

α -Olefin oligomers with narrow molar mass distributions from zirconocene/methylaluminumoxane catalysts — An examination of the structure-reactivity relationship

Dedicated to Prof. Dr. *Herbert Schumann* on the occasion of his 60th birthday

Christoph Janiak^{a)}*, *Katharina C. H. Lange*^{a)}, *Peter Marquardt*^{b)}

^{a)} Institut für Anorganische und Analytische Chemie, and

^{b)} Institut für Technische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

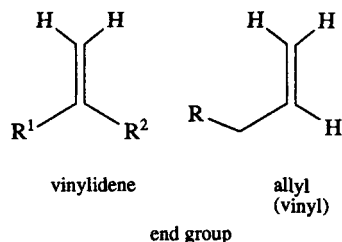
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SUMMARY:

A series of *tert*-butyl substituted zirconocene/methylaluminumoxane catalysts illustrates the potential for the tailoring of olefin oligomers with extremely narrow molar mass distributions, which are explained on the basis of a chain-length dependent propagation rate. Comparative oligomerization experiments provide a means to estimate the relative rates for chain propagation versus chain transfer as well as a correlation with the metallocene structure.

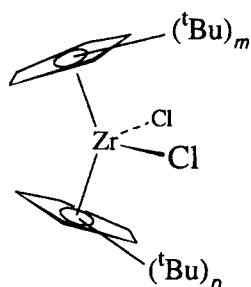
Introduction

Homogeneous, single-site metallocene/MAO catalysts (MAO = methylaluminumoxane) are of high academic and industrial interest as a new generation of Ziegler-Natta catalysts¹⁾. We study here the oligomerization of α -olefins in an attempt to expand their potential applications and to gain a more detailed insight into the central problem of metallocene catalysis, namely the relation of chain transfer versus chain propagation. Higher C_{6–20} α -olefins are of increasing importance as a source of many industrially important chemicals. Various metals and methods are described for the oligomerization of α -olefins, albeit relatively little attention has been paid to the possibility of applying zirconocene/MAO systems^{2–4)}. The finding of low-molar-mass products from propene polymerizations with (achiral) zirconocenes at elevated temperature was generally regarded as unfortunate⁵⁾. Yet, for the olefin *oligomerization* metallocene catalysts should also advantageously combine high activity with the possibility to tailor oligomer properties such as molar mass, molar mass distribution,



as well as the stereoregularity through a rational ligand design at the transition metal center. Depending on the chain-transfer process the type of olefinic end group (vinylidene from β -hydrogen elimination or vinyl/allyl from β -CH₃ elimination) may also be controlled.

We demonstrate here the potential of zirconocene/MAO catalysts to fine-tune the oligomer characteristics, such as the molar mass, together with a very narrow molar mass distribution. In addition a model is provided for a relative quantification of chain transfer versus chain propagation. As a starting point we have studied the oligomerization capabilities of the *tert*-butyl-substituted zirconocene dichloride series (**1b–f**) which offers a wide range of steric variability to study the structure-reactivity relationship. Propene and 1-hexene were employed as monomers.



1a-f

- 1a:** $m = n = 0$: $(C_5H_5)_2ZrCl_2$
1b: $m = 1, n = 0$: $(C_5H_4^tBu)(C_5H_5)ZrCl_2$
1c: $m = n = 1$: $(C_5H_4^tBu)_2ZrCl_2$
1d: $m = 2, n = 0$: $(C_5H_3-1,3-^tBu_2)(C_5H_5)ZrCl_2$
1e: $m = 3, n = 0$: $(C_5H_2-1,2,4-^tBu_3)(C_5H_5)ZrCl_2$
1f: $m = n = 2$: $(C_5H_3-1,3-^tBu_2)_2ZrCl_2$
 (^tBu = *tert*-butyl)

Experimental part

Materials

The zirconocene dichlorides were obtained as follows: **1a:** Purchased from Merck. **1b:** P. Renaut, G. Tainturier, B. Gautheron, *J. Organomet. Chem.* **148**, 35 (1978). **1c:** M. F. Lappert, C. J. Pickett, P. I. Riley, P. I. W. Yarrow, *J. Chem. Cos., Dalton Trans.* 805 (1981). **1d:** From $C_5H_3-1,3-^tBu_2Li$ and $(C_5H_5)ZrCl_3(dme)^8$ in toluene; correct analytical data. **1e:** H. Sitzmann, P. Zhou, G. Wolmershäuser, *Chem. Ber.* **127**, 3 (1994). **1f:** see ref.⁷

Methylaluminoxane (MAO) was obtained from Witco (Bergkamen, Germany) as a 10 wt.-% toluene solution (4.9% wt.-% aluminium, density ≈ 0.9 g/mL, number-average molar mass of the MAO oligomers 900–1100 g/mol). Toluene was refluxed over sodium metal for several hours, followed by distillation and storage under argon. Propene (BASF AG) was polymerization-grade and used without further purification. 1-Hexene (97%) was obtained from Aldrich.

Oligomerizations

Propene oligomerizations were carried out in a 1-L Büchi-glass autoclave, thermostated at 50 °C and charged with 200 mL of toluene, 8.2–8.3 L gaseous propene, and the catalyst solution consisting of 19 mL of methylaluminoxane and $3 \cdot 10^{-5}$ mol of the zirconocene dichloride (mole ratio Al:Zr = 1000, activation time 10 min) for a reaction time of 1 h. After this time the propene was vented off.

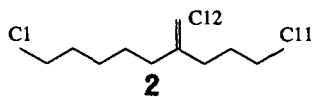
1-Hexene oligomerizations were carried out in a 100 mL Schlenk-flask, thermostated at 50 °C, and charged with 50 mL of 1-hexene and the catalyst solution consisting of 8 mL of methylaluminoxane and $3 \cdot 10^{-6}$ mol of the zirconocene dichloride (mole ratio Al: Zr = 4000, activation time 1 h) for a reaction time of 24 or 48 h.

In both cases the reaction was stopped and the catalyst deactivated by addition of methanol and slightly acidified water. The organic phase was separated and the toluene removed in vacuo (ca. 1 Torr) at 40 °C to leave the oligomer.

Results and discussion

Tab. 1 compiles the oligomerization results. The trends in the productivities can be explained by a combination of the steric hindrance of the bulky *tert*-butyl groups, and by the tendency of prochiral α -olefin monomers to show higher activities in more stereospecific environments⁶). The latter leads to high oligomer yields with zirconocene **1d** in the case of propene and with **1b** for hexene. The low productivities of **1e** and **1f** correlate with other observations on the reactivity of hindered cyclopentadienyl-zirconium compounds⁷). It is evident that well-defined oligopropenes and oligo-1-hexenes with remarkably narrow molar mass distributions and molar masses covering the range $200 < \bar{M}_n < 2000$ are readily available with *tert*-butyl substituted zirconocenes, thereby not taking into account process parameters, such as temperature and olefin or catalyst concentrations, as additional tuning variables.

An olefinic end group analysis of the oligomers shows the sole presence of a vinylidene type double bond ($R^1R^2C=CH_2$) as based on infrared ($\nu_{C=C} = 888 \text{ cm}^{-1}$), ^1H ($\delta = 4.7$ and 4.8 ppm, broad singulets) and ^{13}C NMR studies [$\delta \approx 112$ ($C=CH_2$) and 145 ppm ($C=CH_2$)]. For the low molar mass oligohexene from **1f** the NMR analysis underscores the dimeric character of the product. The ^{13}C NMR spectrum simplifies to essentially 12 major lines with similar intensities except for the quarternary carbon and can be assigned to the dimeric species **2** [^{13}C NMR (50.4 MHz, CDCl_3): $\delta = 14.0, 14.1$ (C1/11), $22.7, 22.8$ (C2/10), $28.0, 29.3, 30.2, 32.0$ (C3/4/5/9), $35.9, 36.2$ (C6/8), 108.6 (C12), 149.8 (C7)]. See also ref.⁹].



We note here that a $\text{Zr}-\text{CH}_3$ starting group (from Cp_2ZrCl_2 and MAO) leading to a 2-methylpropyl and a 2-methylhexyl end group with propene and 1-hexene, respectively, is only important for the synthesis of the first oligomeric molecule, here. For all subsequent catalytic cycles, a $\text{Cp}_2\text{Zr}^+-\text{H}$ species which is formed by β -H elimination as the only discernable chain transfer process here (see below), gives then rise to unbranched propyl and hexyl end groups, respectively.

We can rule out other chain transfer processes, such as chain transfer to aluminium or β -alkyl elimination⁴) to be of any importance for the *tert*-butyl substituted zirconocenes. Chain transfer to aluminium would not only regenerate the $\text{Zr}-\text{CH}_3$ species but also give oligomers with saturated end groups. The latter can be deemed negligible by the reasonable agreement between the \bar{M}_n values from NMR and

Tab. 1. Catalyst activities and oligomer characteristics for **1a-f**^{a)}

Catalyst	Activity in kg oligomer/(gZr · h)	\bar{M}_n /(g · mol ⁻¹)		Dispersity $Q = \bar{M}_w/\bar{M}_n$ ^{e)}		
		¹ H NMR ^{b)}	GPC ^{c)}		cryosc. ^{d)} average	
Oligopropenes:						
1a (C ₃ H ₇) ₂ ZrCl ₂	4.5	340	470	380	400	1.3
1b (C ₃ H ₇ ^t Bu)(C ₃ H ₇)ZrCl ₂	4.4	290	400	350	350	1.2
1c (C ₃ H ₇ ⁱ Bu) ₂ ZrCl ₂	4.4	410	510	370	430	1.3
1d (C ₃ H ₇ ^t Bu) ₂ (C ₃ H ₇)ZrCl ₂	7.3	680	960	750	800	1.7
1e (C ₃ H ₇ ⁱ Bu) ₃ (C ₃ H ₇)ZrCl ₂	1.0	1100	1300	1000	1100	2.3
1f (C ₃ H ₇ ⁱ Bu) ₂ ZrCl ₂	0.01	580	470	n. d.	520	2.2
Oligohexenes:						
1a (C ₄ H ₉) ₂ ZrCl ₂	3.4	230	360	250	280	1.3
1b (C ₃ H ₇ ^t Bu)(C ₃ H ₇)ZrCl ₂	3.7	260	370	250	300	1.2
1c (C ₃ H ₇ ⁱ Bu) ₂ ZrCl ₂	0.7	310	410	300	340	1.2
1d (C ₃ H ₇ ^t Bu) ₂ (C ₃ H ₇)ZrCl ₂	2.5	670	740	650	690	1.6
1e (C ₃ H ₇ ⁱ Bu) ₃ (C ₃ H ₇)ZrCl ₂	0.2	430	670	450	520	2.0
1f (C ₃ H ₇ ⁱ Bu) ₂ ZrCl ₂	0.1	200	n. d.	180	190	n. d.

a) To ensure reproducibility the oligomerizations were carried out at least twice. n. d. = not determined.

b) Based on the integral ratio of the vinylidene protons relative to the alkyl protons.

c) Gel permeation chromatography: Waters 150-C, μ -styrigel columns (10⁶–5 · 10² Å), eluent toluene, Temp. = 60 °C, flow rate 2 mL · min⁻¹, sample volume 100 μ L, concentration 0.5–1 wt.-%, polyethylene standards with a universal calibration according to Benoit et al.¹²⁾ (Mark-Houwink coefficients: polyethylene: $k_{\eta} = 1.27 \cdot 10^{-2}$ mL/g, $A = 1.04$ [polyalkene, C₁₀–C₁₈]; polypropylene: $k_{\eta} = 2.7 \cdot 10^{-2}$ mL/g, $A = 0.71$ [poly(propylene), atactic, solvent benzene, Temp. = 25 °C])¹⁴⁾ and Waters 410, 5 MIXED B-polystyrene gel columns (7.5 · 300 mm, PL-gel 10 μ), eluent tetrahydrofuran, Temp. = 35 °C, flow rate 1.2 mL · min⁻¹, calibration with ethylbenzene, 1,3-diphenylbutane, 1,3,5-triphenylhexane, 1,3,5,7-tetraphenyldecane and 1,3,5,7,9-pentaphenyldecane, lower limit 180 g · mol⁻¹.

d) Cryoscopic molar mass determination in benzene.

e) From gel permeation chromatography (GPC).

GPC/cryoscopy, especially since the molar masses obtained by ^1H NMR are always smaller (saturated end groups would contribute only to the major oligomer peaks between 0.9 and 2.2 ppm and nothing to the vinylidene end group integral, thus ensuing a larger than “real” molar mass). Furthermore, methyl carbon signals in oligopropenes based on the vinylidene end groups ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{R}$, ≈ 22.35 ppm) and propyl start groups ($\text{CH}_3-\text{CH}_2\text{CH}_2-\text{R}'$, ≈ 14.6 ppm) are almost equal in intensity⁹. A β -alkyl elimination would lead to vinyl (or allyl, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{R}-$) end groups, for which no peaks (near 5.0 and 5.8 ppm) could be observed in the proton NMR.

The dispersity of the oligomers is rather narrow (cf. Tab. 1), with values of Q ($=\bar{M}_w/\bar{M}_n$) around and even well below 2. Although dispersities smaller than 2 seem to contradict a Schulz-Flory (or most probable) distribution, such narrow distributions cannot be dismissed as being due to a removal of low-boiling oligomers in the work-up process. In the case of oligohexenes, the dimer **2** (b. p. 88–89 °C/14 Torr)¹⁰ is already too high boiling to be evaporated under the conditions applied. For oligopropenes the narrow dispersities were verified by additional GPC measurements on the toluene product solution *before* solvent evaporation and product isolation. It should be remembered that Schulz-Flory demands a propagation rate independent of the chain length — a prerequisite which is not fulfilled during about the first five insertion steps. Instead for the oligomers one will have a decrease in the rate during the first insertions as could be demonstrated by Fink and Schnell in ethylene oligomerizations with the soluble catalyst system (C_5H_5)₂TiRCl/Al(C_2H_5)₂Cl¹¹). We were able to reproduce such narrow molar mass dispersions with a model which takes in account chain propagation and β -hydrogen elimination (for the chain transfer) and which is based on the decrease in the propagation rate over the first five insertions.

With β -H elimination assumed as the only chain-transfer mechanism the probability of chain growth calculates to $a = k_w \cdot c_M / (k_w \cdot c_M + k_{\beta\text{-H}})$ with k_w = rate constant for propagation, c_M = concentration of monomer (here: $3.4 \text{ mol} \cdot \text{L}^{-1}$ for propene), and $k_{\beta\text{-H}}$ = rate constant for β -H elimination. With constant growth probability a the mole fraction of oligomers which have reached the degree of oligomerization P is given as $x(P) = a^{P-1} \cdot (1 - a)$ with $1 - a$ being the probability of chain transfer. On the other hand, when the growth probability depends on the chain length or $k_w = f(P)$ and subsequently $a = f(P)$, this equation converts to $x(P) = \prod_{i=1}^{P-1} \alpha_i \cdot (1 - \alpha_P)$.

A variation of the gradient for this decrease in propagation together with a variation of the relative rates for propagation and β -H elimination enabled us to reproduce the molar masses together with the narrow molar mass distribution obtained. Subsequently, the relative rates as a function of the steric ligand environment can be estimated. For propene as a monomer, Fig. 1 a illustrates how the dispersity Q is affected by both the gradient (given here as $k_w(P=1)/k_w(P \rightarrow \infty)$) as well as by the relative rate of chain transfer and propagation ($k_{\beta\text{-H}}/k_w(P \rightarrow \infty)$). An increase lowers the dispersity. Values of Q at around 1.3 are calculated here for an about ten-fold rate of the first versus the sixth insertion (with an exponential drop-off in-between) and for a chain transfer rate about equal to the propagation rate. The molar mass, on the other hand, is only little affected by changes in the initial propagation rate but is considerably lowered by an increase in chain transfer rate (Fig. 1 b). Similar diagrams (not shown

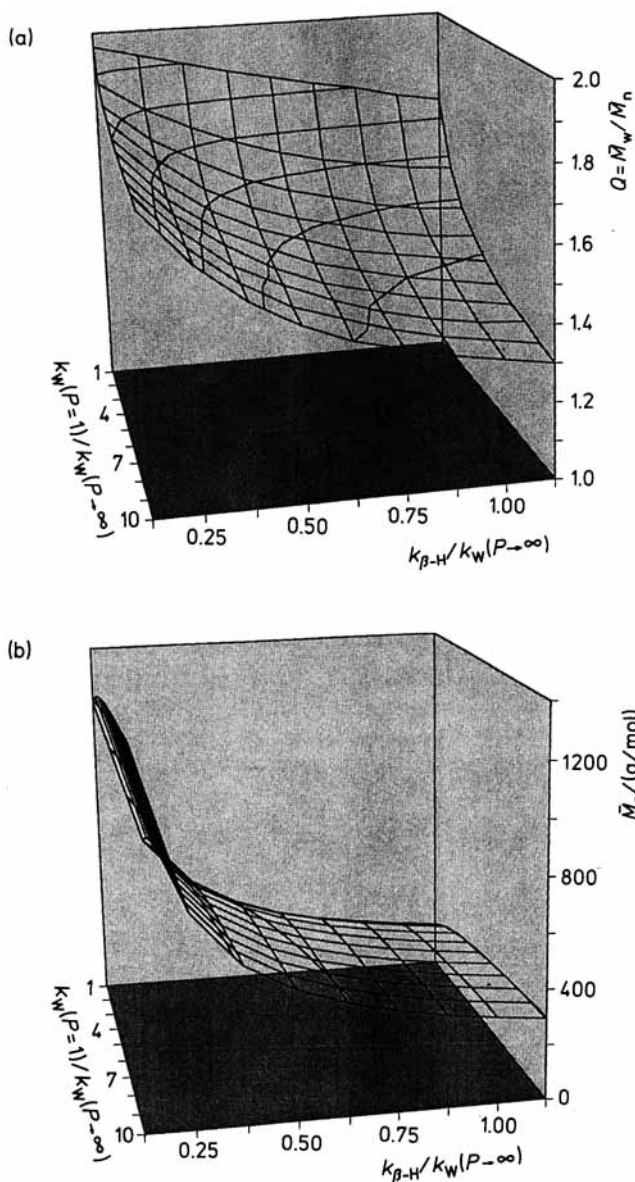


Fig. 1. Dependence of the dispersity Q (a) and the number-average molar mass \bar{M}_n (b) upon the change in propagation rate during the first five insertions ($k_w(P=1)/k_w(P \rightarrow \infty)$) and the ratio for chain transfer (β -hydrogen elimination) versus propagation ($k_{\beta-H}/k_w(P \rightarrow \infty)$)

here) can be calculated for the catalytic synthesis of the oligohexenes, thereby taking into account the different monomer concentrations. We just note here that in order of a dimeric species ($\bar{M}_n = 170 \text{ g} \cdot \text{mol}^{-1}$) to be the major product (80–90 mol-%; cf. entry 1f in Tab. 1) a very steep decrease of the insertion rate for the first over the second and all subsequent insertions has to be assumed together with the rate of the β -hydrogen elimination in the range of k_w . From our modelling calculations we

estimated $k_w(P = 1)/k_w(P \geq 2) \approx 20$ and $k_{\beta-H}/k_w(P = 1) \approx 5$. The strong decrease in the insertion rate can be understood on the basis of molecular mechanics studies by comparing the space for monomer coordination provided in the species $(C_5H_3^tBu_2)_2Zr-H^+$ and $(C_5H_3^tBu_2)_2Zr-(n-C_6H_{13})^+$ (Fig. 2).

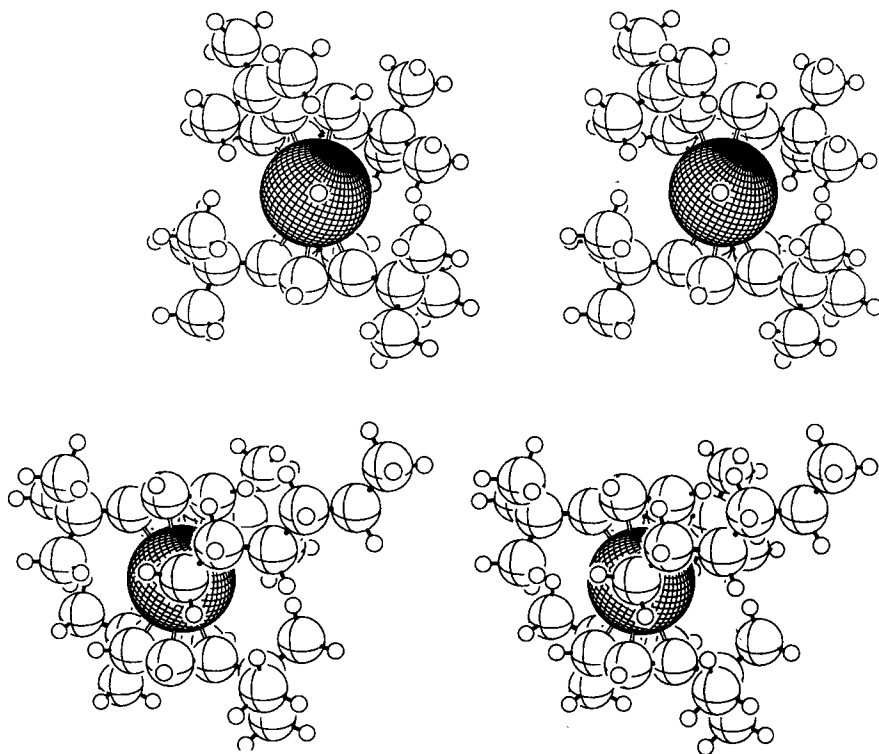


Fig. 2. Stereoscopic view of the spatial conditions around the zirconium center in $(C_5H_3^tBu_2)_2Zr-H^+$ (top) and $(C_5H_3^tBu_2)_2Zr-(n-C_6H_{13})^+$ (bottom) (PLUTON¹³). In comparison to the $Zr-H$ species, monomer coordination in the $Zr-(n-C_6H_{13})$ -derivative, which is obtained after the first insertion, is exceedingly more difficult. Together with the four *tert*-butyl ligands, the hexyl group further restricts the space left for monomer coordination. The sudden blocking of the zirconium coordination site after the first insertion step illustrates the strong decrease of the insertion rate from $k_w(P = 1)$ to $k_w(P = 2)$ (molecular-mechanics optimized structures, mm+ force field, HyperChem 3.0). The molecules are not shown in the full space-filling mode, but the spheres are drawn at the covalent radii to allow for a better recognition of the underlying structure

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