Macromol. Symp. **2004**, *213,* 79-88

Sterically Demanding Bis(2-silylindenyl)zirconium(IV) Dichlorides as Polymerisation Catalyst Precursors

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Summary: A set of different 1- and 2-silyl-substituted zirconocene dichloride/MAO catalyst systems was investigated with respect to their performance in ethene/1-hexene copolymerisations. In-depth studies of bis(2-dimethylsilylindenyl) zirconium(IV) dichloride (**1**) revealed a multi-site behaviour, illustrating sensitivity to the reaction temperature and the comonomer mole fraction. Surprisingly, an upper limit is observed for the latter, leading to complete catalyst inhibition. Analysis of the chain termination processes implies the possibility of a predominant, although in general less favourable, *β*-hydride elimination route under certain polymerisation conditions.

Keywords: copolymerisation; end group analysis; ethene-*co*-1-hexene; metallocenes; multi-modal polymers

Introduction

The control of polymer microstructure by design of the catalyst ligand framework symmetry has been strongly exploited since the first discoveries in the 1980s.[1-3] Sterically rigid and bulky structures have been synthesised and successfully employed for the tailoring of tacticity and comonomer incorporation of homo- and copolymers.[4-6] When Waymouth et al.[7] introduced the concept of oscillating stereocontrol for the production of elastomeric polypropylene (ePP) as an alternative to the stereoblock ePP discovered by Kaminsky et al.,[8] conformationally flexible metallocenes attracted new attention in the community.[9] In the former system, it has been claimed that the observed elastomeric properties could be attributed to a *rac*/*meso* interconversion of the active site during chain growth, leading to atactic/isotactic sequences.[7] Results obtained by molecular mechanics and DFT calculations suggested that the afore mentioned *rac* and *meso* conformers represented actual energy minima for the catalyst precursors.[10,11] However, experimental evidence for the

DOI: 10.1002/masy.200450909

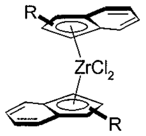
interconversion could not be provided, and recent studies of the polymer microstructure conducted by Busico et al. by means of advanced high-field ^{13}C NMR clearly show that atactic sequences are not contributing to the phenomenon. Isolated stereoerrors due to a *rac*/*rac** interconversion seem to be the most suitable explanation.[12]

Regardless of the validity of the suggested mechanisms of polymerisation, the idea of controlling the number and type of several possible active sites of a conformationally flexible zirconocene remains an intriguing challenge. In the present study we investigate bis-indenyl zirconocenes bearing a silyl moiety in 2-position, which can be substituted with different functionalities. The silyl group appeared to us as a natural choice for the systematic variation and study of different substitution patterns in the 2-position. To our knowledge there are only few reports on the corresponding 1-isomers and therefore these have been synthesized as well. Details on the preparation and structural as well as catalytic characterisation with respect to ethylene homopolymerisations of these zirconocenes will be reported elsewhere.[13] We herein wish to report a screening of different catalysts in the ethene/1-hexene copolymerisation and some aspects of in-depth copolymerisation studies of bis(2-dimethylsilylindene) zirconoium(IV) dichloride (**1**).

Results and Discussion

Comparative Ethene/1-Hexene Copolymerisation Studies

In order to obtain a general idea of the catalyst characteristics of the metallocenes, a comparative copolymerisation screening was run to account for activity. The bis(indenyl)zirconium(IV) dichloride/MAO catalyst was chosen as a standard, since polymerisation activities might vary due to different experimental setups and procedures. A concise overview over the catalysts employed is given in Figure 1.



Acronym	R	2-isomer	meso 1-isomer	rac 1-isomer
DMS	Me$_2$HSi	**1**	**4**	-
TMS	Me$_3$Si	**2**	**5**	**7**
TBDMS	^{t}BuMe$_2$Si	-	-	**8**
DMPS	Me$_2$PhSi	**3**	**6**	**9**

Figure 1. Numbering scheme for the *rac*-like conformer of bis(1/2-silylindenyl)-zirconocene(IV) dichloride metallocenes.

The copolymerisations were run at a comonomer mole fraction of $X_H = 0.60$ in the feed at a reaction temperature of 30°C. The results presented in Table 1 indicate that for the 2-isomers, the DMS moiety (**1**) yields the highest activity. Introduction of one additional methyl group at the silyl moiety (**2**) causes a decrease of 60%, whereas total catalyst inhibition occurs for a phenyl group (**3**). As for the 1-isomers, the *rac* diastereomer of the sterically most demanding DMPS system **9** displays an activity comparable to that of **1**, the least congested 2-isomer. This is in agreement with the results obtained for the homopolymerisation.[13] A striking contrast is that **3** and **9** show complementary copolymerisation activities simply due to a change from the 2- to the 1-isomer. The unsubstituted bis(indenyl)zirconocene is slightly more active than any of the silyl substituted-indenyl zirconocenes considered here.

Table 1. Average activities with absolute standard deviations for the several zirconocene/MAO systems in ethene/1-hexene copolymerisations, using 30°C, 1.2 bar ethene, $X_H = 0.20$, $c(Zr) = 10^{-6}$ mol/L, Al/Zr = 1000, 30 min, toluene.

No.	Compound	Activity [$t/mol_{Zr} \cdot mol_{E+H} \cdot h$]
1	2-DMS	115 ± 12
2	2-TMS	47 ± 1
3	2-DMPS	0
Ref	$[Ind]_2ZrCl_2$	151 ± 6
4	*meso* 1-DMS	53 ± 4
5	*meso* 1-TMS	22 ± 1
6	*meso* 1-DMPS	13 ± 1
7	*rac* 1-TMS	19 ± 0
8	*rac* 1-TBDMS	62 ± 9
9	*rac* 1-DMPS	107 ± 5

Bis(2-DMS)zirconium(IV) Dichloride in Ethene/1-Hexene Copolymerisation

Activity Response on 1-Hexene Mole Fraction and Temperature

In general, zirconocene/MAO catalysts can show a polymerisation rate enhancement at certain temperatures upon the addition of comonomer to the reaction feed. In the case of **1**, the activity decreases rapidly as a function of the comonomer mole fraction in the feed at 80°C. After an initial activity drop down to 60% at $X_H = 0.20$, it stabilises between 3-5%

relative to the homopolymerisation for $0.80 \leq X_H \leq 0.90$. Complete catalyst inhibition is achieved at higher values for X_H. For the same set of experiments at a reaction temperature of 30°C, the slope of inhibition is steeper, although it is qualitatively of the same form, and complete catalyst inhibition is not achieved until X_H exceeds 0.95.

The effect of a variation in temperature is less pronounced and more complicated. In the temperature series all parameters except for the temperature were constant, but the activity ranged from 148 to 245 $t/mol_{Zr} \cdot mol_{E+H} \cdot h$ without any apparent correlation. Conditions used: $c(E) = 0.14$ mol/L, $c(Zr) = 5 \cdot 10^{-7}$ mol/L, Al/Zr = 8700, 30 min polymerisation time.

Polymer Microstructure and Molecular Weights

The polymer microstructure of the LLDPE samples has been analysed by means of FT-IR and ^{13}C NMR, and the homogeneity of the products was investigated by DSC and high-temperature GPC. The polymers obtained under the various experimental conditions are strongly affected by the polymerisation temperature.

The comonomer enchainment was between 1.0 and 0.3 mol% at constant concentration in the reaction feed, $X_H = 0.20$ and a temperature range from 10 to 80°C. Based on the results from the end group analysis (Figure 2) and molecular weights (Table 2), the reason for these values becomes apparent. The ratio of vinyl to *trans*-vinylene termination is larger than unity at all temperatures. While the concentration of vinyl terminations is higher than that of vinylidene up to 30°C, a reversal of the situation is observed from 40°C upwards. Vinylidene bonds originate by hydrogen transfer to monomer or β-hydride elimination after 1-hexene enchainment. Here, the latter process is considered to be dominating for two reasons. Firstly, the activation entropy for a bimolecular hydrogen transfer to monomer is negative and this process becomes less favourable with increasing temperature. Secondly, the activation enthalpy, estimated to be on the order of 155 kJ/mol (±17 kJ/mol),[14] is in reasonable agreement with the calculated reaction energy of 113 kJ/mol, as predicted by Støvneng and Rytter.[15]

Interestingly, the concentration of vinylidene double bonds does stabilise around 0.36/1000C at 70 and 80°C (Figure 2). At 80°C the average number of comonomer units per polymer chain is about 2, based on a molecular weight of 17 kg/mol, *i.e.* $P_n \cong 600$. This implies that 32% of all chains will be terminated after comonomer enchainment or, in other words, enchainment of 1-hexene will lead to chain growth termination one out of five times. Hence,

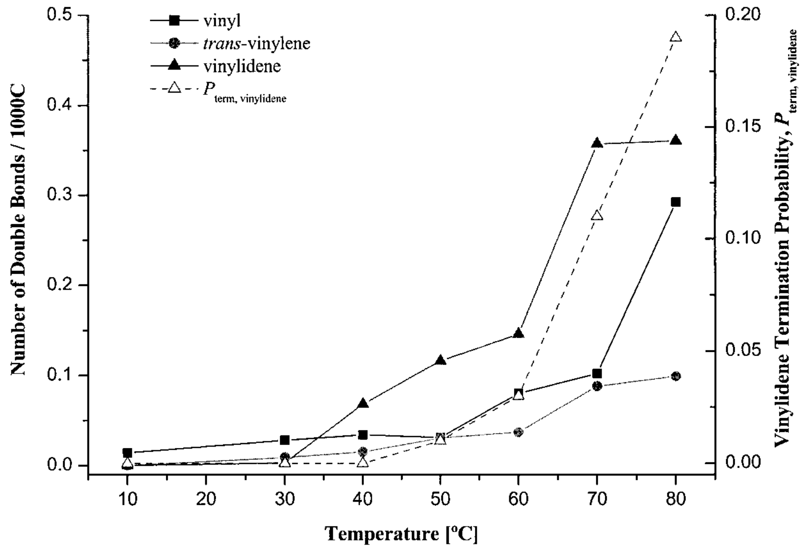


Figure 2. End group analysis as a function of the polymerisation temperature, catalysed with 1/MAO, $X_H = 0.20$, 30 min polymerisation time, Al/Zr = 8700. Left ordinate shows number of double bonds / 1000C, right ordinate the calculated probabilities for chain termination after 1-hexene insertion.

the catalytic process is approaching dimensions of quantitative conversion relative to the usually rather unlikely vinyl termination process.

The increase in the termination rate to vinyl and *trans*-vinylene end groups at elevated temperatures indicates a superposition of mechanisms, *i.e.* β-hydride elimination occurs in addition to chain-transfer to monomer.[17] That is in agreement with thermodynamics which call for faster and more frequent termination, while comonomer insertion should slow down. Further, chain termination by transmetalation to aluminium loses significance with increasing temperature, since the contribution of the negative activation entropy depresses the Gibbs' free energy and makes this process unfavourable. A comparison of the molecular weights determined by means of FT-IR and GPC reveals that there is virtually no termination through transmetalation to be considered at 70 and 80°C (Table 2).

Similar end group effects have been observed for the variation of the 1-hexene mole fraction in the feed at elevated temperatures, but the inhomogeneity of the products obtained made an interpretation more ambiguous.

Table 2. Variation of temperature at constant 1-hexene concentration. The 1-hexene incorporations x_H reported here approach the detection limit for ^{13}C NMR and IR analysis. The uncertainty in these figures is difficult to estimate. We assume ±0.003 for x_H and ±10% for the M_n. PDI = polydispersity index.

T [°C]	$x_{H,\text{NMR}}$	M_n [kg/mol]$_\text{IR}$	M_n [kg/mol]$_\text{GPC}$	PDI
80	0.003	21	17	15
70	0.005	33	16	25
60	0.006	58	17	37
50	0.008	79	35	21
40	0.009	133	47	18
30	0.010	370	58	13
10	0.010	974	208	3.4

Homogeneity of Products and Dual-Site Hypothesis

Since rotationally flexible zirconocenes offer at least in theory the possibility of conformer interconversion during the polymerisation, the question of the accessibility and conversion rate of these conformers arises. Taking into account the polydispersity index (PDI) for the previously discussed copolymerisation, we observe indications for non-ideal single-site catalysis at 10°C. Quijada and Dupont reported a PDI of 3.5 for a copolymerisation with $[\text{Ind}]_2\text{ZrCl}_2$/MAO at 60°C,[17] while **1**/MAO yields a ten-fold PDI at three times the M_n under similar reaction conditions. The response of the PDI as a function of the temperature, shown in Table 2, is rather systematic and passes a maximum around 60°C.

Complications arise when the effect of the comonomer concentration is studied at constant temperatures (Table 3). For the interval $0.00 \leq X_H \leq 0.90$, the PDI ranges between 16 and 1.9 at 80°C. After an initial increase at low concentrations of 1-hexene, the PDI undulates between 8 and 5 and finally displays single-site character at the highest comonomer concentration. In contrast to this, the PDI lies one order of magnitude higher when X_H exceeds 0.60 for the same set of experiments at 30°C and does not exhibit the initial increase at low comonomer concentrations. It has to be emphasised that these inhomogeneous products complicated sample preparation for FT-IR, DSC and GPC analysis. However, comonomer incorporations determined by means of ^{13}C NMR and FT-IR are in good agreement. A comprehensive summary of the polydispersities under the several reaction conditions is presented in Table 3.

Table 3. Polydispersities of LLDPE samples as derived from GPC. Catalyst system **1**/MAO.

	Polydispersity Index	
X_H	**30°C**	**80°C**
0.00	3.6	5.9
0.20	5.7	16.0
0.40	8.5	12.0
0.60	7.0	8.1
0.70	43	4.5
0.80	38	5.0
0.83	29	6.6
0.87	58	5.3
0.90	34	1.9
0.95	15	-

Figure 3 illustrates the superimposition of the GPC analyses for the comonomer variation at 80°C. The product distribution is clearly a function of the comonomer and multimodal. Surprisingly, a smooth transition from the rather monomodal product to at least bimodal products occurs between $0.60 \leq X_H \leq 0.90$ and implies that the different sites are either

a) discriminated with respect to population as a function of the comonomer mole fraction rather than the temperature, or

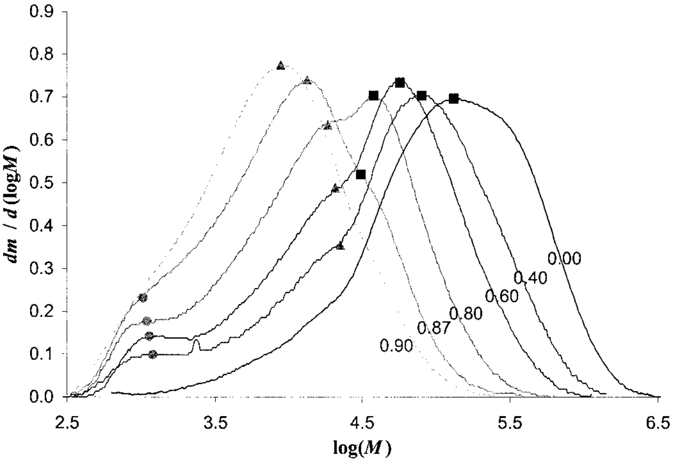


Figure 3. Superimposition of GPC elution curves for different 1-hexene mole fractions in the feed. Main fractions are marked with square, triangles and circles. T = 80°C.

b) respond to the change in comonomer mole fraction by a change in the propagation rate.

A less ambiguous case is presented in Figure 4, which resembles a bimodal product distribution at $X_H = 0.80$ and 30°C. The composition consists of an oligomeric fraction around log(M) = 3.4 and a polymeric fraction at log(M) = 5.8.

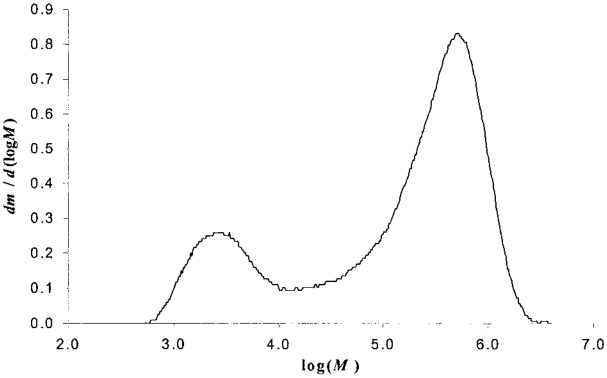


Figure 4. GPC trace of a bimodal product composition obtained with **1**/MAO at X_H = 0.80 and 30°C.

The observed product compositions suggest more than one active site during the polymerisation process. Inspired by the works of Brintzinger et al.,[11] we applied molecular mechanics calculations to analyse the energy profile of the rotamer interconversion of the catalyst precursor. Preliminary results unambiguously show that the dichlorides have different accessible conformers, but these calculations have to be extended to active sites with attached polymer chain and associated olefins for a thorough picture to be drawn. Nevertheless, it can be pointed out for the case of compounds **1** and **2** that no stabilisation of the *meso*-like conformer is expected, accounting for the fact that our computations predict conformational transition states for the sterically less congested catalyst precursors.

Conclusions

The results presented here suggest that the enchainment of 1-hexene in the copolymerisation with ethene as catalysed by **1**/MAO is hindered, although our incorporation rates are somewhat higher than those reported by Quijada for the bis-indenylzirconium(IV)-

dichloride/MAO catalyst.[18] Waymouth made similar observations for his catalyst systems in ethen-1-hexene copolymerisation.[19] While sterically demanding silyl moieties in the 2-position of an indene ring can, in the case of the DMPS group, lead to complete catalytic inhibition in the presence of 1-hexene, inhibition can be achieved at high comonomer mole fractions for even the smaller silyl moieties. Molecular weights increase by the introduction of a functional group in the 2-position. Despite the fact that the system investigated in detail here shows a temperature dependence on the active site population, there is no indication to believe that these sites interconvert rapidly enough to resemble a rotationally dynamic single-site catalyst. Quantum chemical calculations, which we are currently carrying out, suggest different, non-stabilised active sites, which matches the high polydispersity indices found by means of GPC. Still, the analysis of the polymer products remains difficult due to their inhomogeneity and display the non-SSC character of these zirconocenes.

Acknowledgement

We thank Jens Kjær Jørgensen for high-temperature GPC measurements and Aud M. Bouzga for NMR instrument support. A.C.M. gratefully acknowledges Dr.-Ing. scholarship grant no. 145544/431 by NFR (The Research Council of Norway).

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