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The influence of cyclopentadienyl ring substituent steric and electronic effects on the ethylene– α -olefin copolymerisation behaviour of $(\text{CpR})_2\text{ZrCl}_2$ /ethylalumoxane catalysts

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Abstract

A series of $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{ZrCl}_2$ ($\text{R} = \text{H, Me, Et, }^i\text{Pr, }^t\text{Bu, SiMe}_3, \text{Me}_2\text{Ph.}$) complexes have been used in combination with ethylalumoxane to copolymerise ethene with α -olefins ($\text{C}_5\text{--C}_{14}$) under constant conditions ($P = 9\text{--}12$ bar; $T = 50\text{--}80^\circ\text{C}$). Activity decreased substantially for olefin $> \text{C}_8$. Variations of the 1-hexene concentration ($(\text{CpEt})_2\text{ZrCl}_2$ as catalyst) revealed rate enhancement at a 1-hexene/ethylene ratio of 1.0. Copolymer incorporation was low ($< 6\%$) as detected by melting points and ^{13}C NMR spectroscopy. A statistically designed approach (2^3 factorial) was used to investigate the influence of P, T and [1-hexene] on copolymer formation with $(\text{CpR})_2\text{ZrCl}_2$ ($\text{R} = \text{H, }^t\text{Bu}$). Complex interaction between the variables was detected but the results ($\text{R} = ^t\text{Bu}$) were dominated by [1-hexene].

Keywords: Alumoxane; Copolymerisation; Cyclopentadienyl complexes; Substituted cyclopentadienyl rings; Zirconocene; Statistical design

1. Introduction

The copolymerisation of ethylene with higher α -olefins is an industrially important process. The introduction of side chains into the polymer, the lengths of which are determined by the comonomer, allows the manufacture of linear low density polyethylene (LLDPE). LLDPE has a lower density and melting point than high density polyethylene (HDPE), and these properties can be varied with a high degree of control [1–4]. It has been shown that the comonomer acts as a chain transfer agent, lowering the polymer molecular weight

(MW) and narrowing the molecular weight distribution (MWD) [5,6]. There are no long-chain branches on the polymer chains [7], and short-chain branches are determined solely by the comonomer [7]. The LLDPE copolymers have superior film and processing properties due to their increased mechanical and tear strength [2,8,9]. All these factors contribute towards added product value [3,4]. Ethylene–1-hexene (EH) copolymers are used industrially for the manufacture of stretch-wrap, laminated films, and mail and newspaper bags [9].

Surprisingly, few investigations with homogeneous zirconocene catalyst systems have been reported on ethylene– α -olefin copolymerisations, particularly with longer α -olefins. Most of the

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work done in this area has concentrated on the copolymerisation of ethylene with propene. $\text{Cp}_2\text{ZrX}_2/\text{MAO}$ ($\text{X} = \text{Cl}, \text{Me}$) has been used for ethylene–1-hexene [10–12], ethylene–1-octene [13] and ethylene–4-methyl-1-pentene [14] copolymerisation reactions. To our knowledge, no reports have been published on the use of catalysts containing substituted cyclopentadienyl rings for the copolymerisation of ethylene with higher, linear α -olefins.

We have thus undertaken an investigation of the influence of ring substituents, R, in $(\text{CpR})_2\text{ZrCl}_2$ on the polymerisation of ethylene with a range of linear $\text{C}_5\text{--C}_{14}$ α -olefins. Specific systems ($\text{R} = \text{Et}, \text{H}, \text{}^i\text{Bu}$) have been explored in some detail for the ethylene–1-hexene and ethylene–1-octene copolymerisation reaction. Although methylalumoxane (MAO) is the cocatalyst of choice in zirconocene polymerisation reactions we have chosen, as in our earlier studies [15], to use ethylalumoxane [EAO] as the cocatalyst. The EAO is less active than MAO but has advantages which include less sensitivity to impurities (H_2O , air) and safety of use.

In most catalytic studies variables are changed one at a time. Herein we have explored the use of statistically designed (2^3 factorial) experiments on factors affecting copolymerisation behaviour and the properties of the resulting polymers [16]. These types of experiments have many advantages which include (i) the determination of the effect

of principal variables as well as variable interaction terms in maximizing a result and (ii) a reduction of the total number of experiments required to fully understand a system. Very few reports on the use of statistically designed experiments have appeared in the literature [16b].

2. Results and discussion

2.1. $(\text{CpEt})_2\text{ZrCl}_2/\text{EAO}$ catalysed ethylene–1-hexene (EH) and ethylene–1-octene (EO) copolymerisation reactions

In previous studies [15] on ethylene polymerisation using a range of $(\text{CpR})_2\text{ZrCl}_2$ complexes the $\text{R} = \text{Et}$ catalyst displayed intermediate ethylene polymerisation activity. It also displays intermediate values of steric and electronic parameters when compared to other ring substituents [15].

A series of EH and EO copolymerisation experiments was carried out by varying the comonomer concentration in the polymerisation mixture. All other reaction conditions were kept constant and the solubility of ethylene in the reaction medium was near constant over the range of 1-hexene concentrations used. Table 1 shows the experimental conditions employed and the results obtained.

Table 1
Ethylene–1-hexene (EH) and ethylene–1-octene (EO) copolymerisation reactions with $(\text{CpEt})_2\text{ZrCl}_2/\text{EAO}$ ^a

| Copolymer | [comonomer]/ $\text{mol}\cdot\text{l}^{-1}$ | Activity/ $\times 10^5$ g PE ($\text{mol Zr}\cdot\text{h}$) ⁻¹ | $T_m/^\circ\text{C}$ | $\Delta H_m/\text{J}\cdot\text{g}^{-1}$ |
|----------------------|---|---|----------------------|---|
| Ethylene homopolymer | 0.00 | 3.7 ^b | 135.7 ^c | 238 |
| Ethylene–1-hexene | 0.32 | 3.9 | 134.9 | 214 |
| | 0.53 | 4.7 | 130.0 | 180 |
| | 0.75 | 5.0 | 129.7 | 177 |
| | 1.07 | 8.5 | 126.4 | 160 |
| | 1.49 | 2.4 | 124.8 | 114 |
| | Ethylene–1-octene | 0.32 | 4.2 | 131.8 |
| | 0.75 | 4.3 | 128.2 | 75 |
| | 1.17 | 0.35 | 126.3 | 57 |

^aExperimental conditions: $T = 60^\circ\text{C}$, $P_E = 10$ bar, $t = 45$ min, $[\text{Zr}] = 4.55 \times 10^{-6}$ M, $[\text{Al}] = 2.93 \times 10^{-1}$ M, $[\text{Al}]/[\text{Zr}] = 64$ 500.

^b $\pm 0.6 \times 10^5$ g PE ($\text{mol Zr}\cdot\text{h}$)⁻¹

^c $\pm 1.0^\circ\text{C}$

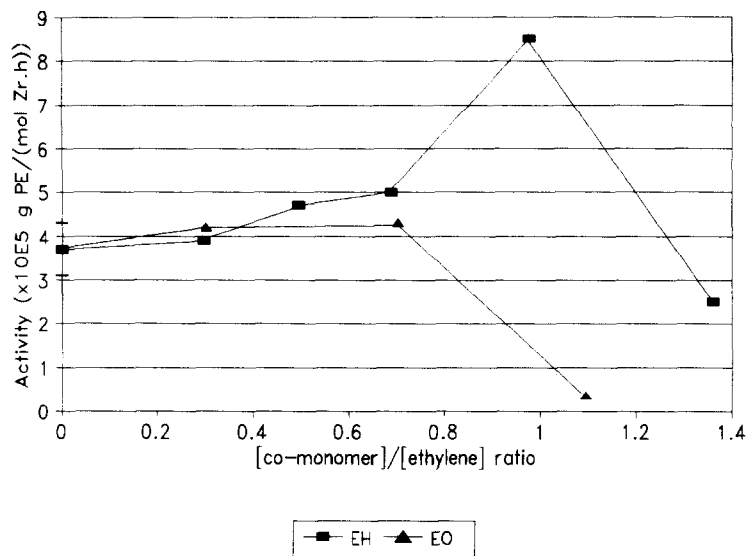


Fig. 1. The effect of the [comonomer]/[ethylene] concentration ratio on polymerisation activity for EH and EO copolymerisation with $(\text{CpEt})_2\text{ZrCl}_2/\text{EAO}$. The error bar is shown by the pair of horizontal bars.

2.1.1. Catalytic activity

Fig. 1 shows a plot of copolymerisation activity versus the [comonomer]/[ethylene] concentration ratio. For the EH copolymerisation series, the activity increased slightly with 1-hexene concentration up to $[1\text{-hexene}] = 1.07\text{ M}$ ($[1\text{-hexene}]/[\text{ethylene}] = 1.0$) and then dropped off sharply. A rate enhancement effect is thus observed. In the EO series, no rate enhancement (within the limits of experimental error) was observed, but the activity again decreased sharply above $[1\text{-octene}] = 0.75\text{ M}$ ($[1\text{-octene}]/[\text{ethylene}] = 0.70$).

An enhancement of polymerisation activity in the presence of a suitable amount of comonomer has been noted for many hetero- and homogeneous polymerisation systems eg. involving ethylene and 1-hexene [11]. For bulkier comonomers, such as 4-methyl-1-pentene, it has been shown that as the monomer ratio increases, there is at most a slight increase in activity, followed by deactivation [14]. Similar behaviour is evident in our studies on the less active EO polymerisations. Rate enhancement effects are also reported to decrease as the polymerisation temperature (and thus catalytic activity) decreases [17].

Since all the metal centres in homogeneous systems are expected to be polymerisation active [18], the effect of added comonomer cannot be to increase the number of active sites nor to modify catalyst fragmentation patterns as proposed for heterogeneous systems [1,19]. The effect of the comonomer must hence be to increase the rate of polymerisation rather than the number of active centres [19b],[20] but the method by which this could be achieved is at present unknown. The decrease in activity on further increase in comonomer concentration is probably due to the relative decrease in ethylene concentration in the system. Even systems which do not exhibit this phenomenon eventually deactivate as the comonomer concentration is increased.

2.1.2. Polymer characterisation

Since the relative incorporation of α -olefin into the polymer was much less than anticipated from the amount of comonomer present during the reaction [10,14], a constant comonomer concentration was assumed throughout the reaction.

The ^{13}C NMR spectrum (Table 2, Copolymer A), of the EH copolymer prepared at $[1\text{-hexene}] = 1.07\text{ M}$ was difficult to measure and not

Table 2
 ^{13}C NMR analyses of ethylene–1-hexene copolymers

| | Copolymer A | Copolymer B |
|-----------------------------------|-----------------------|-------------------------------------|
| Catalyst: | (CpEt) $_2$ ZrCl $_2$ | (Cp ⁱ Bu) $_2$ ZrCl $_2$ |
| $T_m/^\circ\text{C}$ | 127.2 | 127.3 |
| 1-hexene content (mol%) | 1.6 | 1.3 |
| Estimated r_E^a | 98 | 43 |
| r_H | 0 | 0 |
| Triads (mol%): | | |
| EEE | 96.0 | 97.2 |
| EEH | 2.4 | 1.5 |
| HEH | 0.0 | 0.0 |
| EHE | 1.6 | 1.3 |
| EHH | 0.0 | 0.0 |
| HHH | 0.0 | 0.0 |
| No. of 1-hexene runs per molecule | 0.014 | 0.010 |
| Average sequence lengths: | | |
| n_E | 70.3 | 98.7 |
| n_H | 1.14 | 1.3 |
| Monomer dispersity ^b | 87.5 | 76.9 |

^a Ref. [11].

^b High monomer dispersity indicates a high degree of randomness in comonomer incorporation.

well-defined because the comonomer content of the polymer was so low (approximately 1.6 mol%). This value does however fit into the range of 1-hexene content data quoted in the literature for a Cp $_2$ ZrCl $_2$ /MAO system at the same [1-hexene] level [10]. The NMR data show no evidence of any HH diads and hence the copolymer is random. Estimations of the reactivity ratios of ethylene and 1-hexene, r_E and r_H , from the NMR spectrum, according to the method of Uozumi [11], showed that the 1-hexene reactivity ratio was close to zero. This agrees with the low level of 1-hexene incorporation into the polymer. Published reports of EH copolymerisation with the Cp $_2$ ZrCl $_2$ /MAO system at 20°C cite the reactivity ratios as $r_E = 50$ and $r_H = 0.005$ [10]. Analysis of comonomer content by both IR spectroscopy [21,22] and X-ray diffraction were not found to be helpful.

The melting points (T_m) of the polymers (Table 1), determined by DSC, did, however pro-

vide information about copolymer composition. Fig. 2 shows the melting point data for the EH and EO copolymers as a function of the [co-monomer]/[ethylene] concentration ratio. In both cases T_m decreased monotonically with increasing comonomer concentration, which was also found for other homogeneous systems [5,10,23]. This decrease either reflects increasing comonomer incorporation [4,17,24] or a decrease in MW of the polymer (α -olefins are chain transfer agents) [5,10,11,18,19,25,26].

The T_m range is fairly large (124–136°C) and falls within the range quoted for a similar system [10] which indicates that these copolymers have a 1-hexene content of up to 6 mol%. The DSC analyses for the various copolymers showed that the copolymers were homogeneous in composition since only one well-defined sharp melting endotherm was observed. The enthalpies of melting (ΔH_m) for the copolymers are shown in Table 1 and are plotted against the [comonomer]/[ethylene] concentration ratio in Fig. 3. The values decrease monotonically with increasing comonomer concentration as expected [7], and the values for the EO copolymers are well below those for the EH copolymers. This is due either to longer side branches (butyl versus hexyl branches) or to shorter polymer chains (lower MW), both of which would destabilise the packing of the poly-

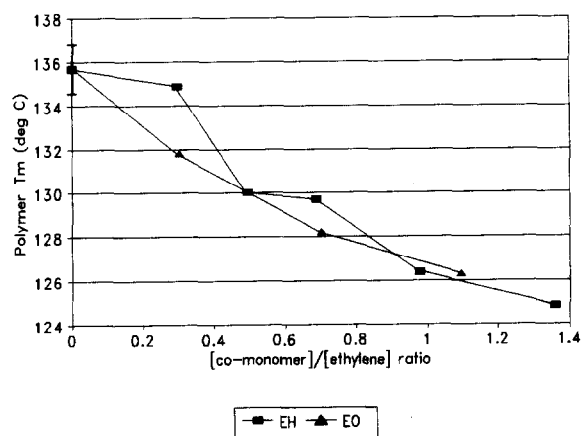


Fig. 2. The effect of [comonomer]/[ethylene] concentration ratio on polymer melting points for EH and EO copolymers produced with the (CpEt) $_2$ ZrCl $_2$ /EAO catalyst system.

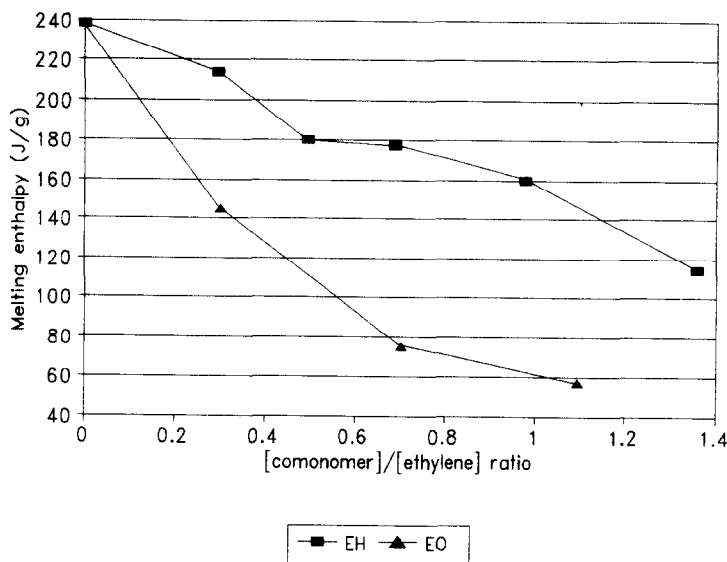


Fig. 3. DSC enthalpies of melting (ΔH_m) versus the [comonomer]/[ethylene] concentration ratio for EH and EO copolymers produced with the $(\text{CpEt})_2\text{ZrCl}_2/\text{EAO}$ system.

mer chains and lower the energy needed for melting. Although polymer molecular weight measurements would assist in the interpretation of the T_m results these were not performed in this work.

2.2. Investigation of experimental factors which affect ethylene–1-hexene copolymerisation in the presence of $(\text{CpR})_2\text{ZrCl}_2/\text{EAO}$ ($R = \text{H}, \text{'Bu}$)

To further explore the copolymerisation reaction, the ethylene–1-hexene reaction was studied as a function of reaction temperature and pressure since these two factors have been observed to be dominant in determining product properties in related studies [27]. Two catalysts with different steric and electronic parameters associated with the substituents on the cyclopentadienyl rings were chosen for this study, viz. $(\text{Cp}^t\text{Bu})_2\text{ZrCl}_2$ and Cp_2ZrCl_2 . $(\text{Cp}^t\text{Bu})_2\text{ZrCl}_2$ showed the highest ethylene homopolymerisation activity, while by contrast the unsubstituted Cp_2ZrCl_2 catalyst showed the poorest ethylene homopolymerisation activity [15].

Three experimental factors (pressure, temperature, 1-hexene concentration) were investigated by means of a set of statistically designed exper-

iments using a 2^3 factorial experimental design for each catalyst. The two catalysts were modelled separately, to permit separate investigation of the response surface for each catalyst. Replicate midpoint experiments were performed to obtain a measure of the error associated with each set of results. The chosen levels for each variable are shown in the footnote to Table 3. The low and high settings for reaction temperature and pressure were based on previous experiments [27] and the values for 1-hexene concentration were based on the extremes of the levels used in the set of experiments described in Section 2.1.

The results of the two sets of experiments are given in Table 3. The measures of error obtained at midpoint conditions are the results of three replicated experiments in each case. The replicate results revealed that the data were reproducible and the measure of the variability in the system thus obtained was used to test the significance of the main effects and interactions obtained from statistical treatment of the data. Fig. 4 shows the results of these experiments in the form of cube plots. A cube plot is a three-dimensional plot, each axis representing one of the variables. Each cube corner represents a combination of the levels of

Table 3
2³ factorial statistically designed EH copolymerisation experiments^a

| Catalyst | Factor levels ^b | | | [1-hexene]/[ethylene] | Activity × 10 ³ g PE (mol Zr·h) ⁻¹ | T _m /°C |
|---|-----------------------------------|----------------|------------|-----------------------|--|--------------------|
| | T _{pol} | P _E | [1-hexene] | | | |
| (Cp ⁱ Bu) ₂ ZrCl ₂ | m | m | m | 0.83 | 1.2 ^c | 120.3 ^d |
| | – | + | – | 0.21 | 9.1 | 128.6 |
| | + | + | – | 0.30 | 7.4 | 127.3 |
| | – | – | – | 0.34 | 1.6 | 126.2 |
| | + | – | – | 0.48 | 0.04 | 125.3 |
| | – | + | + | 0.90 | 0.04 | 116.4 |
| | + | + | + | 1.30 | 0.6 | 116.1 |
| | – | – | + | 1.43 | 3.8 | 111.3 |
| | + | – | + | 2.06 | 0.04 | 119.3 |
| | Cp ₂ ZrCl ₂ | m | m | m | 0.83 | 1.9 ^e |
| – | | + | – | 0.21 | 2.7 | 132.4 |
| + | | + | – | 0.30 | 0.16 | 127.3 |
| – | | – | – | 0.34 | 0.16 | 131.6 |
| + | | – | – | 0.48 | 2.9 | 132.4 |
| – | | + | + | 0.90 | 0.12 | 129.8 |
| + | | + | + | 1.30 | 2.3 | 125.4 |
| – | | – | + | 1.43 | 0.12 | 121.4 |
| + | | – | + | 2.06 | 0.98 | 123.3 |

^a Experimental conditions: *t* = 45 min, [Zr] = 4.55 × 10⁻⁶ M, [Al] = 2.93 × 10⁻¹ M, [Al]/[Zr] = 64 500.

^b Factor levels: – T_{pol}/°C = 50; P_E/bar = 8) [1-hexene]/mol l⁻¹ = 0.32; + T_{pol}/°C = 80, P_E/bar = 12) [1-hexene]/mol l⁻¹ = 1.38; m T_{pol}/°C = 65; P_E/bar = 10) [1-hexene]/mol l⁻¹ = 0.85.

^c ± 0.8 × 10³ g PE (mol Zr·h)⁻¹.

^d ± 5.0°C.

^e ± 1.4 × 10³ g PE (mol Zr·h)⁻¹.

^f ± 1.6°C.

the three variables. Midpoints have been excluded from the plots for clarity.

2.2.1. Catalytic activity

The (CpⁱBu)₂ZrCl₂ catalyst shows a large variation in activity over the range of conditions employed. At the 95% significance level, there is a significant temperature effect and a pressure–[1-hexene] interaction. The response surface is curved. In the case of the Cp₂ZrCl₂ catalyst the range of activities is much smaller, due to the low activity values obtained. Statistical analysis of the data shows the three-factor interaction (T_{pol}–P_E–[1-hexene]) to be significant at the 90% significance level. No other variable effects or interactions were found to be statistically significant.

The two catalysts behave very differently, and the results obtained are quite complex. The situation can be simplified greatly by considering each

combination of the three factors under investigation as providing a different [1-hexene]/[ethylene] concentration ratio in the reaction. Increase in [1-hexene] clearly increases this ratio, as does increasing temperature or decreasing pressure, both of which lower the solubility of ethylene in toluene. The Peng–Robinson [28] calculations show that the solubility of ethylene in the reaction mixture is increased by only ca. 2% by the presence of 1-hexene in the solution, under constant temperature and pressure. The changes in the experimental factors over the range of conditions investigated do, however, make a large difference in the [1-hexene]/[ethylene] ratio. The magnitude of this effect decreases in the order [1-hexene] > pressure > temperature.

Figs. 5 and 6 show the plots of activity for each catalyst as a function of the [1-hexene]/[ethylene] concentration ratio, i.e. the deconvolution of the cube plots. The error bars shown are those

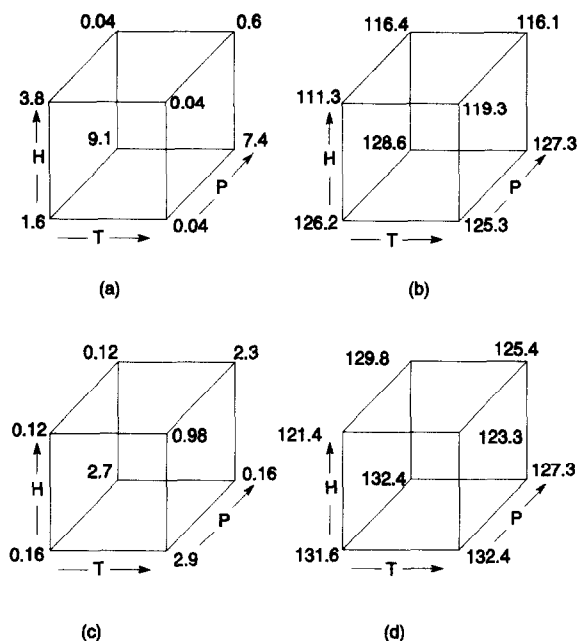


Fig. 4. Cube plots for 2^3 factorial experiments: $(\text{Cp}^i\text{Bu})_2\text{ZrCl}_2$ (a) activity and (b) T_m and Cp_2ZrCl_2 (c) activity and (d) T_m . $T = T_{\text{pol}}$, $P = P_E$, $H = [1\text{-hexene}]$. Midpoint results are omitted for clarity.

from the midpoint experiments. For the $(\text{Cp}^i\text{Bu})_2\text{ZrCl}_2$ catalyst, the plot of activity versus $[1\text{-hexene}]/[\text{ethylene}]$ (Fig. 5) is very similar to that for the $(\text{CpEt})_2\text{ZrCl}_2$ catalyst shown in Fig. 1. There is an initial drop in activity due to the presence of a small amount of 1-hexene followed by a rate enhancement effect at $[1\text{-hexene}]/[\text{eth-}]$

ylene] = 1.43. The initial drop is not seen for the $(\text{CpEt})_2\text{ZrCl}_2$ catalyst, which implies that the $(\text{Cp}^i\text{Bu})_2\text{ZrCl}_2$ catalyst system is more sensitive to the presence of 1-hexene in the reaction [11,17]. The monomer ratio for the maximum rate enhancement for the ^iBu -substituted catalyst is higher than that of the Et-substituted catalyst, which means that the former catalyst is a better copolymerisation catalyst. The variability in the midpoint values is low because we are operating on a linear part of the curve (cf. results for the unsubstituted catalyst). This approach provides an understanding of the pressure–1-hexene interaction. The activity at each pressure–[1-hexene] combination is higher (or the same within experimental error) at lower temperature because lower temperature increases ethylene solubility and thus decreases the $[1\text{-hexene}]/[\text{ethylene}]$ ratio for that combination of conditions.

For the unsubstituted Cp_2ZrCl_2 catalyst, the plot of activity versus $[1\text{-hexene}]/[\text{ethylene}]$ (Fig. 6) shows no clear trend and accounts for the complex three-factor interaction observed. Since this catalyst shows poor activity for copolymerisation it seems unlikely that the activity should depend on the $[1\text{-hexene}]/[\text{ethylene}]$ ratio. It has also been observed in other systems [17] that a decrease in polymerisation temperature (and catalytic activity) leads to a flattening of the activity–

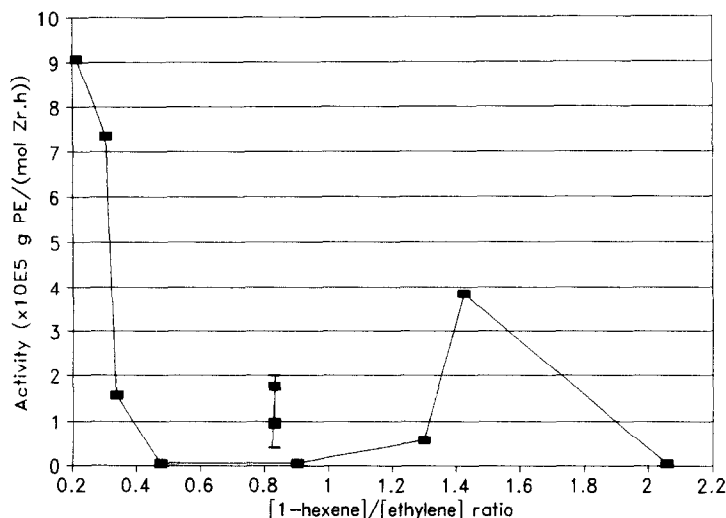


Fig. 5. Activity versus the $[1\text{-hexene}]/[\text{ethylene}]$ concentration ratio for the $(\text{Cp}^i\text{Bu})_2\text{ZrCl}_2/\text{EAO}$ catalyst system.

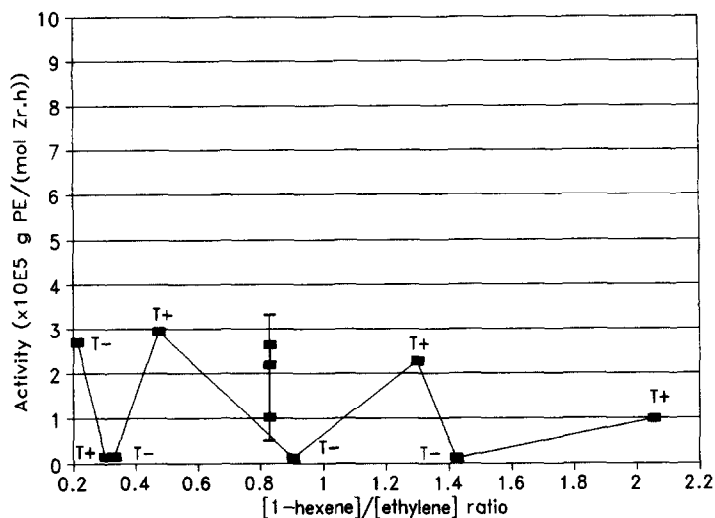


Fig. 6. Activity versus the [1-hexene]/[ethylene] concentration ratio for the $\text{Cp}_2\text{ZrCl}_2/\text{EAO}$ catalyst system.

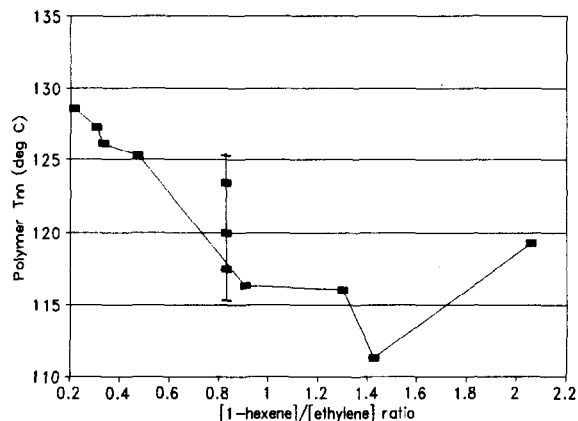


Fig. 7. Polymer T_m versus the [1-hexene]/[ethylene] concentration ratio for the $(\text{Cp}^t\text{Bu})_2\text{ZrCl}_2/\text{EAO}$ catalyst system.

monomer ratio curve. The midpoint values fall on a steeply descending part of the curve, explaining the larger variability compared to the $(\text{Cp}^t\text{Bu})_2\text{ZrCl}_2$ catalyst system.

2.2.2. Polymer characterisation

The deconvoluted plots of polymer T_m versus the monomer ratio for each of the catalysts are shown in Figs. 7 and 8. The melting points of the polymers produced by the $(\text{Cp}^t\text{Bu})_2\text{ZrCl}_2$ catalyst show a significant drop on moving from low to high 1-hexene concentration at any combination of the other two factors. This is to be expected, since the more 1-hexene present in the reaction,

the more is incorporated into the copolymer. A comparison of the Et- and ^tBu -substituted catalysts with respect to their melting points (Figs. 2 and 7) indicates that the T_m 's for the ^tBu substituted catalysts are, on the whole, lower than those for the Et-substituted catalyst. This means that, although the Et-substituted catalyst is more active at any given monomer ratio, the ^tBu -substituted catalyst is presumably better at incorporating 1-hexene. Similar findings were noted for EH polymerisations carried out with Cp_2ZrCl_2 and $\text{C}_2\text{H}_4(\text{tH-Ind})_2\text{ZrCl}_2$ [11]. The reported 1-hexene contents of copolymers formed by the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system lie in the range 2–5

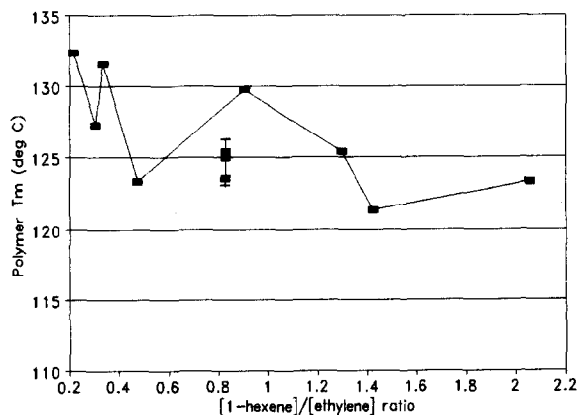


Fig. 8. Polymer T_m versus the [1-hexene]/[ethylene] concentration ratio for the $\text{Cp}_2\text{ZrCl}_2/\text{EAO}$ catalyst system.

Table 4
Ethylene homopolymerisation and ethylene–1-hexene copolymerisation experiments with $(CpR)_2ZrCl_2/EAO$ catalysts

| R in $(CpR)_2ZrCl_2$ | Homopolymerisation ^a activity/ $\times 10^5$ g PE (mol Zr·h) ⁻¹ | Copolymerisation ^b activity/ $\times 10^5$ g PE (mol Zr·h) ⁻¹ | Homopolymer $T_m/^\circ C$ | Copolymer $T_m/^\circ C$ |
|----------------------|--|--|----------------------------|--------------------------|
| H | 1.9 | 1.9 ^c | 131.4 | 124.7 ^d |
| Me | 1.7 | 1.1 | 133.8 | 126.9 |
| Et | 4.8 | 0.5 | 134.7 | 126.5 |
| ⁱ Pr | 3.2 | 1.0 | 133.4 | 124.3 |
| ^t Bu | 8.6 | 1.2 ^e | 135.3 | 120.3 ^f |
| SiMe ₃ | 4.9 | 3.4 | 133.9 | 122.0 |
| CMe ₂ Ph | 1.7 | 0.6 | 130.6 | 126.8 |

^a Experimental conditions: $T = 70^\circ C$, $P_E = 10$ bar, $t = 45$ min, $[Zr] = 6.25 \times 10^{-6}$ M, $[Al] = 2.66 \times 10^{-1}$ M, $[Al]/[Zr] = 42$ 500.

^b Experimental conditions: $T = 65^\circ C$, $P_E = 10$ bar, $t = 45$ min, $[1\text{-hexene}] = 0.85$ M, $[Zr] = 4.55 \times 10^{-6}$ M, $[Al] = 2.93 \times 10^{-1}$ M, $[Al]/[Zr] = 64$ 500.

^c $\pm 1.4 \times 10^5$ g PE (mol Zr·h)⁻¹.

^d $\pm 1.6^\circ C$.

^e $\pm 0.8 \times 10^5$ g PE (mol Zr·h)⁻¹.

^f $\pm 5.0^\circ C$.

mol%, and have similar T_m 's to those of the copolymers prepared in this investigation [11].

In the case of Cp_2ZrCl_2 , the melting points of the copolymers fall into a much smaller range, and are on the whole higher than the corresponding values for the ^tBu-substituted catalyst (Fig. 8). This indicates that this catalyst is a much poorer copolymerisation catalyst under these conditions. There are significant temperature–pressure and pressure–[1-hexene] interactions for the melting points, and the response surface is also curved. The midpoint values do not fall on the curve, con-

firmed curvature of the response surface. For both catalysts, the best 1-hexene incorporation is found at $[1\text{-hexene}]/[\text{ethylene}] = 1.4$ (low pressure and temperature and high [1-hexene]).

A ¹³C NMR spectrum of the copolymer obtained from the ^tBu-substituted catalyst at conditions of high temperature and pressure and low 1-hexene concentration indicated a 1-hexene content in this copolymer of approximately 1.3 mol%. Other data obtained from the NMR spectrum are very similar to those for the polymer formed by the Et-substituted catalyst described above (Table 2, Copolymer B).

2.3. Ethylene–1-hexene copolymerisation with $(CpR)_2ZrCl_2/EAO$ ($R = H, Me, Et, ^iPr, ^tBu, SiMe_3, CMe_2Ph$)

Since the experimentally designed study above showed that different catalysts exhibited very different copolymerisation behaviour, both in activity and copolymer characteristics, a wider range of $(CpR)_2ZrCl_2$ catalysts was tested for EH copolymerisation under constant conditions.

Table 4 shows the results obtained, together with homopolymerisation results [15] as well as the experimental conditions. Some of the copolymerisation results are expressed as averages; these are derived from the midpoint experiments

Table 5
Results of regression analysis of (homopolymerisation–copolymerisation) activities and melting points of $(CpR)_2ZrCl_2/EAO$ catalysts on θ_1 and F ^a

| Coefficients in equation | | R^2 | F | p | Mean square error | |
|--------------------------|--------|----------|------|------|-------------------|-------|
| θ_1 | F | Constant | | | | |
| Activity | | | | | | |
| 0.029 | -79.16 | - | 0.76 | 10.2 | 0.0172 | 3.23 |
| 0.084 | - | -8.90 | 0.00 | 0.61 | 0.48 | 7.15 |
| - | -78.23 | 3.78 | 0.45 | 5.87 | 0.0599 | 3.69 |
| Melting point | | | | | | |
| 0.080 | -116.6 | - | 0.95 | 52.3 | 0.0004 | 5.68 |
| 0.097 | - | -4.28 | 0.00 | 0.38 | 0.57 | 15.23 |
| - | -116.9 | 10.79 | 0.51 | 7.23 | 0.043 | 6.70 |

^a For definitions of statistical terms, see Ref. [39].

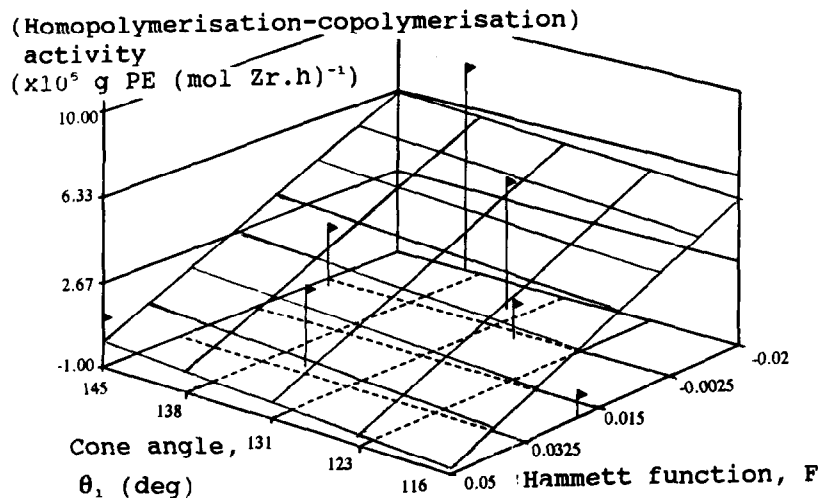


Fig. 9. The effect of steric (θ_1) and electronic (F) parameters on the (homopolymerisation–copolymerisation) activity for the ($\text{CpR}_2\text{ZrCl}_2$)/EAO catalyst series.

determined above. For practical reasons, the reaction conditions for the homo- and copolymerisation studies were not exactly the same. The purpose of the study, however, was to make a relative comparison over the range of R-groups. In this study, a [1-hexene]/[ethylene] ratio of approximately 0.73 was used. The experimental conditions were chosen so as to coincide with the midpoint conditions of the 2^3 factorial experiments.

2.3.1. Catalytic activity

All the catalysts tested exhibited a marked drop in polymerisation activity on moving from homo- to copolymerisation (except for $\text{R} = \text{H}$, where the activity remained the same) (see Table 4). As the reaction conditions for the two sets of experiments were different no further comparison of the data can be made.

Regression analysis of the copolymerisation activities with respect to steric (measured by cone

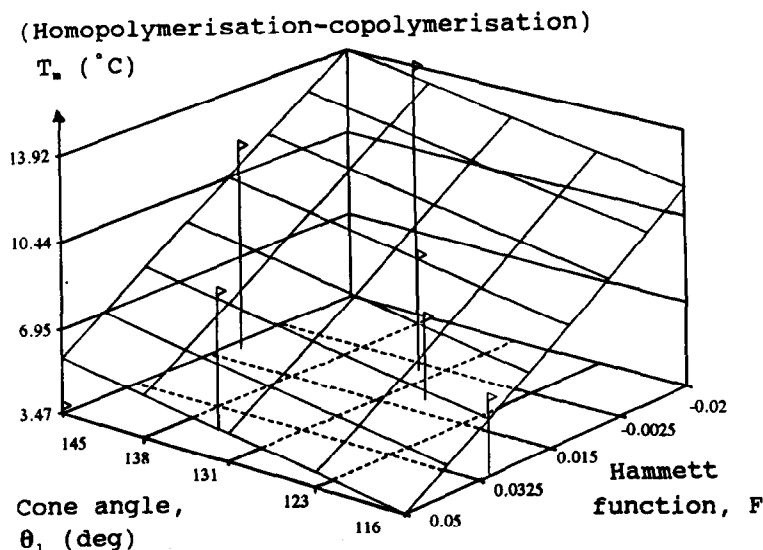


Fig. 10. The effect of steric (θ_1) and electronic (F) parameters on the (homopolymerisation–copolymerisation) activity for the series of ($\text{CpR}_2\text{ZrCl}_2$) catalysts.

Table 6
Ethylene- α -olefin polymerisations with $(\text{CpEt})_2\text{ZrCl}_2/\text{EAO}^a$

| Comonomer | Activity $\times 10^5$ g PE $(\text{mol Zr}\cdot\text{h})^{-1}$ | $T_m/^\circ\text{C}$ |
|---------------|---|----------------------|
| – | 3.7 ^b | 135.7 ^c |
| 1-pentene | 5.4 | 128.0 |
| 1-hexene | 4.8 | 128.2 |
| 1-heptene | 0.16 ^d | 127.5 |
| 1-octene | 4.7 | 128.4 |
| 1-nonene | 0.43 | 128.2 |
| 1-decene | 1.7 | 128.1 |
| 1-undecene | 0.04 | 125.3 |
| 1-dodecene | 0.04 | 126.2 |
| 1-tetradecene | 0.78 | 127.6 |

^a Experimental conditions: $T=60^\circ\text{C}$, $P_E=10$ bar, $t=45$ min, $[1\text{-hexene}]=0.75$ M, $[\text{Zr}]=4.55 \times 10^{-6}$ M, $[\text{Al}]=2.93 \times 10^{-1}$ M, $[\text{Al}]/[\text{Zr}]=64\ 500$.

^b $\pm 0.6 \times 10^5$ g PE $(\text{mol Zr}\cdot\text{h})^{-1}$.

^c $\pm 1.0^\circ\text{C}$.

^d The unexpected low (reproducible) result for 1-heptene can be explained by the presence of internal olefins in the comonomer, as detected by gas chromatography, even after distillation. This was not true of the other α -olefins. It is well-known that internal olefins act as catalyst poisons, and this could account for the low activity observed for this comonomer.

angle [29]) or electronic (measured by Hammett functions [30]) parameters, or a combination of both, was unsuccessful. The same series of analyses using the ratio between the co- and homopolymerisation activities for each catalyst also gave no useful results. However, the *difference*

between the homo- and copolymerisation activities gave a quantifiable relationship. The steric (θ_1) and electronic (F) factors used are the same as those employed in the rationalisation of ethylene homopolymerisation results published previously [15]. This implies that the same factors which regulate homopolymerisation activity also affect copolymerisation behaviour. The overall regression has an R^2 value of only 0.76 (which means that 76% of the variability is explained by the model). Considering the variability in some of the polymerisation results (see Table 4), this is not unexpected. The final regression equation obtained was:

(homopolymerisation–copolymerisation)

$$\text{activity } (\times 10^5 \text{ g PE } (\text{mol Zr}\cdot\text{h})^{-1})$$

$$= 0.029(\theta_1) - 79.16(F)$$

$$(R^2 = 0.76, F = 10.2, p = 0.0172)$$

The full results of the statistical analysis, including the regressions on the steric and electronic parameters separately, are contained in Table 5. The coefficients of the steric and electronic parameters are very similar to those used in the equation to describe the homopolymerisation behaviour. The product of the coefficient of the

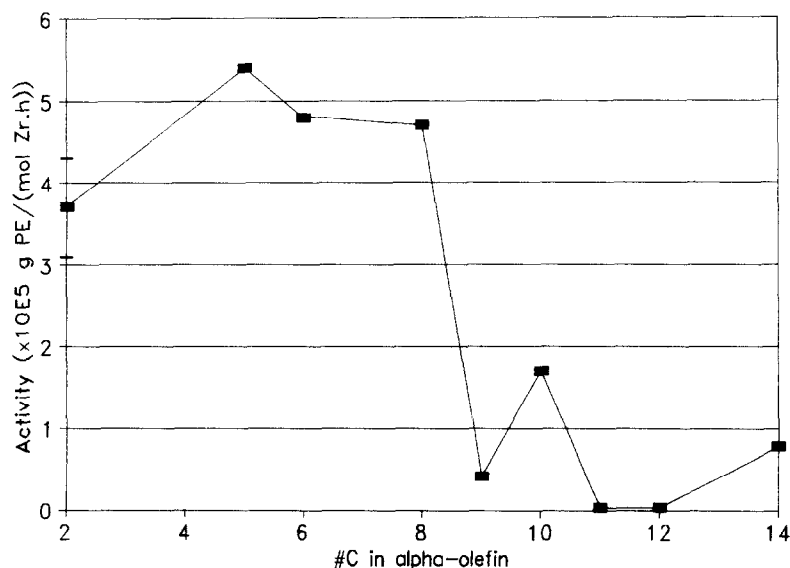


Fig. 11. Polymerisation activity versus comonomer carbon chain length for ethylene- α -olefin copolymerisations.

electronic factor (79.16) with the range of Hammett function values (0.07) is 5.54 while the product of the coefficient of the steric factor (0.029) with the range of cone angle values (29) is 0.84. This means that the electronic effect contributes about 87% to the change in activities which is even more than its contribution was in the case of the analysis of the ethylene homopolymerisation results [15].

The plane described by this equation above is shown in Fig. 9. The plane slopes in both the x - and y -directions, which means that both steric and electronic factors are responsible for the differences in change of activity between each of the catalysts. In fact, the regression of activity on either the steric or electronic parameter alone is non-significant (Table 5).

The difference in activity between the homo- and copolymerisation reactions increases as the steric bulk of the catalyst increases, which means that the relative copolymerisation ability of the catalyst decreases as its bulk increases. This can be understood in terms of the increased difficulty of 1-hexene incorporation as the catalyst becomes bulkier. The difference in activity also increases as the electron-donating ability of the R-substitu-

ents increases. A possible explanation is that electron-donating substituents stabilise the active cationic centre and hence bonding with 1-hexene may be improved. This could cause the catalyst to deactivate, since more energy is needed to activate an α -olefin than is required for ethylene activation [31].

2.3.2. Polymer characterisation

In all cases there is a marked drop in polymer melting point on moving from homo- to copolymerisation, showing that 1-hexene is incorporated into the polymers. The copolymer T_m 's are not related to the homopolymer T_m 's or to the homo- or copolymerisation activities.

Regression analysis was undertaken in the search for a quantitative relationship between T_m and a steric or electronic factor, as was done for the homopolymerisation T_m data. However, no statistically significant simple linear regression relationship could be found for either the copolymer T_m or the difference between the homo- and copolymer T_m 's. However, a three dimensional regression between the cone angle θ_1 and the Hammett function F and the T_m difference values was found to be significant. The steric and elec-

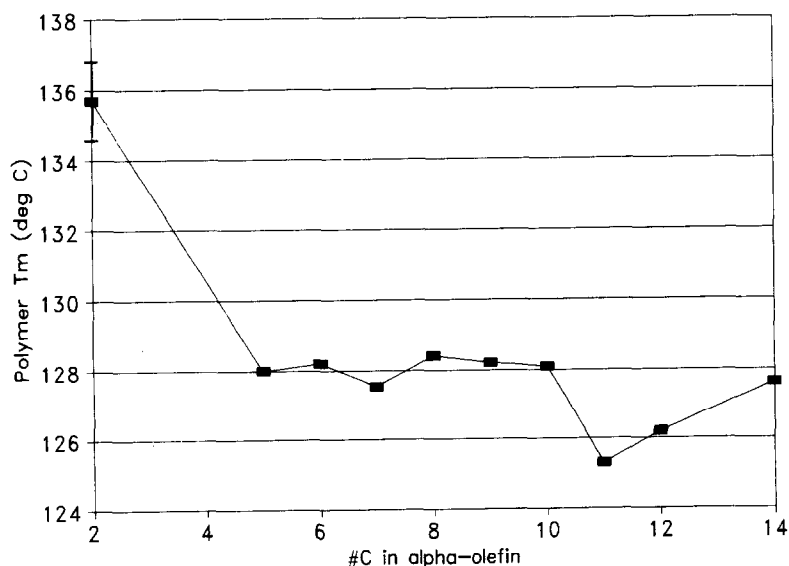


Fig. 12. Copolymer T_m vs. the comonomer carbon chain length for the ethylene- α -olefin polymerisations.

tronic factors are the same as those used in the polymerisation activity regressions. The equation of the plane is

(homopolymerisation–copolymerisation)

$$T_m = 0.08(\theta_1) - 116.6(F)$$

$$(R_2 = 0.95, F = 52.3, p = 0.0004)$$

Full regression data are contained in Table 5. The plot of the plane and the experimental points is shown in Fig. 10. The electronic effect contribution to the overall change in T_m difference is about 78%. The change in T_m increases with increasing steric bulk of the catalyst, which implies that the copolymer 1-hexene content increases, or the copolymer MW decreases, as the steric bulk of the catalyst increases. The latter seems more likely in view of the fact that increasing steric bulk decreases catalytic activity. Increasing electron-donation by the R-substituents also increases the difference in T_m , which means that as the active centre is more stabilised by increased electron-donation, so the polymer MW is lowered. It would seem unlikely that such a situation would increase comonomer incorporation as the catalyst becomes less active.

2.4. Ethylene– α -olefin copolymerisation with $(CpEt)_2ZrCl_2/EAO$

A range of liquid α -olefins from C_5 to C_{14} was copolymerised with ethylene using the $(CpEt)_2ZrCl_2/EAO$ catalyst. The experiments were carried out under the constant conditions employed for the EH copolymerisations. The α -olefin concentration was kept constant at 0.75 M, giving an average [comonomer]/[ethylene] concentration ratio of 0.7. The results from this series of experiments are presented in Table 6.

2.4.1. Catalytic activity

Fig. 11 shows a plot of the polymerisation activities versus the carbon chain length of the α -olefin comonomer. The graph shows that good activities are obtained up to C_8 after which the polymerisation activity drops considerably. There seems to

be a steric threshold in the copolymerisation of ethylene with α -olefins. It is known that bulky comonomers are inserted into the polymer chain with greater difficulty [14,32–34] and that the level of incorporation decreases as the comonomer chain length increases [35,36], since higher α -olefins react more slowly [4].

2.4.2. Polymer characterisation

Fig. 12 shows the relationship between the comonomers used and the melting points of the copolymers produced. There is a sharp drop initially, on moving from homo- to copolymerisation, as expected. However, the nature of the α -olefin makes very little difference to the melting points of the polymers. It should be noted that the T_m value for the ethylene–1-heptene copolymerisation falls into the expected range, which shows that, although the internal olefins kill off catalytic activity, the copolymer produced is not affected to any great extent. The gradual decrease in T_m over the range of comonomers used probably reflects the decrease in MW which results from increased chain termination brought about by the increased bulk of the comonomers.

3. Conclusion

In this publication the role of catalyst steric and electronic effects in ethylene– α -olefin copolymerisation reactions using $(CpR)_2ZrCl_2$ has been explored.

Whereas most experiments are conducted by variation of one variable at a time the effects of three experimental factors (polymerisation temperature and pressure and 1-hexene concentration) on the EH copolymerisation behaviour of two catalysts, $(CpR)_2ZrCl_2$ ($R = H, ^iBu$), were investigated by means of experiments designed to permit statistical analysis. Single variable effects and interactions between variables were observed and explained by considering the monomer ratio at each combination of conditions. The $(Cp^iBu)_2ZrCl_2$ was found to be the better copolymerisation catalyst of the two, exhibiting higher

polymerisation activity and comonomer incorporation (lower T_m) than the unsubstituted catalyst. The latter was found to be a poor copolymerisation catalyst and required high temperatures for reasonable activity.

A series of $(CpR)_2ZrCl_2$ catalysts ($R = H, Me, Et, ^iPr, ^iBu, SiMe_3, CMe_2Ph$) were also investigated for EH copolymerisation under constant conditions. Statistical data analysis indicated that the difference between the homo- and copolymerisation activity for each catalyst was related quantitatively to the same steric (θ_1) and electronic (F) parameters that were used to correlate ethylene homopolymerisation data. The electronic effect was again found to be the dominant effect. Copolymerisation activity decreased with increasing steric bulk of the catalyst. It is proposed that this is related to the steric hindrance of the comonomer approach by the cyclopentadienyl ligand. Activity also decreased with increasing electron-donating ability of the substituents.

The $(CpEt)_2ZrCl_2$ catalysed copolymerisation of ethylene with C_5 – C_{14} α -olefins was also investigated. Copolymerisation activity decreased substantially for olefins larger than 1-octene.

These studies have revealed the complexities involved in investigating polymerisation catalysts. However they do indicate how catalytic activity and polymer properties can be selectively controlled by subtle variations in experimental conditions, catalyst structure and choice of comonomer.

4. Experimental

The synthesis and characterisation of the $(CpR)_2ZrCl_2$ catalysts ($R = H, Me, Et, ^iPr, ^iBu, SiMe_3, CMe_2Ph$) and EAO has been described previously [15]. Comonomers (α -olefins) were dried over sodium and distilled and deoxygenated before use. Their purity before and after distillation was checked by gas chromatography.

Polymerisation reactions were carried out as described previously [15] but with the following modifications: The required amount of α -olefin

was injected into the reactor just prior to catalyst addition. The volume of toluene solvent used was adjusted to keep the total liquid volume constant at 75 ml. Typical reaction conditions were $[Zr] = 4.55 \times 10^{-6}$ M, $[Al]/[Zr] = 64\ 500$ and polymerisation time = 45 min. Specific reaction conditions may be found in the appropriate Tables and in the text. Polymer analysis by DSC was carried out as described previously [15]. Enthalpies of melting (ΔH_m) were measured by integration of the melting endotherm on the second melting run.

^{13}C NMR spectra were recorded at 113°C in 1,2,4-trichlorobenzene and analysed according to the method outlined by Randall [37]. Calculation of the amount of ethylene dissolved in the reaction mixture at various combinations of temperature, pressure and [comonomer], was carried out using the Peng–Robinson equation of state [28]. StatGraphics [38] was used for statistical analyses.

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