

Zirconium *bis*-cyclopentadienyl compounds

An investigation into the influence of substituent effects on the ethene polymerisation behaviour of $(\text{CpR})_2\text{ZrCl}_2/\text{MAO}$ catalysts

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Abstract

A comparative investigation into the ethene polymerisation behaviour of several mono-substituted metallocene catalysts ($(\text{CpR})_2\text{ZrCl}_2/\text{MAO}$; R = H, Me, Et, *i*Pr, *t*Bu, SiMe₃, CMe₂Ph) was performed. The activity of the catalysts was found to be dependant on both steric (quantified using the Tolman cone angle, analytical solid angle and numerical solid angle measurement methods) and electronic effects (Hammett substituent parameters). The highest activity was found for the catalysts with R = Et and SiMe₃.

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1. Introduction

It has long been realised that the steric and electronic parameters of a particular ligand cannot be viewed in isolation and it is usually a combination of the two effects that can be correlated with the properties and behaviour of a compound. Tolman proposed the use of a multivariate approach where, for example a measurable parameter *Z* could be analysed with respect to both steric and electronic parameters according to the following equation:

$$Z = a\theta + b\nu + c \quad (1)$$

In this equation θ is a steric parameter; ν an electronic contribution; and *a*, *b* and *c*, the regression co-

efficients [1]. The percentage contribution of the steric effect could then be determined using the following equation:

$$\text{steric effect (\%)} = \frac{a}{a+b} \times \frac{100}{1} \quad (2)$$

Over the years, the polymerisation activities of metallocenes have been rationalised in terms of both steric and electronic effects. Chien and Razavi [2] have, for example, argued that steric bulk stabilises a catalyst while the electron donating substituents on the ligand increase activity. In their 1971 review article, Henrici-Olivé and Olivé [3] highlighted the importance of electronic effects in catalytic reactions. These influence not only the σ -bond formed between the olefin and the metal, but also the retrodonative back donation of electron density into the π^* -antibonding orbital of the olefin. Clearly all these factors, steric and

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electronic, influence the rate of insertion of an olefin into a growing polymer chain.

A previous investigation by our group into the polymerisation behaviour of a set of $(\text{CpR})_2\text{ZrCl}_2$ ($\text{R} = \text{H}$ (1), Me (2), Et (3), *i*Pr (4), *t*Bu (5), SiMe_3 (6) and CMe_2Ph (7)) catalysts showed that their activities could be *quantitatively* rationalised in terms of steric and electronic effects [4,5]. The study was, however, carried out using ethylaluminumoxane (EAO) as the co-catalyst.

Most polymerisation studies involving metallocene catalysts reported in the literature have been performed using methylaluminumoxane (MAO) as the co-catalyst. Interestingly only scattered reports in which a *systematic* study of the effect of ring substituent steric and electronic effects have on the polymerisation activity of metallocene catalysts, using MAO as the co-catalyst, have appeared in the literature [2,6–10]. The objective of this study was to assess by a systematic study whether the relative contributions of ring substituents to steric and electronic effects could be determined for the $(\text{CpR})\text{ZrCl}_2/\text{MAO}$ system.

2. Results and discussion

2.1. Steric measurements

Two fragment types were set up for the various steric calculations. In one set of fragments, all the $\text{Zr}-\text{C}_{\text{Cp}}$ (C_{Cp} : carbon atom in cyclopentadienyl ring) bond lengths were left the same length. In the other, bond lengths that were unequal (as obtained from X-ray crystallography data) were left unchanged. Only small differences between the results could be found. Therefore, the effect of slight differences in bond lengths and by implication ring-tilt, can be ruled out in the measurement of the size of mono-substituted cyclopentadienyl rings.

The results from the various calculations of the steric sizes of the $(\text{C}_5\text{H}_4\text{R})-\text{Zr}$ ($\text{R} = \text{H}$, Me, Et, *i*Pr, *t*Bu, SiMe_3 and CMe_2Ph) fragments, as determined from the Tolman cone angle (θ), analytical solid angle (Ω) and numerical solid angle (Ω_{N}) calculations are collected in Table 1 [1,11–14].

As can be seen from the data in Table 1, the different steric calculations give remarkably different results and depend on the steric measurement used. Generally the ligand size decreases in the following order:

Table 1

Table of steric measurements for a set of $(\text{C}_5\text{H}_4\text{R})-\text{Zr}$ fragments^a

R	θ_1 (°) ^b	θ_2 (°) ^c	Ω (°) ^d	Ω_{N} (°) ^e	cga (°) ^f
H	135	116	117	120	96 ^g
Me	140	128	122	125	91
Et	143	132	126	129	87
<i>i</i> Pr	143	135	128	130	86
<i>t</i> Bu	148	139	133	135	81 ^h
SiMe_3	146	144	131	134	85
CH_2Ph	146	–	129	131	81
CMe_2Ph	147	145	136	136	83

^a The size of the $\text{C}_5\text{H}_4\text{R}$ ligands were determined from the perspective of the zirconium nucleus. Three of the structures that were retrieved from the CSD, namely the ethyl, *tert*-butyl and benzyl substituted ligands, were reported without their hydrogen atoms placed. The average $\text{C}_{\text{Cp}}-\text{H}$ (C_{Cp} : carbon atom in the 5-membered cyclopentadienyl ring) bond length in those structures that had their H-atoms placed is 0.940 Å. This distance was used to place the H-atoms, at 180° to the cyclopentadienyl ring, in the aforementioned compounds.

^b The Tolman cone angle [1,11,47].

^c Cone angle previously used to calculate the size of cyclopentadienyl ligands [4,10].

^d Solid angle calculated using analytical methods [13].

^e Numerical solid angle [14].

^f Co-ordination gap aperture [15,16].

^g Refs. [16] and [10] report values of 95° and 92°, respectively.

^h Ref. [10] reports a value of 58°.

$\theta > \Omega_{\text{N}} > \Omega$. The solid angle calculations measures smaller sizes than that of the Tolman cone angle because the latter calculation overestimates the size of a ligand by assuming it has *cylindrical* symmetry. The numerical solid angle calculation by contrast traces a non-cylindrical cone around the outer van der Waals radii of the atoms in the ligand. The analytical solid angle algorithm measures an even smaller size by also subtracting out the spaces within a ligand. In our case, the small difference between the two solid angle calculations results from the small space found at the centre of the cyclopentadienyl group.

The differences in the values for the Tolman cone angle reported previously for the CpR ligands (θ_2 in Table 1) [4] result from the different bond length and angular values used in the calculations.

Figs. 1 and 2 depict the ligand profiles (a plot of the size of a ligand as a function of distance from the metal) of two cyclopentadienyl ligands ($\text{R} = \text{H}$ and *t*Bu) using the three measurement methods and illustrate the differences in results obtained from

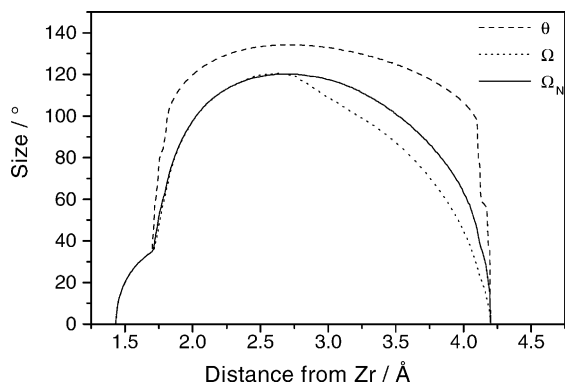


Fig. 1. Ligand profile plots for the Zr-Cp fragment.

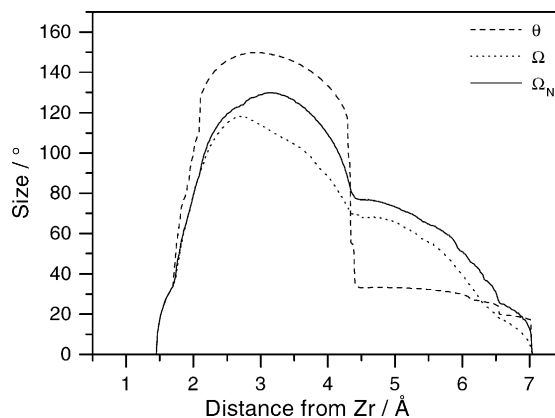


Fig. 2. Ligand profile plots for the Zr-Cp' Bu fragment.

the respective calculations. For the unsubstituted cyclopentadienyl ring, the disparities between the different calculation procedures are not large. However, upon ring substitution marked differences are observed. The non-cylindrical nature of these ligands can be seen in the three-dimensional numerical solid angle plot for an unsubstituted cyclopentadienyl ligand (Fig. 3).

Brintzinger has proposed the concept of the co-ordination gap aperture (cga) to rationalise the olefin polymerisation results of *ansa*-metallocenes [15,16]. It was used to quantify the space available to a monomer approaching an active catalytic site. The co-ordination gap differs from the $C_{p_{cen}}-Zr-C_{p_{cen}}$ ($C_{p_{cen}}$: centroid of cyclopentadienyl ligand) angle, in that it is the largest angle formed by the inter-

section of the two planes at the metal centre, which touch the inner van der Waals radii of the two cyclopentadienyl groups. Clearly, the size of this angle is intimately linked to the nature of the ligand and its substituents.

The cga was originally designed for use with *ansa*-metallocenes where it was found that the β -substituents on the C_5 rings influenced the size of the gap aperture. The ligands on unbridged metallocenes on the other hand are usually free to rotate about the $Zr-C_{p_{cen}}$ axis making the choice of one specific β -carbon on the C_5 ring less meaningful. We have therefore employed the use of Tolman cone angles, using a *rotating* cyclopentadienyl ligand (see Table 1) as proposed by Janiak et al. [10], to measure

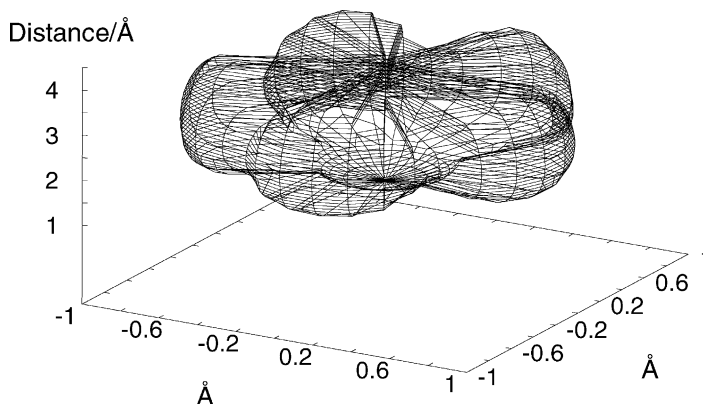


Fig. 3. Three-dimensional, numerical solid angle profile plot for the cyclopentadienyl ligand.

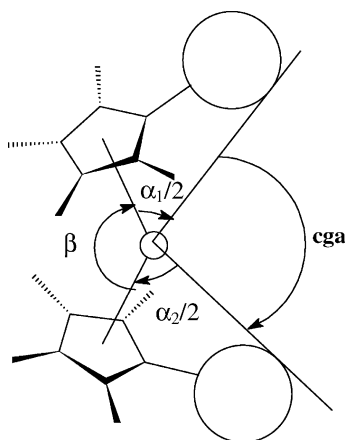


Fig. 4. Diagram illustrating the cga measurement.

the cga (Eq. (3), Fig. 4).

$$\text{cga} = 360^\circ - \frac{\alpha_1}{2} - \frac{\alpha_2}{2} - \beta \quad (3)$$

where α_1 and α_2 are the cone angles for the ligand in question, and β the angle between the metal and the two ring centroids.

Using this procedure, we calculated the cga for Cp_2ZrCl_2 to be 96° . This value is very close to that calculated by Brintzinger's, viz. 95° [16]. Clearly use of the solid angle values would have given too large an aperture (114° for the solid angle measurement). An important point that must be kept in mind, however, is that these calculations depend on the assumption of

unhindered ring rotation. Although the bulky *tert*-butyl substituted cyclopentadienyl rings in the $(\text{CpR})_2\text{ZrCl}_2$ metallocene displays unhindered rotation this does not hold true once the chlorine atoms are replaced by a bulkier entity [17,18]. Erker has demonstrated that even the co-ordination of a modest butadiene ligand to the zirconium atom results in a substantial barrier to rotation in the $(\text{Cp}^t\text{Bu})_2\text{Zr}$ entity [17–21]. Thus in polymerisation reactions, where a bulky polymer chain occupies the open sector of the bent metallocene, rotation of the cyclopentadienyl ligands with bulky substituents is expected to be restricted.

2.2. Polymerisation studies

The polymerisation reaction conditions chosen in the study were selected not to optimise the amount of polymer produced, but to obtain an insight into the effect that the R-groups have on the polymerisation behaviour of the $(\text{CpR})_2\text{ZrCl}_2$ complexes *under similar reaction conditions*. Although it is an easy task to select conditions where the catalysts would produce polymer at a high rate during the entire reaction period, conditions were employed that resulted in an initial high uptake of ethene followed by a deactivation curve after a certain period of time. This time period is dependent on the nature of the CpR ligand. The choice of reaction conditions also avoided the production of excessive polymer in the reactor, minimising diffusion-controlled processes in which

Table 2

Ethene polymerisation data for a set of $(\text{CpR})_2\text{ZrCl}_2/\text{MAO}$ catalysts^a

R	Activity ($\times 10^7$ g PE (mol Zr h) ⁻¹) ^b	T_m ($^\circ\text{C}$) ^c	M_w (g mol ⁻¹)	M_w/M_N	θ ($^\circ$) ^d	cga ($^\circ$) ^e	F^f
H (1)	6.68	136.5	314 400	1.9	135	96	0.03
Me (2)	7.54	136.4	329 400	2.0	140	91	0.01
Et (3)	9.72	137.7	577 600	2.2	143	87	0
ⁱ Pr (4)	8.70	138.9	446 200	2.4	143	86	0.04
^t Bu (5)	2.06	135.4	276 700	2.1	148	81	-0.02
SiMe ₃ (6)	9.23	137.2	232 100	2.0	146	85	0.01
CMe ₂ Ph (7)	0.192	135.4	512 300	2.2	147	83	0.05

^a Conditions: 400 ml toluene; mol Zr = 4.16×10^{-8} mol; [Al]:[Zr] = 30 000:1; T_p = 50°C ; P_p = 2 bar C_2H_4 ; t_p = 45 min.

^b The activities reported are the average of three or more polymerisation reactions per catalyst.

^c Melting point determined by DSC. These values have been obtained from the remelted samples at a heating rate of $10^\circ\text{C}/\text{min}$.

^d Tolman cone angle of CpR ligand as measured from the perspective of the metal.

^e Co-ordination gap aperture measured according to Ref. [10].

^f Hammett substituent parameter, F [48].

the reaction becomes heterogeneous in nature due to the precipitation of polymer during the polymerisation reaction. The reaction conditions eventually used, which met these requirements, were a very low catalyst concentration (4.16×10^{-8} mol) and a high [Al]:[Zr] ratio (30 000:1). The polymerisation data is collected in Table 2.

It is now widely accepted that the polymerisation of olefins by metallocenes is effected through a cationic metallic species. It has however been demonstrated that the polymerisation mechanism of Henrici-Olivé and Olivé [22], which assumes that all the metal species are initially capable of participating in the polymerisation reaction, is not correct. Kinetic studies by Fink et al. [23,24] have shown that a much more complex situation arises where successive equilibria convert alkylaluminium and metallocene species between Lewis acid–base and dissociated ion pairs. Only the separated ion pairs are capable of inserting olefin molecules, whereas the non-separated species can be regarded as “dormant” and not capable of contributing to polymer growth. It is likely that polymerisation reaction conditions and the metallocene ligands have a direct impact on the equilibria described in the aforementioned papers by Fink. In this study, we have not investigated this issue. Instead, the activities of the metallocenes under investigation have only been related to the steric and electronic properties of their ligands by measuring the amount of polymer formed at the end of the polymerisation reaction. Thus, an attempt has been made to associate *ground state effects* with polymerisation activity.

The activities of the $(\text{CpR})_2\text{ZrCl}_2$ complexes decrease in the following order: Et(**3**) \sim SiMe₃(**6**) > ⁱPr(**4**) > Me(**2**) > H(**1**) > ^tBu(**5**) > CMe₂Ph(**7**). As a first assumption, it is tempting to assume that electronic parameters are predominantly responsible for the activity differences. This is illustrated by the greater polymerisation activity exhibited by **6** when compared to the metallocenes **5** and **7**, all of which are similarly sized ligands. However, the lower activity exhibited by the latter two compounds is more likely to result from *intramolecular* co-ordination of the ligand substituents to the active polymerisation centre, thereby inhibiting the polymerisation reaction. Metallocene complexes demonstrating intramolecular co-ordination of ^tBu or CMe₂Ph to a cationic metal centre have been reported in the literature [25–27].

There does appear to be an optimum electron density needed on the metal to ensure high activity, with this requirement seemingly being met in our case by the most active catalysts, **3** and **6**. This ideal value is associated with a cyclopentadienyl ligand in which the ring substituent has a Hammett constant of $F = 0$.

The stability of the M–C bond (the bond formed by the metal to the growing polymer chain) has long been recognised as being important in catalytic reactions [3,22]. For example, donor ligands destabilise the M–C bond, increasing the rate of monomer insertion in the process. Other researchers have also pointed out the same correlation of activity to electron density at the metal. Chien and Razavi [2] and Jordan and co-workers [28] have, for example, related the increased insertion rate of monomer to an increased electron density at the active site. It is interesting to note the sensitivity of the polymerisation reaction to electronic effects over the small range of Hammett substituent constants, F , investigated (-0.02 to 0.05). Chlorine and fluorine have F -values which are far removed from this range ($F_{\text{Cl}} = 0.42$ and $F_{\text{F}} = 0.45$). These values explain the very low polymerisation activity of metallocenes with chlorine and fluorine substituted indenyl ligands [29,30].

Steric effects are also expected to play a significant role in these catalytic reactions. For example, steric bulk has been proposed to contribute to catalyst stability by limiting reductive disproportionation reactions that lead to catalyst deactivation [2]. In our results, the higher activity of **3** and **6** compared to **2** seems to support this proposal. All three catalysts have similar Hammett constants, but there is a vast difference in their activities. This probably results from the added protection of the metal site provided by the bulkier ethyl and trimethylsilyl groups. As with electronic effects, there appears to be an optimum value that results in high activities, this angle size lies between $\theta = 143^\circ$ and 146° . Thus, ligands with a θ -value in this range have a cga sufficiently wide to allow polymerisation to efficiently take place and still protect the catalyst from deactivation pathways.

It is evident from the above discussion that there is no simple correlation between activity and either the steric size or the electronic parameters of the substituents. Attempts to correlate the polymerisation activity simultaneously to both the Hammett substituent constants and steric size using multiple regression

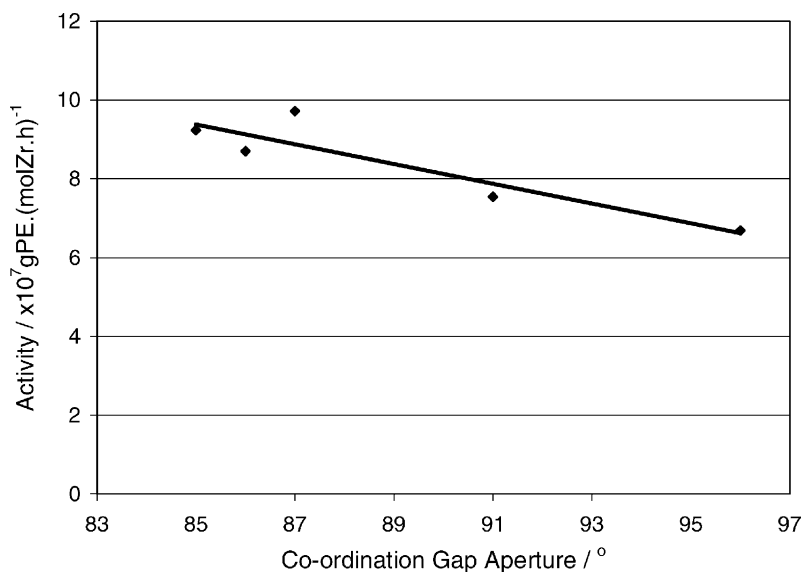


Fig. 5. Correlation between cga and activity.

analysis also failed to deliver statistically acceptable results. This suggests that there is a more complex, non-linear relationship between the substituent parameters and activity.

In our procedure, we have simplified the approach by considering the effect of R on the structure $(\text{CpR})_2\text{ZrCl}_2$ —it is appreciated that the actual structure is almost certainly of the type $(\text{CpR})_2\text{ZrR}^{+/}$ and this simplification may have some influence on the results. Further, we have assumed that the influence of MAO is a constant for all the complexes studied. The structure of MAO is complicated [31] and this assumption of a constant effect of MAO on the different catalysts will have to be confirmed.

If the polymerisation results for catalysts **5** and **7** are excluded (both of which are affected by intramolecular co-ordination of their ligand substituents to the metal [25–27]), there appears to be a modest correlation ($R^2 = 0.83$) between increasing activity and decreasing cga (Fig. 5). This suggests that bulkier substituents protect the active polymerisation site on the metal, thus prolonging the life of the catalyst. It should be borne in mind that the observed trend of increasing activity with decreasing co-ordination gap is related to *mono-substituted or cyclopentadienyl ligands with small substituents*. Janiak et al. [10,32]

have shown that large substituents or multi-substituted cyclopentadienyl ligands, as expected, inhibit polymerisation activity.

The results from several polymerisation studies similar to ours, but with a smaller ligand set, are summarised in Table 3 and corroborate our findings that both steric and electronic effects influence the activity of $(\text{CpR})_2\text{ZrCl}_2$ /aluminoxane catalysts. What can also be seen is that small alkyl and electron donating substituents increase polymerisation activity, whilst the size of the cyclopentadienyl ligands severely inhibits activity. Reaction conditions employed during a polymerisation reaction certainly affect the activity series by influencing the equilibria described by Fink et al. [23,24] and leads to the differences reflected in Table 3. The steric and electronic parameters of some of the substituents are very similar and different reaction conditions could result in an inversion of their position in an activity series.

What is interesting is the effect that changing the co-catalyst has on the activity series. In a previous study by our group [4,5], metallocene **5** exhibited the highest activity when EAO was used as the co-catalyst. In this study, it is the second least active catalyst. In addition to this, **6** was observed to be less active than **5**, also contrary to our current

Table 3

Comparison of ethene polymerisation results from studies on the $(C_5H_{5-n}R_n)_2ZrCl_2/MAO$ system

Activity series ^a (R ^b)	Co-catalyst ^c	Polymerisation conditions	Reference
Et ~ SiMe ₃ > ⁱ Pr > Me > H > ^t Bu > CMe ₂ Ph	MAO	[Al]:[Zr] = 30 000; T _p = 50 °C; P _p = 2 bar; t _p = 45 min	This work
H > Me ₄ + H > Me ₅ + H > ^t Bu + H > Me ₄ > Me ₅ > ^t Bu ₂ + H > ^t Bu > ^t Bu ₃	MAO	[Al]:[Zr] = 160 000:1; T _p = 70 °C; P _p = 5 bar; t _p = 30 min	[10]
Me > Et > H > Me ₅	MAO	[Al]:[Zr] = 24 000; T _p = 80 °C; P _p = 4 bar; t _p = 30 min	[6]
ⁱ Pr > Et > H > ⁿ Pr	MAO	[Al]:[Zr] = 17 083; T _p = 70 °C; P _p = 7.5 bar	[7]
SiMe ₃ > H > ^t Bu	MAO	[Al]:[Zr] = 11 176; T _p = 70 °C; P _p = 7 bar	[9]
Cy > ⁱ Pr > ⁿ Bu > ⁿ Pr > Et > Me	MAO	Not given	[8]
^t Bu > SiMe ₃ > Et > ⁱ Pr > H > Me ~ CMe ₂ Ph	EAO	[Al]:[Zr] = 42 500; T _p = 70 °C; P _p = 10 bar; t _p = 45 min	[4,5]
ⁱ Pr > Me > ^t Bu > ^t Bu ₂ > H	EAO	Not given	[8]

^a Catalyst activities listed in descending order.^b Most entries are for mono-substituted cyclopentadienyl groups, if there is more than one ring substituent on a ring, this is indicated by a subscript (*n*) after the R-group. If the two Cp rings are not the same, this is indicated by two R-groups separated by “+”.^c The co-catalyst used in the polymerisation, EAO or MAO.

findings. The bulkier ethyl groups and lower degree of oligomerisation in EAO may prevent an effective interaction of the aluminoxane Al–O–Al groups with the active catalyst site. The action of EAO activated catalysts may therefore provide a greater insight into the action of the CpR ligands.

The molecular weights of the polymers are slightly higher than those reported elsewhere in the literature for mono-substituted and unsubstituted zirconocene catalysts [33–36]. It has been argued previously that low concentrations of catalyst, as used in this study, favour dissociated active polymerisation sites, resulting in chain propagation instead of chain termination [10,37,38]. Bimolecular deactivation pathways involving two catalytic centres, which result in lower molecular weights, are also limited at lower catalyst concentrations [10,37,38].

3. Conclusions

The factors governing the activity of a catalyst are complex and not easily understood. We have shown that both ground state steric and electronic effects influence catalytic activity of $(CpR)_2ZrCl_2$ metallocenes and when MAO is used as a co-catalyst, a fine control of steric and electronic parameters are required to ensure optimum activity. The catalysts are stabilised by small substituents on the cyclopentadienyl rings

that helps prevent their deactivation by bimolecular disproportionation. However, these substituents cannot be too large as the cga, the space around the catalyst in which polymerisation occurs, becomes too crowded and monomer insertion is inhibited. Substituent electronic parameters are also important in governing the activity of a catalyst as the cyclopentadienyl substituent affects the electrophilicity of the metal as well as the strength of the M–C bond (the bond to the growing polymer chain).

4. Methods section

4.1. Steric size measurements

The size of this substituted cyclopentadienyl ligands was determined using the Tolman cone angle [1,11], analytical solid angle [12,13], and numerical solid angle methods [14]. The steric measurements were made using the co-ordinates of the crystal structures retrieved from the Cambridge Structural Database [39,40]. As we were concerned with assessing the size of the C₅H₄R ligand, measured from the perspective of the metal, the structure had to be modified so as to facilitate the calculations. The two chlorine atoms and one of the C₅H₄R rings were removed from the crystal data file leaving the remaining cyclopentadienyl ring attached to the zirconium atom.

No crystallographic structure for $(\text{CpCMe}_2\text{Ph})_2\text{ZrCl}_2$ has as yet been determined. However, the structure of an analogous compound $(\text{CpCMe}_2\text{-}p\text{-tolyl})_2\text{HfCl}_2$, has been reported [41]. The co-ordinates of this structure were used in the steric measurements, after the methyl group had been removed from the *p*-tolyl ring to give the appropriate $-\text{CMe}_2\text{Ph}$ ring substituent. The assumption of its similarity to the structure of $(\text{CpCMe}_2\text{Ph})_2\text{ZrCl}_2$ is supported by the observation that the ring centroid–hafnium ($\text{Cp}_{\text{cen}}\text{-Hf}$) length of 2.207 Å, is close to the average $\text{Cp}_{\text{cen}}\text{-Zr}$ length of 2.202 Å for the above zirconocenes. The last modification made to the structures was to ensure that the $\text{C}_{\text{Cp}}\text{-Zr}$ bond lengths in the individual fragments were all of the same length so as to eliminate ring-tilt. This modification is unnecessary as the calculations reveal that both ring-tilt corrected and uncorrected fragments give similar results.

The fragments that were generated by the above procedures were then submitted to the program ‘Steric’ [42], which calculates the Tolman cone, solid and numerical solid angles according to the appropriate algorithm. In addition to these standard measurements of size, the algorithms have been developed so as to provide steric profiles of the ligands under investigation. These profiles provide a measure of the size of the ligand as a function of distance from the point of observation, which in our case is the zirconium atom. The Bondi data set of van der Waals and covalent radii were used in all calculations [43]. The results from the calculation are collected in Table 1.

The last steric measurement made was that of the cga [15,16]. The procedure used here is similar to that employed by Janiak et al. [10] (Eq. (3), Fig. 4). We have used the size for the cyclopentadienyl ligand given by the Tolman cone angle generated in our studies to calculate the cga. These results are also listed in Table 1.

4.2. Polymerisation studies

Cp_2ZrCl_2 (**1**) was purchased from Aldrich and used without further purification. The remaining $(\text{CpR})_2\text{ZrCl}_2$ metallocenes were synthesised according to published procedures (R = Me (**2**) [44], Et (**3**), *t*Bu (**5**) and SiMe₃ (**6**) [45], *i*Pr (**4**) and CMe₂Ph (**7**) [46]).

Toluene was used as the solvent in all of the polymerisation reactions. The solvent was collected in a still after heating under reflux over molten sodium for 6 h. When fresh toluene was added to the still, its contents were heated under reflux for a minimum of 72 h before use in any polymerisation reaction. The reactor was prepared for each polymerisation reaction by heating for 13 h at 80 °C under vacuum, cooled to 60 °C, and then filled with argon. The MAO used in the reactions was obtained from Witco as a 10% solution in toluene and was used as received.

Under argon counter-flow, 360 ml of toluene was added to the reactor via cannula tubing from a measuring cylinder, the reactor pressurised to 2 bar ethene pressure and cooled to the polymerisation temperature of 50 °C. The required amount of catalyst (4.16×10^{-8} mol) was taken from a stock solution of metallocene in toluene and mixed with MAO ([Al]:[Zr] = 30 000:1) in 40 ml of toluene. This was stirred for 10 min at 50 °C and then added under ethene counter-flow to the reactor via cannula tubing. The reactor was sealed, pressurised to 2 bar ethene pressure and the polymerisation reaction carried out over 45 min. Venting the reactor to the atmosphere and adding a solution of 10 ml 32% HCl in 90 ml methanol terminated the reaction. The entire contents from the polymerisation reactor were stirred at room temperature for 3 h before being collected by filtration onto a glass frit. The polymer was washed with methanol until no longer acidic and dried under reduced pressure to constant mass.

Polymer melting points were determined on a DuPont 910 differential scanning calorimeter, from the remelted samples at a heating rate of 10 °C min⁻¹. Polymer molecular weights were determined by the Deutsche Kunststoffinstitut, Darmstadt.

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