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Synthesis and Properties of Poly-1-olefins

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SUMMARY: The oligomerization and polymerization of 1-pentene using Cp_2ZrCl_2, Cp_2HfCl_2, $[(CH_3)_5C_5]_2ZrCl_2$, *rac*-$[C_2H_4(Ind)_2]ZrCl_2$, $[(CH_3)_2Si(Ind)_2]ZrCl_2$, $(CH_3)_2Si$(2-methylbenz[e]indenyl)$_2ZrCl_2$, $Cp_2ZrCl\{O(Me)CW(CO)_5\}$, $Cp_2ZrCl(OMe)$ and methylaluminoxane (MAO) has been studied. The degree of polymerization was highly dependent on the metallocene catalyst. Oligomers ranging from the dimer of 1-pentene to polymers of poly-1-pentene with a molar mass M_w = 149000 g/mol were formed. $Cp_2ZrCl\{O(Me)CW(CO)_5\}$ is a new highly active catalyst for the oligomerization of 1-pentene to low molecular weight products. The activity decreases in the order $Cp_2ZrCl\{O(Me)CW(CO)_5\} > Cp_2ZrCl_2 > Cp_2ZrCl(OMe)$. Furthermore, poly-1-olefins ranging from poly-1-pentene to poly-1-octadecene were synthesized with $(CH_3)_2Si$(2-methylbenz[e]indenyl)$_2ZrCl_2$ and methylaluminoxane (MAO) at different temperatures. The temperature dependence of the molar mass can be described by a common exponential decay function irrespective of the investigated monomer.

Introduction

The South African resource situation differs significantly from that in the rest of the world, since SASOL's fuel production is based on coal. In the course of the coal conversion via the Fischer-Tropsch process, 1-olefins are generated as primary products. While even-numbered 1-olefins are readily available on the world market due to the fact that these compounds are synthesised from ethylene e.g. via the Shell Higher Olefin Process (SHOP), the bulk production of odd-numbered 1-olefins, e.g. 1-pentene, is unique to South Africa (SASOL). Utilizing the SASOL streams, Polifin Ltd. recently commenced the production of propene/1-pentene copolymers. An alternative approach to utilize the linear 1-olefins can be envisaged in the homooligomerization or homopolymerization of the respective monomers. Polymers of 1-hexene, 1-octene and 1-decene have found applications as adhesives$^{1)}$. Furthermore, high

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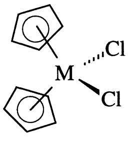
molecular weight poly-1-olefins are added to nonpolar organic liquids in order to enhance the fluidity e.g. high molecular weight isotactic poly-1-octene dissolved in diesel oil (10 ppm) increases oil fluidity by 40 to 60 %[1]. Hungenberg et al. suggested various applications for functionalized oligomers of 1-olefins with a reactive vinylidene group, such as adhesives, fuel additives, copolymers, lubricants and fragrances[2].

Metallocenes are well known to polymerize ethylene and propylene when activated with MAO, whereas isospecific metallocenes based on zirconium convert the less reactive higher 1-olefins normally only to oligomeric products or to polymers with low molar masses at room temperature[3-6].

In this paper the oligomerization and polymerization of 1-pentene with the various metallocenes **1-8** and the synthesis of high molar mass poly-1-olefins with $(CH_3)_2Si(2\text{-methylbenz[e]indenyl})_2ZrCl_2$ (**6**) are reported.



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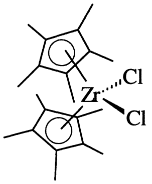
M = Hf **2**



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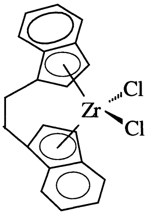

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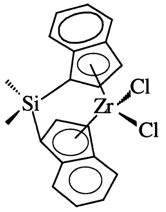

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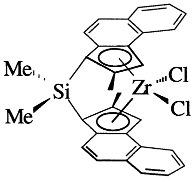

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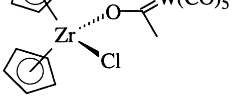

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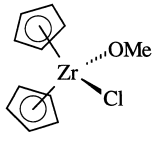

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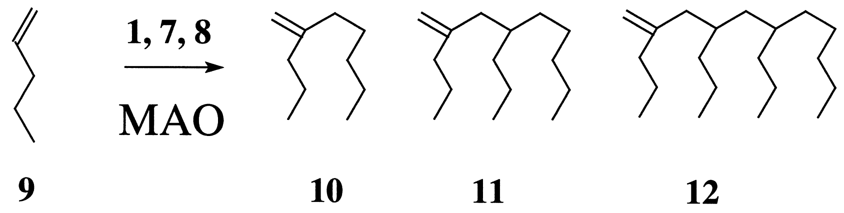
Oligomerization and polymerization of 1-pentene with metallocenes

1-Pentene was oligomerized and polymerized with different bridged and non-bridged metallocenes and methylaluminoxane (MAO)[3)]. The use of Cp_2HfCl_2 (**2**) and $[(CH_3)_5C_5]_2ZrCl_2$ (**3**) (metallocene/MAO ratio 1 : 1000) led to the formation of atactic poly-1-pentene. The bridged catalysts *rac*-$[C_2H_4(Ind)_2]ZrCl_2$ (**4**), $[(CH_3)_2Si(Ind)_2]ZrCl_2$ (**5**) and $(CH_3)_2Si(2\text{-methylbenz[e]indenyl})_2ZrCl_2$ (**6**) afforded the formation of isotactic poly-1-pentene. The degree of polymerization P_n was highly dependent on the metallocene catalyst. Oligomers ranging from the dimer of 1-pentene to polymers of poly-1-pentene with a molar mass M_w = 149000 g/mol were formed (Tab. 1).

Table 1. Molar mass M_w [g/mol], polydispersity M_w/M_n, degree of polymerisation P_n and intensity of the mmmm-pentad of poly-1-pentene synthesized with **1**-**6**.

catalyst	M_w	M_w/M_n	P_n	[mmmm]
1, 7, 8			2-4	
2	8700	1.85	67	
3	8200	2.22	53	
4	20800	4.08	73	0.91
5	17600	3.52	71	0.45
6	149000	2.08	1029	0.64

The stereoregularity of the isotactic poly-1-pentene obtained with the ethylene-bridged metallocene **4** ([mmmm] = 0.91) was significantly higher than that of the poly-1-pentene synthesized with the silyl-bridged metallocenes **5** and **6** ([mmmm] = 0.45 and 0.64, respectively). The appearance of the oligomers produced with **4** and **5** differed strikingly at the macroscopic level, despite similar molar masses. The less isotactic oligomer formed with **5** appeared to be stickier than the more wax-like product synthesised with **4**, whereas the atactic poly-1-pentene prepared with **2** and **3** appeared as a sticky oil.



The utilization of Cp_2ZrCl_2 (**1**), $Cp_2ZrCl\{O(Me)CW(CO)_5\}$ (**7**) and $Cp_2ZrCl(OMe)$ (**8**) yielded products with a low degree of polymerization P_n = 2-4. The dimer **10**, trimer **11** and tetramer **12** of 1-pentene (**9**) can be separated via distillation[3)]. The conversion of 1-pentene with **1** was strongly temperature dependent and the highest catalyst activity was observed at medium oligomerization temperatures (50 – 100°C). The decrease in activity at higher temperatures is most likely due to the degradation of the catalyst. In general, higher yields were achieved with increasing MAO ratio (Fig. 1).

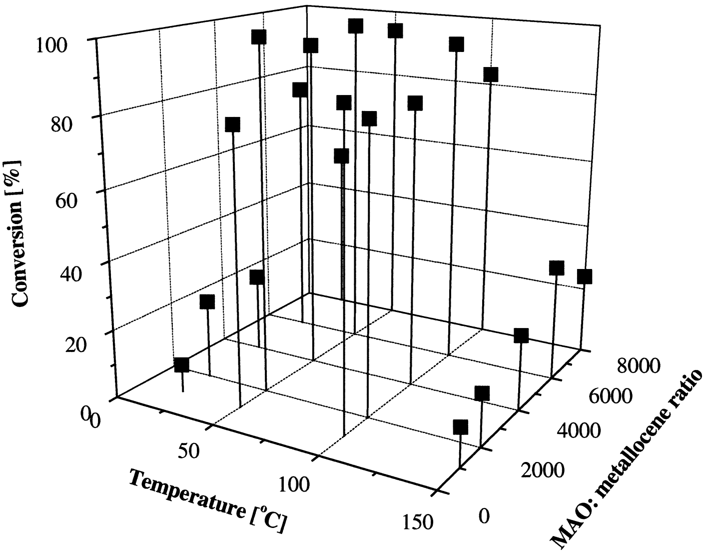


Fig. 1: Conversion of 1-pentene (**9**) to **10**-**12** with Cp_2ZrCl_2 (**1**) as function of the MAO/metallocene ratio and the oligomerization temperature.

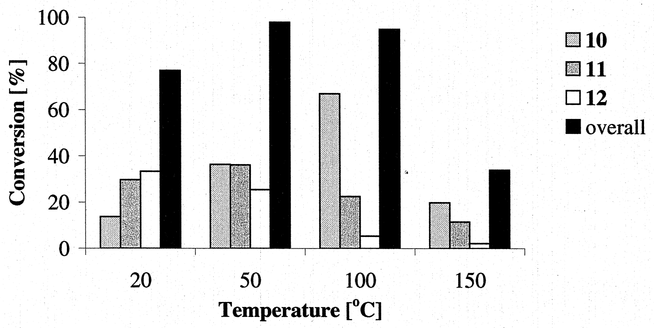


Fig. 2: Temperature dependence of the conversion of 1-pentene (**9**) to **10-12** with Cp_2ZrCl_2 (**1**) at a MAO/metallocene ratio (6000 : 1).

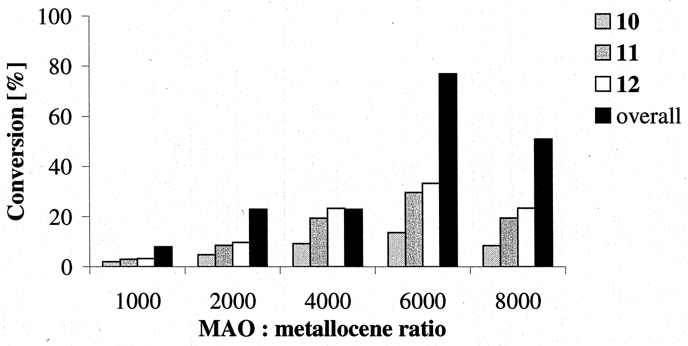


Fig. 3: Conversion of 1-pentene (**9**) to **10-12** with Cp_2ZrCl_2 (**1**) as function of the MAO/metallocene ratio at a constant temperature (20°C).

The product distribution was strongly dependent on the temperature as well as on the MAO ratio. An increase in the oligomerisation temperature favoured the formation of the dimer **10** due to readily occurring ß-elimination (Fig. 2). The higher oligomerisation products **11** and **12** were predominately formed at lower temperatures and higher MAO ratios (Fig. 3).

Oligomerization of 1-pentene with a bimetallic complex

The new bimetallic complex **7** was synthesized in our group and utilizied to oligomerize 1-pentene. Activation with MAO furnished the dimer (**10**), trimer (**11**) and tetramer (**12**) of 1-pentene. The rate of conversion with **7** was significantly higher than with zirconocenedichloride (**1**) under comparable conditions. Compound **8**, however, was almost inactive in the oligomerization of 1-pentene. The activity decreases in the order $Cp_2ZrCl\{O(Me)CW(CO)_5\}$ (**7**) > Cp_2ZrCl_2 (**1**) > $Cp_2ZrCl(OMe)$ (**8**) (Fig. 4).

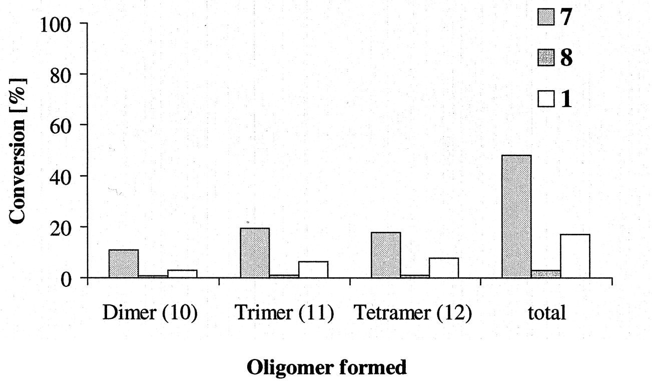
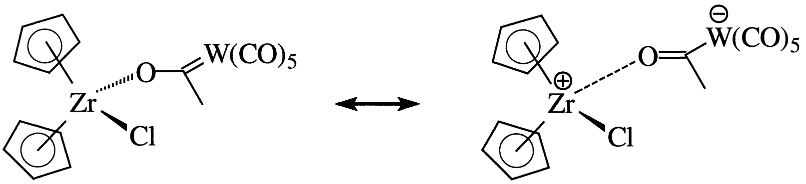


Fig. 4: Conversion of 1-pentene (**9**) to **10-12** with $Cp_2ZrCl\{O(Me)CW(CO)_5\}$ (**7**), $Cp_2ZrCl(OMe)$ (**8**) and Cp_2ZrCl_2 (**1**) under comparable conditions (20°C, 24 h, 1-olefin/MAO/catalyst ratio 30000 : 1000 : 1).

Assuming a strong Zr-O bond in **8,** a free coordination site, which is required for the chain propagation, is unlikely to be generated. In order to understand the high activity of the bimetallic complex we like to propose the presence of a partially ionic species. At the moment further experiments are being carried out in our group to understand the high activity of **7**.



Polymerization of higher linear 1-olefins with $(CH_3)_2Si$(2-methylbenz[e]indenyl)$_2ZrCl_2$ (6)

Poly-1-olefins ranging from poly-1-pentene to poly-1-octadecene with narrow polydispersities were obtained with $(CH_3)_2Si$(2-methylbenz[e]indenyl)$_2ZrCl_2$ (**6**) and methylaluminoxane (MAO) at temperatures between −15 and 180°C at a ratio 1-olefin/ MAO/ metallocene 30000 : 2000 : 1. The molar masses of the homopolymers obtained with $(CH_3)_2Si$(2-methylbenz[e]indenyl)$_2ZrCl_2$ at 20°C were notably higher than those of poly-1-olefins synthesized with other zirconium-based metallocenes under similar conditions (Table 2)$^{3-6)}$.

Table 2. Molar mass M_w [g/mol], polydispersity M_w/M_n, degree of polymerization P_n, melting points T_{m1} and T_{m2} of poly-1-olefins synthesized with **6** at 20°C.

	M_w	M_w/M_n	P_n	T_{m1}	T_{m2}
Poly-1-pentene	149000	2.08	1029	53	95
Poly-1-hexene	153000	2.04	893	Amorphous	
Poly-1-octene	155000	2.15	643	Amorphous	
Poly-1-decene	182000	2.56	507	10	26
Poly-1-tetradecene	173000	2.40	367	13	54
Poly-1-octadecene	126000	2.86	174	17	38

Plotting the molar mass versus the polymerization temperature (Fig. 5), shows that the molar mass of the polyolefin decreases exponentially with increasing temperature. Despite the fact that the number of repeating units in the poly-1-olefins is strongly dependent on the nature of the monomer and the polymerization temperature, it is a striking observation that the molar mass obtained at a specific temperature is independent of the chain length of the monomer.

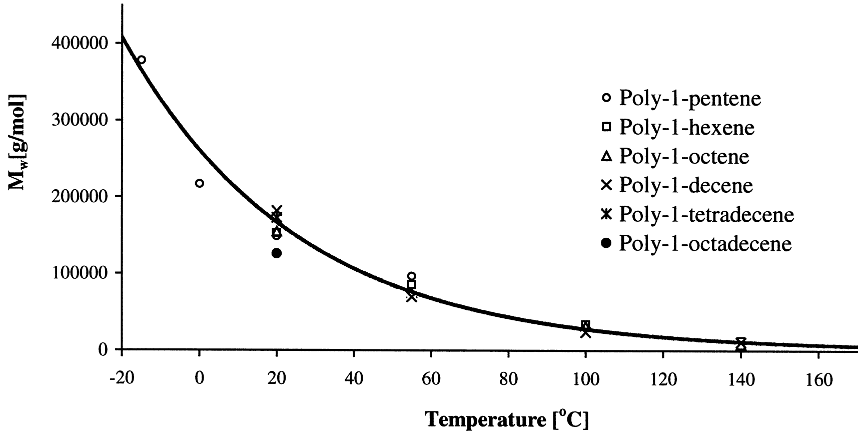


Fig. 5: Molar mass of poly-1-olefins synthesized with **6** as function of the polymerization temperature.

It is known that the thermal properties of polymers derived from 1-olefins depend largely on the length of the alkyl substituent$^{7)}$. Starting from polypropylene, melting points of isotactic poly-1-olefins decrease rapidly with increasing side-chain length. A minimum is reached at poly-1-heptene and subsequently the melting points increase with the length of the side-chain$^{7)}$. Henschke et al. attributed the two melting points of poly-1-pentene synthesized with $Me_2Si[Ind]_2ZrCl_2$ to different crystal modifications$^{4)}$. Poly-1-hexene and poly-1-octene prepared with **6** are amorphous materials without a distinct melting point. Poly-1-olefins with long alkyl chains possess typically two melting points that are generally attributed to the melting of crystals formed by the long side-chains and the helical main-chain$^{4, 7, 8)}$. The melting points for the poly-1-olefins prepared with **6** are listed in Tab. 2.

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