08	
	3	118.2	0.86	7.27	0.12	
	4	121.7	1.02	8.89	0.19	
	5	125.7	1.28	12.06	0.35	
	6	128.7	1.57	24.98	0.75	
	7	132.1	2.14	35.59	1.00	
	106	1	82.1	0.34	0.43	0.01
		2	86.8	0.37	1.52	0.02
		3	90.1	0.39	0.11	0.03
		4	91.4	0.40	1.14	0.05
5		95.6	0.44	2.64	0.07	
6		100.4	0.49	3.93	0.10	
7		104.9	0.55	4.40	0.14	
8		109.7	0.63	7.76	0.20	
9		114.6	0.75	10.88	0.33	
10		119.9	0.93	21.58	0.54	
11		125.4	1.25	45.61	1.00	
212	1	76.6	0.31	0.76	0.04	
	2	81.3	0.33	2.09	0.07	
	3	85.7	0.36	2.92	0.10	
	4	90.1	0.39	3.98	0.15	
	5	94.5	0.43	5.34	0.21	
	6	98.9	0.47	7.90	0.31	
	7	103.6	0.53	12.75	0.46	
	8	108.4	0.61	15.54	0.72	
	9	113.2	0.71	27.99	1.00	
	10	117.4	0.84	15.09	0.81	
	11	121.9	1.03	5.64	0.44	

Conditions: temperature = 60 °C, monomer pressure = 404 kPa, [Al]/[Zr] = 700 : 1, toluene = 450 mL, [catalyst] =  $1.0 \times 10^{-5}$  mol Zr.

SSA and stepwise crystallization, as easier alternative characterization methods.<sup>9</sup>

During isothermal crystallization steps the separation takes place of the crystalline material into groups of lamellae of different thicknesses depending on the amount and distribution of the  $\alpha$ -olefin units in the macromolecular chain.<sup>56,59,60</sup> The presence of  $\alpha$ -olefin in the backbone of the copolymer increases the heterogeneity of the copolymer which decreases the relative lamellar thickness.<sup>60,61</sup> The lower the number of temperature endotherms the greater is the number of short-chain branches in the copolymer backbone. As can be seen in Fig. 4, the DSC curves were deconvoluted to weighted summation of standard Lorentzian distribution functions. The multiplicity of the endotherm peak is related to different lamellar thicknesses of the sample under investigation. For determination of the heterogeneity of a copolymer, the DSC index (DSCI) is very often used.<sup>7,16,59</sup> This value can be obtained from the ratio of the peak height to the greatest peak height. Using the DSCI concept, it is possible to make a semi-quantitative estimation of the heterogeneity of the copolymers. Similar DSCI values close

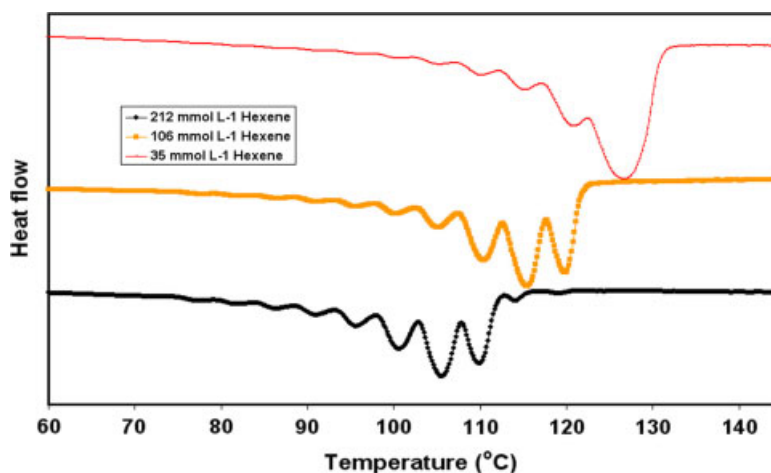
to unity indicate relatively homogeneous incorporation of the comonomer in the copolymer chain. Calculated DSCI values for ethylene/1-hexene and ethylene/1-octene copolymers are listed in Tables 3 and 4, respectively. It is observed that on increasing the comonomer content, the heterogeneity of the copolymer obtained is increased. This trend is also seen when the molecular weight of the comonomer is increased (Figs 5–7) within the range of the comonomers studied.

The multiple melting peaks observed in the DSC heating curves arise due to the segregation of the crystallizable sequence lengths. The longer segments recrystallize to longer lamellar crystals, which melt at higher temperatures. Thus, the number of peaks is related to the CCD.<sup>16,59–61</sup>

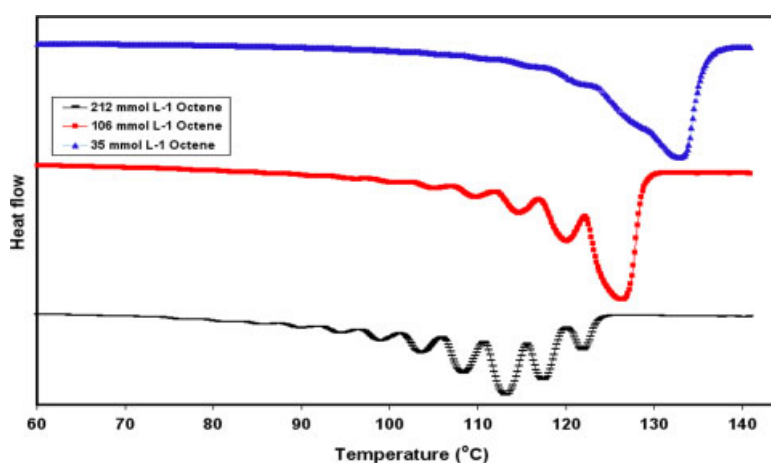
The thickness of different lamellae can be calculated from the Thomson–Gibbs equation:<sup>6</sup>

$$T_m = T_m^\circ \left( 1 - \frac{2\delta_e}{\Delta H \times l_c} \right) \quad (1)$$

where  $T_m$  is the observed melting point (K),  $T_m^\circ$  is the equilibrium melting point of an infinite polyethylene crystal (414.5 K),  $\delta_e$  is the surface energy of a polyethylene crystal ( $70 \times 10^{-3}$  J m<sup>-2</sup>),  $\Delta H$  is



**Figure 5.** Effect of 1-hexene concentration on the melting curves of ethylene copolymers obtained using bis(2-PhInd)ZrCl<sub>2</sub> catalyst and the SSA method.



**Figure 6.** Effect of 1-octene concentration on the melting curves of ethylene copolymers obtained using bis(2-PhInd)ZrCl<sub>2</sub> catalyst and the SSA method.

the enthalpy of fusion of 100% crystalline polyethylene per unit volume ( $288 \times 10^6 \text{ J m}^{-3}$ ) and  $l_c$  (m) is the thickness of the lamellae with melting point  $T_m$ .

The relative amounts of lamellae of various thicknesses were calculated based on the area of the thermogram peaks. The results are listed in Tables 3 and 4.

### Effect of phenyl substitution of the catalyst on comonomer incorporation

Physical properties and comonomer composition distribution of copolymers synthesized using bis(2-PhInd)ZrCl<sub>2</sub> and bisindenylzirconium dichloride (bisIndZrCl<sub>2</sub>) catalysts are compared in Table 5 and Fig. 8. It is observed that phenyl substitution at the 2-position on the indenyl ligand leads to the incorporation of more comonomer, which could affect copolymer characters including  $T_m$  and crystallinity. Figure 8 shows that bis(2-PhInd)ZrCl<sub>2</sub> has higher reactivity towards comonomer insertion in copolymerization. In addition, the CCD of copolymers synthesized using bis(2-PhInd)ZrCl<sub>2</sub> is more homogeneous than that of copolymers synthesized using bisIndZrCl<sub>2</sub>. As can be seen from Fig. 9 the copolymer produced using the bis(2-PhInd)ZrCl<sub>2</sub> catalyst contains a narrower distribution of lamellae (0.3–0.9 nm) than the polymer produced using the bisIndZrCl<sub>2</sub> catalyst (0.5–3.6 nm). Before the studies of the Waymouth group<sup>3,62–66</sup> of the synthesis

**Table 5.** Comparison of some physical properties of copolymers obtained using bisIndZrCl<sub>2</sub> and bis(2-PhInd)ZrCl<sub>2</sub> (1-hexene concentration in feed = 106 mmol L<sup>-1</sup>)

Property	bis(2-PhInd)ZrCl <sub>2</sub>	bisIndZrCl <sub>2</sub>
$T_m$ (°C)	107.8	133.5
Crystallinity (%)	23.4	49.4

of elastomeric polypropylene, the general belief was that only bridged catalysts could improve comonomer incorporation, but their results showed that bis(2-PhInd)ZrCl<sub>2</sub> is very successful in incorporation of comonomer. This is related to sterically restricted conformations in which the indenyl groups block the metal coordination sites, thus making these sites more open for coordination of the larger comonomer. It was suspected that having atmosphere near the metal coordination site also plays a role in comonomer coordination.<sup>3</sup> The results obtained in the present study are similar to those previously reported.<sup>3</sup>

### CONCLUSIONS

The activity of bis(2-PhInd)ZrCl<sub>2</sub> catalyst synthesized using an indirect method for copolymerization of ethylene with propylene, 1-

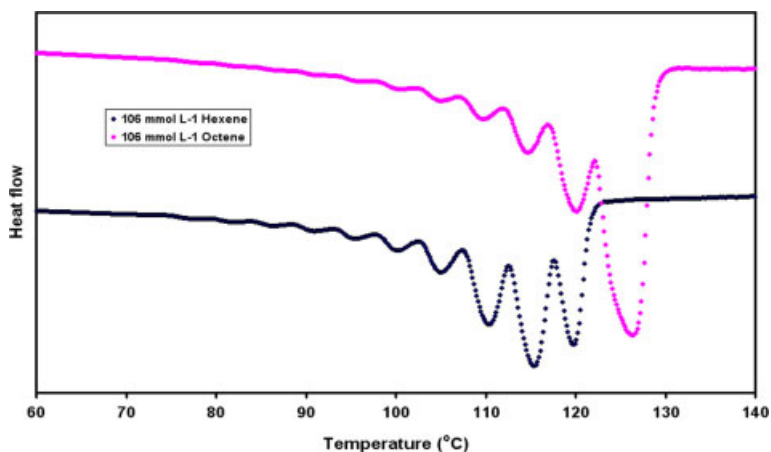


Figure 7. Comparison of the melting curves of ethylene/1-octene and ethylene/1-hexene copolymers using bis(2-PhInd)ZrCl<sub>2</sub> catalyst and the SSA method.

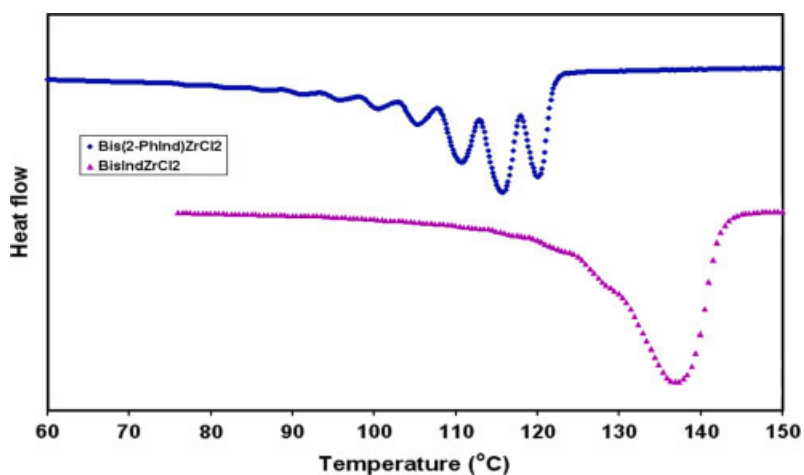


Figure 8. Comparison of the melting curves of ethylene/1-hexene (106 mmol L<sup>-1</sup>) copolymers obtained using bisIndZrCl<sub>2</sub> and bis(2-PhInd)ZrCl<sub>2</sub> catalysts via the SSA method.

hexene and 1-octene was investigated. The effects of comonomer length and concentration on the copolymerization behaviour and on the microstructure of the copolymers obtained were also investigated. The following conclusions can be drawn from the study.

Addition of 1-hexene and 1-octene comonomers decreased the polymerization activity, crystallinity, density, molecular weight and melting point of the copolymers obtained. This could be due to branching of the polymer chain. The CEF and DI both

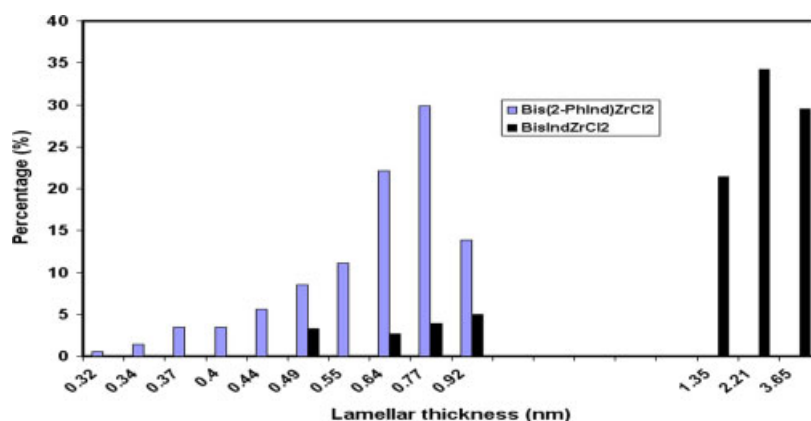


Figure 9. Comparison of the lamella distribution in ethylene/1-hexene (106 mmol L<sup>-1</sup>) copolymers obtained using bisIndZrCl<sub>2</sub> and bis(2-PhInd)ZrCl<sub>2</sub> catalysts (crystal size calculated based on Eqn (1) by considering  $T_m$  from deconvolution of DSC peaks).

decreased with increasing comonomer concentration. The higher the concentration of the comonomers, the smaller the lamellar thickness and the smaller the crystalline length. The lower value of CEF indicated that a negative comonomer effect prevailed in the copolymerizations. The heterogeneity of the copolymer distribution was more pronounced on increasing comonomer content and comonomer length.

It was found that phenyl substitution at the 2-position of the indenyl ligand plays a key role in comonomer incorporation, and the copolymers produced using bis(2-PhInd)ZrCl<sub>2</sub> catalyst were more homogeneous than those produced using bisIndZrCl<sub>2</sub> catalyst. It was found that the bis(2-PhInd)ZrCl<sub>2</sub> catalyst provides copolymers with narrower lamella distributions than the bisIndZrCl<sub>2</sub> catalyst.

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