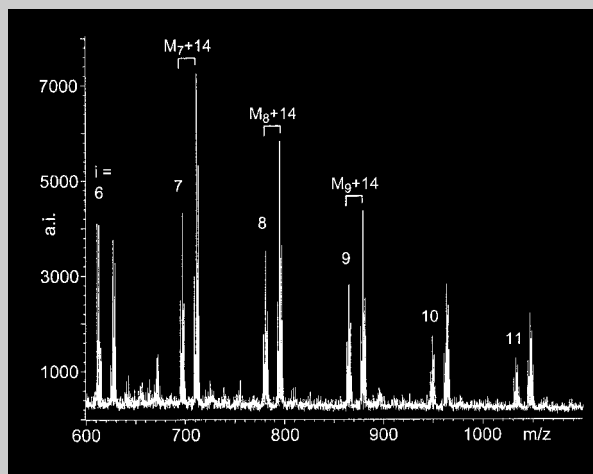


Full Paper: A series of $\text{Cp}'(\text{C}_5\text{H}_5)\text{ZrCl}_2$ and $\text{Cp}'_2\text{ZrCl}_2$ pre-catalysts ($\text{Cp}' = \text{C}_5\text{HMe}_4$, $\text{C}_4\text{Me}_4\text{P}$, C_5Me_5 , $\text{C}_5\text{H}_4^i\text{Bu}$, C_5H_3 -1,3- $^i\text{Bu}_2$, C_5H_2 -1,2,4- $^i\text{Bu}_3$) together with $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ was used for the directed oligomerization of propene and 1-hexene in comparative experiments. Oligomer characterization was carried out by ^1H NMR, SEC (GPC), MALDI-TOF MS, cryoscopy and Raman spectroscopy. From ^1H NMR the nature and relative ratio of the double-bond end group is determined together with \bar{M}_n if every oligomer molecule contains such a double-bond end group. Normally vinylidene double bonds (from β -hydrogen elimination) are found. From ^1H NMR and MALDI-TOF MS also vinyl end groups (from β -methyl elimination) are observed in the case of oligopropenes with $(\text{C}_4\text{Me}_4\text{P})$ - $(\text{C}_5\text{H}_5)\text{ZrCl}_2$ and with the symmetrical methyl containing $\text{Cp}'_2\text{ZrCl}_2$ pre-catalysts. The vinylidene/vinyl ratio depends on the ligand and increases from C_5HMe_4 (65/35) over $\text{C}_4\text{Me}_4\text{P}$ (61/39) to C_5Me_5 (9/91). A comparison of \bar{M}_n from ^1H NMR and SEC together with MALDI-TOF MS shows that the phospholyl-zirconocenes and $(\text{C}_5\text{HMe}_4)_2\text{ZrCl}_2$ also exhibit chain transfer to aluminium, thereby giving saturated oligomers.



MALDI-TOF mass spectrum for an oligohexene terminated in part by chain-transfer to aluminum (note the M_i+14 peak).

Analyses of Propene and 1-Hexene Oligomers from Zirconocene/MAO Catalysts – Mechanistic Implications by NMR, SEC, and MALDI-TOF MS

Dedicated to Prof. Dr. *Walter Kaminsky* on the occasion of his 60th birthday in recognition of his seminal work on metallocene catalysis

Christoph Janiak,*¹ *Katharina C. H. Lange*,² *Peter Marquardt*,³ *Ralph-Peter Krüger*,⁴ *Ralf Hanselmann*⁵

¹ Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany
E-mail: janiak@uni-freiburg.de

² Institut für Anorganische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

³ Institut für Technische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

⁴ Institut für Angewandte Chemie Adlershof, Abt. Zentrale Analytik, Rudower Chaussee 5, D-12484 Berlin, Germany

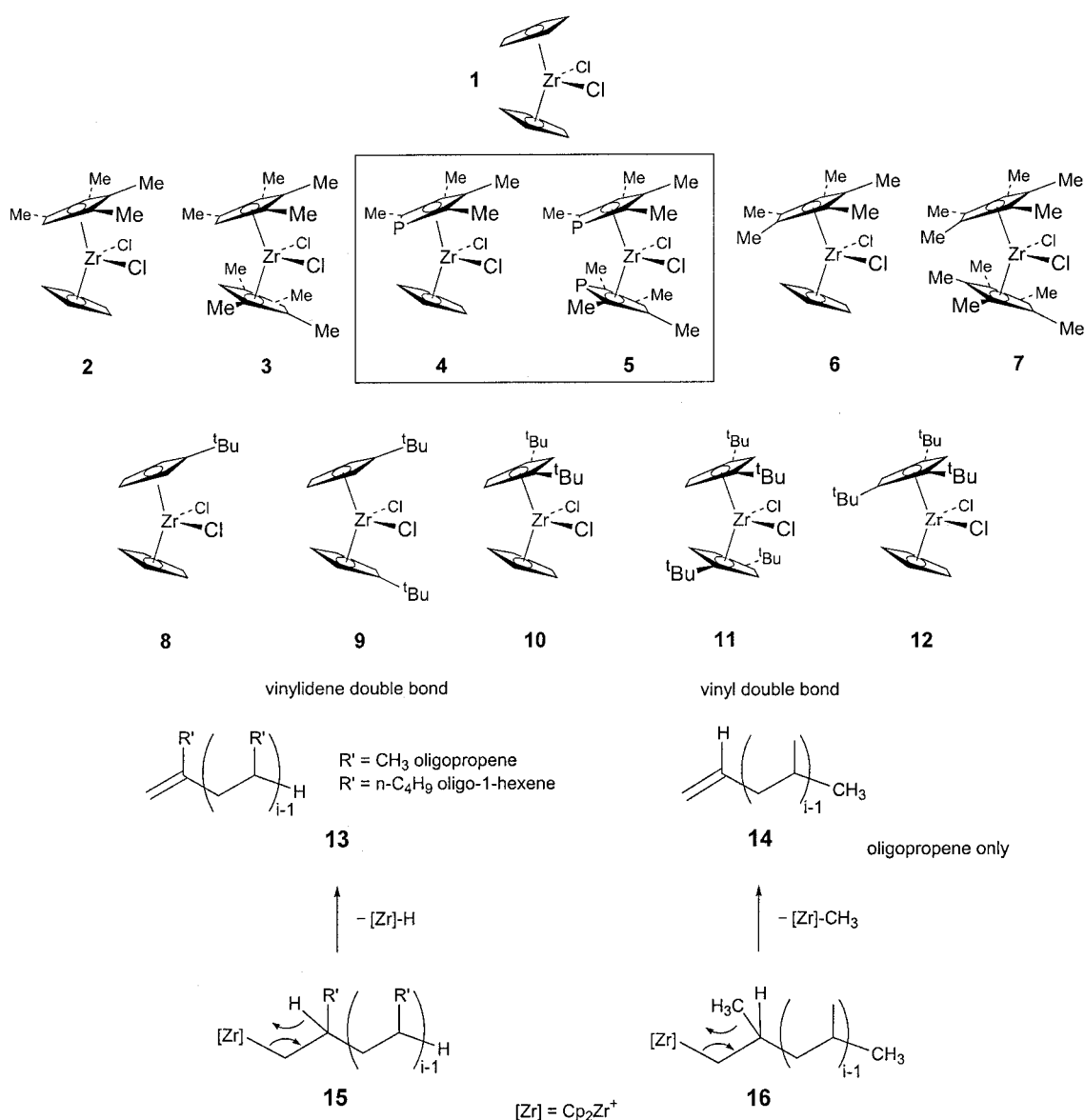
⁵ Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Str. 31, D-79104 Freiburg, Germany

Keywords: chain transfer; MALDI; metallocene catalysts; oligomers; polyolefins

Introduction

Single-site metallocene-methylalumoxane (MAO) catalysts are currently introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins.^[1–3] We investigated the oligomerization of propene and 1-hexene of 12 different systematically alkyl-substituted zirconocenes and phospholyl-zirconocenes (**1–12**) in combination with MAO.^[4]

The use of olefin oligomers as intermediates for specialty chemicals drives the interest in the catalytic oligomerization.^[5] Ethene oligomers are well established and nickel chelate complexes used in the SHELL-higher-olefin-process (SHOP) feature prominently in their manufacturing.^[5,6] A variety of metals and methods are available for the oligomerization of α -olefins,^[4] but feasible processes involving well-defined catalysts are rare.^[7]



In the beginning of metallocene catalysis the finding of low molar-mass products from propene polymerizations with zirconocene catalysts was generally regarded as unfortunate.^[8–11] Following in part the communication of our earlier results,^[12] it is now more and more recognized that metallocene catalysts can be used effectively for the directed oligomerization of α -olefins.^[7, 13–19] The chain-termination reaction gives oligomers with mostly double-bond end groups, predominantly of the vinylidene type (**13**). In special cases also a vinyl double-bond (**14**) can be formed (see below).

A variety of functionalization reactions with such double bonds are possible leading to organic specialties with possible applications as adhesives, blend compatibilizers,^[20] fragrances, lubricants, additives for fuels or in the paper and leather industry.^[7] Also, α -olefin oligomers or derivatives thereof can be used as (macro)monomeric building blocks for novel graft copolymers containing oligo-olefin side

chains.^[15] The functionality of a double bond at the end of each chain together with the product homogeneity are the advantages of oligomers from metallocene catalysis. In addition, olefin oligomerization is used to study mechanistic aspects of metallocene catalysis because of the homogeneity of the reaction mixture (no heterogenation through polymer precipitation) and because the oligomeric products are easier to investigate than high-molar-mass polymers.^[21–27] Here, we critically evaluate and use different methods for the oligomer characterization.

Oligomer Analyses

Size Exclusion Chromatography (SEC) (Gel Permeation Chromatography, GPC)

SEC/GPC is widely used for determining the molar mass and distribution of polymer samples. Recent work has

shown the use of SEC together with the universal calibration method to be problematic when molar masses are small (less than 5000) and particular in the oligomer range, because of the asphericity of individual oligomer configurations.^[28] Also, for methyl methacrylate oligomers a non-linear response to UV and DRI detection was demonstrated, i.e. the extinction coefficient and relative index of refraction was found to be chain length-dependent. This resulted in systematic errors in detection, such that without extensive calibration for chain length, the content of the low molar mass oligomers was determined too low. As the role of end groups becomes increasingly important with lower molar mass, this caveat may be general to other oligomeric systems.^[29] To avoid the potential pitfalls of SEC measurements we have employed a variety of methods for the molar mass determination. The oligomer dispersity $Q = \overline{M}_w/\overline{M}_n$ could, however, only be determined by SEC.

¹H NMR Spectroscopy

Assuming that each oligomer possesses a double-bond end group, the ratio of olefinic protons to total protons can be determined by integration of the ¹H NMR spectrum. From this an average chain length is derived which translates into the number average molar mass, \overline{M}_n .^[30] Furthermore, the relative content of different types of double bonds (if present) can be determined. Among the methods used here, NMR spectroscopy is the fastest and simplest procedure, requiring only a small amount of sample. The protons of the vinylidene double bond (**13**) appear as broad singlets at 4.67 and 4.75 ppm. The vinyl group (**14**) protons feature two overlapping doublets at 4.95–5.05 ppm and a multiplet (ddt) at 5.70–5.92 ppm (Figure 1).^[27, 31]

Viscosity

The kinematic viscosity together with the density of the oligomer solutions in toluene has been measured for some oligomer samples. From this the reduced viscosity η_{red} (in ml/g) has been calculated but failed to show a linear correlation to the molar mass obtained by other methods.

Cryoscopy

The molar mass obtained through the melting point depression corresponds to the number average molar mass, \overline{M}_n . With the help of molecular standards, a considerable deviation to lower mass values was seen starting above 500 g/mol. Hence, the experimental values of the oligomers had to be corrected according to this calibration. In addition, the high amount of sample required (300 to 500 mg) and the lower solubility of the higher molar mass oligomers proved disadvantageously.

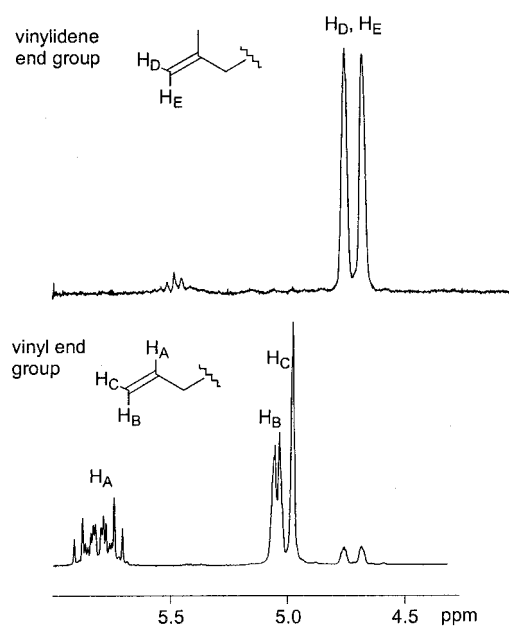


Figure 1. Proton NMR spectra of the olefinic end group of a vinylidene (top) and vinyl (bottom) terminated oligopropene (200 MHz, CDCl₃). The vinyl terminated oligopropene was obtained with catalyst **7**/MAO, cf. Table 1.

Raman Spectroscopy

For 1-decene oligomers the relative content of double bonds could be determined by the integrated intensities of the C=C vibrational bands around 1660 cm⁻¹ when referenced to the intensity of $\nu(\text{C}=\text{C})$ of trans-4-decene.^[32] Assuming that each oligomer chain contains a double bond, the relative intensity of the C=C vibration can be compared to an external standard and is then inversely proportional to the average chain length from which \overline{M}_n can be obtained. For the vinylidene-terminated propene and 1-hexene oligomers, 2-ethyl-1-butene, H₂C=C-(C₂H₅)CH₂CH₃, was used as a reference whose molar mass corresponds to a dimer or monomer unit, respectively. The C=C stretch lies at 1650 cm⁻¹ for the vinylidene (**13**) and at 1642 cm⁻¹ for the vinyl group (**14**). Alternatively, IR spectroscopy could be applied for the same purpose by using the peaks at 888 cm⁻¹ (vinylidene) and 910, 992 cm⁻¹ (vinyl).^[33] The error in the reproducibility of the peak integral was found to be 3% for the standard material and up to 10% for the oligomers, depending on the peak area.

MALDI-TOF MS

Matrix assisted laser desorption ionization – time of flight mass spectrometry (MALDI-TOF MS) is a relatively new method but quite successful for the characterization of large biopolymers and recently also synthetic polymers.^[34, 35] It offers the possibility to determine the accurate molecular mass and the molar mass distribution.

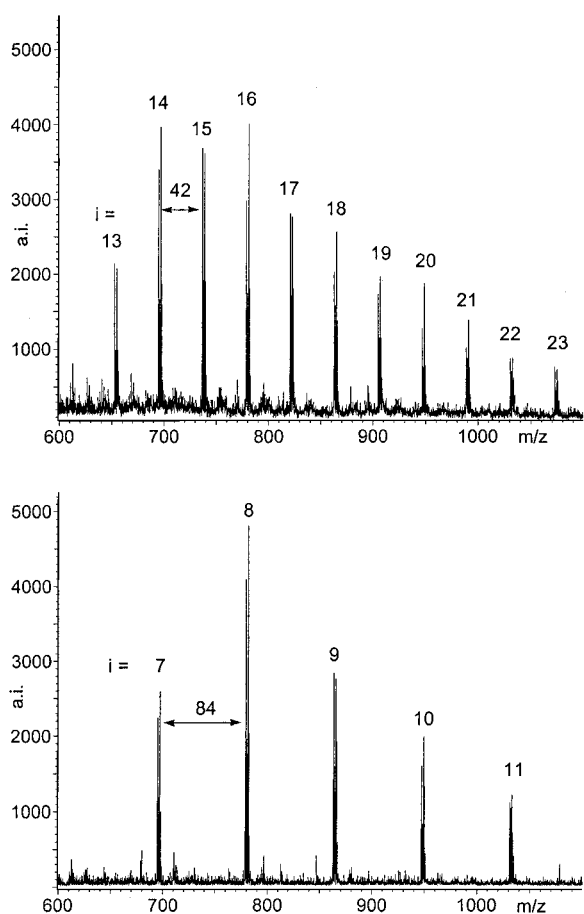


Figure 2. MALDI-TOF mass spectra for samples of oligopropene (top) and oligo-1-hexene (bottom). The oligopropene was obtained with catalyst **2**, the oligohexene with catalyst **8**. Peaks correspond to the silver adduct of M_i (i = degree of oligomerization, number of monomer units) (a.i. = arbitrary intensity).

The ionization technique allows for the investigation of very large and/or thermolabile molecules without fragmentation of the molecular ions. A prerequisite for the application of MALDI is the presence of functional groups in the polymer which are necessary for the adduct formation with silver (sodium or potassium) ions used for the ionization. Hence, polyolefins are in principle not susceptible to the MALDI technique. The reason that the oligomers promised a potential for analysis by MALDI-TOF MS was because of their double-bond end-group functionality. MALDI-TOF MS investigations of such unpolar samples are very rare.^[36]

Figure 2 shows a typical MALDI-TOF mass spectrum for an oligopropene and an oligohexene material. The peak separation corresponds to the monomer mass. From the mass/charge minus a whole-numbered multiple of the monomer mass, the residual mass is obtained which corresponds to the start group. Normally the intensity of mass peaks in mixtures is proportional to the molar amount of each species and therefore the mass spectra should yield \bar{M}_n and Q . Indeed the mass spectra in Figure

2 represent a mass distribution curve. However, it quickly became apparent that the method and the apparatus conditions impose severe limitations with respect to interpreting the olefin oligomer spectra in this direction. The vacuum which is applied before ionization already removes the very low molar mass content from the sample, which is rather critical here. At the same time, the high molar mass end of the sample is also not well reproduced because of the single double-bond functionality together with the detection of the molecular ion as a metal adduct. Thus, all propene and hexene oligomers which were investigated with MALDI-TOF MS gave a dispersion Q of about 1.1. This small value does not reflect the real molar mass distribution. Still, MALDI-TOF was able to provide valuable information concerning the start and end group of the oligomers and the mechanism of chain transfer.

Results and Discussion

Oligomerization activities and oligomer parameters for the catalyst systems **1–12**/MAO are summarized in Table 1 and 2 for propene and 1-hexene, respectively. The trends in the activities will be discussed elsewhere.^[4]

Molar Mass

Generally, it can be remarked that the catalyst behavior has changed drastically when applying α -olefins instead of ethene as a monomer: From a high-molar mass polyethene-producing system the zirconocenes, presented here, become low-molar mass oligomer-forming catalysts.

Figure 3 gives a display of the \bar{M}_n values from ^1H NMR and SEC of oligopropenes and oligohexenes obtained with catalysts **1–7**/MAO. From the molar mass data in Table 1 and 2 and in Figure 3 it can be seen that usually the agreement between molar mass values from different methods is reasonable. However, \bar{M}_n from ^1H NMR is much too high compared with the value from SEC for the propene and 1-hexene oligomers produced with the phospholyl zirconocenes **4** and **5** and for the oligohexene from octamethylzirconocene **3**. Estimation of \bar{M}_n by ^1H NMR is based on the relative ratio of the olefinic to the aliphatic protons. Thus, less than 100% double-bond end groups will give too large a value for \bar{M}_n . The saturated groups can arise from transfer of the oligomer chain to aluminium and hydrolyzation upon quenching of the mixture (Equation (1)). Chain transfer to aluminium creates a new $[\text{Zr}]-\text{CH}_3$ start species due to the exchange of the alkyl chain with a methyl group on aluminium in MAO or TMA (Scheme 1b and d). A chain-transfer to aluminium makes sense for **4** and **5** because adduct formation to phosphorus brings aluminium moieties close to the zirconium reaction center and the oligomer chain end.

Table 1. Results for propene oligomerization with **1–12**/MAO.

Pre-catalyst ^{a)}	Activity		¹ H NMR ^{b)}	\bar{M}_n		Raman ^{f)}	Dispersity $Q = \bar{M}_w/\bar{M}_n^{d,g)}$	End group ratio vinylidene/vinyl %	MALDI-TOF MS ^{j)}
	kg oligomer/(mol Zr · h)	(Conversion/%)		SEC ^{c,d)}	Cryosc. ^{e)}				
Methyl-substituted zirconocenes									
1	960 (51)		330	350/260		250	1.5/1.7	100/0	M_i
2	1300 (66)		620	530/410		440	2.5/2.8	100/0	M_i
3	1300 (63)		1600	1500/1600		n.a.	2.9/2.7	65/35	$M_i, M_i \pm 14$
4^{h)}	10 (4)		640	380/200		460	1.5/1.5	79/21	$M_i, M_i \pm 14$
5^{h)}	10 (4)		1200	300/260		740	2.0/1.7	61/39	$M_i, M_i \pm 14$
6	870 (46)		1300	1300/1500		n.a.	2.4/1.8	100/0	M_i
7	600 (28)		190	320/210		n.a.	1.3/1.4	9/91	$M_i, M_i \pm 14$
<i>tert</i> -Butyl-substituted zirconocenes									
1	410 ^{h)} (43)		350	470/n.a.	380		1.3/n.a.	100/0	M_i
8	400 (42)		290	400/n.a.	350		1.2/n.a.	100/0	M_i
9	400 (42)		410	510/n.a.	370		1.3/n.a.	100/0	M_i
10	670 (70)		680	960/n.a.	750		1.7/n.a.	100/0	M_i
11	1 (4)		580	560/n.a.	n.a.		1.9/n.a.	100/0	M_i
12	84 (9)		1100	1300/n.a.	1000		2.3/n.a.	100/0	M_i

^{a)} Al:Zr = 1000:1, $T = 50^\circ\text{C}$, reaction time = 1 h, pre-activation time = 10 min. Methyl-substituted zirconocenes: **1–3**, **6**, **7**: A pre-catalyst amount of 1.5×10^{-5} mol yielding a concentration of 7.1×10^{-5} mol/L together with a reaction time of 1 h was employed, so that the conversion did not exceed 70% of the monomer. Only in the case of the very low-active phospholyl systems **4** and **5** twice the amount of catalyst and a reaction time of 4 h was employed; cf. footnote h). *tert*-Butyl-substituted zirconocenes: **1**, **8–12**: A pre-catalyst amount of 3×10^{-5} mol yielding a concentration of 1.4×10^{-4} mol/L and a reaction time of 1 h were employed; the conversion did not exceed 70%.

^{b)} Molar mass based on the integral ratio of the vinylidene and vinyl protons relative to the alkyl protons.

^{c)} SEC = size exclusion chromatography (GPC), see *Experimental Part* for details.

^{d)} First value corresponds to worked-up oligomer/second value is from quenched reaction mixture without removal of toluene; n.a. = not available.

^{e)} Cryoscopic molar mass determination in benzene.

^{f)} Molar mass by Raman spectroscopy based on the relative intensity of the C=C stretch at about 1650 cm^{-1} for vinylidene.

^{g)} From SEC.

^{h)} Because of the low activity of this catalyst system, a zirconocene concentration of 1.4×10^{-4} mol/L and a reaction time of 4 h was used here.

ⁱ⁾ The change in polymerization activity for **1** is due to the change in catalyst concentration; see footnote a).

^{j)} Peaks seen in MALDI-TOF MS; peaks correspond to the silver adduct of M_i , $M_i =$ multiples of 42, $\Delta M_i = 42$, $i =$ degree of oligomerization, number of monomer units; more intense peaks given in bold.

An indication of formation of these P–Al adducts in an equilibrium reaction was provided by ³¹P NMR.^[37]

The MALDI-TOF MS investigation supports the assumption of a chain-transfer to aluminium because it features $M_i + 14$ peaks in addition to M_i peaks, in particular in the spectra for oligo-1-hexenes ($M_i =$ multiples of 42 for propene and 84 for 1-hexene). A sample spectrum is displayed in Figure 4. Chain-transfer to aluminium actually will give rise to saturated end groups which do not show as peaks in the MALDI-TOF MS due to lack of the double-bond functionality (Scheme 1b and d). The M_i and $M_i + 14$ peaks correspond to oligomers from [Zr]–H

and [Zr]–CH₃ start groups, respectively, which are still terminated by β -hydrogen elimination (Scheme 1a and c). The relative intensities of the M_i and $M_i + 14$ peaks are a direct measure of the chain-termination pathway. This assumes that the relative probabilities for β -H elimination and chain-transfer to aluminium are the same for a [Zr]–H and [Zr]–CH₃ start group. Thus, in 1-hexene oligomerization the bis-phospholyl zirconocene **5** exhibits about 80% chain transfer to aluminium. Catalysts **3** and **4** give over 60% saturated oligomers through chain transfer. For the less congested tetra- and pentamethylzirconocenes **2** and **6** chain transfer is less important (below 10

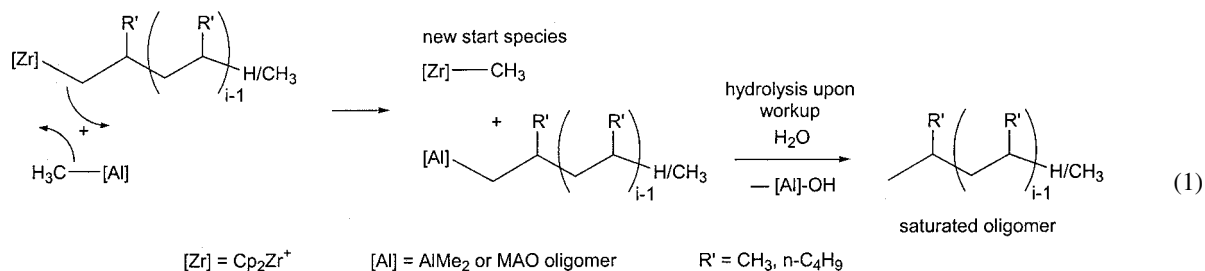


Table 2. Results for 1-hexene oligomerization with 1–12/MAO.

Pre-catalyst ^{a)}	Activity kg oligomer/(mol Zr · h) (Conversion/%)	¹ H NMR ^{b)}	\bar{M}_n SEC ^{c, d)}	Raman ^{e)}	Dispersity $Q = \bar{M}_w/\bar{M}_n^{d, f)}$	MALDI-TOF MS (ratio) ^{b)}
Methyl-substituted zirconocenes						
1	5000 (44)	410	300/n.a	310	1.8/n.a	M_i
2	6300 (55)	1200	1100/n.a		1.9/n.a	$M_i, M_i + 14 (\approx 8:1)$
3	5500 (49)	7000	1500/n.a	2100	2.3/n.a	$M_i, M_i + 14 (1:\approx 2)$
4	120 (1)	2700	500/n.a		1.2/n.a	$M_i, M_i + 14 (1:\approx 2)$
5	70 (1)	5600	500/n.a		1.3/n.a	$M_i, M_i + 14 (1:\approx 5)$
6	3300 (29)	3800	3300/n.a		2.6/n.a	$M_i, M_i + 14 (\approx 4:1)$
7	2900 (24)	1600	1400/n.a		2.0/n.a	$M_i, M_i + 14 (\approx 2:1)$
<i>tert</i> -Butyl-substituted zirconocenes						
1 ^{g)}	5900 (52)	510	530/650		1.7/1.5	M_i
8	7900 (70)	480	540/505		1.5/1.5	M_i
9	1700 (13)	330	390/390		1.4/1.4	M_i
10	2700 (24)	1200	970/770		2.0/2.4	M_i
11	260 (2)	200	240/220		1.1/1.2	M_i
12	310 (3)	240	270/280		1.2/1.5	M_i

a) A pre-catalyst amount of 3×10^{-6} mol yielding a concentration of 5.2×10^{-5} mol/L together with a reaction time of 1 h was employed, so that the conversion did not exceed 70% of the monomer. Al:Zr = 4000:1, $T = 50^\circ\text{C}$, reaction time = 1 h, no pre-activation time.

b) Molar mass based on the integral ratio of the vinylidene and vinyl protons relative to the alkyl protons.

c) SEC = size exclusion chromatography (GPC), see *Experimental Part* for details.

d) First value corresponds to worked-up oligomer/second value is from quenched reaction mixture without removal of toluene; n.a. = not available.

e) Molar mass by Raman spectroscopy based on the relative intensity of the C=C stretch at about 1650 cm^{-1} for vinylidene.

f) From SEC.

g) The slight change in polymerization activity for **1** is due to ageing of MAO in the course of time.

h) Peaks seen in MALDI-TOF MS; peaks correspond to the silver adduct of M_i , $M_i =$ multiples of 84, $\Delta M_i = 84$, $i =$ degree of oligomerization, number of monomer units; more intense peaks given in bold (approximate intensity ratio given in parentheses).

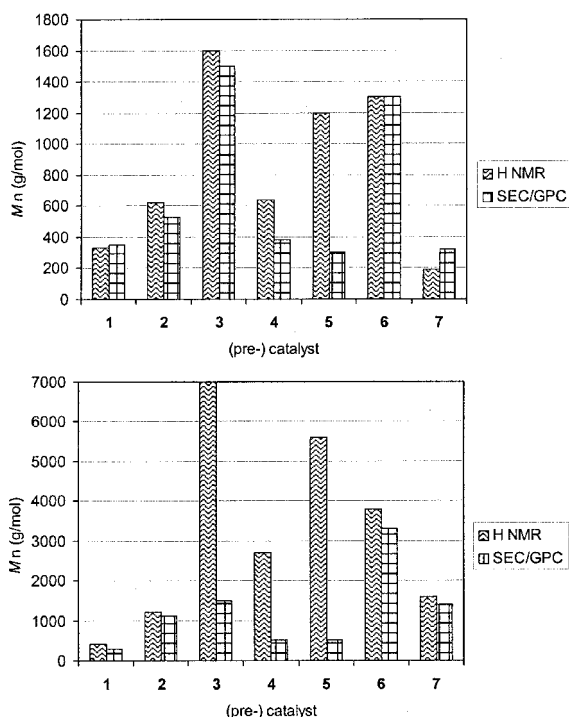
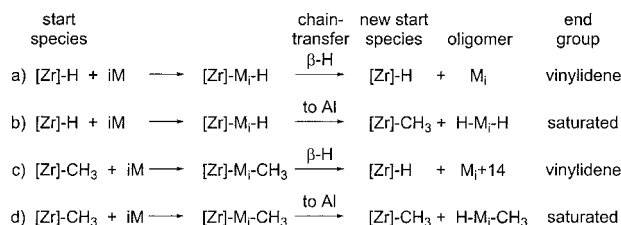
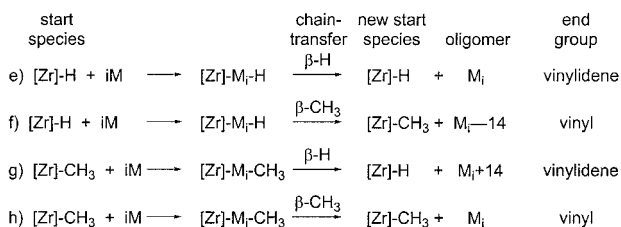


Figure 3. Number average molar mass values (\bar{M}_n) by ¹H NMR and SEC for oligopropenes (top) and oligohexenes (bottom) with catalysts 1–7/MAO. Entries from Table 1 and 2.

M_i and M_i+14 peaks only:



M_i and $M_i\pm 14$ peaks:



M = monomer; M_i = molar mass of oligomer M_i

Scheme 1. Correlation between start and end group for the different chain-termination reactions. Only oligomers with vinylidene or vinyl end groups can be seen in MALDI-TOF MS.

and 20%, respectively). The decamethylzirconocene **7** has over 35% and the parent zirconocene **1** shows no evidence for chain transfer. This type of chain-termination

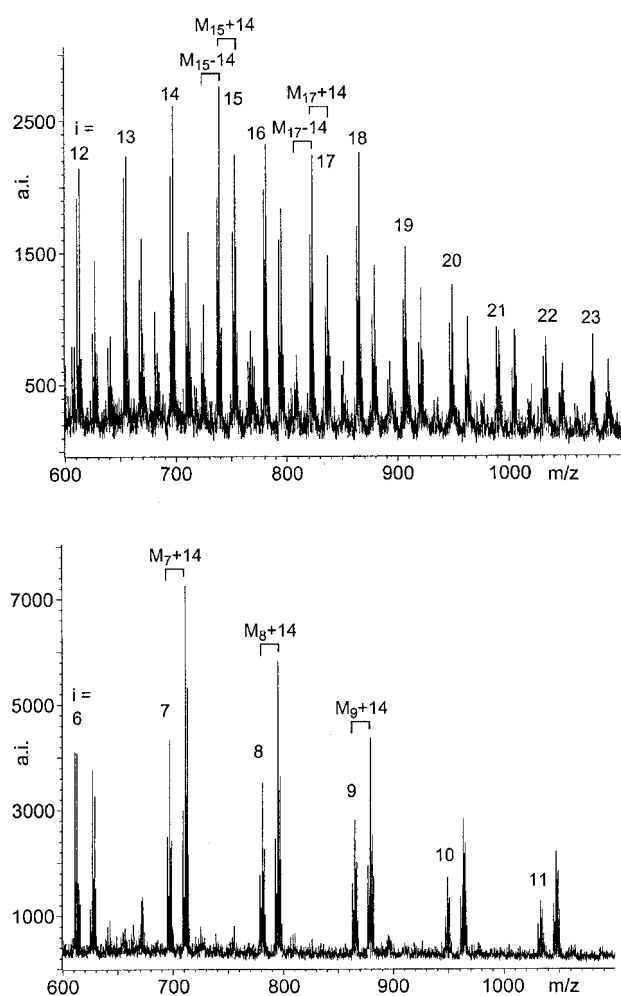


Figure 4. MALDI-TOF mass spectra for samples of an oligopropene with β -methyl elimination (top, note the M_i+14 and M_i-14 peaks) and an oligohexene with chain-transfer to aluminium (bottom, note the M_i+14 peak); see also Scheme 1. Both oligomers were obtained with catalyst **3**. Peaks correspond to the silver adduct of M_i (i = degree of oligomerization, number of monomer units) (a.i. = arbitrary intensity).

mechanism is especially dominant in the oligomerization of 1-hexene with the permethylated zirconocenes. We attribute this to steric causes which make it more difficult for the β -hydrogen to get oriented towards the metal center, so that chain-transfer can become a competing reaction pathway.

With the *tert*-butyl-substituted zirconocenes the steric crowding on the cyclopentadienyl rings is apparently not high enough to sufficiently hamper the β -hydrogen interaction with the metal. This is also evident from the lack of β -methyl elimination with catalysts **8–12** (see below).

End Groups

The majority of end groups contain a double bond. Only with the phospholyl zirconocenes **4** and **5** for both oligoolefins and with **3** for oligohexene were saturated end

groups observed to a significant extent (see above). The usual double bond is of the vinylidene type (**13**) and originates from a β -hydrogen elimination as the typical chain termination reaction (**15**). For *oligopropenes* and per-methylated zirconocenes also double bonds of the vinyl type (**14**) are observed. These are derived from a β -methyl elimination as chain-termination reaction (**16**).^[24] Vinyl double bonds are observed for the octamethylzirconocene (**3**), the mono-phospholyl and the bis-phospholyl zirconocene (**4** and **5**) and for decamethylzirconocene (**7**). The vinylidene/vinyl ratio (from ^1H NMR) was included in Table 1.

Evidence for the β -methyl elimination is also obtained in the MALDI-TOF mass spectra by an M_i-14 and M_i+14 peak around M_i (M_i = multiples of 42 for propene). The M_i-14 peak originates from an oligomer with a $[\text{Zr}]-\text{H}$ start group and chain termination by β - CH_3 elimination (Scheme 1f). Since the latter gives rise to $\text{Zr}-\text{CH}_3$ start groups an M_i+14 peak is also seen for those oligomers who are then terminated by β -H elimination (Scheme 1g). The oligomers which start with $[\text{Zr}]-\text{CH}_3$ and end with β - CH_3 elimination feature the M_i peak (just like those with a $[\text{Zr}]-\text{H}$ start group and β -H elimination) (Scheme 1e and h). A sample spectrum is included in Figure 4.

It is difficult to assess the importance of chain-transfer to aluminium with MALDI-TOF MS if β -methyl elimination is operating simultaneously. The ratio of the M_i-14 and M_i+14 peak might be used as a measure. However, both peaks possess a different double-bond (vinyl vs. vinylidene) which may not have the same ion-coordination and, thus, ionization probability.

In the case of oligohexenes, only vinylidene double bonds are found, based on ^1H NMR studies. For oligohexenes double bonds of the vinyl type would have required an *n*-butyl elimination and are not observed.

With the *tert*-butyl-substituted zirconocenes it was hoped for that β -methyl eliminations could also be initiated. This was not the case, however. The NMR and MS spectra of the oligomer products from **8–12** did not show any evidence for the formation of vinyl double bonds (cf. Table 1). Apparently, the steric bulk of up to four *tert*-butyl groups in a zirconocene is not high enough to sufficiently hamper the β -hydrogen elimination.

Dispersity, Molar Mass Distribution

The dispersity of many oligomers is rather narrow. Values of Q ($= \bar{M}_w/\bar{M}_n$) below 2 can be found in Table 1 and 2. Although dispersities smaller than 2 seem to contradict a Schulz-Flory (or most probable) distribution, such narrow dispersities cannot be dismissed as being due to a removal of low-boiling oligomers in the work-up process. This was tested by subjecting the quenched reaction mixture to a SEC analysis before and after the

removal of toluene (and possibly the low-boiling fraction). In most cases the effect of work-up on the molar mass distribution is rather small. A dispersity of $Q < 2$ can be explained by a chain-length dependent insertion rate.^[12]

It is evident that a combination of methods is necessary for the elucidation of chain-termination mechanism and of the oligomer parameters. The methods ¹H, SEC (GPC) and MALDI-TOF MS each give different necessary pieces of information. Here, ¹H NMR provides information on the end-group structure, hence the chain termination mechanism, and on the number-average molar mass if every chain end carries a double bond. SEC gives the different molar mass values and the polymer dispersity. MALDI-TOF MS proves chain-transfer to aluminium in combination with β -hydrogen elimination as chain-transfer pathways. In addition, MALDI-TOF offers independent evidence for chain termination by β -methyl elimination.

Experimental Part

General Procedures

All experiments which involved air- and moisture sensitive reagents were carried out under argon with standard Schlenk techniques. Solvents were dried over sodium metal (toluene and benzene), sodium benzophenone ketyl (pentane and diethyl ether) or potassium metal (hexane and THF) followed by distillation and storage under argon.

Materials

The known zirconocene dichlorides were prepared according to literature procedures, or slight modifications thereof: (C₅HMe₄)(C₅H₅)ZrCl₂ (**2**),^[38] (C₅HMe₄)₂ZrCl₂ (**3**),^[38, 39] (C₄Me₄P)(C₅H₅)ZrCl₂ (**4**),^[38] (C₄Me₄P)₂ZrCl₂ (**5**),^[38, 40] (C₅Me₅)(C₅H₅)ZrCl₂ (**6**),^[38, 41] (C₅Me₅)₂ZrCl₂ (**7**),^[38, 42] (C₅H₄^tBu)(C₅H₅)ZrCl₂ (**8**),^[43] (C₅H₄^tBu)₂ZrCl₂ (**9**),^[44] (C₅H₃-1,3-^tBu₂)(C₅H₅)ZrCl₂ (**10**),^[37] (C₅H₂-1,2,4-^tBu₃)(C₅H₅)ZrCl₂ (**11**),^[45] (C₅H₃-1,3-^tBu₂)₂ZrCl₂ (**12**).^[46] All complexes were purified by sublimation and the purity was checked by elemental analysis, NMR, and mass spectrometry.^[37, 38] The analytical data matched the literature values. (C₅H₅)₂ZrCl₂ was purchased from Merck and used as such. Methylalumoxane (MAO) was obtained from Witco (Bergkamen, Germany) as a 10 wt.-%-toluene solution (4.92 wt.-% aluminium, density \approx 0.9 g/ml, average molecular weight of the MAO oligomers 900–1100 g/mol). Propene (BASF AG) was polymerization grade and 1-hexene (97%) was obtained from Aldrich, both monomers were used without further purification.

Oligomerizations

Propene oligomerizations were carried out in a 1-L Büchi-glass autoclave, thermostated to 50 °C and charged with 200 ml of toluene, 8.1 liter gaseous propene, and the catalyst solution consisting of 19 ml of methylalumoxane and 1.5 or 3×10^{-5} mol of the zirconocene dichloride (see footnotes in

Table 1 and 2 for details; molar ratio Al:Zr = 1000:1, activation time 10 min). After a reaction time of 1 h the propene was vented off. 1-Hexene oligomerizations were carried out in a 100 ml Schlenk-flask, thermostated to 50 °C and charged with 50 ml of 1-hexene and the catalyst solution consisting of 8 ml of methylalumoxane and 3×10^{-6} mol of the zirconocene dichloride (molar ratio Al:Zr = 4000:1, no activation time) for a reaction time of 1 h, unless mentioned otherwise. 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 vacuum (\approx 1 Torr) at 40 °C to leave the oligomer. To ensure reproducibility, oligomerizations were carried out at least twice with each zirconium complex, thereby also including the full range of oligomer analyses. A series of polymerization runs was performed by using the same toluene and MAO batch. To avoid ageing effects of MAO,^[47] a series of comparative polymerizations was run within a week.

For the comparative oligomerization runs we tried not to have the conversion exceed 50% so as to avoid drastic insertion rate changes when the monomer concentration becomes too low.

Oligomer Analyses

¹H and ¹³C NMR were obtained on a Bruker ARX 200 or ARX 400 in CDCl₃ (¹H and ¹³C chemical shifts are referenced to TMS via the solvent signal).

Size exclusion/gel permeation chromatography (SEC/GPC) was carried out either on a Waters 150-C equipped with μ -styrigel columns (5×10^2 – 10^6 Å), eluent toluene, $T = 60$ °C, flow rate 2 ml min⁻¹, sample volume 100 μ l, concentration 0.5–1%, polyethene standards with a universal calibration according to Benoit^[48] (Mark-Houwink coefficients: polyethene: $k_{\eta} = 1.27 \times 10^{-2}$ ml/g, $A = 1.04$ [polyalkene, C₁₀–C₁₈]; polypropene: $k_{\eta} = 2.7 \times 10^{-2}$ ml/g, $A = 0.71$ [polypropene, atactic, solvent benzene, $T = 25$ °C])^[49] or on a Waters 410 equipped with 5 MIXED B-polystyrene gel columns (7.5 \times 300 mm, PL-gel 10 μ), eluent THF, $T = 35$ °C, flow rate 1.2 ml \cdot 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 \cdot mol⁻¹.

Cryoscopic molar mass determinations were carried out in benzene.

Kinematic viscosities (ν in mm²/s) were measured with an Ubbelohde capillary viscosimeter (capillary type 0c) on toluene solutions of the samples. Together with the density (ρ) and the known concentration (c) of these sample solutions (density meter DMA 48 from chempro/PAAR), the reduced viscosity (η_{red} in ml/g) could be calculated according to $[(\nu\rho/\eta_1)-1]/c$ (η_1 dynamic viscosity of the solvent).

Raman spectra were collected on a Bruker RFS 100 (slit width 2.4 mm, laser power 260 mW, 500 scans per sample, measuring time 1 h), spectrum evaluation with the program OPUS21.

MALDI-TOF-MS: Spectra were recorded with a Bruker REFLEX II time-of-flight mass spectrometer using a nitrogen laser for MALDI ($\lambda = 337$ nm). The measurements were performed in reflector mode with ion source and reflector lens potentials at 20 and 21.5 kV. The matrix was dithranol

(20 mg/mL), the cationizing agent silver trifluoroacetate (10 mg/mL). The polymer concentration was 10 mg/mL and the ratio polymer:matrix:cation = 1:2:1.

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