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Living Ziegler-Natta Polymerizations: True or False?

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Summary: Based on the recent literature, the synthesis of novel polyolefin architectures via Ziegler-Natta chemistry under living conditions appears to be a promising and fast-growing area. In this paper, the appropriateness of the term "living" as applied to the said context is discussed in mechanistic terms, and the potential and the limitations of the field are outlined with the aid of two paradigmatic case histories (i.e., propene polymerization in the presence of bis(phenoxy-imine)Ti and bis(phenoxy-amine)Zr catalysts).

Keywords: controlled; living; polypropylene; Ziegler-Natta polymerization

Introduction

Transition-metal-mediated olefin polymerizations under living conditions have become a field of rapidly growing interest and importance, as is witnessed by the recent literature.[1]

Such a development is by no means obvious. It may be worth recalling that a living polymerization is *"a chain polymerization from which chain transfer and chain termination are absent"*.[2] In reality, only few cases conform rigorously to the definition; however, it has become fairly common to extend it to *"controlled"* polymerizations, in which chain initiation is rapid relative to propagation, and chain termination and transfer are "negligible" in the time scale of the experiment, with the result that polymer molecular mass increases linearly with monomer conversion, and M_w/M_n is 1 or slightly higher.[3]

Even in this enlarged context, though, catalytic olefin polymerizations used to be uncommon until very recently; with just a few exceptions, indeed, olefin polyinsertion into transition

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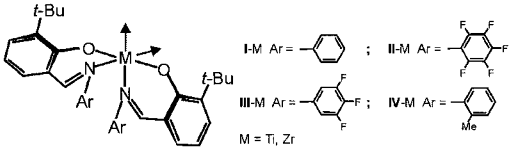
metal – carbon bonds is normally limited by fast β-H transfer. As a matter of fact, in typical cases the average chain growth time is well below 1 s,[4] which is all but controllable, and incompatible with applications like, e.g. block copolymerization. Therefore, the discovery of several new families of single-center Ziegler-Natta catalysts able to promote the living/controlled homo- and copolymerization of ethene, propene and higher 1-alkenes[1] can be regarded as surprising.

Of special interest are octahedral C_2-symmetric complexes of Column 4 metals bearing two phenoxy-imine ligands (see examples in Chart 1), developed independently by Fujita and coworkers[5] and by Coates and coworkers.[6]

Chart 1

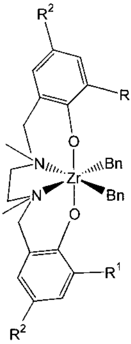


The former authors, in particular, noted that the living behavior seems to require that M = Ti, and that the aryl substituent on the imine N is *ortho*-F substituted (like in **II** of Chart 1). According to them, the function of this *ortho*-fluorination would be to prevent β-H transfer from the growing polymer chain, by establishing with it an *attractive* $^{\beta}$C-H$\cdots$^{o}F-C interaction.[7] On the other hand, Coates *et al.* claimed living ethene polymerization also in the absence of the said *ortho*-F.[8] We shall comment on the origin of this discrepancy in the final remarks.

Bis(phenoxy-imine)Ti systems have been used to prepare well-defined diblock copolymers of the type PP-*block*-PE and PP-*block*-EPR (with PP = polypropylene, PE = polyethylene, EPR = ethylene/propylene rubber).[1] A draw-back is that the PP blocks are *syndiotactic*, due to a very peculiar propene insertion mechanism entailing a 2,1 regiochemistry,[9] whereas an *isotactic* configuration is definitely more relevant for applications, e.g. aimed at phase compatibilization in poorly miscible polypropylene blends.

With a proper fine-tuning and activation of stereorigid C_2-symmetric Zr complexes with tetradentate bridged bis(phenoxy-amine) ligands (Chart 2; Bn = Benzyl), originally developed by Kol and coworkers and applied to the isotactic and living polymerization of 1-hexene,[10] in our laboratory we have recently been able to achieve the controlled polymerization of ethene and propene, the latter to highly isotactic polypropylene (iPP), and to prepare the first samples of iPP-*block*-PE and iPP-*block*-EPR.[11,12]

Chart 2



	R^1	R^2
1	^{t}Butyl	^{t}Butyl
2	Methyl	Methyl
3	1-Adamantyl	Methyl
4	9-Anthracenyl	Methyl

In this paper, reasoning on the said achievements, the factors that make a Ziegler-Natta catalyst suited to controlled olefin polymerization will be discussed, and common mechanistic features will be pointed out between catalyst structures that apparently have little in common. In particular, with the aid of experimental results and of computer modeling, it will be shown that *steric* – more than *electronic* – factors dominate catalyst performance (also) in this respect.

Results and Discussion

i) Bis(phenoxy-imine)M Catalysts

With proper activation of dichloride or dialkyl precursors, complex **II**-Ti of Chart 1, and its homologue with additional *p*-^{t}Bu groups on the phenoxide rings, have been reported as catalysts for the "living" homo- and copolymerization of ethene and propene, the latter to a highly syndiotactic polymer.[1,5-7] As already noted in the Introduction, based on DFT calculations it has been proposed that the reason for such a remarkable and atypical behavior is an *attractive* interaction between the *ortho*-F and a β-H of the growing polymer chain, making the latter less prone to be transferred to the metal and/or to the monomer; this has been described as a new strategy for the control of catalyst behavior, as opposed to the "classical" one making use of *repulsive* non-bonded contacts in the coordination sphere of the transition metal.[7] Recent results of solution NMR studies on model compounds seemingly provided an independent validation to the concept.[13]

We have been intrigued by such a possibility, which would substantially expand the available tools in catalyst design. Therefore, we have carried out a combined experimental and theoretical investigation on some of the new catalysts.[14] In this section, we report on the main results obtained.

We focused on propene polymerization, because the nature of the competing reaction paths is reasonably well-identified. In particular, a large body of experimental and theoretical results indicates that: i) propene insertion is the rate limiting step in chain propagation (i.e. the insertion transition state is the highest point of the reaction path); and also that ii) solvent and counterion effects, although undoubtedly important, are rather indiscriminate and do not largely affect the *relative* rates of the various possible insertion modes.[15,16] As a matter of fact, calculations which do not consider solvent and counterion explicitly, including those reported in previous papers on catalysts belonging to the very same class considered here,[9,17] are in very nice agreement with the experiments. For ethene, instead, it is still unclear whether the rate limiting step in chain propagation is monomer insertion or anion displacement from the active cation; very recent calculations are actually more consistent with the latter hypothesis.[18,19]

For reasons that will become clear in the following section, two different computational strategies were used to model the systems of Chart 1. In a first approach, referred to as "full-QM" from here on, all atoms were treated at Quantum Mechanics level. In a second approach, labeled as "QM/MM", the ^{t}Bu and Ar-on-N fragments were treated at Molecular Mechanics level. As an exemplification, the partitioning used in the QM/MM calculations for the specific case of **II**-Ti (Chart 1) is shown in Figure 1 (for more "technical" details, see Ref. [14]).

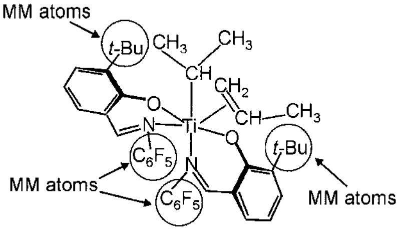


Figure 1. Partitioning between QM and MM treatment in the QM/MM approach for system **II**-Ti-^{i}Pr of Chart 1.

For Ziegler-Natta catalysts in general, β-H transfer *to the monomer* is normally much faster than to the metal.[15] We found experimentally[14] that bis(phenoxy-imine)M catalysts are no exception in this respect. In fact, the fraction of olefinic ends in the polypropylene chains turned out to be independent of propene concentration within the experimental uncertainty, which implies that chain propagation and β–H transfer have the same reaction order on the monomer.

As is well-known, the nature of M in these systems affects profoundly the regiochemistry of chain propagation. While M = Ti entails predominantly 2,1 (secondary) propene insertion into Ti-CH(CH_3)-CH_2-P (secondary chain),[5,6,17,20,21] for M = Zr 1,2 (primary) insertion into Zr-CH_2-CH(CH_3)-P (primary chain) is favored.[17,22] On the other hand, our calculations indicate that the lowest energy pathway of β-H transfer to propene involves the latter *always* in 1,2 orientation. This is fully consistent with (and at the same time explains) the experimental results of chain end-group analysis reported by Coates *et al.*[21] for non-*ortho*-F-substituted Ti-based catalysts, and by Fujita *et al.*[22] for Zr-based ones.

Assuming that the average polymer molecular mass is dictated by the competition between propene insertion and propene-induced chain transfer, we computed the internal energy difference ($\Delta E^{\ddagger}_{\text{T-P}}$) between the corresponding two transition states. In particular, the $\Delta E^{\ddagger}_{\text{T-P}}$ values relevant to this investigation correspond to β-H transfer to 1,2 propene from a secondary chain (simulated with an *iso*-propyl group) for M = Ti, and from a primary chain (simulated with an *iso*-butyl group) for M = Zr (Table 1).[23] It should be noted that the calculations did not include ZPE, thermal corrections, solvent and counterion effects; therefore, the results of Table 1 cannot be expected to predict absolute average polymerization degrees, but – rather – to reproduce trends, because (as noted before) the aforementioned corrections and effects can be safely assumed to be similar when comparing similar reaction profiles.

For a separate evaluation of electronic and steric contributions to $\Delta E^{\ddagger}_{\text{T-P}}$, we compared the results of a full-QM analysis (Table 1, column 3) with those of QM/MM calculations, in which the Ar substituents were treated at MM level, thus considering their steric effects only (Table 1, column 4).

Let us then examine the data, and in particular how $\Delta E^{\ddagger}_{\text{T-P}}$ is affected by the possible presence of *ortho*-F atoms on the Ar ring bound to the imine N (systems **I**-M and **II**-M).

Table 1. Calculated $\Delta E^{\ddagger}_{\text{T-P}}$ (in kcal/mol) for the systems of Chart 1 (see text).

System	Alkyl chain	$\Delta E^{\ddagger}_{\text{T-P}}$ (full-QM)	$\Delta E^{\ddagger}_{\text{T-P}}$ (QM/MM)
I-Ti	Secondary	4.0	4.8
I-Zr	Primary	-0.2	0.5
II-Ti	Secondary	8.8	9.9
II-Zr	Primary	0.4	1.6
III-Ti	Secondary	4.4	4.8
IV-Ti	Secondary	7.4	7.8

When M = Zr, $\Delta E^{\ddagger}_{\text{T-P}}$ is always close to 0, in line with the experimental finding that catalysts based on **I**-Zr and **II**-Zr are able – at most – to oligomerize propene.[22]

The picture changes remarkably when M = Ti. Both for **I**-Ti and **II**-Ti, $\Delta E^{\ddagger}_{\text{T-P}}$ is substantially larger than for the Zr homologues.[24] Importantly, however, the full-QM-calculated $\Delta E^{\ddagger}_{\text{T-P}}$ jumps from 4.0 kcal/mol for **I**-Ti to almost 9 kcal/mol for **II**-Ti. This is also in nice agreement with the experiments; indeed, catalysts based on **I**-Ti afford propene polymers of relatively low average molecular mass, whereas a “living” behavior is reported for catalysts based on **II**-Ti.[5-7]

In order to find a rationale for this, it is very instructive to compare the full-QM $\Delta E^{\ddagger}_{\text{T-P}}$ values with those resulting from the QM/MM approach. *The fact that they are very similar indicates that the main effect of the ortho-F in **II**-Ti is steric.* In fact, examining the relevant transition state geometries reveals that one of the said F atoms is at close non-bonded contact *with the monomer* in the transition states of both competing processes (Figure 2); another, in turn, is at critically short distance *from the growing chain* in the transition state of β-H transfer to the monomer (Figure 2b), but *not* in that of monomer insertion (Figure 2a).

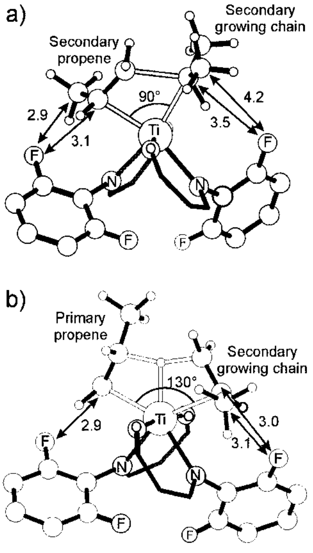


Figure 2. Transition states for 2,1 propene insertion, a) and β-H transfer to 1,2 propene, b) for **II**-Ti-^{i}Pr. For the sake of clarity, only the *ortho*-F atoms of the perfluorinated phenyl rings are shown, and the phenoxide rings are simply sketched in wire frame. Distances (in Å) between the *ortho*-F and the nearest-in-space C atoms of monomer and growing chain are given.

Remarkably, the remaining two *ortho*-F atoms, which point away from the active pocket, are by no means sterically irrelevant. In fact, their hindrance decreases the rotational freedom of the aromatic ring, which is in practice conformationally locked. As a matter of fact, if such two F's are removed,[5,25] according to our calculations the full-QM $\Delta E^{\ddagger}_{\text{T-P}}$ value drops from 9 to 6 kcal/mol, that is only 2 kcal/mol higher than for **I**-Ti. On the other hand, by replacing the remaining two *ortho*-F's with two larger methyl groups (system **IV**-Ti), $\Delta E^{\ddagger}_{\text{T-P}}$ goes up again (last row of Table 1).[26] In our opinion, all this provides a consistent picture on the steric nature of the *ortho* effect.

How crucial the *ortho*-substitution of Ar is on the balance between chain propagation and transfer is further indicated by the fact that **III**-Ti (with F atoms in *meta* and *para*, but not in *ortho*) and **I**-Ti have similar full-QM and QM/MM $\Delta E^{\ddagger}_{\text{T-P}}$ values.[5]

Interestingly, though, we did find out that the *ortho*-F atoms on Ar in **II**-Ti are not completely innocent from the electronic standpoint. Molecular orbital analysis gave evidence for a *partial attractive interaction* between one of them and the nearest α-H atom of the chain in the transition state of β-H transfer to the monomer, which is therefore slightly *stabilized* (Figure 3). This feature, on the other hand, turned out to be negligible in the (sterically more open) transition state of monomer insertion. Natural bond order (NBO) analyses[27] aimed at estimating the extent of this H···F bonding interaction resulted in a bond order of 0.02 only, which roughly corresponds to a stabilizing interaction of about 1 kcal/mol. It can be worth adding at this point that a similar weak intramolecular attractive H···F interaction has been detected experimentally in the aforementioned solution NMR study on model (phenoxy-pyridine)Zr-benzyl species with a -CF_3 ligand fragment at close non bonded contact with an α-(methylene)H of a benzyl group.[13]

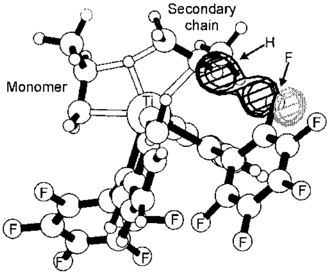


Figure 3. Transition state for β-H transfer to 1,2 propene at **II**-Ti-^{i}Pr, showing the attractive interaction of an *ortho*-F atom with an α-H atom of the growing chain. For clarity, only the MO portion which involves the H···F interaction (*ortho*-F···H distance, 2.1 Å) has been sketched.

Summing up all the above, we conclude that the "*ortho*-F effect" in propene polymerization promoted by bis(phenoxy-imine)Ti catalysts represents one more application of a general and consolidated concept, i.e. that chain propagation and chain transfer to the monomer have very different space requirements, and therefore react differently to ancillary ligand substitution. The former process has a compact four-center transition state, and the reacting atoms, which span an angle of ca 90°, can be accommodated in relatively small active pockets. The latter instead has a bulkier six-center transition state spanning an angle of ca 130°, which is more easily destabilized by the steric pressure of substituents suitably located in the ligand framework.[15,28,29] Previous cases of highly successful applications of the same concept are the pseudo-tetrahedral 2,2'-substituted *rac*-bis(1-indenyl) *ansa*-metallocenes,[30] and the square-planar Brookhart-type Ni and Pd catalysts.[31] In the following section, we shall see how to extend it usefully to stereorigid octahedral Zr complexes with bis(phenoxy-amine) ligands (Chart 2).

ii) Bis(phenoxy-amine)Zr Catalysts

Kol and coworkers reported[10] on the living and highly isotactic polymerization of 1-hexene promoted by the C_2-symmetric complex **1** of Chart 2, after activation by $B(C_6F_5)_3$.

In our hands, **1**/$B(C_6F_5)_3$ turned out to be inactive towards propene; on the other hand, with **1**/methylalumoxane (MAO) and **1**/$[HMe_2N(C_6H_5)][B(C_6F_5)_4]/Al(^iBu)_3$ we obtained moderately isotactic polypropylenes of very low average molecular mass in reasonable yields. ^{13}C NMR end-group analysis of samples prepared at different propene concentrations revealed a 1,2 insertion regiochemistry, and pointed to trans-alkylation by the Al-alkyl and β-H transfer *to the monomer* as the dominating chain transfer pathways.[32]

The former process was easily suppressed by reacting MAO or $Al(^iBu)_3$ with a sterically hindered phenol.[11,33] Contrasting the latter and improving the stereoselectivity, instead, required a fine-tuning of the ancillary ligand.[12]

Simple Quantum Mechanics/Molecular Mechanics (QM/MM) calculations (for details, see Ref. [12]) on models of active cations led us to conclude that the alkyl substituent R^1 (Chart 2 and Figure 4) is crucial not only for the enantioselectivity (which is expected, based on the well-known growing chain orientation mechanism of stereocontrol[15,32,34]), but also on the ease of monomer-induced chain transfer. Indeed, a bulkier R^1 makes chain mis-orientation (i.e., with the first C-C bond pointing *towards* the nearest-in-space R^1, rather than *away* from it) more difficult, and at the same time enhances the steric pressure on the space-demanding six-center transition state of β-H transfer to propene, which is therefore severely destabilized (Figure 4).

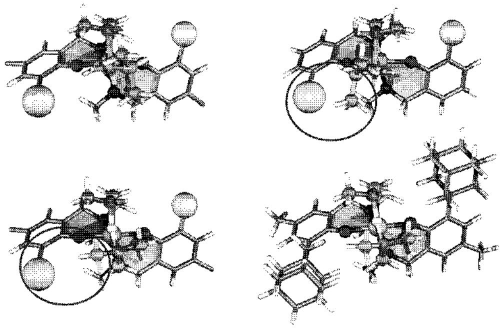


Figure 4. QM/MM transition states for propene insertion with the *re* (top, left) and *si* (top, right) enantioface, and for β-H transfer to the monomer (bottom, left), at an active bis(phenoxy-amine)Zr-^{i}Bu cation (Chart 2) with Λ configuration. Bulky R^1 substituents (generically represented with yellow spheres) disfavor the latter two processes, due to the repulsive contacts evidenced with circles. The extreme case of β-H transfer to the monomer when R^1 = 1-Adamantyl is explicitated (bottom, right).

In Table 2, we summarize the main results of our calculations, for the cases of R^1 = Methyl, ^{t}Butyl, 1-Adamantyl, and 9-Anthracenyl. In particular, for each model system we report the difference in internal energy between the transition states of 1,2 propene insertion with opposite enantiofaces ($\Delta E^{\#}_{\text{enantio}}$), and that ($\Delta E^{\#}_{\text{T/P}}$) between the transition states of chain transfer to the monomer and of chain propagation via 1,2 insertion with the favored enantioface. The values of $\Delta E^{\#}_{\text{T/P}}$ are scaled to the case with $R^1 = R^2 =$ H, used as a reference ($\Delta E^{\#}_{\text{T/P}} = 0$) and computed at full-QM level; once again, this means that such values can be used to predict relative trends, but not absolute average polymerization degrees. In all cases, R^1, R^2 = Alkyl (Chart 2) were modeled at MM level, and the growing polypropylene chain was simulated with an ^{i}Butyl.

Table 2. Calculated values of $\Delta E^{\#}_{\text{enantio}}$ and $\Delta E^{\#}_{\text{T/P}}$ (for definitions, see text) for propene polymerization at model active cations derived from **1-4** of Chart 2. All energy values in kcal/mol.

Precursor	R^1	R^2	$\Delta E^{\#}_{\text{enantio}}$	$\Delta E^{\#}_{\text{T/P}}$
Reference	H	H	0	0
2	Methyl	Methyl	0	0.2
1	^{t}Butyl	^{t}Butyl	1.7	1.8
3	1-Adamantyl	Methyl	4.1	3.5
4	9-Anthracenyl	Methyl	1.0	-1.5

From the table, it is immediate to note that for "spherical" R^1s $\Delta E^{\#}_{\text{enantio}}$ and $\Delta E^{\#}_{\text{T/P}}$ follow parallel trends. Indeed, both parameters increase regularly with increasing Van der Waals radius, the highest values corresponding to R^1= 1-Adamantyl. At the other extreme, system **4**, with the big but flat R^1= 9-Anthracenyl, was predicted to afford a non stereoregular polymer of lower average molecular mass than that obtained with R^1 = Methyl.

Complexes **3** and **4** of Chart 2 were prepared on purpose (see Ref. [12] for the synthetic procedure), and tested in propene polymerization at 25°C, comparatively with the known[10,11,32] complexes **1** and **2**. The results, summarized in Table 3, are in very nice agreement with the QM/MM-predicted trends.

Table 3. Selected results of propene polymerization (at 25°C, [C_3H_6] = 1.36 M) promoted by **1-4** (experimental details are available from the author).

	R_p(a)	k_p, M^{-1} s^{-1}	$f_{t,m}$,(b) s^{-1}	t_{cg},(c) min	M_n,(d) kDa	[*mmmm*](e)	T_m,(f) °C
2(g)	0.9	n.d.	n.d.	n.d.	4	0.02	Am.(i)
1(g,h)	1.6	0.045	6×10^{-4}	28±5	4	0.80	123
3(g)	4.1	0.053	3×10^{-5}	550±150	110±40	0.985	151
4(g)	32	n.d.	n.d.	n.d.	0.8	0.02	Am.(i)

(a)Productivity, in kg(polymer)/[mol(Zr)×[C_3H_6]×h]. (b)Frequency of chain transfer to the monomer. (c)Average chain growth time. (d)Upper limit of M_n, calculated as $M_1k_p[C_3H_6]/f_{t,m}$, and reached approximately at t_p >3 t_{cg}. (c) ^{13}C NMR fraction of isotactic pentads in fully regioregular sequences. (f)Maximum of the melting endotherm in 2nd DSC heating scan for polypropylene samples at the upper limit of M_n. (g)Cocatalyst, $[HMe_2N(C_6H_5)][B(C_6F_5)_4]/Al(^iBu)_3/2,6\text{-di-}^tBu\text{-phenol}$. (h)Data from Ref. [11]. (i)Amorphous.
n.d. = not determined (M_n and stereoregularity too low for accurate measurements).

The catalytic performance of **3**, in particular, is truly remarkable. It produces an isotactic polypropylene which, at the ^{13}C NMR characterization (Figure 5), reveals only very low amounts of *rr* stereodefects (0.3 mol%), and of isolated 2,1 regiodefects in *erythro* configuration (0.4 mol%).[15,34] The melting temperature of 151°C and enthalpy of 110 J g^{-1} are among the highest ever reported for "single-site" iPP.[15,34] Moreover, ^{13}C NMR end-group analysis of samples obtained at reaction times up to 3 hours indicated a linear increase of M_n (9.5×10^3 Da at 1 h, 2.0×10^4 Da at 2 h, 2.8×10^4 Da at 3 h), with the initial benzyl ends and the saturated ends deriving from reaction quenching with acidified methanol in 1:1 mole ratio within the experimental error (see again Figure 5); consistently, M_w/M_n values ≤1.3 were measured by GPC (Supporting information). Traces of terminal vinylidenes became detectable in the ^{1}H NMR spectra for reaction times in excess of 3 hours.

Compared with the original catalyst **1**,[32] the above corresponds to an increase in enantioselectivity from 96% to 99.7%, in average chain growth time (at 25°C and under the conditions described) from less than 0.5 to 9 hours, and in the limiting value of M_n from 4 to 110 kDa. This opens the door to the synthesis of block copolymers of highly isotactic polypropylene (for iPP-*block*-PE, in particular, see ref. [12]).

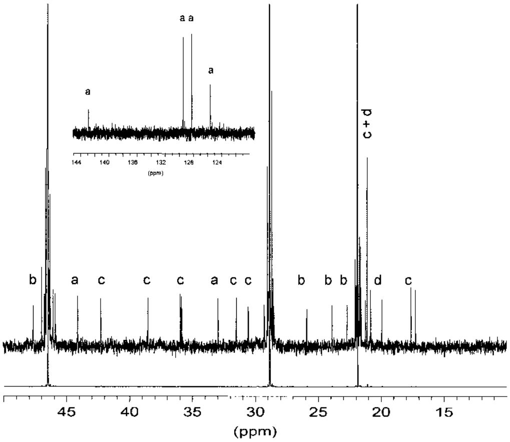


Figure 5. 100 MHz ^{13}C NMR spectrum (in tetrachloroethane-1,2-d_2 at 120°C) of an isotactic polypropylene sample prepared at 25°C with **3**/$[HMe_2N(C_6H_5)][B(C_6F_5)_4]/Al(^iBu)_3$/2,6-di-^{t}Bu-phenol (reaction time 1 h). The chemical shift scale is in ppm downfield of TMS. Resonances labeled with a, b, c, d are due to Benzyl ends, ^{t}Butyl ends, 2,1 regiodefects and *rr* stereodefects, respectively.[11,12,34]

In striking contrast, but consistently with the QM/MM prediction, complex **4** turned out instead to afford an oligomeric, oily polypropylene, with just a slight enrichment in *syndiotactic* diads ([*r*]=0.6, measured by ^{13}C NMR) due to a weak stereocontrol exerted by the growing chain,[34] similarly to **2**.[32]

Concluding Remarks

In conclusion, we have shown in the previous sections that the key to the high molecular weight capability of the new bis(phenoxy-imine)[5-7] and bis(phenoxy-amine)[10-12] Column 4 metal catalysts, at least in propene polymerization, is a suitable substitution of the ancillary ligand framework resulting in the destabilization of the sterically demanding transition state of chain transfer to the monomer. With the aid of computer modeling, this concept was usefully applied in rational ligand fine-tuning, ending up with novel catalyst structures with improved performance.[12]

Whether or not the result can be plausibly defined (and practically utilized) as a "living"[2] (or, more properly, controlled[3]) polymerization depends primarily on the TOF of monomer insertion. For a limiting number average degree of polymerization of (indicatively) 1.0×10^4, the time interval during which the polymerization is controlled is 10 s for TOF = 1 ms^{-1} (which is typical of, e.g. *ansa*-metallocenes[4b,4c]), 3 hours for TOF = 1 s^{-1} (which is instead representative of propene polymerization with **II**-Ti[35]).

Applying definitions, though, is always somewhat subjective. In particular, the apparent discrepancy between Refs. [7] and [8] on the structural requirements of bis(phenoxy-imine)Ti catalysts for a living behavior, of which we have said in the Introduction, is simply the result of a different viewpoint on the time scale at which a controlled polymerization reaction can plausibly be labelled as "living" (minutes for the authors of Ref. [8], hours – more reasonably – for those of Ref. [7]).

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