Microstructure of polypropene samples produced with different homogeneous bridged indenyl zirconium catalysts. Clues on the structure and reactivity relation

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Abstract

Propene bulk polymerization with rac-ethylenebis(1-indenyl) zirconium dichloride, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, dimethylsilylbis(1-indenyl)zirconium dichloride, dimethylsilylbis (4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride/methylaluminoxane (MAO) were carried out at polymerization temperatures from 0 to 60°C. The regio-irregularities, racemic placements and their succession, which are known to cause depression of the melting point of isotactic polypropene produced with homogeneous catalysts, were studied and compared. Only stereospecific 2,1-insertions were detectable and found to increase with temperature. 1,3-insertion shows up only for catalyst with tetrahydroindenyl ligands and replaces the 2,1-insertions at elevated polymerization temperatures. A racemic propene placement occurring after a 2,1-insertion sequence is found to a minor extent compared to regular meso enchainment.

Keywords: Ethene–propene copolymer; Indenyl derivatives; Isotactic polypropene; Microstructure; Regio-irregular insertion; Ziegler–Natta catalysis; Zirconium

1. Introduction

The degree of stereocontrol and the physical properties of polymers produced with stereorigid bridged homogeneous catalysts have been a point of much consideration. Compared with heterogeneous catalysts their polymers lack of lower melting points even so the homogeneous catalysts show a higher degree of stereospecifity in terms of isotacticity rates. The insertion of regio-irregular units has been claimed to be one of the reasons of this drawback [1,2]. In this paper five different indenyl catalysts were compared with respect to the microstructure of the resulting polymers over a broad range of polymerization temperatures. Emphasis has been put on the polymerization temperature dependence of the occurring misinsertions. Such considerations can give valuable hints for the interpretation of the structure/reactivity relation.

2. Experimental

The catalysts were prepared according to the literature [3,4]. Propene (quality 99.8%) was further purified while condensing it into the reactor by passing it through 10 Å molecular sieves

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and BASF copper catalyst R3-11 columns at 80°C. The propene bulk polymerization was carried out in a dry steel reactor equipped with a mechanical stirrer. The catalyst (10^{-6} to 10^{-8} mol depending on polymerization temperature) and methylaluminoxane (MAO) 300 mg, both in toluene solution, were prereacted with each other at room temperature for 12 min in a lock and injected into the liquid propene with argon pressure. The polymerization was stopped after 100 min by

degassing. One polymerization series was complete after three repeated polymerization runs each at 0, 15, 30, 45 and 60°C. The resulting polymer was stirred with a 5% hydrochloric acid/water/20% ethanol solution, washed with water/20% ethanol, neutralized and finally vacuum dried at 60°C.

All ^{13}C NMR spectra were obtained by using a Bruker MSL 300 operating at 75.47 MHz, pulse width 60°, relaxation delay 6 s, > 1000 scans and
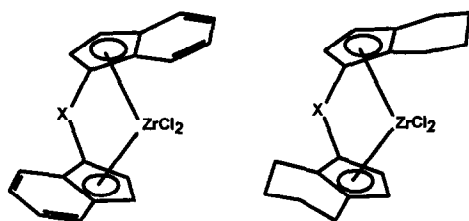
X = CH₂CH₂	**1**	[et(1-indenyl)₂]ZrCl₂	**2**	[et(H₄-1-indenyl)₂]ZrCl₂
X = Si(CH₃)₂	**3**	[(CH₃)₂Si(1-indenyl)₂]ZrCl₂	**4**	[(CH₃)₂Si(H₄-1-indenyl)₂]ZrCl₂

Fig. 1. Catalyst used for polymerization, the catalysts being referred to in the text with the given numbers.

Table 1
Polymerization results: activity, viscosity-average molecular weight M_v, melting temperature T_m, mmmm pentads and regio-irregularities in ‰; in propene bulk polymerization for runs of 100 min, catalyst concentration of 10^{-6} to 10^{-8} mol, depending on polymerization temperature, and methylaluminoxane (MAO) 300 mg

Catalyst	T_p	Activity	M_v	DSC 2.heat	NMR mmmm	1,3 i	2,1-i	2,1 r-i
	(°C)	(kg/mol h)	(g/mol)	(°C)	(%)	(‰)	(‰)	(‰)
1	0	2500	109100	152	95	0	2	1
[et(indenyl)₂]ZrCl₂	30	90000	53000	142	93	0	3	1
	60	150000	34000	134	90	0	13	2
	−20	100	280400	159	98	0	5	0
2	0	600	167700	152	96	0	7	0
[et(H₄-indenyl)₂]	30	15000	38000	149	96	9	3	0
ZrCl₂	45	55000	34800	142	90	12	3	0
	60	70000	25200	136	85	19	0	0
2a	0	150	91000	144	95	0	10	0
[et(H₄-indenyl)₂]Zr	30	4000	46000	140	94	9	2	0
(acetylmandelat)₂	60	16000	15500	127	89	40	0	0
3	0	300	140000	156	96	0	3	0
[(CH₃)₂Si(indenyl)₂]	30	10000	78000	149	93	0	4	2
ZrCl₂	60	51000	47000	140	91	0	5	2
4	0	200	147000	159	94	0	6	0
[(CH₃)₂Si(H₄-indenyl)₂]	30	4000	45000	154	96	2	3	0
ZrCl₂	60	65000	21000	142	91	5	0	0

BB decoupling. The samples were dissolved in 1,1,2,2-tetrachlorethane-D_2 DSC melting isotherms were recorded with a Perkin Elmer DSC IV with heating rates of 20°C/min. All reported melting points are DSC minima of the second complete cycle. Viscosity measurements (M_v = viscosity-average molecular weight) were performed in decalin (decahydronaphthalene) at 135°C using an Ubbelohde viscosimeter Schott type 0a and Mark–Houwink constants derived by Scholte et al. [5]. Gel-permeation chromatography (GPC) was performed on a Waters 150-C ALC/GPC with 1,2,4-trichlorobenzene as a solvent at 135°C.

3. Results

3.1. Polymerization

The following catalysts were used in propene bulk polymerization (Fig. 1).

The polymerization results are summarized in Table 1. By GPC polydispersities M_w/M_n of 1.8 to 2.5 were found. In bulk polymerization molecular weights and melting points exceed those of solvents polymerization especially at higher T_p [6]. For example a polymerization using catalyst **2**, at a T_p of 66°C and 1.6 mol/l propene results in a PP sample with a isotacticity index ($II = (S_{mm} + 0.5S_{mr})/(S_{mm} + S_{mr} + S_{rr})$) of 81%, a melting point of 97°C and a M_v of 11000 g mol^{-1} [7].

3.2. Microstructure

It is well known that besides heterotactic misinsertions at least one other type of regio-aspecific insertion occurs. In Table 2 are listed all observed and calculated shifts. The calculations were done using the additive rules for ^{13}C NMR shift calculation and the 01 nomenclature according to Cheng and Bennett [8]. Each sequence was con-

Table 2
Observed and calculated ^{13}C NMR shifts for propene regio-irregularities, + = peak is overlapping with one of the main peaks, P = primary, S = secondary, T = tertiary carbon, − = racemic placement

2,1-i	meso 2,1-insertion followed by a regular meso 1,2-insertion								
	01·*10*·01								
sequence	1 (S)	2 (T)	3 (P)	4 (T)	5 (P)	6 (S)	7 (S)	8 (T)	9 (P)
calculated (ppm)	41.87	35.89	17.83	38.38	17.14	30.22	35.54	31.36	21.04
observed (ppm)	41.9	35.6	17.7	38.3	17.0	30.1	35.4	31.1	+
r2,1-i	racemic 2,1-insertion								
	01·$\overline{10}$·01								
sequence	1 (S)	2 (T)	3 (P)	4 (T)	5 (−P)	6 (S)	7 (S)	8 (T)	9 (P)
calculated (ppm)	43.57	35.20	16.05	37.6	14.76	32.19	34.95	31.27	20.94
observed (ppm)	not detected								
2,1-r-i	meso 2,1-insertion followed by a racemic 1,2-insertion								
	0$\overline{1}$·*10*·01								
sequence	1 (S)	2 (T)	3 (−P)	4 (T)	5 (P)	6 (S)	7 (S)	8 (T)	9 (P)
calculated (ppm)	43.02	34.92	15.12	38.08	15.34	32.13	35.09	31.32	20.96
observed (ppm)	43.1	34.8	15.1	38.1	15.2	32.4	35.1	31.1	+
1,3-i	1,3-insertion								
	01·*000*·01								
sequence	1 (S)	2 (T)	3 (P)	4 (S)	5 (S)	6 (S)	7 (S)	8 (T)	9 (P)
calculated (ppm)	45.95	30.96	20.83	37.31	27.61	27.61	37.31	30.96	20.83
observed (ppm)	45.9	31.0	20.8	37.3	27.5	27.5	37.3	31.0	20.8
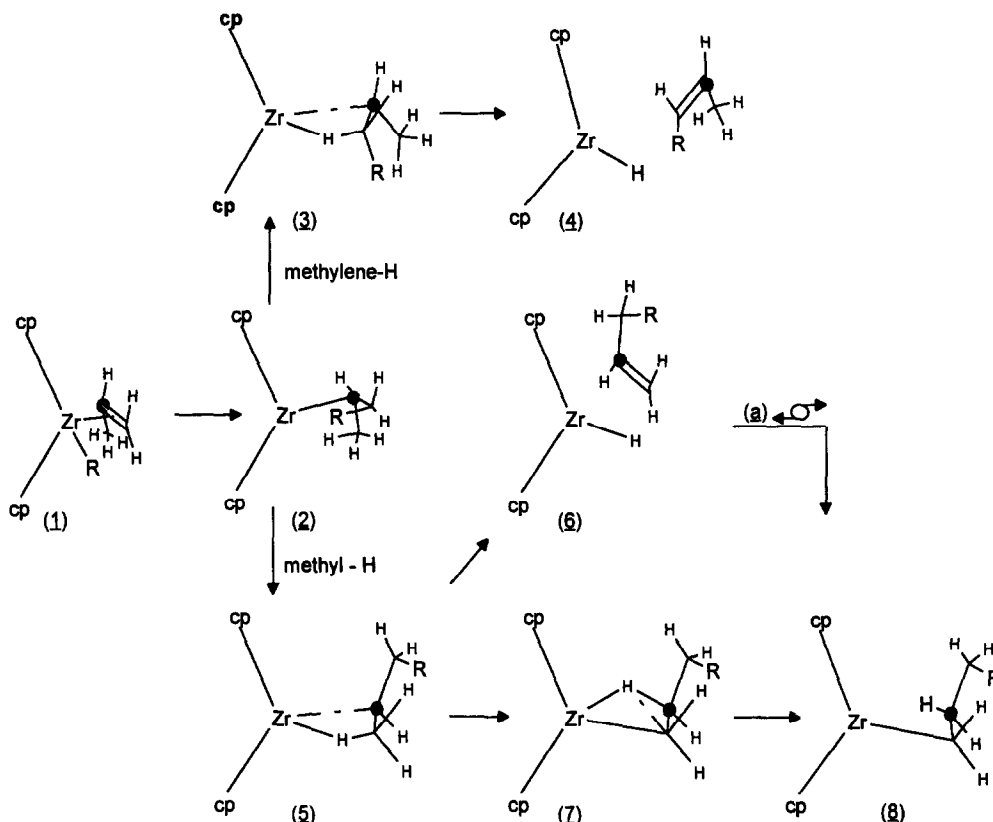
Scheme 1. Mechanistic scheme rationalizing a potential pathway to 1,3-inserted propene units (8) initiated by a 2.1-insertion process (1 → 2). 1,3-Inserted propene can originate from a methyl–H Zr interaction (5) via a hydride shift (7) or alternatively (a) needs rotation and recoordination followed by 1,2-insertion of the terminal olefin of structure (6) into the Zr–H bond. In contrast the pathway via methylene–H participation is leading to an internal olefin causing chain termination. C(2) atom = ●.

sidered to be part of a regular 01-sequence. For the best fit of the calculation a 010101 unit was placed before and behind the sequence in question. A racemic insertion of the 2,1-inserted monomer as disclosed by others is not observed at all [9].

A 2,1-insertion leaves the active site in a deactivated state for further olefin insertion and is a preferred mode for chain termination by β-hydride elimination. One aim of this work was to study this deactivated catalyst state.
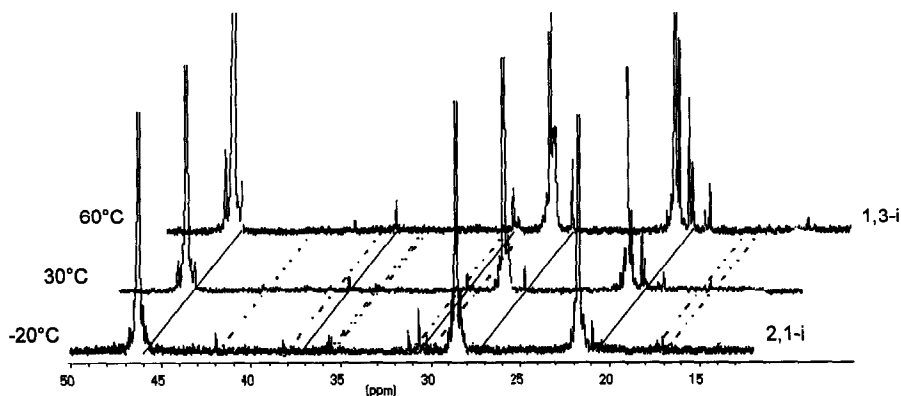

Fig. 2. Temperature dependence of 2,1- and 1,3-insertions in propene polymerization with catalyst 2 Et(H_4-indenyl)$_2$ZrCl$_2$, 2,1-insertion = — · —, 1,3 insertion = —
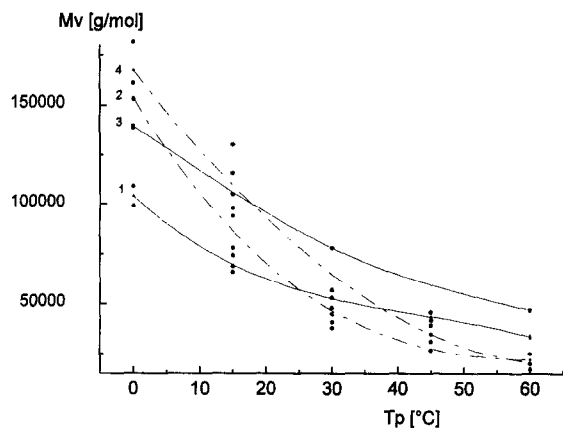
Mv [g/mol]

Fig. 3. Temperature dependence of viscosity-average molecular weight M_v for catalysts 1, 2, 3 and 4. H_4-indenyl catalysts = — · —, indenyl catalysts = — —

One way to overcome this state of hindrance for the catalytic activity is a β-hydride mediated change of the zirconium coordination as illustrated in Scheme 1 which leads from a Zr–C(2) (Scheme 1, 2) bond to a zirconium atom bonded to the C(1) atom (Scheme 1, 8) of the chain as a concerted process going along with a methyl hydride shift. It is an open question if a terminal olefin and a Zr–H structure exist as intermediates (Scheme 1, 6) [10], staying in close proximity ready to coordinate and continue chain growth and not to cause chain transfer, when the olefin is leaving the coordination sphere. This type of insertion is called a 1,3-insertion and originates from a 2,1-insertion.
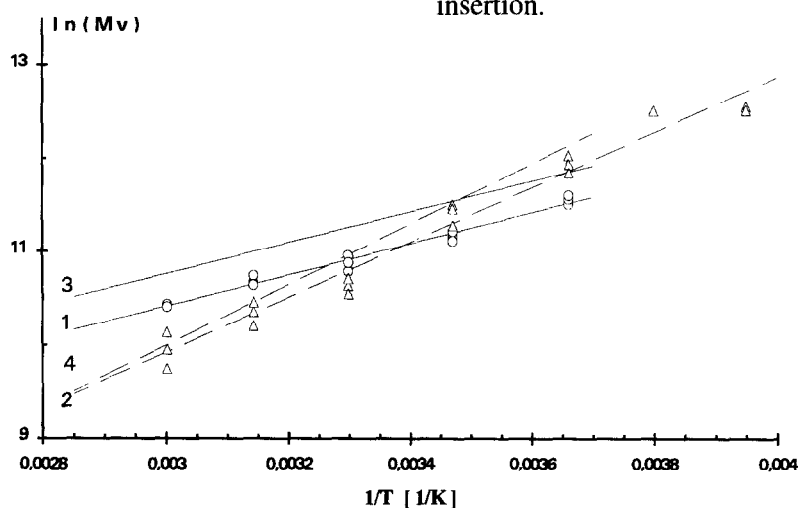

Fig. 4. Arrhenius plot of M_v versus T^{-1} for catalyst 1, 2, 3 and 4. For 1 and 2 every single measurement is indicated as a point (1 = O, 2 = △). H_4-indenyl catalysts = — · —, indenyl catalysts = — —

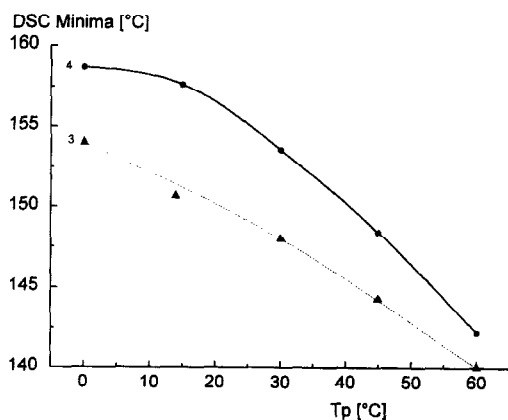Fig. 5. Variation of melting temperature T_m with T_p for polypropene samples obtained with catalyst 3 = ▲ and 4 = ●

For bridged H_4-indenyl catalysts the 2,1-insertion becomes the predominant type of regio-specific mistake at higher polymerization temperatures. At $T_p = 60°C$ one exclusively finds 1,3-insertion, while all the 2,1-insertions detectable at low polymerization temperatures ($-20°C$) have disappeared (Fig. 2).

Bridged indenyl catalysts do not show any 1,3-insertion at all, at least when bulk polymerization is applied and therefore the monomer concentration is high. 2,1-Insertions are increasing with T_p. One is able to detect a racemic placement of the next 1,2-inserted olefin at higher polymerization

Table 3
Copolymerization of propene with ethene at $T_p = 0°C$, $t_p = 100$ min and catalyst **2**

Catalyst	T_p	Activity	inc. ethene	M_v	DSC melting point
	(°C)	(kg/mol h)	(mol%)	(g/mol)	(°C)
2	0	560	1.5	360000	149

temperatures. However preferentially to about 70% 2,1-insertions are flanked by regular meso placement.

In the case of a 2,1-insertion a stereocenter is built up in the α-position of the chain next to the zirconium atom. The mechanism responsible for enantiomorphic site control is said be predominant causing a 3 times higher rate of regular meso enchainment after a 2,1-insertion defect.

Molecular weights were found to be higher for the H_4-indenyl catalyst at low polymerization temperatures (Fig. 3) but decrease more rapidly with T_p compared to the indenyl catalyst, which can be expressed in higher rates of β-hydride elimination for the H_4-indenyl catalyst. As already shown the same tendency to stronger β-hydride agostic interaction causing the 1,3-insertion on one site is responsible for elimination by β-hydride transfer causing chain transfer and there-

fore lowering the molecular weight at elevated temperatures.

In a logarithmic diagram M_v against T^{-1} a steeper slope of the Arrhenius equation can be taken as a measure for an increased temperature dependent tendency to β-hydride elimination compared to chain growth (Fig. 4).

Comparing the degree of melting point reduction caused by the different irregularities the 1,3-insertion reduces crystallinity to a lesser extent than the 2,1-insertions when polymer samples of the same T_p and mmmm ‰ pentad concentration are compared (Table 1 and Fig. 5).

3.3. Ethene–propene copolymers with very low ethene contents

Polymers with very low ethene contents (< 3 mol%) were found to have 2 times higher molecular weights while their melting points are only slightly lower. To study this phenomenon emphasis was placed on the microstructure of the polymer [11] (Table 3).

The insertions that were found are listed in Table 4.

By NMR it can be proved that almost 3/4 of the occurring 2,1-insertions are followed by an

Table 4
Observed and calculated ^{13}C NMR shifts for ethene–propene copolymers + = peak is overlapping with one of the main peaks

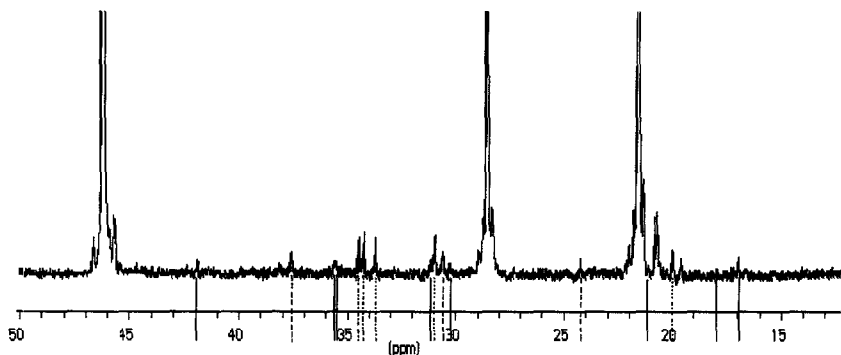| 2,1-i	2,1 insertion										
	01·*10*·01										
	see Table 2										
2,1-e-i	2,1-insertion followed by ethene insertion 01·00 *10* 01										
sequence	1 (S)	2 (T)	3 (P)	4 (S)	5 (S)	6 (T)	7 (P)	8 (S)	9 (S)	10 (T)	11 (P)
calculated (ppm)	45.65	31.32	20.99	34.79	34.49	33.98	20.31	34.49	34.79	31.32	20.99
observed (ppm)	45.5	31.0	+	34.6	34.3	33.8	20.1	34.3	34.6	31.0	+
e-i	ethene insertion 01·*00*·01										
sequence	1 (S)	2 (T)	3 (P)	4 (S)	5 (S)	6 (S)	7 (T)	8 (P)			
calculated (ppm)	45.95	31.00	20.88	37.73	24.51	37.73	31.00	20.88			
observed (ppm)	+	30.7	20.8	37.6	24.3	37.6	30.7	20.8			

Fig. 6. Monomer insertions other than regular 1,2-insertions in propene–ethene copolymerization at $T_p = 0°C$, $t_p = 100$ min and catalyst 2, e-i = - - -, 2,1-e-i = — · — · · —, 2,1-i = —

ethene insertion. Regular ethene insertions are in a lower order of magnitude (Fig. 6).

4. Conclusions

Propene bulk polymerization leads to a higher degree of stereocontrol especially at elevated polymerization temperatures compared to solution polymerization, which is reflected in higher melting points of the resulting polymer samples.

The 2,1-insertion leads to β-hydride elimination and chain growth termination. One way to overcome this is to incorporate ethene as a comonomer to activate the catalysts sites blocked by 2,1-insertion. The resulting polymers have two times higher molecular weights.

Indenyl and H_4-indenyl ligands produce polymers of different stereochemistry. 2,1-Insertion is found for all catalysts. At higher polymerization temperatures the H_4-indenyl catalyst can or has to overcome the hindrance to chain growth by a 2,1-insertion via a β-hydride shift initiated transformation of the Zr–chain bond (Scheme 1, 5), which leads to a 1,3-insertion. No 2,1-insertions are detectable any more. The indenyl-catalysts however simply produce more 2,1-insertions with increasing T_p. A racemic propene insertion after a 2,1-insertion becomes more probable for T_p's of 60°C but is still – due to predominantly enantio-

morphic site control – of minor occurrence as compared to a regular meso enchainment.

The last effect can best be explained electronically. The metal center of the H_4-indenyl catalyst system must to be of a stronger cationic nature therefore favoring the β-hydride agostic interaction. At elevated temperatures side reactions with participation of β-hydride agostic interaction become noticeable leading to either 1,3-insertions or chain transfer which is reflected in lower molecular weights of the obtained polymer.

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