

Highly isotactic polypropene prepared with rac-dimethylsilyl-bis(2-methyl-4-*t*-butyl-cyclopentadienyl)zirconiumdichloride: an NMR investigation of the polymer microstructure

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Abstract

Isotactic polypropene was prepared using rac-dimethyl-silylbis(2-methyl-4-*t*-butyl-cyclopentadienyl)zirconiumdichloride (**1**) and methylalumoxane (MAO) at temperatures between 0 and 80 °C and with Al/Zr ratios of 300 and 1500. The polymers, prepared at temperatures below 30 °C had melting points of 162 °C and above. The chain ends were determined by means of distortionless enhancement by polarization transfer (DEPT)-NMR spectroscopy. The pentad intensities were corrected according to the chemical shifts of the end groups. The intensity distributions are shown to arise from enantiomeric site control of the chiral catalyst species.

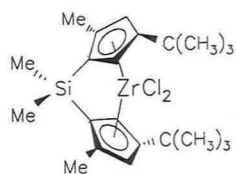
Key words: chiral zirconocenes; isotactic polypropene; stereospecific olefin polymerization

Introduction

Chiral zirconocenes have attracted great interest as polymerization catalysts. The title compound **1** [1,2] is able to produce polypropenes with melting points of 160 °C and higher, but the molecular weights of the polymers are low, however. A thorough clarification of the modes of stereocontrol by ¹³C-NMR analysis is hindered by end group signals superimposed on pentad resonances. In order to provide a basis for the correction of the pentads of low molecular

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weight polypropenes we have determined the end group signals by means of DEPT-NMR spectroscopy.



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Results and discussion

Propene polymerization with catalyst 1

Results obtained at some selected polymerization temperatures are summarized in Table 1.

The stereoregularity of the polymers prepared with catalyst 1 is remarkably high. Even at a polymerization temperature (T_p) of 80°C the polymer consists of 96% mmmm-pentads. Below 30°C the polymer melting points increase significantly, probably due to the higher molecular weight of the polymer chains. Compound 1 is the first metallocene catalyst known to produce isotactic polypropene with melting transitions above 160°C [3].

The molecular weight distributions of the polyolefins are typical of single site metallocene catalysts [4]. However, the molecular weights decrease rapidly with increasing T_p : at $T_p=80^\circ\text{C}$ the number average molecular weight (M_N) is about 500 g/mol with a mean chain length of 11 monomer units.

End group determination

For a detailed analysis of the pentad distribution of polypropene prepared with 1 the end groups were determined by comparison with literature data

TABLE 1

Some polymerization properties of catalyst 1

Run	T_p^a [°C]	Activity ^b	mmmm [%]	m.p. ^a [°C]	M_N [10 ³ g/mol]	M_w/M_N
1	0	300	98	163	49	2.31
2	25	1200	98	162	21	2.10
3	50	5000	97	149	4	2.65
4	80	23000	96	136	0.5	2.38

^a T_p = polymerization temperature; m.p. = melting point.

^bActivity in kgPP/(mol Zr atm h).

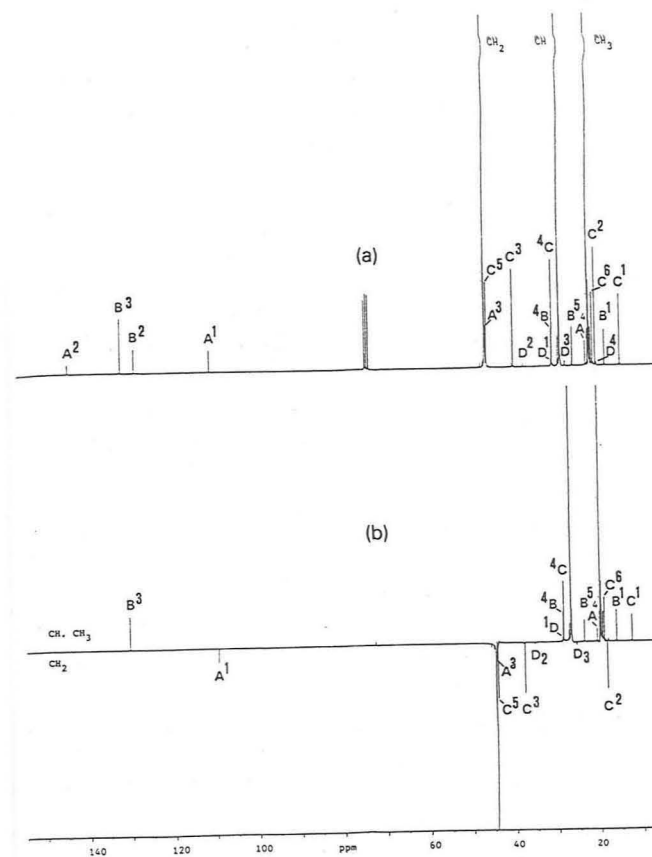


Fig. 1. Conventional ^{13}C -NMR (a) and DEPT spectrum (b) of polypropene prepared with 1.

[5–8] and by means of DEPT-NMR-spectroscopy. Fig. 1 sets a conventional ^{13}C -NMR (1a) against a DEPT-NMR spectrum (1b) of polypropene prepared at 80°C. The structural elements A–E were identified.

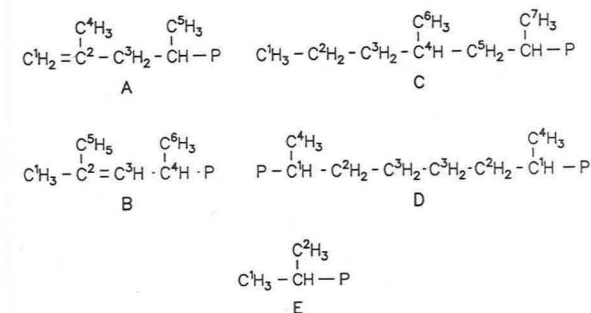


Fig. 2. Formation of end groups.

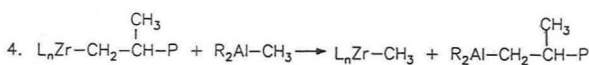
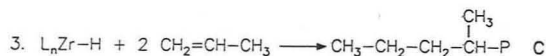
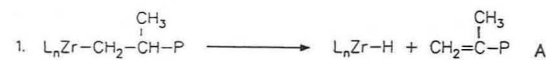


Fig. 2. Continued.

TABLE 2

End group concentrations

Entry	T_p^a	Al/Zr	[A] ^b	[B]	[C]	[D]	[E]
1	25	300	0.1	<0.1	0.1	<0.1	0.2
2	50	300	0.8	0.3	1.0	0.2	0.3
3	50	1500	0.8	0.1	0.8	<0.1	1.2
4	80	300	4.4	3.1	7.7	0.3	0.2

^a T_p = polymerization temperature.^b Concentrations given in mole-% propene.

β -Hydride elimination produces the vinylidene group A. This chain termination process is dominant in metallocene polymerization and was found for different metallocene catalysts [5,6,9,10]. Group B results from an isomerization of A under the influence of some acid, during work up or during the NMR experiment. This assignment is supported by the observation that treatment of a polymer sample with gaseous HCl increases the ratio of B/A. The *n*-propyl group C is formed by insertion of a monomer into the Zr-H bond. Accordingly, the concentration of *n*-propyl groups equals the concentration of groups with C=C bonds (A + B), since one Zr-H unit is formed for each C=C bond. Group D ('1,3-insertion') results from the isomerization of a 2,1-insertion unit [10]. The formation of isopropyl groups E after hydrolysis indicates chain transfer to aluminum as an active chain transfer reaction [8,11,12], especially at high Al/Zr ratios (cf. Table 2, entry 3). The chain termination reactions are summarized in Fig. 2.

TABLE 3

Pentad distribution of polymers prepared with 1 [13]

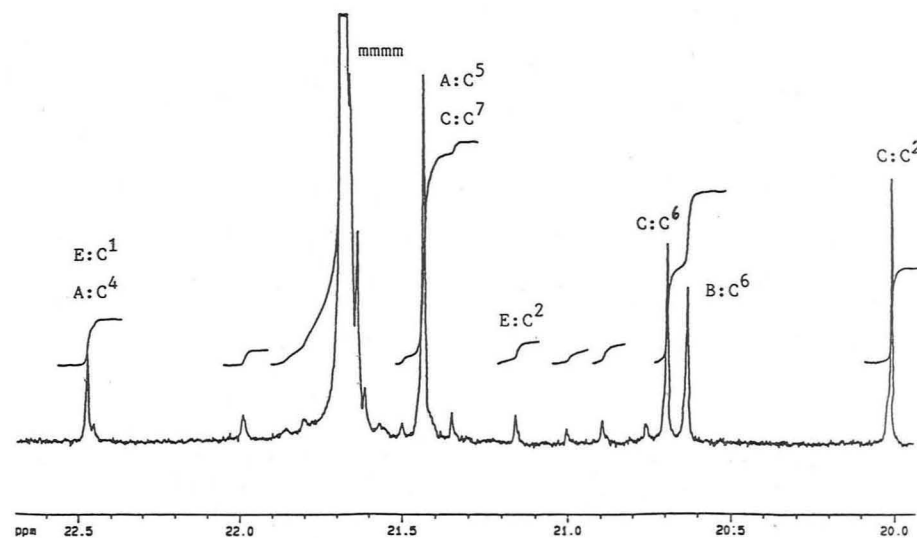
Cat.	T_p	mmmm	mmmr	rmmr	mmrr	mrmm	mrmr	rrrr	mrrr	mrrm
1	25	0.98	0.01	0	0.01	0	0	0	0	0
1	50	0.97	0.02	0	0.01	0	0	0	0	0
1	80	0.96	0.03	0	0.01	0	0	0	0	0

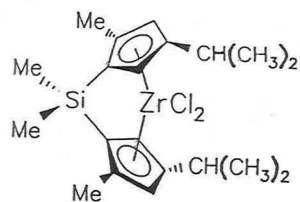
Pentad distributions of polymers prepared with 1

Figure 3 shows the expanded methyl region of a polypropene sample prepared at 80°C [13]. In addition to the mmmm-resonance at 21.7 ppm several end group signals appear which are superimposed on the chemical shifts of other pentads [14]. By comparison with literature data [5-10] and by performing DEPT-NMR experiments we were able to identify the end group signals marked in Fig. 3. The assignments of peaks which arise from unsaturated end groups were checked by catalytic hydrogenation of relevant polymer samples [15].

Table 3 summarizes the pentad distributions of low molecular weight polypropene produced with catalyst 1 at 25, 50 and 80°C.

The corrected distribution is dominated by the mmmm-pentad. The other four major intensities result predominantly from the end groups, as depicted in Fig. 3. Even at a polymerization temperature of 80°C, catalyst 1 produces

Fig. 3. Pentad region of a ¹³C-NMR spectrum of polypropene prepared with 1 at 80°C [13].



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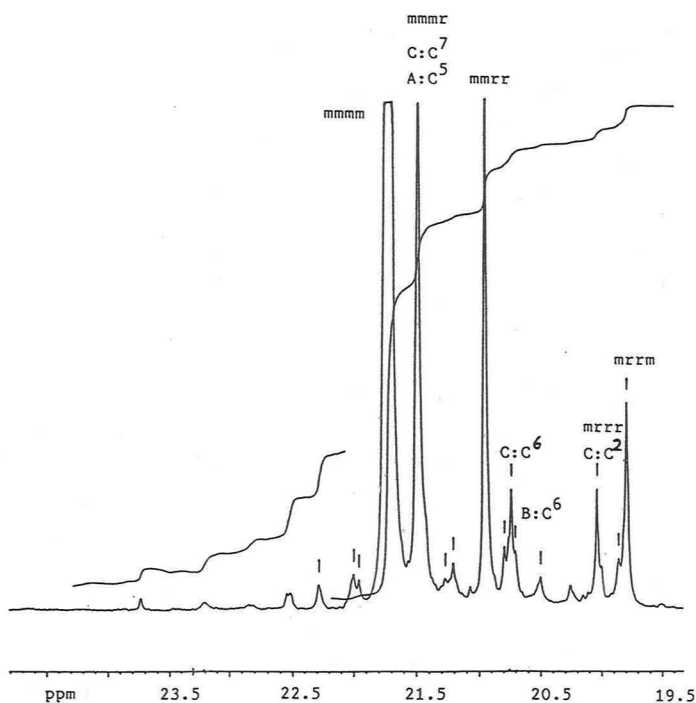
Fig. 4. Pentad region of a ^{13}C -NMR spectrum of polypropene prepared with catalyst 2 [16].

TABLE 4

Pentad distribution of polymers prepared with 2 [16]

Cat.	T_p	mmmm	mmmr	rmmr	mmrr	mrmm	mrrr	rrrr	mrrr	mrrm
2	50	0.70	0.12	0.01	0.09	0.01	0.01	0	0.01	0.05

polypropene with nearly perfect stereoregularity. As a result of this high degree of stereocontrol, the pentad distribution cannot be determined with an accuracy sufficient to investigate the mechanism of the stereoselection.

Polypropene formation with catalyst 2

Propene polymerization was performed with catalyst 2 [1,2], which differs from 1 by substitution of *t*-butyl by isopropyl groups.

This exchange reduces the stereoregularity of the polymers from 98 to 70% mmmm-pentads ($T_p=50^\circ\text{C}$, cf. Fig. 4). Within the error limits the pentad distribution of catalyst 2 follows enantiomorphic site statistics (mmmr/mmrr/mrrm=2/2/1), indicating that the enantiofacial discrimination of the prochiral monomer unit is controlled by the chiral metal complex. Since the structures of compounds 1 and 2 are similar it would be interesting to determine whether the same mechanism is operative for both catalysts.

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