Error formation in *ansa*-zirconocene catalyzed isotactic propylene polymerization

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Abstract

Propylene was polymerized in the presence of the cation bis(O-acetyl-(R)-mandelate) $(1^+(S))$ of (S)-ethylenebis[4,5,6,7-tetrahydro-1-η^5-indenyl]zirconium and $(1^+(R/S))$ of a mixture of diastereomers. Under the same experimental conditions the polymers obtained with the latter exhibit abundant non-homosteric methyl ^{13}C NMR pentads as well as 2,1- and 1,3-misinsertion resonances; these stereo- and regioirregularities are absent in the poly(propylenes) formed by the enantiomeric $1^+(S)$. The stereoselectivity of catalysis by $1(R/S)$ can be significantly raised either by reducing its concentration, lowering the polymerization temperature, or immobilizing it in a silica support; the stereoselectivity of catalysis by $1(S)$ is not similarly affected. These results are consistent with the interchange of polymer chains of opposite β-carbon configuration bound to different chirality metal centers of the racemic mixture causing steric inversions. In the case of catalysis by $1(S)$, the same process does not introduce stereoerror because the growing chains are of the same configuration. Maximum isotactic specificity of an *ansa*-zirconocene precursor is obtained either with a pure enantiomer of the precursor or with a racemic mixture of the zirconium complex which is adequately immobilized on a support.

Keywords: Zirconium; Metallocenes; Polymerization; Propylene; Isospecific; Ziegler–Natta catalyst

1. Introduction

Ziegler-Natta's inventions enable α-olefin polymerization at low monomer pressure, temperature (T_p), and with regio- and stereoselectivity. Many new materials, such as isotactic poly(olefins), linear high and linear low density poly(ethylenes), and poly(olefin) elastomers, were synthesized for the first time, and are now manufactured in tens of billions of pounds per year in the USA. Coordinately unsaturated chiral Ti(III) ions were postulated to be the stereoselective catalytic sites [1], and non-bonded interactions were proposed to provide the selectivities [2,3]. Ziegler-Natta catalysis is undergoing a renaissance initiated by the discoveries of metallocenium species [4] possessing exceedingly high polymerization activity (*A*), and of chiral *ansa*-zirconocene precursor capable of stereoselective polymerization [5,6]. The latter had been attributed also to non-bonded interactions [7–10].

There are similarities and differences between the heterogeneous $TiCl_3$-based catalysts and the homogeneous metallocene-based catalysts. This work was motivated to understand the differences, which have both scientific significance and technological consequences. It is well known that the heterogeneous catalyst produces isotactic poly(propylene) over a broad range of conditions. The polymer is characterized by high crystallinity $(X_c > 60\%)$, melting transition temperature $(T_m > 162°C)$ [11], homosteric pentad distribution $([mmmm] > 0.95)$ [11–13], and solvent resistance. This indicates that the catalytic sites have a fixed ligand environment. In contradistinction, racemic *ansa*-zirconocenes formed poly(propylene), which is inferior in all of the above-mentioned properties [14,15], and even crystallizes in the γ- instead of the usual α-morphology [15]. Polymerization involving the *ansa*-metallocene became more stereospecific when conducted at low T_p [15,16] or high monomer concentration $[C_3H_6]$ [17a]. Multiple β-hydrogen eliminations/reinsertions [17a] and chain-end isomerization [17b] had been proposed for the occurence of erroneous insertions. The possibility of interchange of propagating chains was frivolously waved

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aside [17a]. However, this possible mechanistic pathway can be directly tested by experimentation. The central purpose of this work is to compare the propylene polymerization behavior in the presence of (S)-ethylenebis(4,5,6,7-tetrahydro-1-η^5-indenyl)zirconium bis (O-actyl-(R)-mandelate) (1(S)) and a mixture of diastereomers (1(R/S)) [18,19]. The results show that the interchange of polymer chains belonging to metal centers of opposite chirality is a significant contributing factor to the loss of stereochemical control in isospecific propylene polymerization.

2. Results

Precursor 1 was synthesized in the form of O-acetyl-R-mandelate diastereomers. The polymerization behavior of acetyl mandelates are very similar to that of chloride because they all undergo alkylation and heterolytic cleavage leading to a common zirconocenium species. The cumbersome reference to the configuration and diastereomeric nature of these compounds is omitted hereafter; the precursors are denoted simply as antipodes as if their non-Cp ligands were achiral. In most of the experiments the precursor was activated with an optimum amount of tri-iso-butylaluminum (TIBA) and a stoichiometric quantity of triphenylcarbenyl-tetrakis(pentafluorophenyl)borate (2). The probable reactions are alkylation of 1 by TIBA, followed by abstraction of an anionic ligand by the trityl cation to afford the zirconocenium ion 1^+ rapidly and quantitatively, even at $T_p = -55°C$ [16]. Since the tetrakis(pentafluorophenyl)-borate anion is both inert and non-coordinative, 1^+ may be thought of as a "naked" ion with a minimum of ion-pair interactions.

2.1. Ethylene polymerization

The two precursors 1(S) and 1(R/S) should behave identically when no stereoselection is involved in the

catalysis. This was tested by comparing their catalysis of ethylene polymerization. The experimental conditions were: [Zr] = [2] = 24 μM, [TIBA] = 2 mM, t_p = 5 min, $P_{C_2H_4}$ = 10 psig, T_p = 20°C. The enantiomeric system $1^+(S)$ produced 0.44 g of polyethylene (PE) (T_m = 138.4°C, M_n = 4.04 × 10⁵) at A_E = 1.05 × 10⁷ g PE/(mol Zr · [C_2H_4] · h); the corresponding results for the racemic $1^+(R/S)$ system are 0.42 g of PE (T_m = 137.7°C, M_w = 4.1 × 10⁵) at A_E = 1.01 × 10⁷ g PE/(mol Zr · [C_2H_4] · h). This good agreement shows that the racemic and enantiomeric preparations were pure and equal in chemical activity, i.e. $1^+(S)$ and $1^+(R)$ have the same rate constants of propagation (k_p) and chain transfer (k_{tr}). However, the two systems behave very differently in their stereospecific polymerization of propylene.

2.2. Propylene polymerization catalyzed by the racemic zirconocene precursor

Nearly all stereospecific polymerizations of propylene were conducted with racemic zirconocene precursors except those cited in Refs. [18] and [19]. This is because propylene is only a prochiral monomer; macromolecules produced by the opposite antipodes of a chiral catalyst are indistinguisable. Furthermore, it is a very difficult task to obtain the pure enantiomer. There are ample reports of sensitivity of stereospecificity of propylene polymerization by racemic zirconocene precursors depending on the experimental conditions [14–17]; this is systematically investigated here. We began by investigating the change of stereoselectivity of the catalyst caused by lowering its concentration; the results are summarized in Table 1. In runs 1–5 both [1(R/S)] and [2] were reduced from 25 μM to 2.5 μM. The propylene polymerization activity A_p, which is based on per mol of Zr, remains approximately constant as expected. However, the T_m of the resulting polymers increases by 32°C, while M_w decreases by one-half with a lowering of the catalyst concentration. Therefore,

Table 1

Propylene polymerization catalyzed by $1^+(R/S)$ at different concentrations and temperatures

No.	[Catalyst] (μM)	T_p (°C)	A_p (×10⁻⁶)	T_m (°C)	M_w (×10⁻⁴) [e]
1 [a]	25	0	6.82	116.6	21.1
2 [a]	17.5	0	7.42	127.3	16.7
3 [a]	12.5	0	7.10	131.1	12.3
4 [a]	7.5	0	4.32	142.5	9.9
5 [a]	2.5	0	5.68	148.7	9.0
6 [a]	25	20	3.75	102.7	6.75
7 [b]	40	−20	0.09	148.7	28.6
8 [c]	125/SiO₂	0	0.06	151.2	6.22
9 [c]	150/SiO₂	20	0.14	132.6	1.52
10 [d]	300	0	1.0	144.0	15.06

[a] [Zr] = [2], [TIBA] = 1.5 mM. [b] [TIBA] = 2 mM. [c] 1(R/S) mandelate supported on SiO₂ and activated as in [a]. [d] 1(R/S)Me₂ supported on SiO₂ and activated with 300 μM of 2 without TIBA. [e] M_w by intrinsic viscosity method [20].
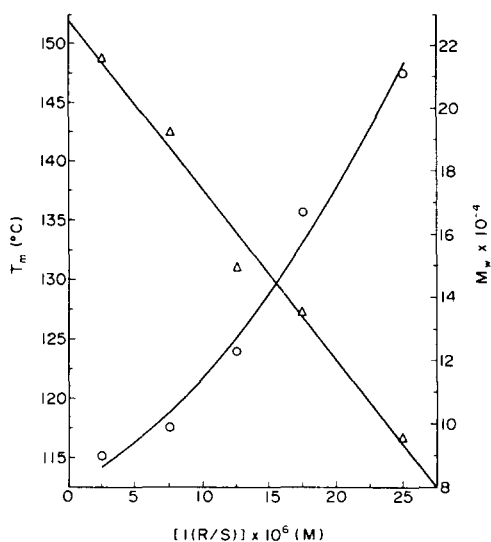
Fig. 1. Poly(propylene) obtained at 0°C 1(R/S)/TIBA/2, variation of T_m (△) and M_w (○) with [1(R/S)].

Fig. 2. ^{13}C NMR spectrum of sample 1.

stereoselectivity is much higher at lower [Zr]; while the polymer M_w suffers at low catalyst concentration as shown in Fig. 1. In the case of variation of M_w vs. [1(R/S)], a trend towards an asymptotic limiting value may be discerned.

Sample 1 has the lowest T_m and should be the most stereoirregular polymer of this study; its ^{13}C NMR spectra (Fig. 2) shows that the [*mmmm*] sequence fraction is only 0.71 (Table 2). Many minor peaks can be seen in the inset, corresponding to regioerrors of 2,1- and 1,3-misinsertions [21]. In comparison, sample 5 obtained at ten times lower catalyst concentration has [*mmmm*] = 0.99 and no regioirregular resonances.

The stereoerror formation increases markedly with an increase in T_p. Run 6 in Table 1, conducted at +20°C, produced poly(propylene) which melted at 14°C lower temperature than the product of run 1. However, at
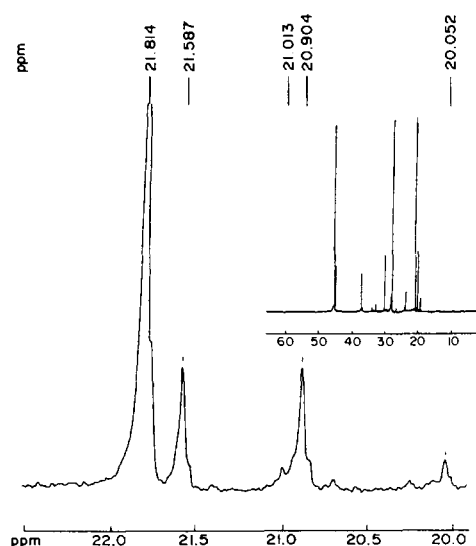
$T_p = -20$°C, high melting poly(propylene) ($T_m = 148.7$°C) was obtained in spite of the high catalyst concentration used. The polymer has a high M_w of 2.86×10^5.

A method often employed to minimize undesirable interactions between catalytic species is to immobilize them on an inert support. We have developed a procedure for this [20]. The surface of macroporous silica was first modified with MAO, then zirconocene was impregnated on it. Supported catalysts 1(S)/SiO$_2$ and 1(R/S)SiO$_2$ were prepared with the two precursors in this manner. Previously, the immobilized zirconocene catalyst was found to behave identically to the dissolved (free) metallocene to produce the same copolymers of ethylene and propylene and exhibit the same activity in the homopolymerization of either monomer [22].

In polymerization run 8, 125 μM of 1(R/S)/SiO$_2$ was used to produce poly(propylene) at 0°C, which has

Table 2
^{13}C NMR of poly(propylenes)

Pentad configuration	Sample 1		Sample 5		Sample 8		Sample 11	
	δ (ppm)	int [a] (%)	δ (ppm)	int [a] (%)	δ (ppm)	int [a] (%)	δ (ppm)	int [a] (%)
mmmm	21.8	71.0	21.8	99	21.8	98.1	21.8	> 99.9
mmmr	21.6	12.3			21.6	1.7		
rmmr								
mmrr								
mrmm and *rmrr*	20.9	14.7			20.9	0.2		
mrmr								
rrrr								
rrrm								
mrrm	20.1	2.0						
mm		83.3		99		99.8		> 99.9
mr		14.7				0.2		
rr		2.0						

[a] Integrated intensity (%) of total ^{13}CH$_3$ resonances.

$T_m = 151.2°C$ and $M_w = 6.2 \times 10^4$. This shows that the immobilization of **1(R/S)** results in a high degree of stereochemical control as compared with run 1, even though the concentration of the supported catalyst was five times higher than the free *rac*-zirconocene. Similarly, run 9, catalyzed by 150 μM of **1(R/S)**/SiO$_2$ at $T_p = 20°C$, produced poly(propylene) with $T_m = 132.6°C$, which is 30°C higher than that of run 6 (Table 1). The ^{13}C NMR spectrum of sample 8 showed it to be exceedingly stereoregular (Table 2, columns 6,7). Therefore, the immobilized racemic catalyst has greater stereochemical control than the racemic catalyst in solution [23].

The possible involvement of alkylaluminum species in stereoerror formation was considered. Therefore, **(S/R)** ethylenebis(4,5,6,7-tetrahydro-1-η^5-indenyl) zirconium dimethyl (**3**) was synthesized by a literature procedure [24]. It was activated by an equimolar amount of **2** to polymerize propylene. In the absence of TIBA, a very large quantity of **3** (300 μM) had to be employed because a major portion of it was consumed unproductively to scavenge impurities in the reaction medium. Run 10 at 0°C produced poly(propylene) of $T_m = 144°C$ and $M_w = 1.51 \times 10^5$. Therefore, in the absence of aluminum alkyl compounds, the racemic dimethyl derivative of **1** is moderately stereoselective, even at high concentration.

2.3. Propylene polymerization catalyzed by the enantiomeric zirconocene precursor

The loss of stereoselectivity of catalysis by **1(R/S)** with an increase of [Zr] or T_p, and a converse effect by the increase of [C$_3$H$_6$] or immobilization of the zirconocene precursor, suggest bimolecular origins in contrast to processes involving a single active complex to be discussed later. Therefore, the chirality of the metal center and the configuration of the growing polymer chain may play a role in the formation of stereoerrors. To shed some light on this question, the polymerization behavior of **1**$^+$(**S**) was investigated. In this case all the active sites have the same **S** configuration and the
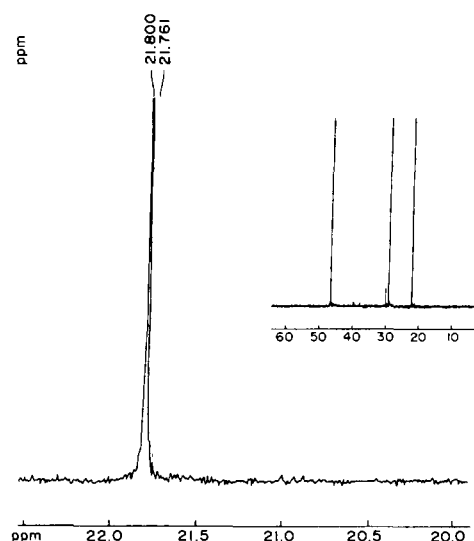

Fig. 3. ^{13}C NMR spectrum of sample 11.

methine carbons are in predominantly the **R** configuration.

The difference between the catalysts derived from **1**$^+$(**S**) and the racemic mixture is obvious and striking. In runs 11 and 12 of Table 3 a ten-fold difference in [Zr] has negligible effect on both the activity and the T_m and M_w of the polymer formed. The T_ms were both above 151°C, indicative of high stereoregularity. The ^{13}C NMR of sample 11 (Fig. 3) obtained at the high [Zr] = 25 μM, is of even higher steric purity than sample 5 produced at low concentrations in the racemic system. Therefore, the stereoselectivity of **1**$^+$(**S**) is invariant to its concentration.

The A_p of **1**$^+$(**S**) is $(1.2 \pm 0.3) \times 10^6$ g PP/(mol Zr $\cdot$ [C$_3$H$_6$] $\cdot$ h) as compared with $6.3 \pm 1.3 \times 10^6$ g PP/(mol Zr $\cdot$ [C$_3$H$_6$] $\cdot$ h) for **1**$^+$(**R/S**). This discrepancy contrasts with the same activity for ethylene polymerization by these two systems (vide supra). Furthermore, the **S** antipode produces poly(propylene) of nearly the same M_w ($\sim 1.5 \times 10^5$) at both high and low concentrations (runs 11 and 12). In comparison the M_w

Table 3
Propylene polymerization catalyzed by 1$^+$(S) at different concentrations and temperatures

No.	[Catalyst] (μM)	T_p (°C)	A_p ($\times 10^{-6}$)	T_m (°C)	M_w [d] ($\times 10^{-4}$)
11 [a]	25	0	0.93	151.9	15.5
12 [a]	2.5	0	1.54	151.4	14.1
13 [b]	300	0	0.11	151.5	18.81
14 [c]	300/SiO$_2$	0	0.01	151.7	10.42
15 [a]	25	20	0.25	133.4	5.3
16 [a]	100	-20	0.01	155.5	20.9

[a] [Zr] = [2], [TIBA] = 1.5 mM. [b] 1(S)Me$_2$ activated with 300 μM of cocatalyst 2 without TIBA. [c] 1(S) supported on SiO$_2$ and activated as in [a]. [d] M_w by intrinsic viscosity method [20].

decreases with a decrease in the concentration of the racemic mixture as shown in Fig. 1.

Runs 11 and 12 (Table 3) were conducted with 1.5 mM of TIBA. To show any effect of the latter, the S enantiomer of the dimethyl derivative, 1(S)(Me)$_2$ (4) was synthesized. Polymerization of propylene at 0°C using [4] = [2] = 300 μM (run 13) gave polymer with the same high T_m (151.5°C) and M_w (1.9 × 10^5) as runs 11 and 12. Therefore, the presence of aluminum species has neither positive nor negative influences on the stereoselectivity.

Immobilization of the 1(S) precursor on silica did not affect its stereoselectivity. Run 14 employed 300 μM of this supported catalyst at 0°C. The poly(propylene) thus obtained has T_m = 151.7°C and M_w = 1.1 × 10^5, which is quite similar to the products of runs 11–13. In conclusion, the stereoselectivity of 1$^+$(S) system is not lowered by intermolecular events since there are no significant changes caused by increasing [Zr], eliminating [Al], or immobilization.

However, increasing T_p still causes loss of stereoselectivity of the 1$^+$(S) system. At −20°C (run 16) the poly(propylene) formed has T_m = 155.5°C and M_w = 2.1 × 10^5; these values are much greater than 133.4°C and 5.3 × 10^4 for the T_p = +20°C polymer (run 15). The changes may represent the contribution of intramolecular processes to stereo-error formation (vide infra). In the case of runs 5–7, both intra- and intermolecular processes were operative to lower the stereoregularity of poly(propylene) formed.

3. Discussion

3.1. Molecular mechanics calculation of steric energies

Isotactic poly(propylene) produced in the presence of 1$^+$(S) is exceedingly high in stereoregularity (Table 2, sample 11). This indicates that an enantiomeric pure C$_2$ ansa-zirconocene cation has very high intrinsic stereoselectivity. The degree of profacial preference by an active species can be estimated from the steric energies of the π-propylene complexed zirconocenium transition states with the relevant configurations for the com-

plexed propylene, the metal center and the growing polymer chain. Several authors [8–10] have employed molecular mechanics modeling to obtain the steric energy differences. The results for Et[1R–IndH$_4$]$_2$Zr$^+$(π-C$_3$H$_6$)P, where P is 2-methylpentyl [10], are given in Table 4. The notations in this table and elsewhere have the following meanings: (re)M^R–S · · · has re monomer π-complexed to the metal in S configuration and β-carbon atom having the R configuration. This transition state leads to normal face addition (NFA) and meso enchainment. The corresponding reverse face addition (RFA) of the si monomer (case 2) results in a racemic enchainment, which has a steric energy about 3.3 kcal mol^{-1} higher than case 1. This difference is the stereocontrol energy $\Delta E_S(r − m) = E_S(\text{RFA}) − E_S(\text{NFA})$, which is a measure of intrinsic stereoselectivity. Cases 3 and 4 are for β-carbon atom in the R configuration. There are four additional cases for the metal in the S configuration; they bear enantiomeric relationship to those given in Table 4 [25].

Knowing the steric energy difference between racemic and meso enchainment, $\Delta E_S(r − m)$, one can obtain the isotactic insertion probability $\rho(m)$, which is given by Eq. (1).

$$\rho(m) = \frac{1}{1 + \exp(-\Delta E_S(r − m)/\text{RT})} \quad (1)$$

The NMR spectroscopically observable microstructural sequences are related to $\rho(m)$ depending upon the steric control model [6] provided there is no other significant source of stereoerrors. The homosteric m-pentad distribution is $\rho(m)^5 + (1 − \rho(m))^5$ for the enantiomorphic site (E) model [26]; and it is $\rho(m)^4$ for the Bernoullian (B) model [27]. The value of $\rho(m)$ for 1$^+$(S) at 25°C is about 0.996, which corresponds to [$mmmm$] = 0.984 for either the E or B control model [10]. The ^{13}C NMR spectrum of sample 11 show this high steric purity. Even the racemic 1$^+$(R/S) produced poly(propylenes) having this level of stereoregularity at either low concentration (sample 5) or on silica support (sample 8).

Sample 1 obtained in the presence of 1$^+$(R/S) at normal concentration and propylene pressure has

Table 4
Steric energies for the transition states of Et[IndH$_4$]$_2$Zr$^+$(C$_3$H$_6$)P

Case i	Configuration	Steric energy (kcal mol^{-1}) [a]			Enchainment type [d]	Relative probability at 25°C
		$E_{s,i}$ [b]	$\Delta E_{s,i}$ [c]	$\Delta E_s(r − m)$ [d]		
1	(re)M^R–S · · ·	66.3	0		m	1
2	(si)M^R–S · · ·	69.7	3.3	3.3	r	3.8 × 10^{-3}
3	(re)M^R–R · · ·	67.9	1.6		r	6.7 × 10^{-2}
4	(si)M^R–R · · ·	71.1	4.9	3.3	m	2.5 × 10^{-4}

[a] Error ±0.1 kcal mol^{-1}. [b] $E_{s,i}$ is the steric energy for the ith case. [c] $\Delta E_{s,i}$ is the relative steric energy with respect to $i = 1$; $\Delta E_{s,i} = E_{s,i} − E_{s,1}$. [d] $\Delta E_s(r − m)$ is the stereocontrol energy.

[*mmmm*] of only 0.71. The steric purity increases to nearly the level expected from Eq. (1) for poly(propylene) obtained at $-55°C$, but decreases precipitonsly as T_p increases to $+80°C$. Furthermore, fractions of even lower isotacticity can be extracted by refluxing acetone and diethylether [15].

3.2. Bimolecular processes affecting stereochemical control

If the stereochemical configuration of an inserted monomer is entirely determined by NFA, (eq. (2)) or RFA, (eq. (3)),

$$(re)M^R-S \cdots \to M^R-SS \cdots NFA \qquad (2)$$

$$(si)M^R-S \cdots \to M^R-RS \cdots RFA \qquad (3)$$
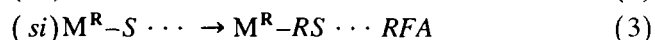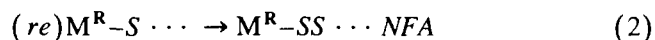
then there will only be a few stereo-errors in the isospecific polymerization promoted by the present catalyst. For a stereocontrol energy of 3.3 kcal mol^{-1}, the relative probability of NFA:RFA at 25°C is only 1:3.8 $\times 10^{-3}$. The high steric purity of polymers formed by the S antipodes is consistent with this preference for NFA, but the $1^+(R/S)$ catalyst forms many more errors. The stereoregularity of poly(propylene) obtained with $1^+(S)$ is independent of its concentration.

There are in the $1^+(R/S)$ system an equal number of $M^R-S \cdots$ and $M^S-R \cdots$ species (type A) which are favored by facial selection [28]. If the propagating chains are allowed to exchange, then species of the form $M^R-R \cdots$ and $M^S-S \cdots$ (type B) are formed. Eq. (4)

$$M^R-S \cdots + M^S-R \cdots \rightleftharpoons M^R-R \cdots + M^S-S \cdots \qquad (4)$$
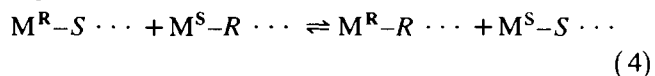
and others like it, provide alternative pathways leading to the B-type species, which are otherwise formed by RFA (Eq. (3)). The steric energies of the A and B species without π-complexed olefin differ by only 0.34 kcal mol^{-1}. The ratio of type A:type B species is 1:0.56 for equilibrium (4). This chain interchange would significantly increase the number of stereoerrors. The observed effect of catalyst concentration and immobilization is consistent with the occurrence of Eq. (4). In the case of $1^+(S)$ catalyst, only one antipode of the precursor is present. Interchange of chains on metal centers of the same chirality has no stereochemical consequence.

The change of stereochemical configuration of the propagating chain with respect to the metal center as depicted by Eq. (4) is an over-simplification. Since organoaluminum compounds are ubiquitously found in Ziegler-Natta catalysis, the exchange may involve L_2Zr^+P and AlP′ species, and between the latter with L_2Zr^+H or with L_2Zr^0P, where L_2 is the bis-hapto ligand and P is the growing polymer chain. Exchange reactions between dialkyl zirconocene (Cp_2ZrMe_2, $(Me_5\text{-}Cp)_2ZrMe_2$, Ind_2ZrMe_2, $(Me_2SiCp)_2ZrMe_2$) and

alkylaluminum compounds (Me_6Al_2, MAO, MeAl(2,6-di-t-butyl-4-methylphenoxy)$_2$) had been measured by Siedle et al. [29] using ^{13}C NMR; they proposed the participation of zirconocenium ionic species in these exchanges. The possible involvement of Al–P is indicated by runs 11 to 13 of Table 1. Exchange between L_2Zr^+P and $P'B^-X_3$, where X is pentafluorophenyl, would have the same consequence of Eq. (4). It is uncertain how much the coulumbic repulsion would affect Eq. (4) involving two L_2Zr^+P species, but the process could occur unimpeded if one of the molecule is a neutral L_2Zr^0P complex.

Steric accessibility to the metal center is obviously important for Eq. (4) to take place. This can explain the observed [17a] sharp increase of stereoregularity of the poly(propylene) formed with the increase of monomer concentration. Complexation of L_2Zr^+P with monomer molecule or molecules would hinder the exchange of its P chain with those of the other species postulated above.

Both Eqs. (3) and (4) introduce one stereochemical inversion. According to the enantiomorphic site control model, this would be followed by another racemic insertion. The resulting macromolecule would have stereochemical error of the rr type, which is flanked by chain segments of the same helix handedness. Such error may be accommodated in the α-crystalline morphology. However, if frequent chain interchange is favored by the experimental conditions, then the polymers would have highly irregular microstructures. They either do not crystallize, as is the case for the acetone soluble fraction, or assume disordered γ morphology [15].

3.3. Other processes affecting stereochemical control

Stereocontrol energy of the magnitude given in Table 4 is too large to account for the temperature dependence of stereoselectivity indicated by the results in Tables 1 and 3, according to Eq. (1). A possible explanation is that at elevated temperature certain conformations and configurations for the catalytic species become accessible which are either more susceptible to chain interchanges or have little or no stereoselectivity.

Several investigators have proposed that agostic interaction can influence the stereoselectivity of Ziegler-Natta catalysts [10,30]. In general, if the agostic interaction stabilizes the intermediate along the reaction coordinate, then this process is rendered more favorable than other competing pathways. For instance, if there is a significant β-hydrogen agostic interaction, then β-hydride elimination is facilitated which tends to lower the polymer molecular weight. Morokuma and coworkers [8] have obtained with ab initio calculations the following atomic separation parameters for α-, β- and γ-hy-
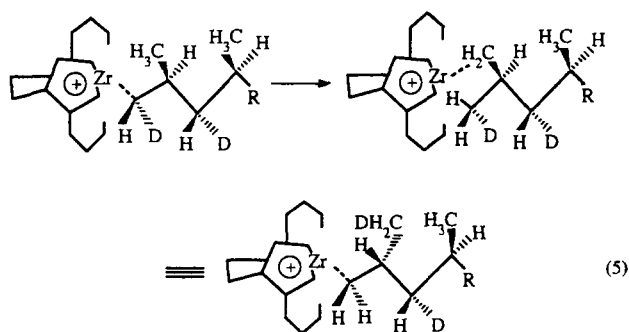
$$(5)$$

drogen agostic interactions: $C_\alpha \overset{1.12}{—} H \overset{2.34}{—} Zr, C_\beta \overset{1.12}{—}$ $H \overset{2.22}{—} Zr$, and $C_\gamma \overset{1.12}{—} H \overset{2.40}{—} Zr$. Molecular mechanics modeling of the catalyst rac-ethylenebis(1-η^5-indenyl)zirconium $(C_3H_6)P$ with these parameters afforded $\Delta E_s(r-m)$ values (kcal mol^{-1}) of 2.9, 3.6, 1.5, 0.7 for no, α-, β- and γ-hydrogen agostic interactions respectively [10]. In other words while the α-agostic interaction enhances stereoselectivity, the γ-agostic interaction almost nullifies it. Therefore, if the conformation enabling γ-agostic interaction is populated at high T_p, then the polymer formed could be of very low stereoregularity.

Leclerc and Brintzinger [17b] performed polymerization of (E)- or (Z)-propene-1-d with 1(R/S)/MAO, and obtained D-atom coupled ^{13}C NMR spectra. They observed in addition to the triplet signal expected for the CHD group of the polymer backbone, another triplet signal for the mrrm methyl resonance (δ 19.4, $J(^{13}C, ^2D) = 18.9$ Hz). The significance of the latter is that most of the methyl group associated with a stereo-error carry a D-atom which must originate from the α-CHD group and not from the CH_3 substituent of the olefin. Eq. (5) was proposed [17b] for this isomerization.We note that in this mechanism the Zr^+ center has migrated to the next carbon in the chain. If this process proceeds further instead of reversing itself, then β-hydride elimination should produce internal double bonds. Appreciable amounts of 1,2 disubstituted and 1,1,2 trisubstituted internal olefins were found by ^{13}C NMR spectra in poly(hexene) obtained with ansa-zirconocene catalysts [31]. This is consistent with the proposed isomerization by Eq. (5).

Rieger et al. [31] suggested that "δ-forward" and "λ-backward" conformational isomerization occurs in some ansa-zirconocene complexes. Burger et al. [32] reported non-axial distortions due to thermally induced excursion of 30° and more from the expected axial symmetry for other zirconocene compounds. At sufficiently elevated temperatures, indenyl ring slippage, dissociation of one η^5 ligand, or isomerization to a meso compound may happen. All these structural changes can adversely affect stereochemical control.
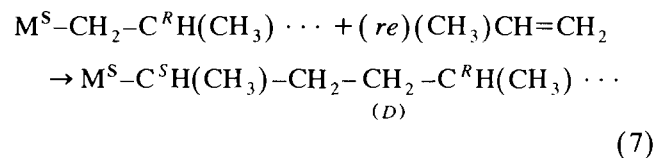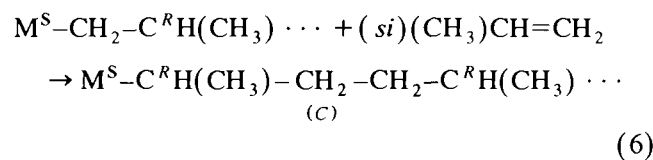
There are other processes which can cause steric inversion and involve only one metal center. Stehling et al. [17c] proposed reversible β-hydride elimination and reinsertion of the oligo-olefin to account for the reversal of the configuration of the methine carbon of the last monomer unit. The facial selectivity for insertion of olefins into Zr–H in these catalysts is opposite from that of insertion into Zr–C bond. Similarly, Busico and Cipullo [17a] postulated that the L_2Zr^+P ion can undergo a sequence of hydride shifts, rotations of the eliminated olefin, followed by reinsertion resulting in the epimerization of the β-carbon of the last insertion monomer unit.

All the processes considered in this section involve only a single active species in contrast to the bimolecular nature of the processes of Section 3.2.

3.4. Regioirregular insertion

Regioirregular 2,1- and 1,3-mis-insertions, seen in Fig. 2, are common for poly(propylene) formed by racemic ansa-zirconocene catalysts [15b,21]. The amount of mis-insertion is between one and a few percent, depending upon experimental conditions. This work has shown that these misinsertions are not detectable in the case of catalysis by $1^+(S)$. Furthermore, the amounts of regioirregular errors are reduced in catalysis by $1^+(R/S)$ if its concentration is low or if it is immobilized. This suggests that there is some commonality between the regiochemical mis-insertions and stereochemical inversions (vide supra). A plausible explanation may be offered as follows.

The secondary insertion of either si propylene (Eq. (6)) or re propylene (Eq. (7)) to the normal propagating species type A

$$M^S-CH_2-C^RH(CH_3) \cdots +(si)(CH_3)CH=CH_2$$
$$\rightarrow M^S-C^RH(CH_3)-CH_2-CH_2-C^RH(CH_3) \cdots$$
$$(C)$$
$$(6)$$

$$M^S-CH_2-C^RH(CH_3) \cdots +(re)(CH_3)CH=CH_2$$
$$\rightarrow M^S-C^SH(CH_3)-CH_2-CH_2-C^RH(CH_3) \cdots$$
$$(D)$$
$$(7)$$

is energetically unfavorable compared with the primary NFA (Eq. (8), case 1 of Table 4).

$$M^S-CH_2-C^RH(CH_3) \cdots +(si)CH_2=CH(CH_3)$$
$$\rightarrow M^S-CH_2-C^RH(CH_3)-CH_2-C^RH(CH_3) \cdots$$
$$(8)$$
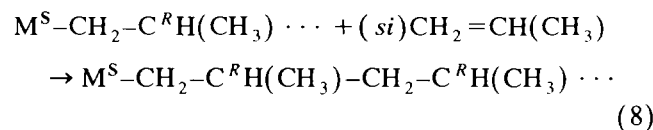
The rates of Eqs. (6) and (7) are about one-hundreth that of Eq. (8) [34]. MM2 calculations estimate the

steric energy differences to be $E_{s,6} - E_{s,1} \approx 6.2$ kcal mol^{-1} and $E_{s,7} - E_{s,1} \approx 6.6$ kcal mol^{-1} in the transition state [10]. In contrast, secondary insertion to type B species formed via Eq. (4) has ΔE_s of only about 2.3 kcal mol^{-1} more than that for the primary NFA (Eq. (8)). Consequently, when interchange Eq. (4) occurs so does regioirregular 2,1-insertion. Species C and D have a strongly reduced propagation rate of the order of 10^3 slower than the normal insertion rate [34]. In fact species C and D preferentially undergo elimination of the β-hydrogen from the α-methyl group, and subsequent reinsertion of this product olefin affords the tetramethylene sequence referred to as 1,3-misinsertion [15b,21].

4. Experimental

4.1. General laboratory materials and equipment

All operations were performed under argon using glove-box or Schlenk techniques. Ethylene and propylene were supplied by Mariam-Graves Co. Argon, ethylene and propylene were deoxygenated with activated BTS catalyst and dried over molecular sieves and P_2O_5. Celite was purchased from Fischer Scientific Co. and used without further treatment. Toluene, pentane, hexane and THF were refluxed and distilled from Na/K alloy. CH_2Cl_2 was dried and distilled from CaH_2.

4.2. Catalysts

The procedure of Schäfer et al. [35] was adapted to synthesize 1,2-ethylenebis(4,5,6,7-tetrahydro-1S-indenyl)$_2$Zr(O-acetyl-R-mandelate)$_2$ (1) and a diastereomeric mixture of 1,2-ethylenebis(4,5,6,7-tetrahydro (1R/S-indenyl)$_2$Zr(O-acetyl-R-mandelate)$_2$. The crystalline product is the S-enantiomer 1; the ^{1}H NMR spectrum is given in column 1 of Table 5. The mother liquor contains some S, and mostly R, isomers. The ^{1}H NMR spectrum of the latter is contained in column 2. The as-prepared 1(R/S) has a spectrum which is consistent with a racemic mixture.

Other literature procedures were applied for the synthesis of rac-Et[IndH$_4$]ZrCl$_2$ [35], 1,2-ethylenebis(4,5,6,7-tetrahydro-1S-indenyl)$_2$ZrMe$_2$ [24], 1,2-ethylenebis(4,5,6,7-tetrahydro–indenyl)$_2$Zr(O-acetyl-R-–mandelate)$_2$ [36] and Ph$_3$CB(C$_6$F$_5$)$_4$ (2) [37].

A silica-supported catalyst 1,2-ethylenebis(4,5,6,7-tetrahydro-1S-indenyl)$_2$Zr(O-acetyl-R-mandelate)$_2$/ MAO/SiO$_2$ was prepared following a modified procedure of Chien and He [22]. Silica (PQ Corp. grade CS-1022) was heated at 400°C under Ar for 12 h and then at 100°C under vacuum for 12 h. At room temperature, 7.07 ml MAO (Akzo, 3.11 M toluene solution, 22 mmol) was added to a suspension of 0.94 g of the calcined SiO$_2$ in 10 ml of toluene. The mixture was vigorously stirred for 30 min. After it was filtered in a Schlenk apparatus and washed with 5 × 50 ml of toluene, the MAO/SiO$_2$ precursor was brought into contact with 74 mg of 1 (0.1 mmol) in 10 ml of toluene and vigorously stirred for 1 h. The solid was then separated by filtration and washed with 5 × 10 ml of toluene. It was then vacuum dried overnight to give the supported catalyst having a Zr content of 8.0×10^{-2} mmol g^{-1} catalyst. Silica-supported catalyst 1,2-ethylenebis(4,5,6,7-tetrahydro1R/S–indenyl)$_2$Zr(O-acetyl-R–mandelate)$_2$/MAO/SiO$_2$ was synthesized by the same approach and was analyzed to have the same Zr content of 8.0×10^{-2} mmol g^{-1} catalyst.

4.3. Polymerization

Polymerization was performed in a 250 ml crown-capped pressure vessel containing 50 ml of toluene, saturated with 15 psig of monomer and containing a magnetic stir bar. Between 1 and 2 mM of TIBA was introduced first, followed by the zirconocene compound and finally by an equimolar amount of the cocatalyst 2. Polymerization was quenched with acidic methanol (2 vol.% of HCl). After stirring for at least 2 h, the polymer was separated by filtration, vacuum dried overnight and characterized.

4.4. Characterization

^{1}H NMR spectra were obtained with a 200 MHz Bruker spectrometer. ^{13}C NMR spectra of polypropylene were obtained with a 500 MHz Bruker spectrometer at 110°C using d_2-Cl$_2$CHCHCl$_2$ as solvent. Elemental analyses were performed by Microanalytical Lab. at the University of Massachusetts, Amherst. Thermal data (melting point T_m and heat of fusion ΔH_f) of polymers were recorded on a Perkin-Elmer DSCIV. The scan rate was 20°C min^{-1} and two scans were made. After the first scan, the temperature was held for 5 min above the melting transition temperature and then cooled down. The data of the second scan were used. Intrinsic

Table 5
^{1}H NMR (CDCl$_3$) data for ethylenebis(tetrahydroindenyl)$_2$-Zr(O-acetyl-R-mandelate)$_2$

S-enantiomer	R-enantiomer	Assignment
7.55(m)	7.56(m)	C$_6$H$_5$
7.35(m)	7.36(m)	
5.83(d)	5.80(s)	CH–COOZr
5.70(d)	5.65(d)	C$_5$H$_2$
5.20(d)	5.40(d)	
3.1–3.0(m)	3.1–3.0(m)	CH$_2$
2.9–1.1(m)	2.9–1.1(m)	CH$_2$
2.24(s)	2.27(s)	CO–CH$_3$

viscosity was measured for PE or PP in decalin at 135°C and the M_w of the polymer was calculated from it [20].

5. Conclusions

Propylene polymerization catalyzed by $1^+(S)$ is highly stereo- and regiospecific. In comparison the racemic $1^+(R/S)$ catalyst produced poly(propylene) with stereo- and regioirregularities. The irregularities diminish with a lowering of T_p, catalyst concentration and catalyst mobility, or with an increase of $[C_3H_6]$. This has been interpreted to mean interchange of chains on metal centers of opposite configurations. How important is this type of process in the introduction of stereoerrors vis-à-vis the other processes of Section 3.3 involving only a single active species? The question was investigated with a σ_S-symmetric syndiospecific precursor diphenylmethylidene $(1-\eta^5$-cyclopenta-dienyl)$(9-\eta^5$-fluorenyl)zirconium dichloride (5) activated with TIBA and 2 [38]. Both the zirconium center and the poly(propylene) chain bound to it in this system are achiral, therefore, processes like Eq. (4) should not be a source of stereoerrors. However, the isomerization and epimerization of Section 3.3 would inject stereoerrors into the syndiotactic microstructure. Variations of T_p, [Zr], and immobilization of 5 on SiO_2 were all found to have a very small effect on the [$rrrr$] fraction in the ^{13}C NMR spectrum of the polymer. There were no observable peaks due to 2,1- and 1,3-misinsertions. These results indicate that Eq. (4) is probably the dominant contributor to stereoerror formation for the polymerization catalyzed by $1^+(R/S)$.

The ligand framework of a precursor can be designed to enchance its stereoselectivity. Some of the successful approaches are the incorporation of bulky or cyclic bridging moieties [16], strategic placement of aliphatic or aromatic substituents on the η^5-ring [39], and annelation to the indenyl group [17c,40]. Very high stereo- and regiospecificity had been achieved with these catalytic systems. Presumably, the accessibility of the metal center for chain interchange or freedom for intramolecular isomerization, eqpimerization, and hydrogen elimination were delimitated. A combination of a specially designed catalyst, immobilized in a support, seems to be the most promising approach for a commercially viable isospecific catalyst suitable for current manufacturing technologies.

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