

Group 4 C_s symmetric catalysts and 1-olefin polymerization

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Abstract

Polymerization of propene and 1-butene promoted by group 4 C_s symmetric metallocene precursors has been tested in different reaction conditions. The stereochemical structure of the polymer is affected by the radius of the transition metal, the substituent of the olefin and in some cases the reaction temperature and the monomer concentration. The results are tentatively rationalized considering the possible catalytic cycles that may produce either syndiotactic or isotactic polymers. A sample of syndiotactic polypropylene melting at 170°C is also reported. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Metallocenes; Syndiotactic; Isotactic; Polypropylene; Poly(1-butene)

1. Introduction

C_s *ansa*-zirconocene-MAO catalysts (MAO = methylaluminoxane) promote syndiotactic specific polymerization of simple 1-olefins such as propene, 1-butene and 4-methyl-1-pentene [1–3]. In contrast crystalline polymers with more or less isotactic microstructures have been obtained with the C-3 branched monomers 3-methyl-1-butene and 3-methyl-1-pentene [4,5]. Asanuma and Tamai [6] claim syndiotactic poly(3-methyl-1-butene) by polymerizing in liquid monomer at low temperature.

A tentative scheme that provides an explanation for the isotactic structure obtained with the latter two olefins is outlined in Fig. 1 where are

reported the configuration of the metal of the active species (according to the rules of Cahn–Ingold–Prelog [7,8] extended to chiral metallocenes as proposed by Schögl [9]) and that of the last unit of the chain end (this latter configuration is primed). The bent arrows represent the two possible chain migratory insertions with the enantioface selectivity dictated by the catalyst configuration levered by chain-end conformation [10,11], while the straight arrows represent olefin-free, Cossee back-skip reactions [12] leading to catalyst isomerizations without insertion. Importantly, the (RR', SS') and (RS', SR') species are mirror image pairs with equivalent free energies, whereas the (RR', SR') and (SS', RS') pairs are diastereoisomeric and of more or less different free energy.

If the difference in free energies between the π -complexes resulting from enantioface selective coordination of the olefin to the (RR'–SR')

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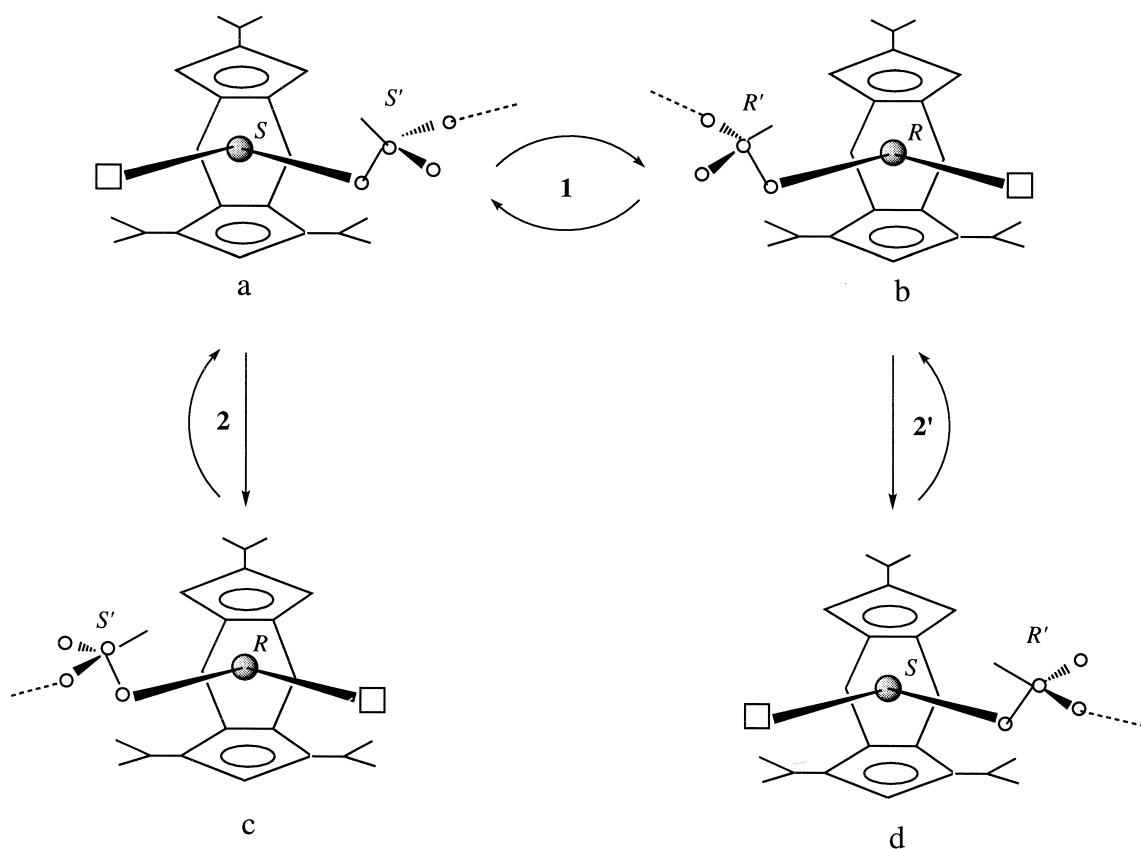


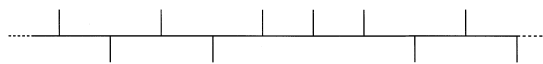
Fig. 1. Stereoisomers of the active species obtained from C_s *ansa*-metalloenes when the configuration of the last unit of the growing chain end is taken into consideration. The absolute configuration of the metal has been attributed assigning the lower rank to the vacant coordination site. The configuration of the methine β to the metal is primed. The bent arrows represents the chain migratory insertions allowed by the active species enantioface selectivity and the straight ones the back skips producing inversion of the configuration of the metal.

and (SS' – RS') diastereoisomers is negligible there is little driving force for the back-skip reaction and polyinsertion can occur essentially through catalytic cycle 1 producing a syndiotactic polymer with occasional *mm* triads due to misinsertion (Fig. 1 and Scheme 1).

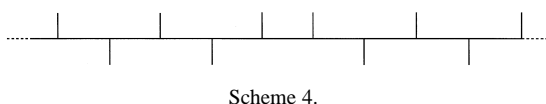
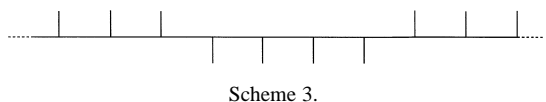
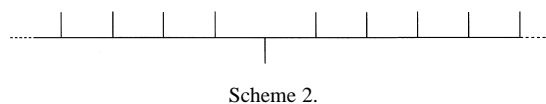
On the other hand, if the differences in free energies between diastereoisomer π -complexes is large and in favor of the SR' – RS' pair there will be a driving force in favor of the back-skip after every insertion and a prevailing isotactic

polymer will arise from cycles 2 and 2' (Cossee's mechanism [12]) with occasional *rr* triads due to misinsertions¹) (Fig. 1 and Scheme 2). Quite possibly, the insertion step for the complexes, arising from enantioface selective coordination of the olefin on the RS' – SR' diastereoisomers, is slower in comparison with the corresponding arising from the SS' – RR' pair, that are assumed to be the lower energy ones.

¹ On the whole the diastereoisomers of the active state are 2³, considering the coordination of the monomer with either one or the other enantioface. For brevity only the preferred enantioface monomer coordination is considered in this discussion (see Fig. 1).



Scheme 1.



Bulky monomer substituents, hindering ancillary ligands, small transition metal radius, and low monomer concentration should slow down the rate of cycle 1, thus favoring cycles 2 and 2'.

In practice the stereochemical structure of the polymer could turn stepwise from syndiotactic to isotactic while increasing the free energy gap

by changing the transition metal, the ancillary ligands, the bridge, the monomer and by decreasing the concentration of the monomer.

Misinsertions are not depicted in Fig. 1. Of course they imply wrong enantioface coordination, e.g., on SS' and insertion to give RS' , followed by enantioselective insertion, $RS' \rightarrow SS'$, producing a mm pair, or other mechanism involving epimerization of the chain (see e.g., Ref. [13]).

Forgetting the misinsertions, the stereochemical structure of the partially stereoregular polymers would be identical to that expected from steric control by the chain end (for both the prevailing isotactic and the prevailing syndiotactic ones) since prevailing isotactic propagation of the same chain could occasionally switch from cycle 2 to 2' through one insertion step occurring according to cycle 1 (Fig. 1 and Scheme 3).

Table 1

Polymerizations of propene in the presence of zirconium catalysts with C_s symmetry

Run ^a	Catalyst ^b (mol · 10 ⁻⁶)	T (°C)	t (m)	Toluene (ml)	Propylene (g)	Yield (g)	Activity ^c	m.p. (°C)	NMR	
									[r]	[rrrr]
1	LZrCl ₂ (5)	-60	420	30	19.0	0.31	1.3 · 10 ³	170 ^d	0.98	0.91
2	LZrCl ₂ (5)	-60	1080	30	5.0	0.05	1.8 · 10 ²	166	0.98	0.95
3	LZrCl ₂ (1)	-17	25	100	28.3	0.10	5.5 · 10 ⁴	160	0.98	0.90
4	LZrCl ₂ (1)	+16	10	100	31.4	7.00	9.1 · 10 ⁶	113	0.93	0.75
5	LZrCl ₂ (0.1)	+50	30	100	26.6	0.15	7.2 · 10 ⁵	85	0.86	0.52
6	L''ZrCl ₂ (5)	-60	1080	35	20.0	0.25	4.4 · 10 ²	156	0.96	0.88
7	L''ZrCl ₂ (1)	+16	30	100	31.0	0.72	3.2 · 10 ⁵	142	0.96	0.87

^aAll the runs were carried out by utilizing 5 · 10⁻³ mol of MAO.

^bLZrCl₂ = Bis(dimethylsilyl)-1,1'-2,2'-diyl-(3',5'-diisopropyl)(4-isopropylcyclopentadienyl)zirconiumdichloride; L''ZrCl₂ = isopropyl-(cyclopentadienyl)(9-fluorenyl)zirconiumdichloride.

^cActivity = yield(g)/mol catalyst · t(h) · [monomer].

^dAnnealed at 140°C (2 h).

Table 2

Polymerizations of propylene in the presence of hafnium catalyst with C_s symmetry

Run ^a	Catalyst ^b (mol · 10 ⁻⁶)	T (°C)	t (m)	Toluene (ml)	Propylene (g)	Yield (g)	Activity ^c	NMR	
								[r]	[rrrr]
8	LHfCl ₂ (1)	+16	60	100	45.6	0.032	5.3 · 10 ³	0.80	
9	LHfCl ₂ (1)	+50	60	100	27.3	0.26	6.3 · 10 ⁴	0.64	

^aAll the runs were carried out by utilizing 5 · 10⁻³ mol of MAO.

^bLHfCl₂ = Bis(dimethylsilyl)-1,1'-2,2'-diyl-(3',5'-diisopropyl)(4-isopropylcyclopentadienyl)hafniumdichloride.

^cActivity = yield(g)/mol catalyst · t(h) · [monomer].

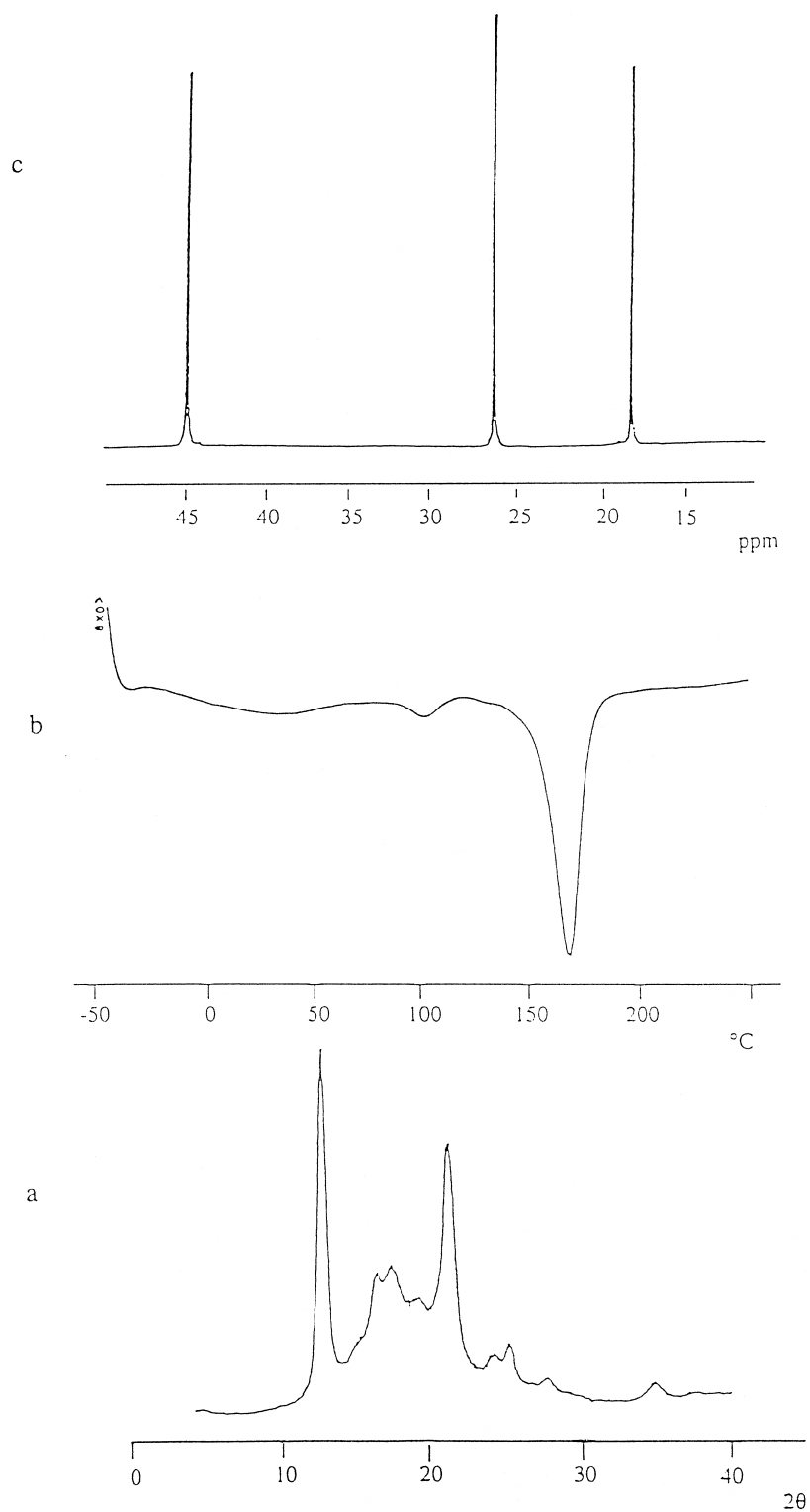


Fig. 2. X-ray powder spectrum (a), DSC diagram (b) and ^{13}C NMR spectrum (c) (HMDS scale), of sample 1.

Table 3

Polymerizations of propylene in the presence of titanium catalysts with C_s symmetry

Run ^a	Catalyst ^b (mol · 10 ⁻⁶)	<i>T</i> (°C)	<i>t</i> (m)	Toluene (ml)	Propylene (g)	Yield (g)	Activity ^c	NMR			
								[<i>mm</i>]	[<i>mr</i>]	[<i>rr</i>]	[<i>r</i>]
10	LTiCl ₂ (5)	-60	2733	35	17.5	1.52	1.1 · 10 ³	0.29	0.49	0.22	0.47
11	LTiCl ₂ (5)	-60	2710	35	1.18	0.23	1.3 · 10 ³	0.21	0.47	0.32	0.56
12	LTiCl ₂ (1)	+16	30	100	35.8	0.81	3.3 · 10 ⁵	0.23	0.51	0.26	0.51
13	LTiCl ₂ (1)	+50	30	100	32.5	1.22	5.2 · 10 ⁵	0.20	0.50	0.30	0.55
14	LTiCl ₂ (5)	+50	1380	30	0.73	0.13	1.9 · 10 ³	0.13	0.48	0.39	0.63
15	L'TiCl ₂ (5)	-60	2733	35	17.5	0.20	1.5 · 10 ²	0.27	0.49	0.23	0.48
16	L'TiCl ₂ (5)	-60	4330	30	1.18	0.02	2.2 · 10 ¹	0.27	0.50	0.22	0.48
17	L'TiCl ₂ (1)	+16	30	100	31.0	0.016	6.8 · 10 ³	0.23	0.50	0.27	0.52

^aAll the runs were carried out by utilizing 5 · 10⁻³ mol of MAO.^bLTiCl₂ = Bis(dimethylsilyl)-1,1'-2,2'-diyl-(3',5'-diisopropyl)(4-isopropylcyclopentadienyl)titaniumdichloride; L'TiCl₂ = Diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)titaniumdichloride.^cActivity = yield(g)/mol catalyst · *t*(h) · [monomer].

Conversely, syndiotactic propagation occurring through cycle 1, could be perturbed by occasional insertions occurring through cycles 2 or 2' (i.e., a skipped insertion) (Fig. 1 and Scheme 4).

It is entirely possible that catalyst intermediates with crowded, sterically hindered β-agostic resting states could have an increased rate of cycle 2 relative to cycle 1. Factors that could in turn influence this crowding include non-bonded forces between bulky monomers, bulky chain-end structures, hindered ancillary Cp ligands, a smaller transition metal radius, and the nature of the Cp bridge. In this contribution we report on variations of the structures of catalysts and monomers leading to syndiotactic, atactic, and isotactic polymers with C_s symmetric metallocenes all of which are in accord with Fig. 1.

It has been suggested that catalyst isomerizations (straight arrows, cycle 2, 2') occur faster

than insertion on the basis of an activation energy estimated at 0.9 kcal/mol from MM2 calculations. It was reasoned that the catalyst isomerizes faster than it can insert; meaning that the chain-end configuration of the last inserted unit controls enantioface selection by dictating the catalyst configuration and subsequent preferred chain-end conformation [14]. This is the same mechanism suggested almost twenty years ago by Corradini for syndiospecific V catalyzed polymerizations with a crowded metal atom following 2,1-insertions [15]. While it is generally not possible to prove a reaction mechanism unequivocally it is frequently possible to disprove one in specific instances. The invalidity of the above scenario with [Me₂C(1-Cp-9-Flu)ZrP]⁺/X⁻ (X = MAO⁻ or B(C₆F₅)₄⁻) is made obvious by the *mm* triads in the syndiotactic polymer microstructure (Scheme 1) and the ordered structure of hemi-isotactic

Table 4

Polymerizations of 1-butene in the presence of titanium catalysts with C_s symmetry

Run ^a	Catalyst ^b (mol · 10 ⁻⁶)	<i>T</i> (°C)	<i>t</i> (m)	Toluene (ml)	Monomer (g)	Yield (g)	Structure
18	LTiCl ₂ (5)	-60	8305	30	1.57	0.06	partially isotactic [<i>m</i>] = 0.74
19	LTiCl ₂ (5)	+15	5615	30	1.57	0.24	truly atactic [<i>m</i>] = 0.51
20	LTiCl ₂ (1.6)	-60	4230	10	4.5	0.40	partially isotactic [<i>m</i>] = 0.67
21	L'TiCl ₂ (5)	-60	4200	30	17.6	0.19	regioirregular and stereoirregular
22	L'TiCl ₂ (5)	-60	4220	30	1.57	0.03	regioirregular and stereoirregular

^aAll the runs were carried out by utilizing Al/Ti = 1000.^bLTiCl₂ = Bis(dimethylsilyl)-1,1'-2,2'-diyl-(3',5'-diisopropyl)(4-isopropylcyclopentadienyl)titaniumdichloride; L'TiCl₂ = Diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)titaniumdichloride.

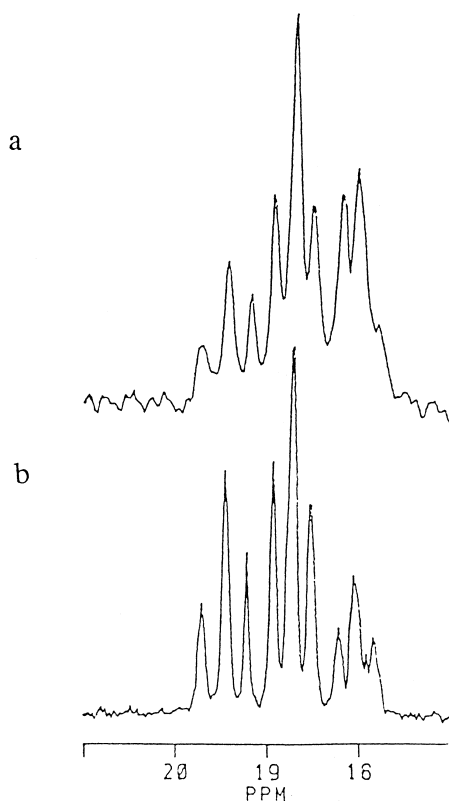


Fig. 3. Methyl region of ^{13}C NMR spectra of samples 10 (a) and 15 (b). (HMDS scale).

polypropylene obtained with $[\text{Me}_2\text{C}(3\text{-Me-1-Cp-9-Flu})\text{ZrP}]^+/\text{X}^-$ ($\text{X} = \text{MAO}^-$ or $\text{B}(\text{C}_6\text{F}_5)_4^-$) [2].

The group of usual suspects which could stabilize the $[\text{Me}_2\text{C}(3\text{-Me-1-Cp-9-Flu})\text{ZrPI}]^+$ catalyst configurations in between propylene in-

sertions in syndiospecific polymerizations include counter-anions, solvent, monomer, chain-ends and β -agostic bonding in the catalyst resting states [16–18]. Evidence for the isotactic-specific cycles in Fig. 1 under very crowded conditions comes from the isospecificity of Zr polymerizations with 3-methyl-1-butene [4] and 3-methyl-1-pentene [5] and some polymerization data in this contribution.

In order to test this hypothesis we have investigated polymerization of propene and 1-butene in the presence of several C_s *ansa*-metallocenes: Bis(dimethylsilyl)-1,1'-2,2'-diyl-(3',5'-diisopropyl)(4-isopropyl)(cyclopentadienyl) MCl_2 (LMCl_2) where $\text{M} = \text{Ti}$, or Zr , or Hf , $(\text{Ph}_2\text{C})(\text{Cp})(1\text{-fluorenyl})\text{TiCl}_2(\text{L}'\text{TiCl}_2)$ and $(\text{Me}_2\text{C})(\text{Cp})(1\text{-fluorenyl})\text{ZrCl}_2(\text{L}''\text{ZrCl}_2)$.

2. Results and discussion

The results of propene polymerizations at different reaction conditions with zirconocene and hafnocene precursors are reported in Tables 1 and 2. In agreement with the previous literature [1,2] the polymers are essentially syndiotactic with isolated *m* diads due to the back-skip and isotactic *mm* triads at least in part due to occasional misinsertions in an enantiomorphic site control mechanism [1,13].

A larger amount of isolated *m* diads (Table 2) in the polymers produced with Hf than Zr

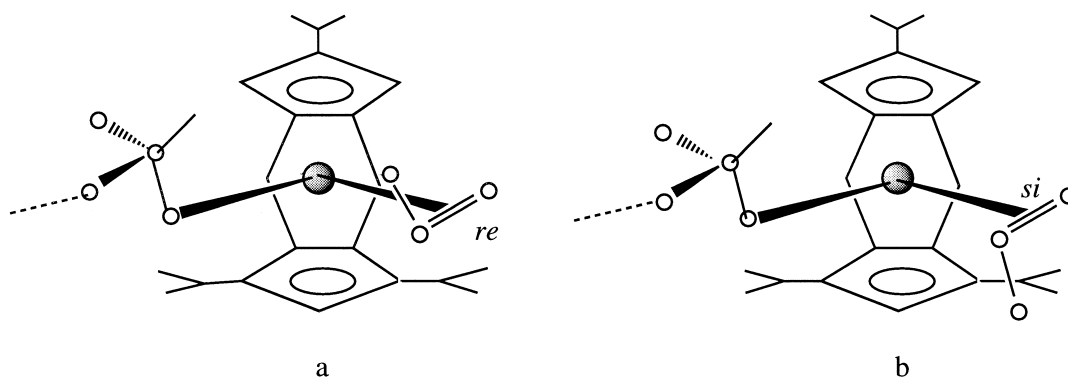


Fig. 4. If the non-bonded interactions experienced by propene with the methine carbon of the last inserted monomer unit of the chain (left) and the isopropyl substituent of the disubstituted Cp ligand (right) are comparable, the enantioface selectivity is lost (the non-superposable coordinations of prochiral olefin has been labeled with the notation *re* and *si* [19]).

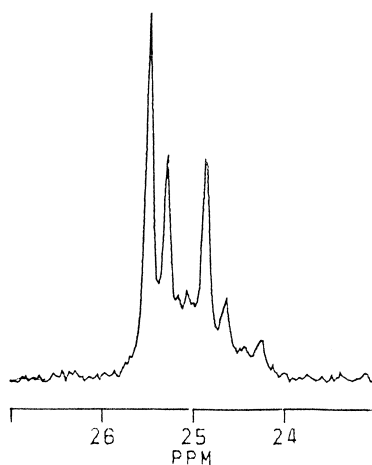


Fig. 5. C3 region of ^{13}C NMR spectrum of sample 18 (HMDS scale).

could have an electronic origin in cycles 2 and 2' of Fig. 1, since the atomic radii of the two metals are very close within each other [3].

Decreasing the reaction temperature leads to very stereoregular polymers and at -60°C with LZrCl_2 an almost completely syndiotactic ($rrrr > 90\%$), very crystalline polypropylene is obtained with an annealed melting point of 170°C and with crystallization rates rivaling those of isotactic polypropylene (see Fig. 2).

A completely different picture emerges when examining the polymerizations performed in the

presence of C_s Ti precursors. The polymerization results with propylene and 1-butene with both titanocenes (LTiCl_2 and $\text{L}'\text{TiCl}_2$) at different reaction temperatures and monomer are collected in Tables 3 and 4. In the case of propylene the polymers are almost completely stereoirregular and almost unaffected by the reaction conditions (Fig. 3).

The lack of stereospecificity of the propylene polymerizations cannot be justified simply considering that the free energy gap arising from the diastereomers of Fig. 1 should be larger for Ti cations due to the much smaller radius in comparison with both Hf and Zr. In fact, if this were the case, by lowering the monomer concentration one would expect to obtain a prevalently isotactic polypropylene. Possibly, the lack of stereoregularity is due to either an extremely rapid back and forth skipping rate for the crowded catalysts (vide supra) or the methyl of the incoming propylene experiences comparable non-bonded interactions with the other Ti appendages [10,11] as shown in Fig. 4.

Increasing the size from CH_3 to C_2H_5 as the substituent on the monomer ligand favors the Cossee type cycles 2 and 2' relative to chain migratory insertion (cycle 1) for some unknown reason. This change apparently increases the

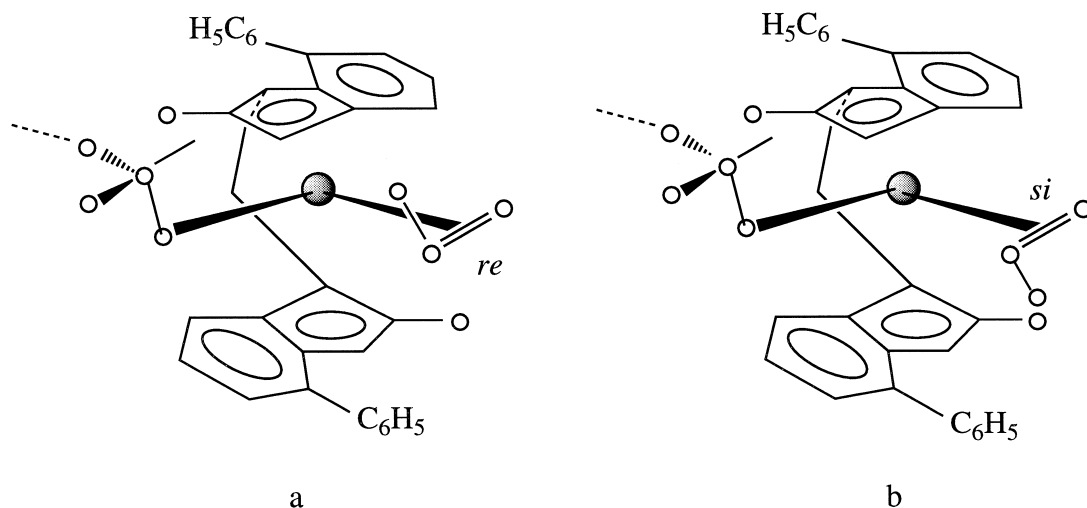


Fig. 6. Coordination of the *re* enantioface of the monomer (a) involves higher non-bonded interactions with both the chain and the ancillary ligand in comparison with coordination of the *si* enantioface (b).

energy gap between the diastereoisomeric active species and also appears to affect the difference between the conflicting non bonded interactions; producing a prevailing isotactic, chain-end control structure (Fig. 5).

It is worth mentioning here that for both homogeneous and heterogeneous catalysts appreciable enantioface-selective non-bonded interactions between incoming propene and the ancillary ligand of the active sites have been previously observed for the initiation step [20–22].

It is also worth noting that, due to the difference in symmetry of the C_2 and C_s symmetric cations, the former produce a higher isotactic stereospecificity with Ti as a result of the smaller radius of the metal. This is because of the co-operative non-bonded repulsion of the methyl of the incoming monomer with the ancillary ligands and the chain [20,23,24], as shown for the ‘wrong’ and ‘right’ presentation in Fig. 6.

3. Conclusion

When C_2 symmetric *ansa*-metallocene precursors are used for promoting polymerization of 1-olefins the polyinsertion is consistently isotactic specific [24] no matter whether the metal is Ti, Zr or Hf and how much bulky is the substituent of the monomer.

On the contrary, the stereochemistry of the polyinsertion promoted by C_s metallocene dramatically depends on the monomer substituent and the radius of the metal.

With Zr precursors 3-branched-1-olefin afford prevailing isotactic polymers while, in the same conditions, all the other 1-olefins afford syndiotactic polymers.

With Ti precursors propene affords stereoirregular polymers, while 1-butene affords moderately isotactic polymers. As discussed in Sections 1 and 2 these results can be rationalized by considering that, at least in some cases, the configuration of the substituted carbon of the chain β to the metal cannot be neglected.

Therefore, the stereoisomers of the active species to be considered for coordination of the monomer are 4 (two diastereoisomer pairs of enantiomers).

The free energy gap between the active state resulting from coordination of the olefin on the different diastereoisomers, when large enough, due to either the small radius of the transition metal, and (or) the bulky substituent of the last monomer unit of the chain, and (or) the very large ancillary ligands, can switch the insertion mechanism from chain migratory to Cossee type leading to a more or less isotactic propagation.

For C_s Ti catalyst the incoming monomer could experience comparable non-bonded interaction with either the ancillary ligands of the active cation or the methine carbon β to the metal, depending on the coordinating enantioface, so that stereospecificity is lost.

4. Experimental part

Reagents: Toluene was dried by refluxing over Na-diphenylketyl and distilling before use. The metallocenes was purchased from Boulder Scientific, MAO was prepared according to literature [25]. Propene and 1-butene were purchased from Società Ossigeno Napoli and used after distilling over $Al(C_2H_5)_3$.

Polymerization runs at $-60^\circ C$ were performed in a 100 ml glass flask equipped with a magnetic stirrer introducing, at room temperature, toluene, MAO and metallocene as reported in the Tables 1–4. The mixture was left to age for 5 min, then the reactor was introduced in liquid nitrogen and gaseous monomer was condensed, finally the flask was thermostated at $-60^\circ C$. The polymerization were stopped by introducing few millilitres of methanol, the polymerization mixture was poured in acidified ethanol, the polymers were recovered by filtration, washed with fresh ethanol and dried in vacuo at $80^\circ C$.

Polymerization runs at higher temperature (-17 , $+16$ and $+50^\circ C$) have been performed

in a 250 ml glass-autoclave introducing the amount of MAO and metallocene dissolved in 100 ml of toluene, as reported in Tables 1–4. The mixtures was fed with the monomer and kept under magnetic stirring over the runs. The autoclave was vented and the polymers were recovered as previously described.

^{13}C NMR spectra were recorded on AM 250 Bruker spectrometer operating at 62.89 MHz. The samples were prepared by dissolving 40 mg of polymer into 0.5 ml tetrachloro-dideuterioethane. The spectra were recorded at 120°C using hexamethyldisiloxane (HMDS) as internal chemical shift reference.

Melting points were measured by using a Du Pont 9900 DSC calorimeter with a heating rate of 20 K/min, on previously melted and recrystallised samples.

Wide angle X-ray diffractogram was obtained with $\text{CuK}_\alpha\text{-Ni}$ filtered radiation by using a PW 1050 Philips powder diffractometer. The scan rate was $2\theta/\text{min}$.

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