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The Strange Case of the "Oscillating" Catalysts

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Summary: The field of stereoselective propene polymerization has been dramatically innovated by the discovery of homogeneous metallocene-based catalysts with well-defined and tunable molecular structure. Of all, "oscillating" metallocenes are probably the most ingenious and challenging example of catalyst design. Their catalytic species were built to "flip-flop" between a chiral and an achiral conformation, at a rate intermediate between those of monomer insertion and chain transfer. The result of this molecular switching would be a polypropylene with an isotactic/atactic stereoblock structure, performing as a thermoplastic elastomer. This essay discusses how the real polymerization mechanism differs from what the catalyst inventors had in mind, but also how - through fortunate circumstances - their optimism has been rewarded.

Introduction

The advent, in the mid-'80s, of metallocene-based catalysis was a true revolution in the world of stereoselective olefin polymerization.[1,2] After thirty years since the initial discoveries of Karl Ziegler and Giulio Natta,[3,4] and five generations of increasingly effective but poorly understood heterogeneous catalysts,[5] it was ultimately found that homogeneous catalytic species with well-defined precursors and a predetermined ligand environment of the active transition metal can promote with high productivity the regio- and enantioselective polyinsertion of 1-alkenes.

Polypropylene synthesis, in particular, became a favorite playground (which is understandable, in view of the enormous industrial significance of this resin[5]). In a comparatively short time, classes of metallocene catalysts were developed with almost any conceivable kind of stereocontrol (isotactic, syndiotactic, atactic, hemiisotactic), and - most importantly - the relationship between selectivity on one

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hand, and symmetry and structure of the catalytic species on the other, was clarified.[1,2]

All of a sudden, the dream to tailor a catalytic species to a desired polymer architecture looked close to reality. Therefore, when a rational route to isotactic/atactic stereoblock polypropylene (a material of high potential interest for applications as a thermoplastic elastomer) was announced,[6] the scientific community was - in a way - prepared and there was little room for skepticism.

The idea behind the catalyst design was elegant and conceptually simple (Chart 1 - P = Polymer chain; only C-C bonds traced in the saw-horse chain representations). As is well-known, stereorigid *ansa*-metallocene catalysts in which two indenyl ligands are locked by a bridge in a *rac*-C_2-symmetric (Chart 1-a) or a *meso*-C_s symmetric (Chart 1-b) configuration afford isotactic and atactic polypropylene, respectively.[1,2] The former is a semicrystalline thermoplastic material, with a melting temperature of up to 165°C; the latter, instead, is uncrystallizable and moderately elastomeric.[5] With this premise, how about preparing *unbridged* bis-indenyl catalysts with substituents of tunable size on the rings, in such a way that hindered ligand rotation is allowed, and a *rac*/*meso* conformational rearrangement occurs at a rate intermediate between those of monomer insertion and chain growth (transfer)?

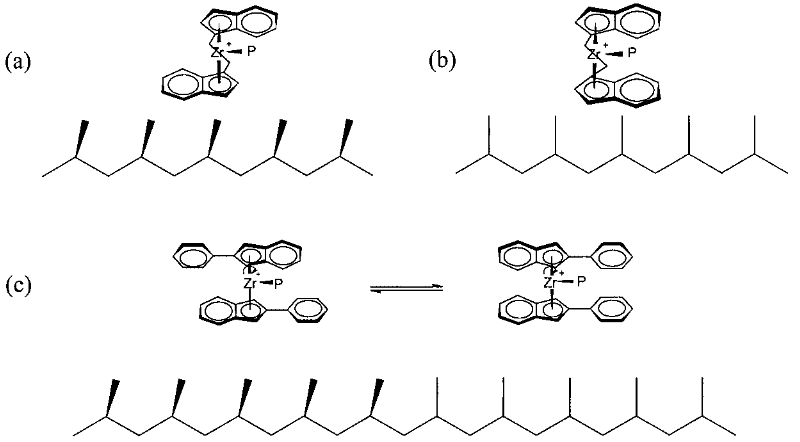


Chart 1

The concept substantiated in the form of (2-Ar-Indenyl)$_2$ZrCl$_2$ complexes, where Ar is an aryl group which can range from a simple phenyl (**1**; Chart I-c)[6] to much more complicated and bulky moieties, like 3,5-di-*tert*-butyl-4-methoxy-phenyl (**2**; Chart 2).[7] Single crystal X-ray diffraction had proved that complex **1** crystallizes in mixed "*rac*-like" and "*meso*-like" conformation.[6] When combined in toluene solution with methyl-aluminoxane (MAO) or another suitable activator,[1,2] it gives rise to a propene polymerization catalyst of decent activity. Remarkably, the polypropylene produced is largely stereoirregular, but also contains a highly isotactic part;[6,7] the fact that it does perform as a thermoplastic elastomer[6-8] was taken as an indication that at least part of the isotactic and atactic sequences are chemically bound, and that crystalline domains act as physical crosslinks between amorphous ones.[8] In turn, this was perceived as a validation of the mechanistic picture of Chart 1-c, and the whole class of (2-Ar-Indenyl)$_2$ZrCl$_2$ catalysts gained the now popular definition of "oscillating", and were credited as clean "molecular switches".[6-10]

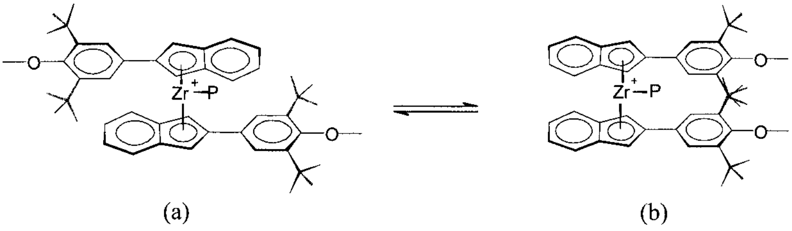


Chart 2

However, the following facts should have suggested that the reality is somewhat more complicated:

i) Solution NMR investigations on model complexes, down to very low temperatures, did not provide evidence for a slow *rac*/*meso* interconversion .[11]

ii) Although even small changes in the ligand framework can affect the stereoselectivity dramatically, no clear structure/performance correlation could be found.[7]

iii) Computer modeling by means of molecular mechanics, alone[12] or combined with quantum mechanics,[13] confirmed that, for complex **1**, the *rac*-like and *meso*-like conformations correspond to energy minima (the former being slightly deeper), but the activation energy for their interconversion was estimated to be fairly low (2-5 kcal/mol),[13] and - at most - comparable with that for monomer insertion (5-15 kcal/mol).[1] Considering that the latter is a bimolecular process (hence with a large negative activation entropy), it is difficult to imagine how it can be (much) faster than the intramolecular *rac*-like/*meso*-like rearrangement. Higher interconversion barriers were calculated for complexes with bulkier Ar substituents, such as **2**,[14] but in that case the *meso*-like conformation turned out to be much less stable than the *rac*-like one, due to unfavorable contacts between the Ar groups (apparent already on inspection of Chart 2-b).

iv) Last but not least, the polymers have broad molecular mass distributions, which is rather unusual with homogeneous catalysts; moreover, they can be solvent separated in fractions largely differing in stereoregularity, from completely amorphous (though not purely atactic) to highly crystalline (though not completely isotactic).[2,7,8] Altogether, this strongly suggests the presence of more than one catalytic species, possibly in equilibrium but with average life-times longer than the average growth time of individual macromolecules.

On the other hand, direct proof (or disproof) of the mechanism in Chart 1-c by means of a microstructural characterization of the polymers was never provided. That is what we decided to achieve.

Reading "oscillating polypropylenese"

Stereoselective polymerization is a very special case of asymmetric synthesis. For a reaction affording low-molecular-mass products, the effectiveness of the asymmetric induction can be measured in terms of the so-called enantiomeric excess (*i.e.*, the difference in fractional abundance of the two resulting enantiomers), but this is practically uninformative on the reaction mechanism. For a polymerization, instead, the fact that the products of individual reaction steps (*i.e.*, the monomeric units) are permanently enchained in the form of macromolecules represents an extraordinary advantage for mechanistic purposes. In fact, from the stereochemical characterization of a polymer, in addition to the degree of stereoregularity (which is the equivalent of the enantiomeric excess), the way each reaction step affected the subsequent one(s) can also be derived. In this respect, a polymer chain contains its complete birth story, sequentially recorded like on a tape; of course, to know that story one must be able to read the tape.

For decades, we Ziegler-Natta chemists have tried to do so with polypropylene, in order to trace the behavior of our complicated and molecularly ill-defined heterogeneous catalysts. Year after year, our reading has become more and more fluent, and our understanding lately deeper and deeper.[15,16]

"Polypropylenese" is a rather weird language, based on two letters only - namely, "*m*" and "*r*" (Chart 3-a) - but with a fairly high number of local dialects. The isotactic version, in particular, makes use predominantly of *m*'s in long strings, with just a few *r*'s usually occurring in couples (*rr*) (Chart 3-b). The atactic form, instead, is much more varied, with an equal number of randomly distributed *m*'s and *r*'s (Chart 3-c).

Understanding the two is not difficult, unless they are intermixed, which is unfortunately the case for polypropylene made with oscillating metallocenes. In particular, to solve the problem introduced in the previous Section one has to judge whether whole polymer chains, or - rather - different segments within individual chains, are written in the two idioms. This requires much more than merely counting the characters (*m* and *r* diads), or even the syllables (*mm*, *mr* and *rr* triads); in fact, one has to look at whole words, and to check for the possible presence of hybrid ones (Chart 3-d).

Our reading eye for "polypropylenese" is ^{13}C NMR.[15] Routine ^{13}C NMR spectra of polypropylene give easy access to the distribution of sequences with up to four characters (pentads; Figure 1, top), but this is not enough yet for the considered case.[9,17] In our laboratory, however, we have recently developed high field (150 MHz) ^{13}C NMR techniques enabling us to go further - in favorable cases up to twelve characters, more typically from six to eight (Figure 1, bottom).[15,16,18]

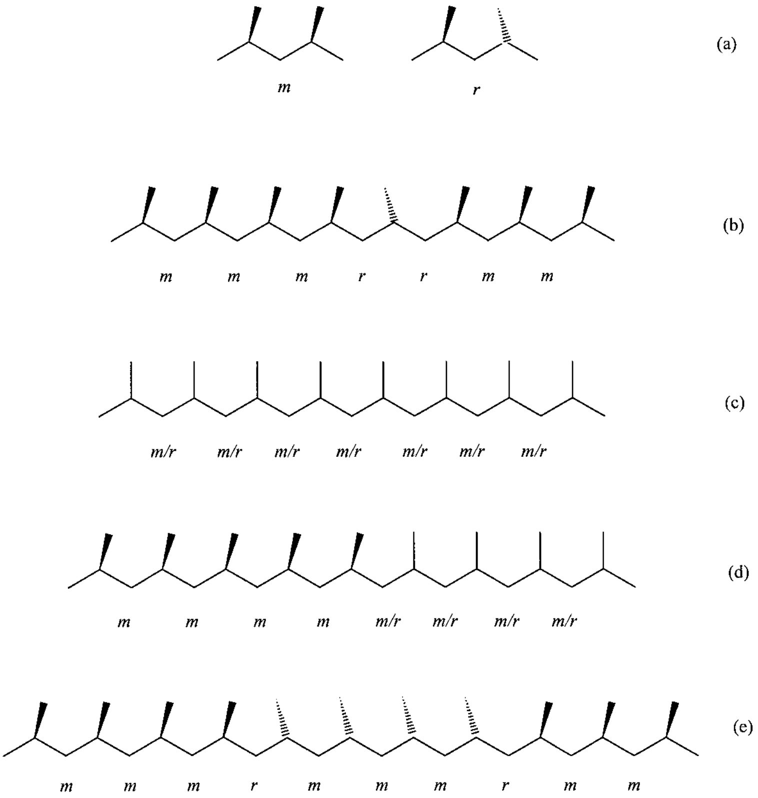


Chart 3

When we applied this tool to samples of polypropylene made with two representative oscillating catalysts, namely **1** and **2** (activated at 20°C in toluene solution with typical co-catalysts such as MAO or N,N-dimethylanilinium *tetrakis*-perfluorophenylborate/Al(*iso*-Butyl)$_3$)[1,2] what we read was partly unexpected.

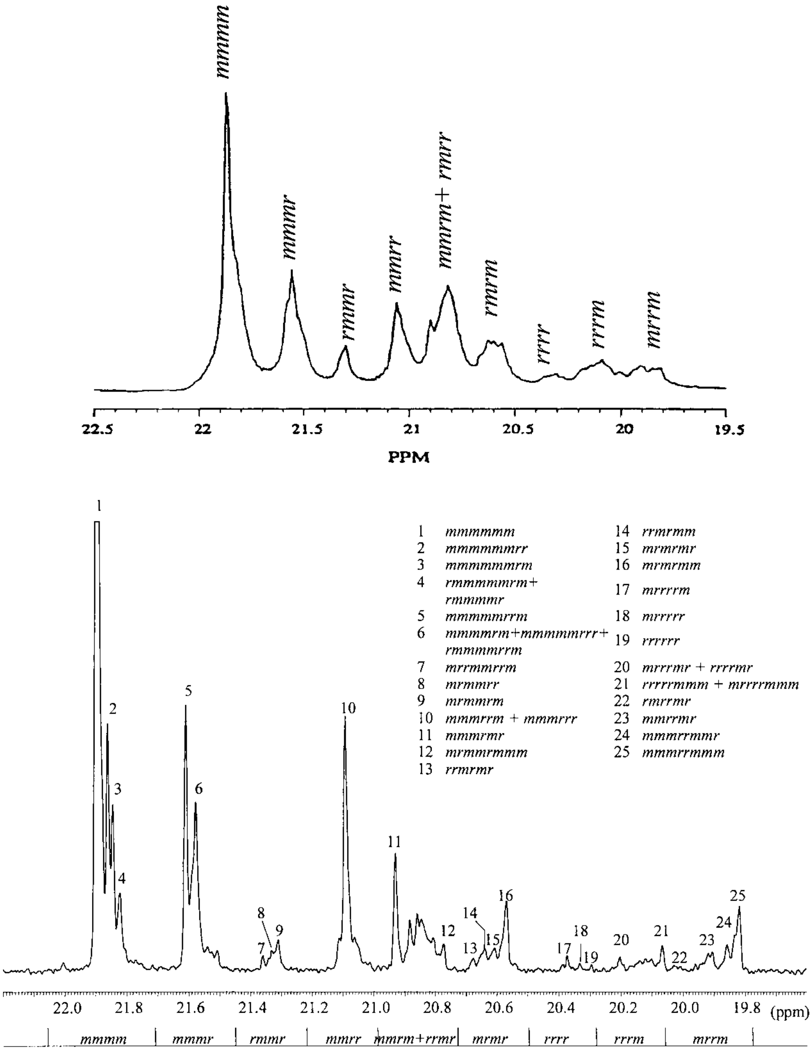


Figure 1. Methyl region of the ^{13}C NMR spectra of typical polypropylene samples prepared with catalyst **1**. Top - 100 MHz (adapted from ref. *9*). Bottom - 150 MHz (this work). The chemical shift scale is in ppm downfield of tetramethylsilane. Thanks to a very high resolution and a full resonance assignment, in the 150 MHz spectrum it was possible to identify for the first time peaks (no. 11 and 16) mostly due to junctions between isotactic and (quasi-)atactic blocks.[19]

In agreement with the literature,[2,7,8] the polymers obtained with **1** could be solvent-separated in fractions according to crystallinity, from nil up to 60%, as measured by X-ray diffraction (Table 1, entries 1-4). In all fractions we found isotactic segments (with traces of *rr* stereodefects), along with largely stereoirregular ones, and it was gratifying for us to be the first to recognize, in the semicrystalline fractions, points of switch between the two (*e.g.*, the intense *mmmrmr* and *mrmrmm* methyl heptads; Table 2 and Figure 1-right).[19] To our surprise, however, we also noted that the non-crystallizable blocks were not truly atactic, but contained a slight excess of *m*'s, although still distributed at random as the atactic grammar requires;[15] this feature was more pronounced the higher was monomer concentration in the feed (compare the values of the P_m parameter for entries 1,2 and 3,4 in Table 1).

Table 1. Results of propene polymerization in the presence of the "oscillating" metallocene catalysts **1** and **2** (see text)

Entry no.	Catalyst/ Co-catalyst	Solvent	$[C_3H_6]$, mol/L	[*mmmmmm*], % a)	P_m b)	T_m, °C c)	Δh_m, J/g c)
1	**1/MAO**	Toluene	1.5	5	0.56	-	-
2	**1/MAO**	Toluene	6.7	8	0.58	-	-
3	**1/Borate** d)	Toluene	1.5	13	0.53	133	7
4	**1/Borate** d)	Toluene	6.7	23	0.59	140	10
5	**2/MAO**	Toluene	1.5	30	0.84	90	4
6	**2/MAO**	Toluene	6.7	52	0.91	140	34
7	**1/Borate** d)	ODCB e)	1.5	4	0.52	-	-

Experimental conditions: T = 20°C; [Zr] = 3×10^{-5} mol/L; [Al]/[Zr] = 1.0×10^{3} (for activation with MAO); [B]/[Zr] = 2.5, [Al]/[Zr] = 3.0×10^{2} (for activation with dimethylanilinium *tetrakis*-perfluorophenylborate/Al(*iso*-Butyl)$_3$); polymerization time, 1.00 h.

a) ^{13}C NMR fraction of isotactic heptads in the whole sample.

b) Conditional probability of *m* diad formation during stereoirregular chain propagation, estimated by statistical analysis of the ^{13}C NMR stereosequence distribution.[15]

c) Measured by Differential Scanning Calorimetry (DSC) on 2nd heating scan.

d) *tetrakis*-perfluorophenylborate/Al(*iso*-Butyl)$_3$).

e) 1,2-dichlorobenzene.

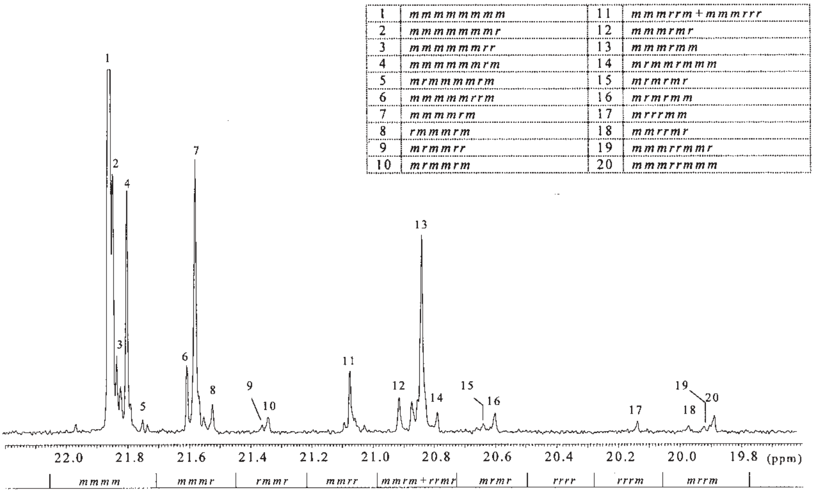
Table 2. 150 MHz ^{13}C NMR stereosequence distribution of the diethyl-ether-soluble/hexane- insoluble fraction of a polypropylene sample prepared with catalyst **1** (Table 1, entry 4), and best-fit calculated one in terms of two stochastic models: one assuming the sample as a physical mixture of isotactic and (quasi-)atactic chains, another as an isotactic/(quasi-)atactic stereoblock polymer.[9,15,16,19] The latter model ends up with a much better agreement, as the reduced-χ^2 test indicates.

Stereosequence	Normalized fraction		
	Experimental	Calculated (physical mixture)	Calculated (stereoblock)
mmmm	0.4854(63)	0.4833	0.4875
mmmmmm	0.3808(66)	0.3832	0.3752
mmmr	0.1453(20)	0.1437	0.1446
mmmmrr	0.0716(39)	0.0705	0.0724
rmmr	0.0212(20)	0.0236	0.0197
mmrr	0.0990(20)	0.1022	0.0989
mmrm+rmrr	0.1096(20)	0.1149	0.1098
mmmrmr	0.0330(20)	0.0226	0.0324
rmrm	0.0521(20)	0.0472	0.0504
mrmrmm	0.0288(20)	0.0226	0.0306
rrrr	0.0093(20)	0.0078	0.0089
rrrrrm	0.0030(20)	0.0027	0.0030
rrrrrr	0.0012(10)	0.0008	0.0009
rrrm	0.0278(20)	0.0262	0.0285
rmrrmr	0.0030(20)	0.0025	0.0019
mmrrmr	0.0128(20)	0.0133	0.0121
mmrrmm	0.0345(20)	0.0353	0.0336
		Isotactic content = = 57 wt.-% $\chi_r^2 = 4.0$	$P_{iso/ata} = 0.19$ [a)] $P_{ata/iso} = 0.33$ [b)] $\chi_r^2 = 0.3$

[a)] Conditional probability of switching from isotactic to (quasi-)atactic propagation.
[b)] Conditional probability of switching from (quasi-)atactic to isotactic propagation.

Even more surprisingly, in polypropylene samples prepared with catalyst **2** the chains turned out to be largely written in a more exotic dialect, made of strings of consecutive *m*'s mostly separated by randomly distributed *single r*'s (Chart 3-e and

Table 3); this can be seen on inspection of the high-field ^{13}C NMR spectrum of Figure 2, showing an intense sharp peak corresponding to the *mmmrmm* heptad.



1	*mmmmmmmm*	11	*mmmrrm+mmmrrr*
2	*mmmmmmmr*	12	*mmmrmr*
3	*mmmmmmrr*	13	*mmmrmm*
4	*mmmmmmrm*	14	*mrmmrmmm*
5	*mrmmmmrm*	15	*mrmrmr*
6	*mmmmmrrm*	16	*mrmrmm*
7	*mmmmrm*	17	*mrrrmm*
8	*rmmmrm*	18	*mmrrmr*
9	*mrmmrr*	19	*mmmrrmmr*
10	*mrmmrm*	20	*mmmrrmmm*

Figure 2. Methyl region of the 150 MHz ^{13}C NMR spectrum (in 1,2-tetrachloroethane-d_2 at 90°C) of a polypropylene sample prepared with catalyst **2** (Table 1, entry 6). The chemical shift scale is in ppm downfield of tetramethylsilane; the assignment is based on Ref. 13. The presence in the sample of isotactic sequences separated by *single r* diads is apparent already on inspection (see, in particular, the intense peaks numbered as 4, 7 and 13).

We can view this as an extreme degeneration of the atactic form, exaggerating the deviation just described for catalyst **1** and thus ending up with a much larger defect of *r*'s. As a matter of fact, in this case too the fraction of *m*'s turned out to increase with increasing propene concentration in the feed (Table 1, entries 5 and 6).

All this combines in an intriguing story, which proves - if needed - that science and common sense are not always good friends.

Table 3. 150 MHz ^{13}C NMR stereosequence distribution of a polypropylene sample prepared with catalyst **2** (Table 1, entry 6), and best-fit calculated one in terms of a stochastic model assuming chain propagation at a *rac*-like catalytic species oscillating between its two enantiomorphous forms (see text).

Stereosequence	Normalized fraction	
	Experimental	Calculated
mmmm	0.6446(125)	0.6495
mmmmmm	0.5178(127)	0.5266
mmmmmr	0.1082(30)	0.1165
mmmr	0.1419(22)	0.1436
mmmmrr	0.0255(20)	0.0267
rmmr	0.0105(20)	0.0079
mmrr	0.0342(20)	0.0329
mmrm+rmrr	0.1336(22)	0.1303
mmmrmm	0.0991(20)	0.1025
mmmrmr	0.0147(22)	0.0116
rmrm	0.0162(20)	0.0143
mrmrmm	0.0098(20)	0.0102
rrrr	0.0009(20)	0.0005
rrrm	0.0045(20)	0.0053
mrrm	0.0145(20)	0.0156
mmrrmr	0.0029(20)	0.0028
mmrrmm	0.0116(20)	0.0127
		$P_{osc} = 0.086$ a) $\sigma = 0.985$ b) $\chi_r^2 = 1.3$

a) Conditional probability of oscillation of the catalytic species.

b) Probability to select the preferred monomer enantioface at each enantiomorphous catalytic species.

From microstructure to mechanism

The presence of isotactic sequences with minor amounts of *rr* stereodefects (Chart 3-b) in polypropylene samples made with (2-Ar-Indenyl)$_2$ZrCl$_2$ catalysts proves unquestionably that the catalytic species can exist in solution in the *rac*-like conformation for a time longer than that required for a single monomer insertion. Conversely, the genesis of stereosequences with an excess of *m* diads separated by *single r* diads (Chart 3-e) is more ambiguous. In principle, they might be ascribed to chain propagation under the chiral control of the growing chain end (1,3-*like* asymmetric induction)[15,20] when the catalytic species is in the achiral *meso*-like conformation. In such a case an occasional failure of stereocontrol, inverting the configuration of the last inserted unit, would be perpetuated until another failure takes place. Sporadic examples of weak isotactic chain-end control have actually been reported for metallocene catalysts with non-chirotopic sites,[1,2,15,21] but only with bis-cyclopentadienyl ligands and at very low temperature (<<0°C); moreover, a dependence of the extent of chain-end control on monomer concentration has never been observed, at least to our knowledge.

A much more plausible hypothesis is that such blocks are formed instead at a *rac*-like catalytic species which oscillates between its two enantiomorphous forms (rather than to and from the less stable *meso*-like form), at a rate (slightly) lower than that of monomer insertion (Chart 4-bottom).[19] Indeed, as is well known for the *rac*-*ansa*-metallocene homologues (Chart 1-a), opposite monomer enantiofaces are inserted at active species with opposite chirality.[1,2] This offers an immediate and simple explanation for the otherwise puzzling increase of the *m* fraction (P_m) - or, equivalently, of the average length of the m_n strands - with increasing monomer concentration (because that speeds up the polyinsertion, but not the oscillation).

From Table 1, one has to conclude that the ratio between the average rates of monomer insertion and ligand rotation (which is roughly coincident with $P_m/(1-P_m)$) is critically dependent on the Ar substituent. In particular, it can be comparatively high ($P_m>0.90$) for the bulky catalyst **2**, whereas for the much less hindered catalyst **1**, in the time scale of monomer insertion, ligand rotation can be regarded as almost free even in liquid propene, and the result is a quasi-atactic chain propagation ($0.50<P_m<0.60$. This obviously implies that, for the latter system, some contribution of the *meso*-like form to the catalytic activity cannot be ruled out). All this fits with the previously discussed results of computer modeling.[12-14]

Now we need to explain why a highly fluxional catalytic species can be frozen occasionally in one of the two mirror images of its *rac*-like conformation for a comparatively long time, and thus produce (long) isotactic blocks. An important clue is the co-catalyst effect: we noted indeed that, in particular for polypropylene made with catalyst **1**, changing MAO for N,N-dimethylanilinium *tetrakis*-perfluorophenylborate/Al(*iso*-Butyl)$_3$ results (*coeteris paribus*) in a significantly higher content of isotactic blocks (Table 1, entries 1,3 and 2,4). Keeping in mind that: i) the active species of metallocene catalysts are cationic;[1,2] ii) the co-catalyst has to be a "poorly coordinating" anion, in order not to form a tight ion couple that would preclude the access to the monomer;[1] and, iii) the polymerization is normally carried out in non-polar or weakly polar solvents (such as toluene or hexane), in which catalyst and co-catalyst are known to give rise to a variety of "loose" ion couples (monomer-separated, solvent-separated, etc.),[1,2,22] we conclude that it is the interaction with the counterion to freeze, in some of the possible arrangements, the oscillation of a *rac*-like $[(2\text{-Ar-Indenyl})_2\text{ZrP}]^+$ cation (Chart 4-top). In this respect *tetrakis*-perfluorophenylborate, which can establish

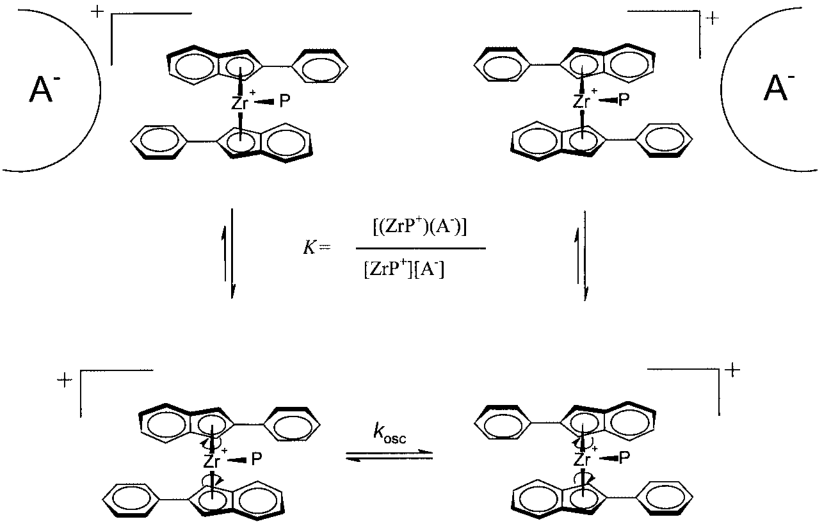


Chart 4

directional interactions with metallocene cations, seems to be more effective than the large and highly delocalized anion of MAO.[22,23]

If such hypothesis is correct, one has to anticipate that an increase in the polarity of the reaction medium will result in a decrease of what, in an admittedly crude attempt of simplification, can be defined as "overall association constant" K (Chart 4), and therefore of the isotactic content in the polymerization product. **This is actually the case.** In fact, we carried out two propene polymerizations with catalyst system **1**/N,N-dimethylanilinium *tetrakis*-perfluorophenylborate/Al(*iso*-Butyl)$_3$, under identical conditions except that toluene (dielectric constant, $\varepsilon = 2.38$ at 25°C) in one case, and 1,2-dichlorobenzene ($\varepsilon = 9.93$) in the other was used as the solvent (Table 1, entries 3 and 7); in the former case, the polymer turned out to be semicrystalline, with a fraction of isotactic heptads [*mmmmmm*] = 13% and a melting temperature $T_m \approx 133$°C, whereas in the latter **it was completely amorphous and atactic-like** ([*mmmmmm*] = 4%).

Moral

In conclusion, we believe that the true picture of an oscillating metallocene catalyst is the one shown in Chart 4. If one compares it with that in Chart 1,[6] one can realize how different (and also, unfortunately, more complicated) it is in molecular terms: rather than involving a *rac*-like and a *meso*-like conformation, the "oscillation" takes place (mainly) between the two enantiomorphous forms of the *rac*-like conformation, provided that the counterion leaves room for that. It is unquestionable that the Ar substituent on the indenyl ligands crucially drives catalyst dynamics; however (apart from possible electronic effects) changing its bulkiness affects, at the same time, the relative stability of the accessible conformations, their interconversion barriers and the cation/anion interlocking, which explains why it is hard not only to predict, but even to rationalize *a posteriori* the result on catalyst selectivity.

Therefore, if this story has a moral, we would say that it is close to the old saying that "Fortune favors the brave", and that the way to rational catalyst design can still be long, even for the "simple" metallocenes.

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