

RAUL QUIJADA<sup>\*)</sup>, RENÉ ROJAS<sup>\*)</sup>,  
JUAN GUEVARA<sup>\*)</sup>, ANA NARVAEZ<sup>\*)</sup>,  
DIANA DELFIN<sup>\*)</sup>, GRISELDA B. DE GALLAND<sup>\*\*)</sup>

## Studies on homo and copolymerizations of long-chained $\alpha$ -olefins over metallocene catalysts

**Summary** — Metallocene catalysts, *viz.*,  $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ ,  $rac\text{-Me}_2\text{-Si(Ind)}_2\text{ZrCl}_2$  and  $\text{Ph}_2\text{C(Flu)(Cp)ZrCl}_2$ , were studied in homopolymerization of 1-octadecene and the first two were used in copolymerization of ethylene with 1-octadecene. They exhibited different activities and  $rac\text{-Et(Ind)}_2\text{ZrCl}_2$  was the most active in the homopolymerization carried out at 70°C. At 30°C, the activities were practically identical. In the copolymerization runs, the catalysts were similarly active, and the Et-bridged catalyst was the more active. The copolymers prepared over  $rac\text{-Me}_2\text{-Si(Ind)}_2\text{ZrCl}_2$  were found to have more comonomer incorporated. The composition of copolymerization products was found (<sup>13</sup>C-NMR) to vary with the catalyst system. DSC thermograms showed poly-1-octadecene prepared over  $rac\text{-Et(Ind)}_2\text{ZrCl}_2$  to vary in properties with polymerization temperature (Figs. 3—5). The homopolymer prepared at 70°C showed endotherms at 41°C and 53°C and that prepared at 30°C produced one broader peak at 67°C. With  $rac\text{-Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$ , the 70°C homopolymer produced one broader peaks at 41°C and 53°C and the 30°C homopolymer gave peaks at 7°C and 67°C. The two peaks in the homopolymer thermograms appear to be explicable in terms of different structural ordering in various homopolymer domains. As the comonomer concentration in the feed was increased, the molecular weight decreased and otherwise was independent of the type of the metallocene used.

**Key words:** homopolymerization, copolymerization, metallocenes, catalyst activity, poly-1-octadecene.

The discovery that metallocene catalysts can polymerize different monomers at very high rates and make it possible to obtain homo and copolymers with well defined structures, has introduced new options into making a wide variety of polymer materials endowed with attractive properties. In contrast to conventional multi-site Ziegler—Natta catalysts, the metallocene based catalysts produce very uniform homo and copolymers. The presence of an aromatic planar ring, steric and electronic effects, and the bridge group that restricts the mobility of the metallocene play an important role in the control of stereochemistry, molecular weight and incorporation of  $\alpha$ -olefin comonomers [1, 2].

Recently much attention has been focused on the preparation of homo and (co)poly( $\alpha$ -olefins) endowed with

novel interesting properties, by using well-known metallocene catalysts. These poly( $\alpha$ -olefins) can be tailored to specific applications by introducing long-chained or well-defined functional groups into the hydrophobic main chain or at the end of each polymer chain. Our earlier investigations have shown several metallocene catalyst to promote copolymerization of ethylene with  $\alpha$ -olefins [3, 4].

In recent years, theoretical models obtained with *ab initio* and semiempirical methods have been used to understand the experimental behavior in metallocene-catalyzed olefinic systems and also to predict the behavior of similar new catalytic systems. Using these methods, several phenomena have been studied [5]. Among them are the tacticity of the resulting polymer, the reaction mechanism and the influence of agostic interactions (where the C-H bond of the growing polymer chain acts as a ligand on the metallic center to form a C-H-metal bond) [6—8]. Other studies make use of molecular mechanics to characterize, from the geome-

\*) Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 2777, Santiago, Chile

\*\*) Instituto de Química, Universidad Federal do Rio Grande do Sul., Av. Bento Gonçalves 9500-90540 Porto Alegre-RS-Brazil

try-optimized standpoint, catalyst molecules for obtaining ring dihedral angles, to observe the influence of ring substituents on the catalytic properties, and to determine possible steric hindrances which are the determinants of polymer chain structure [9–10].

The purpose of this work is to present results obtained in the homopolymerization of 1-octadecene and copolymerization of ethylene with 1-octadecene, by using some racemic and nonracemic catalytic systems. For the homopolymerization, the yield and catalytic activity is related to the metallocene structure. For the copolymerizations, the study is based on the observation of how the comonomer concentration influences the system's catalytic activity and the viscosity of the polymer.

## EXPERIMENTAL

### Materials

Commercial toluene was purified by refluxing over metallic sodium, using benzophenone as an indicator. The 1-octadecene comonomer (Aldrich) was purified by distilling over metallic sodium. Polymerization-grade ethylene was deoxygenated and dried by passing through columns of BASF R3-11 catalyst and 4Å-molecular sieves. Commercial (Witco and Boulder Scientific Co.) methylaluminoxane (MAO) and the catalysts *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and *rac*-(CH<sub>3</sub>)<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> were used without further refinement. All manipulations were carried out in an inert nitrogen atmosphere.

### Homopolymerization of 1-octadecene

Reactions were carried out in a 250-mL flask and a 500-mL glass reactor by using toluene as solvent at a reaction temperature of 70°C and 30°C. The reagents were introduced into the reactor in the following order: toluene, MAO, monomer and catalyst. The reaction was terminated by addition of a 2 vol.% of a HCl/methanol solution and then the reaction mixture was washed with acetone to remove all the unreacted monomer.

### Copolymerization

All copolymerizations were carried out in a 500-mL glass reactor with toluene as solvent at a reaction temperature of 60°C. The reagents were introduced into the reactor in the following order: toluene, comonomer, MAO, and the required amount of a catalyst solution. The reaction mixture was degassed, and then ethylene was introduced until a pressure of 1.6 bar was reached. After 30 min., polymerization was stopped by addition of 2 vol.% of a HCl/methanol solution. The resulting polymer was collected by filtration, washed with a HCl/methanol solution, then with acetone until no comonomer remained unreacted, and finally dried in vacuum at 60°C.

### Characterization

The amount of comonomer incorporated was followed by <sup>13</sup>C-NMR. Measurements were performed at 80°C on a Varian XL-200 or XL-300 spectrometer. Samples were dissolved in *o*-dichlorobenzene. Benzene-d<sub>6</sub> (20%) was used as an internal lock, and chromium(III) triacetylacetonate as a paramagnetic substance to reduce the relaxation time. Intrinsic viscosity was determined in decahydronaphthalene (decalin) at 135°C by using a Viscosimatic-Sofica viscometer.

For poly-1-octadecene, calorimetric analyses were carried out in a Perkin-Elmer DSC-7 calorimeter, connected to a cooling system and calibrated against different standards. Sample weights ranged from 7 to 10 mg. The DSC melting curves were recorded at a heating rate of 10°C/min, after crystallization from the melt at 10°C/min.

## RESULTS AND DISCUSSION

### Homopolymerization of 1-octadecene

#### Activity

Table 1 shows the catalytic activity in homopolymerization of 1-octadecene, obtained with different metallocene catalysts: *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>, and Ph<sub>2</sub>C(Flu)(Cp)ZrCl<sub>2</sub>.

Table 1. Yields and catalyst activities in various times of homopolymerization of C<sub>18</sub> over *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> and Ph<sub>2</sub>C(Flu)(Cp)ZrCl<sub>2</sub> catalysts

Metallocene	Experiment No.	[Zr]x10 <sup>5</sup> mol/L	Time, h	Yield, g polymer	Activity kg pol./mol Zr · h
<i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	1	6.4	0.5	4.5	1,765
	2	6.4	1	6.1	1,200
	3	6.3	3	6.3	420
<i>rac</i> -Me <sub>2</sub> Si(Ind) <sub>2</sub> ZrCl <sub>2</sub>	4	6.6	0.5	1.5	580
	5	6.6	1	2.6	530
	6	6.6	3	6.3	417
Ph <sub>2</sub> C(Flu)(Cp)ZrCl <sub>2</sub>	7	6.5	3	5.8	357

Reaction conditions: C<sub>18</sub> = 7.89 g, n(Zr) = 5x10<sup>-6</sup> mol, n(Al)/n(Zr) = 2,000, temperature: 70°C, solvent: 60 mL toluene, reactor: 250 mL flask.

The results show that the *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> catalyst offers the highest activity. Under the reaction conditions (closed reaction vessel with the same starting amount of 1-octadecene), it was observed that after 30 min the activity of the polymer produced by *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> relative to *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> was approximately 3 times as high. This result is consistent with the theoretical findings where the electronic charge on the Me<sub>2</sub>Si-bridged compound is more positive

than that on the Et-bridged catalyst, and it is the monomer linked more times to the active center [5]. These results are also consistent with a recent study on the correlation between the charge density and dissociation free energy [11].

In order to verify the thermal properties of the poly-1-octadecene, syntheses at different temperatures were carried out in a different reactor (500 mL), characterized by an excellent control of temperature and stirring. Table 2 shows the results of the catalytic activity at different temperatures for the two main catalysts, *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>.

**Table 2.** Yields and catalyst activities values at various temperatures of homopolymerization of C<sub>18</sub> over *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> catalysts

Metalloocene	Experiment No.	[Zr] × 10 <sup>5</sup> mol/L	Temperature °C	Yield, g polymer	Activity kg pol / mol Zr · h
<i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	8	5.8	70	9.2	1,102
	9	6.2	30	3.8	472
<i>rac</i> -Me <sub>2</sub> Si(Ind) <sub>2</sub> ZrCl <sub>2</sub>	10	5.9	70	5.1	609
	11	5.8	30	3.4	408

Reaction conditions: C<sub>18</sub> = 13.4 g, n(Zr) = 8 × 10<sup>-6</sup> mol, n(Al)/n(Zr) = 2,000, solvent: toluene 100 mL, rpm 300, time: 1 h, reactor: 500 mL

The catalytic activity for the *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> shows a great decrease. This can be due to the steric effect related to the loss of mobility of the aromatic ring linked to the zirconium atoms. This makes it difficult for the lefin to be inserted, affecting the catalytic behavior of the metallocene. On the other hand, the *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> has a more rigid structure and the temperature does not change the interaction too much.

### Copolymerization of ethylene with 1-octadecene

#### Activity

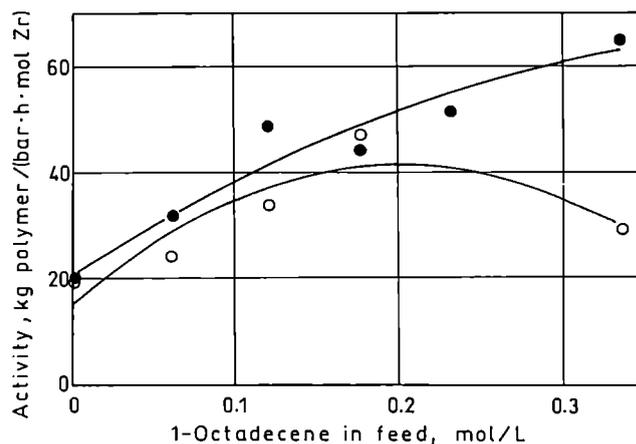
Table 3 and Figure 1 show the catalytic behavior of the system in the presence of the comonomer for two different catalysts, Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>, respectively. The increase of the comonomer fraction is seen to increase the catalytic activity until a maximum value is reached. Several explanations have been given [4] of which the more consistent could be the following two: on the one hand, the presence of the comonomer and its incorporation increase the solubility of the monomer in the liquid phase, thus increasing its insertion rate and, on the other hand, the comonomer activates new catalyst sites by an increased affinity for the metallocene.

Strong differences were observed between the activities of the two catalysts used. In Figure 1, the catalytic activity of the Et-bridged catalyst is seen to be higher than that of the Me<sub>2</sub>Si-bridged catalyst. As mentioned

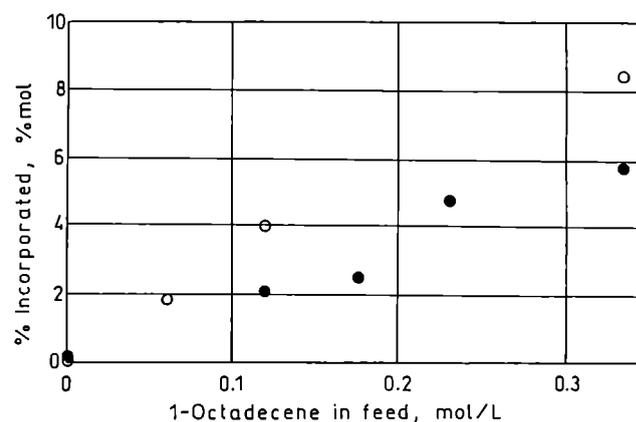
**Table 3.** The effect of comonomer concentration on the catalytic activity and content of 1-octadecene in ethylene copolymers prepared over Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>

Metalloocene	Comonomer feed mol/L	Activity · 10 <sup>3</sup> kg/mol Zr · h · bar	Comonomer incorporated mol %	Viscosity dL/g
<i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	0	18.4	0	2.71
	0.06	32.3	1.1	1.98
	0.12	48.2	2.0	1.80
	0.23	56.6	4.7	1.47
	0.33	61.6	5.7	1.20
<i>rac</i> -Me <sub>2</sub> Si(Ind) <sub>2</sub> ZrCl <sub>2</sub>	0	17.1	0	3.73
	0.06	24.0	1.8	2.36
	0.12	33.9	4.0	1.87
	0.23	—	—	—
	0.33	28.9	8.4	1.42

Reaction conditions: n(Zr) = 1.9 × 10<sup>-6</sup> mol; n(Al)/n(Zr) = 2,620; temperature: 60°C; time: 30 min; ethylene pressure = 1.6 bar



**Fig. 1.** The influence of initial comonomer concentration on catalyst activity in copolymerization of ethylene with 1-octadecene over different metallocenes; ● — Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>; ○ — Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>



**Fig. 2.** The effect of 1-octadecene comonomer feed on the incorporation over different metallocenes; ● — Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>; ○ — Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>

before, this is consistent with the theoretical findings [5].

#### Comonomer incorporation

Table 3 and Figure 2 show the amount of the comonomer incorporated into the copolymer to increase as the 1-octadecene concentration in the reaction medium is raised.

In the copolymerization with other comonomers having shorter chains such as 1-hexene [5], the percentage of comonomer incorporation has been found to be independent of the metallocene catalytic systems. Nevertheless, in the presence of 1-octadecene, some significant differences are observed: the  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$  system has incorporated more comonomer than the  $[\text{Et}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$  system (8.4 mol % for the former, compared with the 5.7 mol % for the latter, at a starting concentration of 0.33 mol/L). This behavior can be explained on the theoretical analysis already discussed [5]: the approach of a 1-octadecene chain to the metallic center finds less opposition in  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$  than in  $[\text{Et}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$ , and therefore the metallic center is more favorable in the first than in the second catalyst.

With respect to the percentage of incorporation as a function of the type of the comonomer, the incorporation of those of larger size such as 1-octadecene was found to be the lower as expected in view of the steric effects of the larger groups [4, 5].

### Polymer properties

#### Homopolymer of 1-octadecene

For the 1-octadecene homopolymer obtained with both catalysts, the DSC melting curves show very interesting results (Figs. 3–5). Figure 3 shows the thermograms for poly-1-octadecene obtained over the  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  catalyst at 70°C and 30°C, respectively. For the 70°C, there are two endotherm peaks at 41 and 53°C; for the 30°C, a single peak occurs at 67°C. The endotherms 53 and 67°C are due to the presence of cry-

stalline regions in the isotactic poly-1-octadecene. The peaks at lower temperatures could result from the disordered regions of the chains, which present a certain crystallinity due to some partial order of the lateral chain of poly-1-octadecene. The inversion of the intensity of the peaks may be due to the increase in the mobility of the structure of the catalyst when it is polymerized at 70°C, affecting the stereoselectivity. When the temperature is reduced to 30°C, the inverse phenomenon is observed. Figure 4 shows the melting curves of

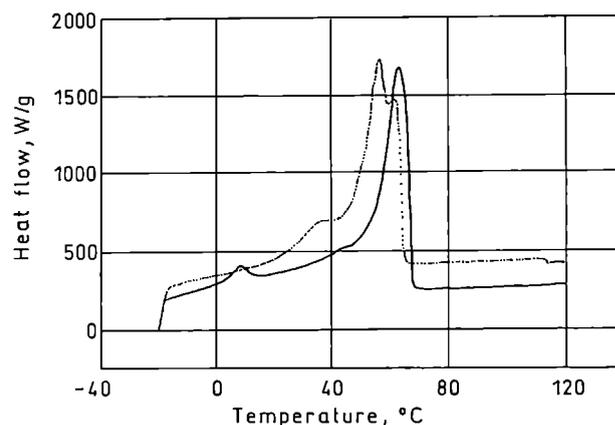


Fig. 4. DSC melting curve of 1-polyoctadecene obtained with  $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  at 70 (···) and 30°C (—)

the poly-1-octadecene synthesized over the  $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  catalyst at 70 and 30°C. The thermograms are similar except that the melting points are different. The curve of the synthesized homopolymer at 70°C shows two endotherms at 40 and 57°C, and the one synthesized at 30°C presents peaks at 7 and 67°C. Clearly, lowering of the temperature implies an increased rigidity in the metallocene structure, allowing a better stereoselectivity control.

The polymer prepared over  $\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$  catalysts produced only one peak at 37°C (Fig. 5), which is

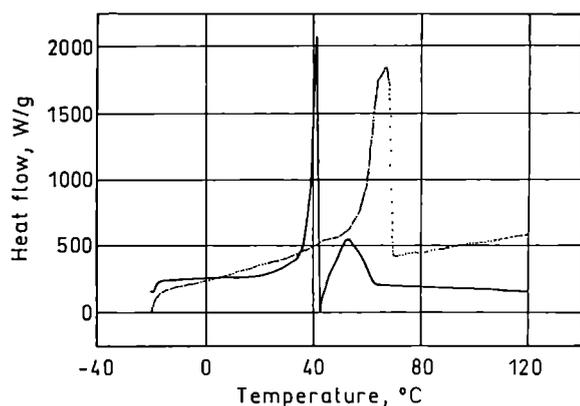


Fig. 3. Thermograms of 1-polyoctadecene obtained over  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  at 30 (···) and 70°C (—)

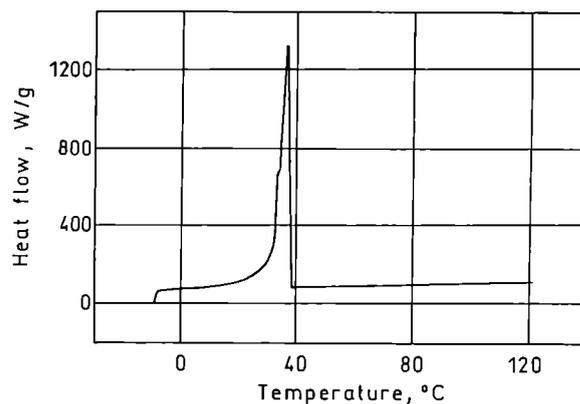


Fig. 5. DSC melting curve of 1-polyoctadecene obtained with  $\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$  at 70°C

due to the syndiotactic order of the chain of poly-1-octadecene, presenting one crystalline phase.

#### Copolymer of ethylene-1-octadecene. Molecular weight

Figure 6 shows that an increase in the comonomer concentration in the reaction medium decreases the intrinsic viscosity and therefore the weight-average molecular weight of the polymer. This can be explained if it

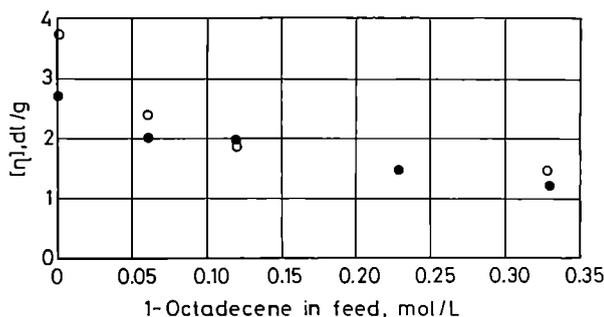


Fig. 6. Effect of 1-octadecene comonomer feed on the intrinsic viscosity  $[\eta]$  of the ethylene/1-octadecene copolymer for different metallocenes; ● —  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ ; ○ —  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$

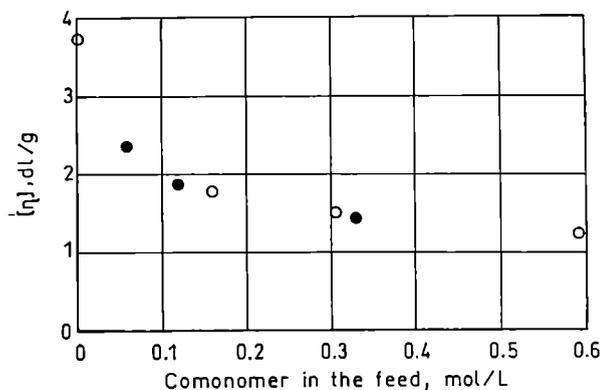


Fig. 7. Effect of the ethylene/ $\alpha$ -olefin comonomer feed on the intrinsic viscosity  $[\eta]$ , with  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  catalyst; ● — 1-octadecene, ○ — 1-hexene

is considered that the ratio of propagation rate to termination rate is decreased by the presence of comonomer, owing to  $\beta$ -type terminations. This is attributed to the

fact that the  $\alpha$ -olefin favors the stabilization of the four center intermediate, thereby allowing more time for interaction with the active site and making  $\beta$ -elimination or monomer transfer reactions possible to occur [4].

The variation in the molecular weight is seen to be independent of the catalytic system (Fig. 6).

Figure 7 shows the variation of the intrinsic viscosity as a function of the comonomer concentration at different ethylene/ $\alpha$ -olefin ratios. The molecular weight is seen to be independent of the type of comonomer.

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