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Giulio Natta and the Development of Stereoselective Propene Polymerization

Vincenzo Busico

Abstract This chapter looks back at the fascinating history of isotactic polypropylene, the first man-made stereoregular polymer, from the largely serendipitous discovery to the modern technologies for the industrial production of reactor blends with high-yield Ziegler–Natta catalysts featuring highly controlled morphology. This is also the story of a great man, Giulio Natta, winner of the 1963 Nobel Prize in Chemistry, and his team of incredibly talented young coworkers at the Milan Polytechnic, who in just a few years at the end of the 1950s elucidated the structure of the new polymer and that of the novel $TiCl_3$-based catalysts leading to its formation. The pioneering studies that followed on chain microstructure and the origin of the stereocontrol, and the first educated guesses on the nature of the active species, are critically reviewed, and re-visited with the aid of modern experimental and computational tools and methods, to highlight the current picture of what still represents a most important and lively area of polymer science and organometallic catalysis.

Keywords Isotactic · Polypropylene · Stereocontrol · Stereoselective polymerization · Titanium trichloride · Ziegler–Natta catalysis

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Fig. 1 Development of global installed capacity of the polyethylene and polypropylene industry (1958–2012) [1]

1 Premise

This chapter focuses on the birth and initial developments of Ziegler–Natta (ZN) catalysts for isotactic polypropylene (iPP). It’s certainly not the first time that this story has been written (and won’t be the last), but its charm has not faded. The dramatic sequence of lucky shots triggering Ziegler’s and Natta’s discoveries contributes some thrill, but the main power of the narration is that it tells about one of the most outstanding achievements of chemistry and the chemical industry, in an absolute sense, with an impact on society that can hardly be overestimated. A quantitative indicator is the global capacity of iPP production, which has been growing exponentially and is now close to an astounding 60 million tons/year, thus almost catching up to polyethylene production (Fig. 1) [1].

Albeit indirectly and ex-post, I was personally involved in the story as a coworker of Paolo Corradini and Adolfo Zambelli, the two associates of Natta who elucidated, respectively, the crystal structure and the microstructure of polypropylene. Moreover, a large part of my professional life (more than three decades, alas) has been dedicated to the stereochemistry of this fascinating polymer. I decided to let all this transpire from the pages, which may imply here and there a subjective opinion but no deliberate bias.

This chapter tries to combine a modern view with a historical perspective. This is because ZN catalysts were invented when polymer science was already robust, whereas the fundamentals of organometallic chemistry were still largely unknown and important elements for a correct interpretation of the early discoveries not yet available. A paradigmatic example is the starting idea of Ti as a cocatalyst [2], plausible at a time when Ziegler's "Aufbau" reaction [3] was the only known process of ethene oligomerization under comparatively mild conditions, but much less so once the foundations of transition metal chemistry were in place. On the other hand, ZN catalysis is the most effective man-made reaction for making polymers, and therefore *any* ZN scientist *should* know about polymer chemistry and physics. In particular, a proper assessment of chain microstructure is key to understanding the properties of polyolefin-based materials and also in investigating the behavior of organometallic catalytic species, which remain elusive even now after 60 years of application. The subject has been treated exhaustively in several books and reviews [4–6].

One last introductory remark concerns the bibliography. Many key achievements of early ZN catalysis for iPP were only disclosed in patents, or appeared first in articles published in Italian journals and language. For the sake of simplicity, I will mainly refer to (more) easily accessible books and reviews in English, wherein interested readers can find detailed citations of the original literature.

2 ZN Catalysts for Polypropylene: Definition and Genealogy

According to Boor, who authored one of the first comprehensive books on the subject [7], a ZN catalyst is a combination of a transition metal compound and a main group metal-alkyl compound. Although the definition may look unrealistically broad (and in fact covers a huge number of combinations that are not active as olefin polymerization catalysts), it is a sensible one because active combinations have been reported for transition metals in almost all groups of the periodic table and a generous number of main group metals. In a sense it is instead too narrow, because it does not include the so-called main group metal-alkyl-free (MAF) catalysts, which are well-documented [8] albeit thus far irrelevant for application (with the very notable exception of heterogeneous Cr-based systems for polyethylene, known as Phillips catalysts [9] and starring in another fascinating story). One may also wonder if molecular (metallocene and post-metallocene) catalysts can or should be included in the definition; my personal view is that they can but they should not, because although the basic catalysis is the same, the activation chemistry and the high electrophilicity of the cationic active species introduce clear aspects of specificity compared with "classical" heterogeneous Ti-based systems [10]. Last but not least is the question of whether or not "Ziegler–Natta" is the correct designation for the latter systems, looking back at history and the patent litigations that went on for decades [11]. On this of course I have an opinion, like most others in the field, but it is a personal one and as such of very limited importance. The reason why I will refer to both catalysts and catalysis as "Ziegler–Natta" is for the *inclusive* character of this choice. This book celebrates the 50th anniversary of the Nobel Prize to two outstanding scientists named Karl Ziegler and Giulio Natta, and when I write about the marvelous chemistry that they started it seems natural to me to merge the two names into one.

Much less pregnant of implications but of some practical relevance is the classification of ZN systems for polypropylene [11]. I have always found it confusing to identify a ZN catalyst in terms of "generations" and in the following I refrain from using a scheme that is not univocal. I prefer to set just one major divide between unsupported (or self-supported) $TiCl_3$-based catalysts [7] and ($MgCl_2$-)supported ones [11], and within the former to classify $TiCl_3$ polymorphs according to their crystal structure, i.e., as fibrillar (β) or layered (α, γ and δ) [12].

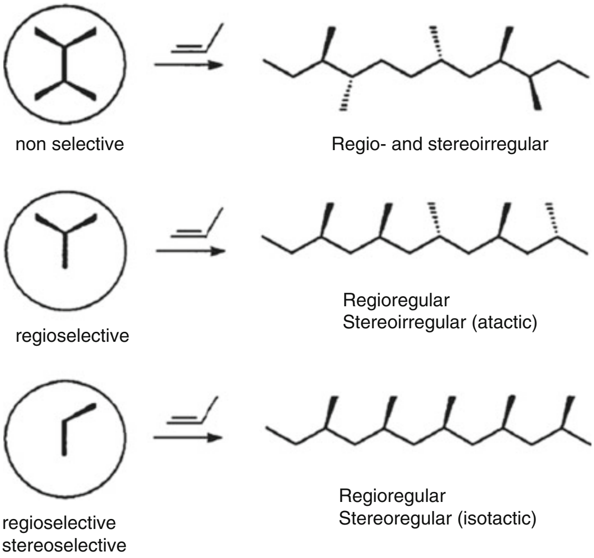
The emphasis of this chapter will be on the basic principles of ZN catalysis for iPP, rather than on iPP properties and applications. In particular, the objective is to illustrate the mechanism of asymmetric induction in the insertion of a monomer that has no functional groups other than a C=C bond, and yet reacts yielding a much larger enantiomeric excess than most highly functional substrates of enantioselective catalysis. That this occurs at the surface of simple and inexpensive inorganic solids is another amazing aspect that contributes to make ZN catalysts "unique and marvelous" [7].

3 From Ziegler's *Metallorganische Mischkatalysator* to ZN Catalysts

It is a fact that the impact of transition metals on olefin polymerization was discovered by accident. The details of how the accident occurred may vary somewhat depending on the literature source, but what is certain is that the fortuitous presence of traces of Ni in a reactor where ethene oligomerization at Al centers was being carried out changed the process into a selective dimerization [13]. I find this an example of how Fate challenges humans. Of all transition metals, Ni is one of the least suited to mediate polyolefin chain growth; the strong propensity of Ni-alkyl bonds to undergo β-H elimination make Ni-based catalysts mainly suited to oligomerization [14]. Indeed, Ni contamination in Ziegler's autoclave led to 1-butene, which is the shortest oligomer that can form from ethene polyinsertion under fast β-H elimination. Decades afterwards, elegant work by Brookhart and coworkers demonstrated that high molecular weight polyethylene can actually form in the presence of Ni-based catalysts bearing a proper ancillary ligand framework [15], but that's yet another story. For the one of interest here, Fate's verdict was: "Ni is no good for the 'Aufbau' reaction." In Ziegler's group, on the other hand, they knew about Sybilline oracles and re-phrased the verdict into a more general "[Transition] Metals can change the course of the 'Aufbau' reaction," and realized its vast implications. The systematic screening that followed was serendipitous and fortunate; nowadays, even a freshman student of organometallics would privilege early transition metals, but in 1953 Zr and Ti were just metals other than Ni. In the modern jargon of high-throughput experimentation [16], Cr was a "hit" and Zr a "lead." The real breakthrough followed, i.e., the combination of $AlEt_3$ and $TiCl_4$ [13]. What that meant for polyethylene can be read in a previous chapter of this book.

Why not polypropylene too? This embarrassing question may be given many different answers, but the simplest probably is that whoever finds a treasure tends to enjoy it for a while before searching for another. On the other hand, once it is known that somebody has found a treasure in a certain place, it is natural for others to

Fig. 2 The four possible insertion modes of propene in polypropylene chain propagation (adapted from [5])



search in the vicinity, just in case… Being a mushroom hunter, I have done that many times, usually with excellent results. Natta too knew about mushrooms, by the way.

Trying propene after ethene may seem obvious, but it actually isn't. The distance between the two monomers is, in a sense, larger than that between the Earth and the Moon. If we forget about the possibility of branches and differences in molecular mass, enchaining ethylene units gives just one chain structure; doing the same with propylene units can produce endless regio- and stereostructures [5, 6] (Fig. 2). It has been noted that a polypropylene chain 1,000-monomeric-units long can have 4^{1000} isomers, and to make all of them there is not enough C in the Universe! In view of this, not even the wildest dreamer would have anticipated that a trivial mixture of $AlEt_3$ and $TiCl_4$ gives rise to a partly stereoselective propene polymerization catalyst, and producing a hypothetical rubbery propene polymer probably did not look like a glorious target after high-melting linear polyethylene. Natta's precedents with butyl rubber may have originated a different opinion; in any case, believing that the process might result in something of interest and trying it out was his first merit. The famous laconic note "*Fatto il polipropilene*" ("Made polypropylene") that he wrote in his agenda on 11 March 1954 [11] to mark the synthesis of the first man-made stereoregular polymer is revealing of the man's character.

The discovery of iPP is a model case history of how a breakthrough can be transferred from a laboratory bench to industrial production. It took some 3 years from that 11 March 1954 to start the first commercial iPP plants in Italy and the USA, which is truly amazing; metallocene catalysts, to make a homogeneous comparison, have been struggling for decades, and those for iPP are not there yet [17]. The ingredients were a chemical company (Montecatini) with a long-term vision and a firm belief in research; a university professor combining uncommon scientific and managerial skills; and a consultancy agreement between the company and the professor enabling the latter, inter alia, to call on bright young chemists and chemical engineers selected from all over Italy for academic or industrial positions (depending on need). The quality of those young scientists, incidentally, is demonstrated by the fact that by the 1960s most of them had become chair-holders and had founded schools of excellence at top Institutes in Italy and abroad, whose legacy has not entirely dispersed after half a century. All that could happen because the company trusted the professor, who fully deserved the trust, and a lean legislation and bureaucracy assisted in the endeavor. In Italy, and not only in Italy, this simple recipe was lost quite a while ago, which may be one reason for the present stagnation. Of course, that Ziegler was also a consultant for Montecatini, which was therefore aware about the "Nickel effect" and passed the information over to Natta almost in real time, was crucial for the following developments [11].

The original Ziegler's catalyst system, i.e., a mixture of $TiCl_4$ and $AlEt_3$ in heptane, was a rather poor catalyst for iPP; typically, less than 40% by weight of the produced polymer had a degree of stereoregularity resulting in high crystallinity and high melting temperature [7, 11]. Understanding that alkylated $TiCl_3$ was the real catalyst, discovering the polymorphism of $TiCl_3$, and finding new highly stereoselective catalyst systems for iPP based on the combination of the right polymorph(s) and Al-alkyl (s) were the achievements of Natta's group on the inorganic and organometallic chemistry side. Elucidating the stereostructure of the unprecedented new polymer (and many more deriving from the stereoselective polymerization of higher 1-alkenes, styrene, and conjugated dienes), on the other hand, was their monumental contribution to polymer science. By the end of the 1950s, the picture was practically complete. In retrospect, I honestly find that even a Nobel Prize is not an adequate reward for such an extraordinary enterprise.

4 The Structure of $TiCl_3$-Based ZN Catalysts for iPP

Under standard conditions, $TiCl_4$ is a readily hydrolyzable molecular liquid miscible with aliphatic and aromatic hydrocarbons, in which its tetrahedral molecules have no tendency to aggregate. When $TiCl_4$ and $AlEt_3$ are in contact in an aliphatic hydrocarbon (e.g., heptane) a reaction occurs, as is indicated by the immediate change of the liquid phase from colorless to yellow, and the progressive separation of a brown solid (rather slow below room temperature; faster above, in which case the color of the precipitate tends to darken and ultimately becomes black) [7, 11, 18, 19]. The process is believed to entail a first step of metathesis, leading to the formation of $TiCl_3Et$ and $AlEt_{3-x}Cl_x$ mixtures. $TiCl_3Et$ is metastable and decomposes homolytically into $TiCl_3$ and Et radicals; the latter mostly disproportionate to ethane and ethene, whereas the former aggregate into highly defective and partly ethylated $TiCl_3$ crystallites, precipitating from the nonpolar liquid in view of the predominantly ionic character of the bonding [7, 11, 18, 19]. Natta and coworkers discovered that this heterogeneous system was an active catalyst for the polymerization of propene, and unexpectedly found by X-ray diffraction that the polymer was partly crystalline, which evidently

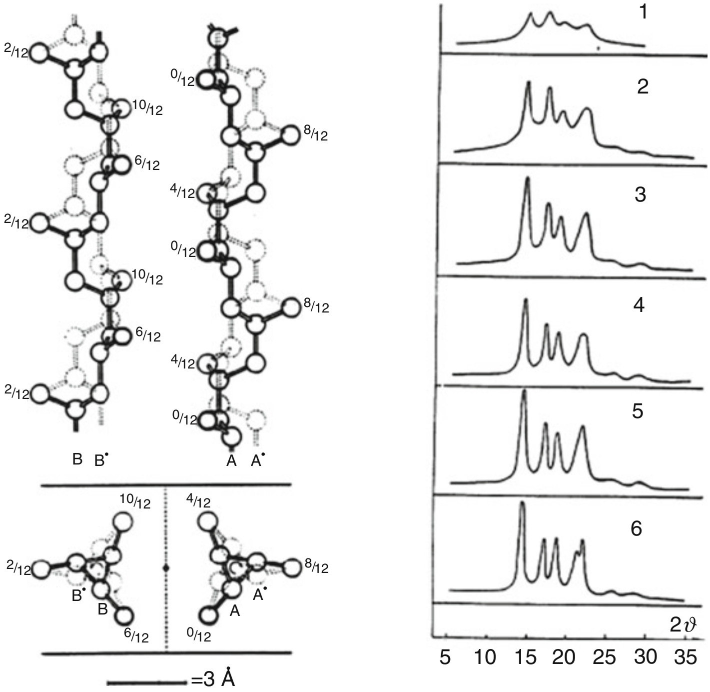


Fig. 3 *Right*: X-ray diffraction patterns of iPP fractions of increasing degree of stereoregularity (increasing from *1* to *6*), as obtained by solvent extraction from a raw sample produced with a $TiCl_4/AlEt_3$ catalyst system. *Left*: Enantiomorphous 3_1 helices in the crystal lattice of the stable iPP α-phase (adapted from [6])

called for chain stereoregularity, and therefore a stereoselective active species [7, 11]. Moreover, the ultimate melting point of the material when observed at the hot stage microscope exceeded 165°C, i.e., well above that of polyethylene!

The team in Milan had to face two major scientific problems: assign the structure of the new polymer and explain its genesis. The first part could be accomplished with a clever analysis of the X-ray diffraction patterns, recognized by Corradini [20; and references therein] as compatible with the 3_1 helical conformation anticipated by Bunn [21] for a hypothetical stereoregular hydrocarbon with the configuration that we now name “isotactic” after the suggestion by Natta’s wife [11] (Fig. 3). I am not a believer in Lukacs’ reflection theory [22], but I find it a fascinating coincidence that Watson and Crick published their fundamental work on the α-helix of DNA at about the same time [23].

Equally fast was the intuition that the formation of stereoselective active sites had to do with specific structural features of the solid catalyst surface, and the consequential decision to investigate its crystal lattice. This rapidly led to the discovery that $TiCl_3$ is polymorphic and that the different modifications can be grouped into two classes, with fibrillar (β) and layered (α, γ, δ) structures respectively [7, 11, 12]. Very recent quantum mechanics (QM) models of the ordered α, β, and γ phases [24], in full agreement with

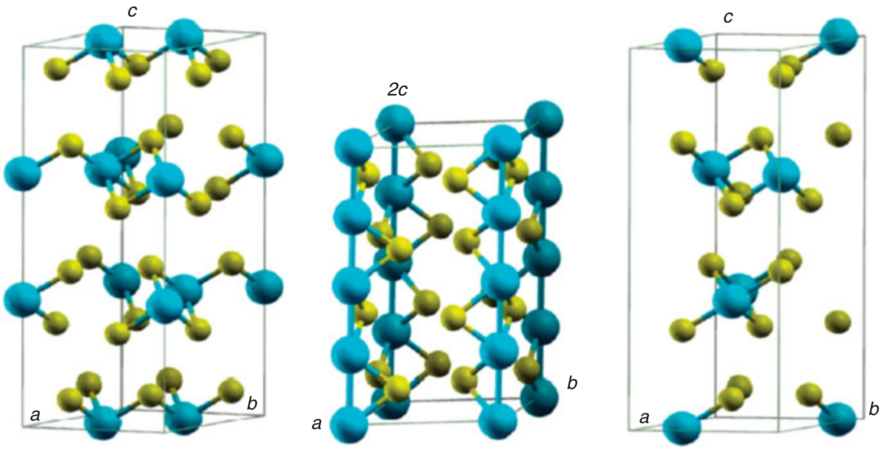


Fig. 4 QM models of unit cell in the crystal lattices of $TiCl_3$ in the α (*left*), β (*center*), and γ (*right*) phase (reproduced with permission from [24]; Ti and Cl are represented as *large dark* and *small light spheres*, respectively)

the conclusions of Natta, Allegra, and Corradini based on powder X-ray diffraction data [12], are shown in Fig. 4. All lattices look rather similar, with (quasi-)close-packed Cl atoms hosting the Ti atoms in one third of the available octahedral cavities. The main difference is the cavity occupation motif. This is mono-dimensional in the β phase, which can be viewed as an inorganic polymer with ideally infinite $(TiCl_3)_n$ chains where every Ti shares three Cl bridges with each first neighbor. In all other phases, the Ti atoms occupy alternate planes of octahedral cavities filled by two thirds, which results in identical Cl–Ti–Cl "sandwiches" (structural layers) held together by comparatively weak dispersive forces; the variable here is the stacking sequence of the Cl planes: $[AB]_n$ or $[ABC]_n$, respectively, in the α and γ phases; disordered in the δ phase.

Importantly, the said structural differences between fibrillar and layered polymorphs produce dramatic diversities with respect to electronic properties (apparent already on inspection: the β phase is brown in color, the layered ones are violet), magnetic behaviors [24], and – most relevant for catalysis – local configuration of Ti (nonchiral in the β phase, chiral in all others). Ziegler's good luck did not cover the latter feature; in fact, testing "violet" $TiCl_3$ (made, e.g., by reduction of $TiCl_4$ with H_2 or Al) in propene polymerization and finding that this was much more stereoselective than the "brown" counterpart (80% or more "highly isotactic" polymer instead of less than 40%) was entirely due to Natta's group [7, 11]. Theirs was also the discovery, a few years later, that using $AlEt_2Cl$ in the place of $AlEt_3$ can push the fraction of highly isotactic polymer up to 95% [7, 11].

Modern readers can hardly imagine the absolute novelty of those findings and the embarrassing inadequacy of vast sectors of the chemical community to assess or even understand them. As a matter of fact, until 1954 it was largely believed that stereoregular polymers can only have natural origin (as can be read in the motivation of the Nobel Prize to Natta [25]). That the world was just not ready is demonstrated

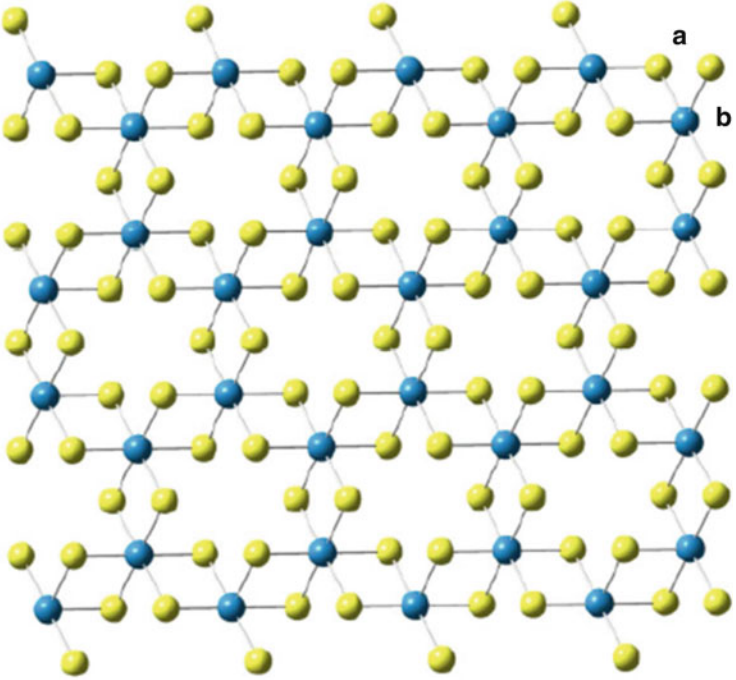


Fig. 5 QM models of 100-type (**a**) and 110-type (**b**) lateral terminations of a violet $TiCl_3$ structural layer (adapted from [27]; Ti and Cl are represented as *blue* and *yellow spheres*, respectively)

by the fact that it took one year for the first paper by Natta et al. to find a scientific journal that would dare to publish something seemingly too revolutionary to be true; on the other hand, the communication to the *J. Am. Chem. Soc.*, which appeared in March 1955 [26], was immediately saluted by unbiased polymer scientists (and in particular by Paul J. Flory) as a groundbreaking announcement.

The Δ or Λ configuration of Ti in violet $TiCl_3$ lattices, with three pairs of bent Cl bridges between first neighbors in the lattice, is shown in Fig. 5; the helical leitmotiv may call for undue but suggestive associations with the chain conformation of iPP. Relating the intrinsic chirality of Ti with the stereoselectivity of the active sites in propene polymerization was an easy logical process. Building up a detailed mechanism of asymmetric induction, on the other hand, took a long time and the contributions of many brilliant scientists [6]. The next milestone was the seminal work of Cossee and Arlman [28]. Moving from the structure of the bulk, they speculated that the basal 001 planes of violet $TiCl_3$ crystals cannot offer chemisorption sites and as such have no interest for catalysis, whereas lateral terminations of the structural layers (e.g., parallel to the 110 or 100 crystallographic directions) expose linear racemic arrays of enantiomorphic Ti centers, with two residual *cis* pairs of Cl bridges toward the crystal interior, one terminal Cl from the third broken bridge pair to ensure the electroneutrality, and one coordination vacancy (Fig. 5). Cossee proposed [29] that the catalytic species would form by metathesis of the terminal Cl with an alkyl group of the Al-alkyl cocatalyst;

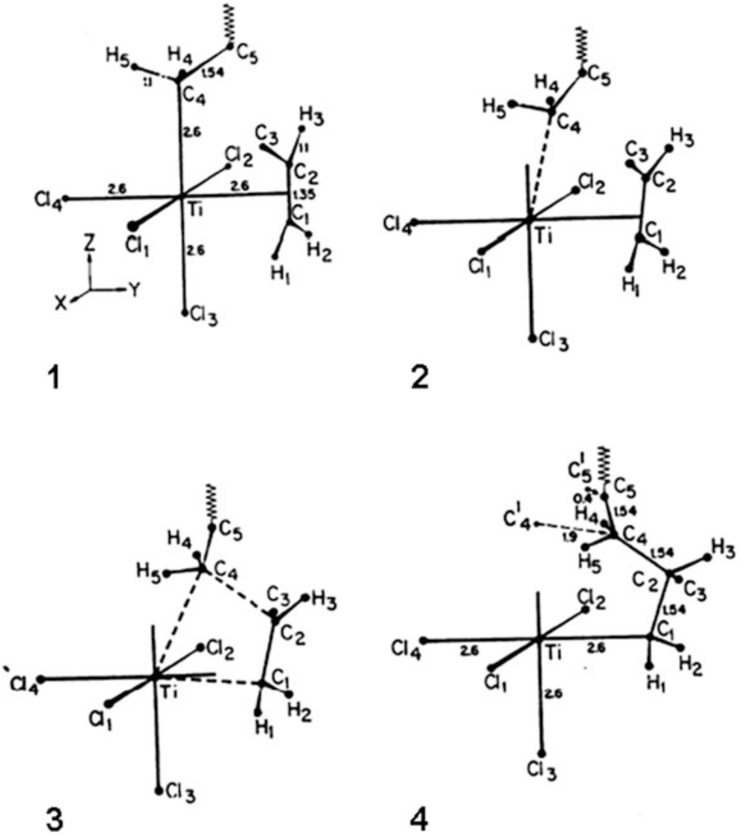


Fig. 6 The Cossee mechanism of chain-migratory propene insertion into a Ti–R bond on the edge of a violet $TiCl_3$ crystal (adapted from [29])

propene would then chemisorb at the remaining empty site of the octahedron and insert into the Ti–R bond, as schematically depicted in Fig. 6. I always found that drawing illuminating and like to make reference to it whenever I can; it elegantly anticipated the concept of "chain migratory insertion" [6], which is now part of the fundamentals of organometallic chemistry. The geometric representation of the reaction path, with the four-center insertion transition state, was incredibly accurate for the time (as a matter of fact, the various steps as depicted could well be snapshots taken from modern molecular dynamics simulations). Yet, that propene insertion would occur with 1,2 regiochemistry and be enantioselective due to site control [5, 6], opposite monomer enantiofaces being preferred at Ti centers of opposite chirality, were all and only educated guesses. Moreover, the steric contacts involved in the chiral recognition were not identified.

In the mid-1970s, with the development of ^{13}C NMR spectroscopy, the insertion regiochemistry and the site-controlled origin of the stereoselectivity could be experimentally confirmed by Zambelli and coworkers [30–32]. The unambiguous identification of predominant . . .*mmmmrrmmmm*. . .-type stereodefects in ZN iPP

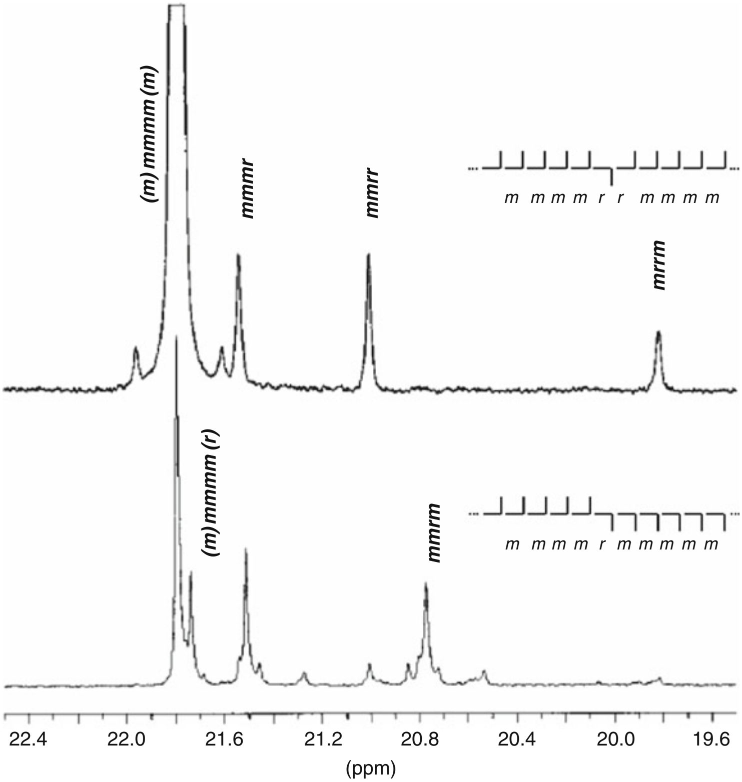


Fig. 7 ^{13}C NMR methyl fingerprints of typical iPP samples obtained under (*top*) enantiomorphic-sites control, and (*bottom*) chain-end control (adapted from [5])

chains by means of steric pentad analysis on the methyl resonance (Fig. 7; [*mmmr*]:[*mmrr*]:[*mrrm*]≈2:2:1, in agreement with the so-called enantiomorphic-sites chain propagation model [33]) was a classical early demonstration of active site "fingerprinting" from the polymer chain microstructure [6].

In the late 1970s, the resolution of the picture was further increased by the school of Corradini, with pioneering applications of molecular mechanics (MM) [34–36] providing a semi-quantitative character to Cossee's speculations. As is well-known, MM cannot evaluate transition states, and also due to the difficulties arising from the poorly defined set of geometries and potentials to be used in the calculations (which were among the first of their kind for organometallic systems) those studies can be viewed as the digital version of traditional stick-and-ball models. This does not diminish their value and rather demonstrates that limitations in tools can be overcome by means of intuition and imaginative thinking.

Figure 8 shows MM models of 100 and 110 terminations for a structural layer of α-$TiCl_3$ [34–36]. In the former case (Fig. 8a), a local C_2 axis relates the two coordination sites available for catalysis at each surface Ti atom, which implies their equivalence (homotopicity). In each of them, a growing polymer chain

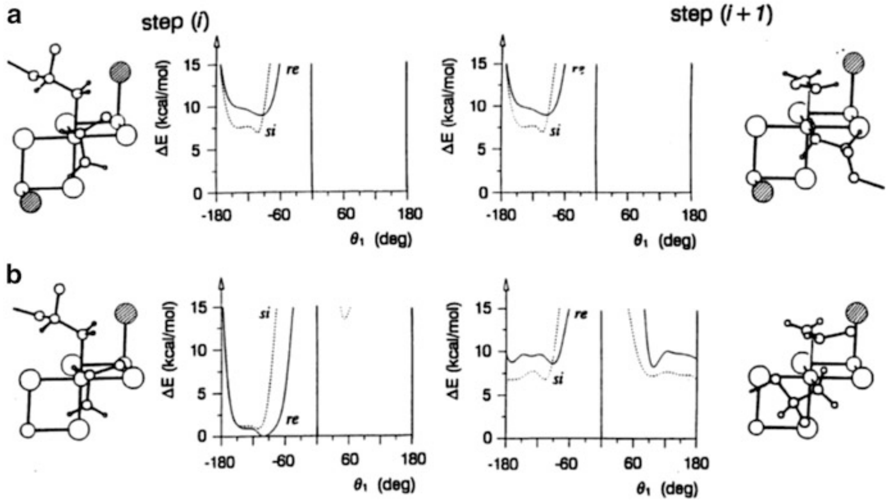


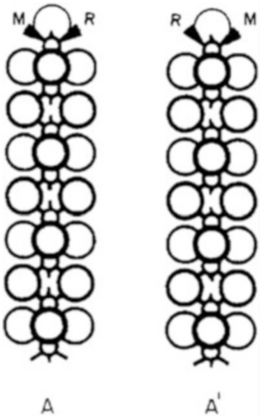
Fig. 8 MM models of catalytic species on 100 (**a**) and 110 (**b**) lateral terminations of an α-$TiCl_3$ structural layer. Consecutive insertion events under chain migratory regime are labeled step *i* and step (*i* + 1) (adapted from [36])

experiences repulsive nonbonded contacts with one of the Cl atoms of the surface (shaded in Fig. 8); as a result, the first C–C bond is conformationally constrained and chirally oriented. In turn, this was proposed to favor the 1,2 insertion of a propene molecule π-coordinated to the other site with the enantioface that directs the methyl substituent *anti* to the said C–C bond. On 110 model terminations (Fig. 8b), on the other hand, the absence of one of the two surface Cl atoms required for the orientation of the growing chain lowers the local symmetry of Ti to C_1, which makes the two active coordination sites non-equivalent (diastereotopic), and propene insertion as represented at step (*i* + 1) non-enantioselective. Therefore, chain propagation here can be isotactic only provided that monomer insertion occurs in preference as shown at step *i* (I will come back to this later).

The experimental confirmation to Corradini's model came, again, from ^{13}C NMR analysis, in this case of the polymer chain ends. In fact, Zambelli and coworkers found that for highly isotactic-selective ZN catalysts, the enantioselectivity of 1,2 propene insertion into initial Ti-[^{13}C-labeled]-alkyl bonds is different from that of the subsequent ones. They observed no enantioselectivity for insertion into a Ti–$^{13}CH_3$ bond and only partial (~80%) enantioselectivity for that into a Ti–$^{13}CH_2$–CH_3 bond, whereas the following propagation steps were almost completely enantioselective [37]. These findings highlighted the steric requirements for the asymmetric induction and proved, in particular, that for the onset of the stereocontrol the alkyl group bound to Ti needs to be a "chain," i.e., consist of at least two C atoms and preferably more [6].

As we shall see in next section, starting from the 1970s, violet $TiCl_3$-based catalysts gave way to $MgCl_2$-supported ones [11] and were practically abandoned before QM modeling had become feasible. To the best of my knowledge, the only

Fig. 9 Models (*A* and *A*′) of enantiomorphic active sites on the surface of a β-$TiCl_3$ crystal (adapted from [19]; *R* alkyl, *M* monomer)



available QM study is a PhD dissertation from my own research group [27] that investigated with periodic DFT-D methods – inter alia – the relative stability of possible crystal terminations for different $TiCl_3$ polymorphs. In brief, the conclusion was that, apart from trivial 001 planes, plausible surfaces indeed have the structures postulated in Figs. 5, 6, and 8. For α-$TiCl_3$, 100-type terminations (Fig. 8a) would be slightly lower in energy than 110-type (Fig. 8b); the calculated values of surface energy after full relaxation were 0.14 and 0.15 $J\,m^{-2}$, respectively. In the same work [27], it was also found that the chemisorption of $AlEt_2Cl$ on 110-type terminations at $\theta = 0.5$ (where θ is the degree of surface coverage), which is the highest allowed by steric interference between neighboring adsorbates, is exergonic and makes the residual exposed Ti centers rather similar to those on 100-type terminations, as far as the local coordination environment is concerned. A weaker chemisorption of $AlEt_3$ compared with $AlEt_2Cl$ might be the reason for the lower stereoselectivity of violet-$TiCl_3$/$AlEt_3$ catalyst systems than for violet-$TiCl_3$/$AlEt_2Cl$ ones. It should be noted, however, that no QM studies of catalytic reactivity for these surfaces have been published so far.

Also pending is an explanation for the partial stereoselectivity of catalyst systems based on β-$TiCl_3$. ^{13}C NMR analysis of the highly isotactic PP fraction demonstrates that the stereocontrol must be traced to inherently chiral active sites [19], but in this case the Ti centers in the bulk of the crystal are not stereogenic [12]. It was noted that the terminal Ti atoms of the fibrils are chiral if they bear three different ligands (e.g., one dangling Cl, the growing chain and the monomer; Fig. 9 [19]), but no quantitative studies of propene insertion were carried out. My own educated guess is that, under polymerization conditions, β-$TiCl_3$ crystallites are likely to reconstruct into more stable layered structures, at least locally. In fact, β-$TiCl_3$ is metastable and changes into the γ polymorph by thermal annealing at moderately high temperature (a few hours at 150–250°C). In the presence of $TiCl_4$, the transformation is much faster and occurs readily well below 100°C [11].

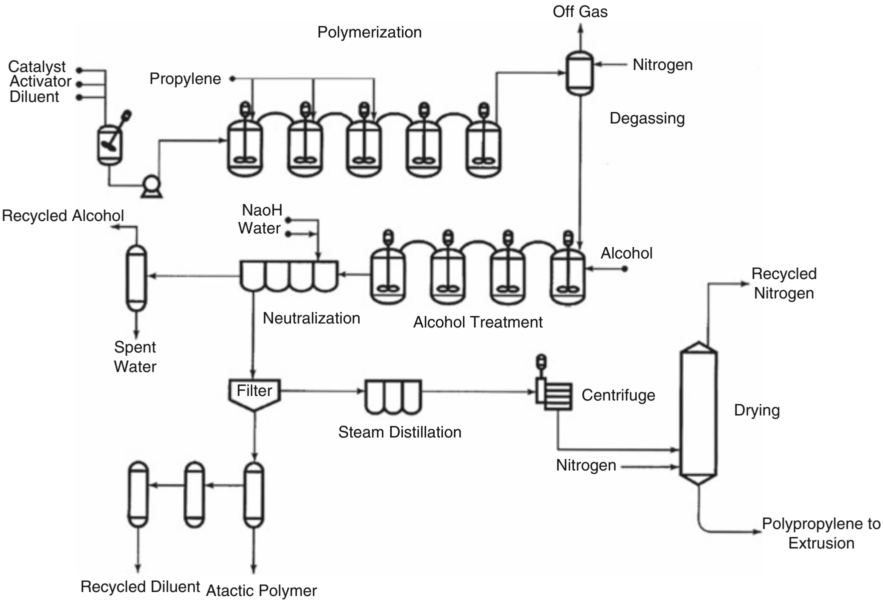


Fig. 10 Flow-chart of an early iPP production plant based on violet $TiCl_3$ catalysis (Hercules technology; reproduced with permission from [11])

5 From "Self-Supported" $TiCl_3$-Based to $MgCl_2$-Supported $TiCl_4$-Based ZN Catalysts

The schematic layout of an iPP production plant based on violet $TiCl_3$ catalysts in the 1960s is shown in Fig. 10 [11]. Notably, a large part of the plant was for operations other than polymerization, such as catalyst alcoholysis and neutralization and separation of the "highly isotactic" PP part from a "less tactic" part by filtration. The latter made it necessary to work in a low-boiling aliphatic hydrocarbon diluent, because the less tactic PP fraction is partly insoluble in liquid propene.

Polyolefins are low-value-added products and simplifying their production technology is of crucial importance. The main weak point of violet $TiCl_3$ was its comparatively low productivity. Even with catalysts characterized by high surface areas (such as those developed by Solvay, including weak Lewis bases such as ethers to stabilize crystallite terminations by means of labile chemisorption), 10–15 kg of iPP per gram of catalyst was the maximum achievable mileage [11]. Due to the acidity of Ti–Cl bonds, which readily hydrolyze liberating HCl, this value was still too low to avoid a cost-intensive polymer de-ashing procedure.

Supporting the active Ti species on an inert matrix, thus increasing the productivity referred to Ti, looked like an obvious solution to the problem. However, one should realize that in violet $TiCl_3$ the bulk of the crystal is not an innocent self-support because its structure determines that of the catalytic surfaces and in particular the stereogenic environment of the exposed Ti centers. As a matter of fact, when typical supports like

Table 1 Typical formulations and performance of $MgCl_2$-supported Ti-based ZN catalyst systems for iPP

Internal donor	External donor	Productivity[a]	Index of isotacticity[b]	M_w/M_n[c]
Aromatic monoester (e.g., ethylbenzoate)	Aromatic monoester (e.g., methyl-*p*-toluate)	0.5	>95	5–6
Aromatic diester (e.g., dibutyl-*o*-phthalate)	Alkoxysilane [e.g., $R^1R^2Si(OMe_2)$]	1–2	>97	5–6
2,2′-dialkyl-1,3-dimethoxypropane	Alkoxysilane [e.g., $R^1R^2Si(OMe_2)$]	>2	>97	3–4
Aliphatic diester (e.g., dialkylsuccinate)	Alkoxysilane [e.g., $R^1R^2Si(OMe_2)$]	1–2	>98	>7

[a] 10^3 kg(PP) g(Ti)$^{-1}$

[b] Wt% of highly isotactic PP

[c] Polydispersity index

calcined silica or alumina were impregnated with $TiCl_4$ and reacted with Al-alkyls for Ti alkylation/reduction, the results were very poor (at most, moderate activity in the polymerization of ethene; low or no activity and no stereoselecivity in that of propene) [11]. The breakthrough came, once again, serendipitously: highly active catalysts for ethene polymerization were obtained when $TiCl_4$ was supported on MgO, and it did not take too long to realize that (1) $TiCl_4$ chlorinates MgO to give $MgCl_2/TiCl_4$ adducts, and (2) $MgCl_2$ has a layered structure very similar to that of violet $TiCl_3$ (i.e., stacked Cl–Mg–Cl sandwiches with all octahedral cavities in between the two Cl planes occupied by Mg) [11].

Using authentic $MgCl_2$ as the support led to even better catalysts for polyethylene, whereas the performance for polypropylene was ambivalent: high productivity (>150 kg of polymer per gram of Ti) but poor stereoselectivity (less than 40% highly isotactic polymer) [11]. However, the addition of proper Lewis bases to the catalyst formulation (Table 1), as components of the solid precatalyst ("internal donor") or complexed with the Al-alkyl cocatalyst ("external donor"), improved both the productivity (up to 2–3 tons of polymer per gram of Ti) and the stereoselectivity (>95% highly isotactic polymer) [11, 38, 39].

Other chapters of this book cover modern "high-yield" $MgCl_2$-supported ZN catalysts [11, 38, 39]; here I will only elaborate on their structural relationships with violet $TiCl_3$. As a matter of fact, it is plausible to imagine that the chemisorption of $TiCl_4$ on lateral terminations of $MgCl_2$ structural layers, followed by alkylation and reduction of the adsorbates by an Al-alkyl, results into local environments mimicking the edges of authentic violet $TiCl_3$ structural layers. In other words, according to this hypothesis, $MgCl_2$ would act as a template for the epitaxial adsorption of $TiCl_n$ species (n=4 or 3) [6].

Giannini [40] and Corradini [41] were the first to extend to the new systems the crystallochemical approach used before by Cossee and Arlman (Sect. 4). Their starting point was the identification of plausible nontrivial $MgCl_2$ crystal surfaces, proposed to be 100 (with penta-coordinated Mg atoms) and 110 (with tetra-coordinated Mg atoms). According to a pioneering paper by Corradini et al. [41], precursors of stereoselective active species would result from the epitaxial chemisorption of $TiCl_4$

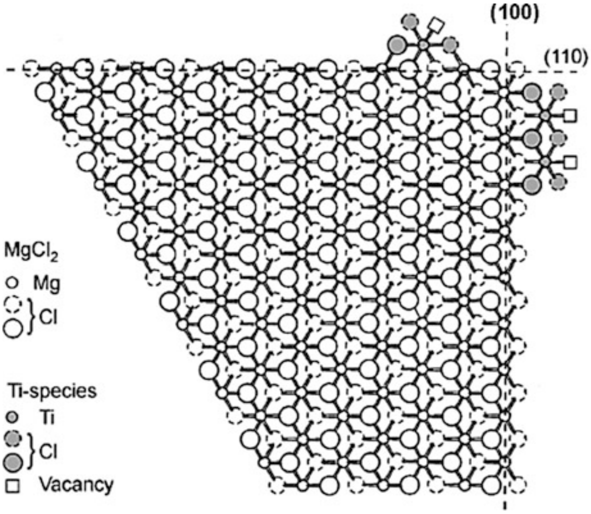


Fig. 11 Models of precursors of active $TiCl_3$ species on (100) and (110) edges of a $MgCl_2$ structural layer (re-elaborated after [41])

in the form of dinuclear Ti_2Cl_8 adducts on 100 $MgCl_2$ surfaces, whereas mononuclear chemisorption on 110 surfaces would lead to non-stereoselective (albeit chiral) active species (Fig. 11). The difference between the two would be the lack of steric hindrance necessary to enforce growing chain orientation in the latter case. In view of a postulated higher Lewis acidity, 110 surfaces were proposed [41] to bind Lewis bases in preference to $TiCl_4$, which would then prevent the formation of non-stereoselective sites; the role of Lewis bases in enhancing catalyst stereoselectivity would thus be *indirect* [6, 41].

^{13}C NMR and temperature rising elution fractionation (TREF) polymer characterization data, on the other hand, pointed to a *direct* effect of Lewis bases on site enantioselectivity; in fact, the highly isotactic polymer fraction yielded by catalysts modified with Lewis bases is not only much more abundant, but also more stereoregular compared with that of Lewis-base-free systems, while keeping the typical fingerprint of enantiomorphic-site control [42]. This suggests that Lewis base molecules are in nonbonded contact with the inherently chiral catalytic species, and shape their active pocket to make them better able to discriminate between the two enantiofaces of propene at the insertion step.

Recent periodic DFT(-D) (dispersion-corrected density functional theory) evaluations of relative stability for different $MgCl_2$ crystal surfaces concluded that well-formed α-$MgCl_2$ crystals should only feature basal planes and lateral terminations with penta-coordinated Mg (104 or equivalent) [43]. Surfaces exposing tetra-coordinated Mg (110 or equivalent) are appreciably higher in energy and should at most constitute a small minority [43]; on the other hand, they turned out to bind Lewis bases much more strongly, which should favor their formation in $MgCl_2$/Lewis base adducts [43–45]. The latest state-of-the-art QM calculations indicated that $TiCl_4$ chemisorption is also much stronger (and possibly even exclusive) on 110-type faces [46], which is in line with the results of recent vibrational spectroscopy studies [47, 48].

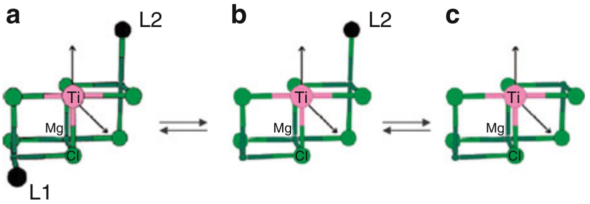


Fig. 12 The three-site model of active species for $MgCl_2/TiCl_4$/Lewis base catalyst systems; *L1* and *L2* generically denote chemisorbed Lewis base molecules. *a*, *b* and *c* are proposed to give rise to highly isotactic, poorly isotactic ("isotactoid") and (chain-end-controlled) syndiotactic polypropylene chain propagation, respectively (adapted from [50])

In view of the above, the current picture of $MgCl_2/TiCl_4$/Lewis base catalysts assigns a dominant role to 110-type $MgCl_2$ crystallite terminations [46–49]. A model of catalytic species reconciling all available experimental and computational evidence, including the observed formation of less tactic polypropylene fractions containing poorly isotactic and syndiotactic stereoblocks, is shown in Fig. 12 [6, 50]. The isotactic-selective species, in particular, is similar to the homologous model for violet $TiCl_3$ (Fig. 8) with respect to the Ti first coordination sphere, but features Lewis base molecules rather than Cl atoms to enforce the orientation of the growing polymer chain necessary for the onset of the enantioselectivity.

An important extra benefit of $MgCl_2$ as a support is the superior control over pre-catalyst morphology that it ensures [39]. Sophisticated technologies have been implemented for the production of activated $MgCl_2$ in the form of spherical secondary particles with controlled shape and porosity, even after the harsh protocols necessary for the chemisorption of $TiCl_4$ and the ID. With a proper pre-treatment (e.g., a mild pre-polymerization process "gluing" the primary particles together), once in the polymerization reactor such particles expand regularly under the hydraulic pressure of the product springing radially from the billions of constituent primary $MgCl_2$ nanoparticles, ending up with polymer granules faithfully replicating pre-catalyst morphology (Fig. 13, left). The advantages of this achievement can hardly be overestimated, ranging from improved control over reactor fluid dynamics to the possibility of production of in-situ finely dispersed polymer blends in reactor cascades (e.g., intimate mixtures of iPP and ethylene/propylene rubber known on the market as "impact-resistant" or "heterophasic" PP; Fig. 13 right) [39]. All this considered, one can conclude that $MgCl_2$ is a rare example of a nanostructured support dictating practically all aspects of catalyst behavior from the atomic to macroscopic scale, i.e., from stereoselectivity to morphology.

6 Concluding Remarks

It has been estimated that up to one half of all scientific discoveries are serendipitous in origin [51]. ZN catalysis, from $TiCl_3$-based to $MgCl_2$-supported, represents an outstanding case history in this respect, but at the same time demonstrates that

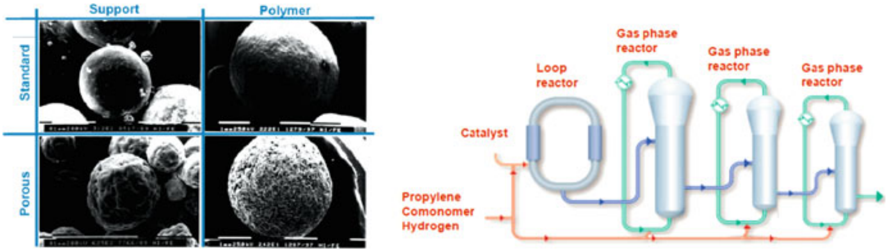


Fig. 13 *Left*: Scanning electron micrographs documenting the replication of pre-catalyst morphology in $MgCl_2$-supported ZN catalysis for PP (courtesy of J. Pater, Lyondellbasell). *Right*: A typical reactor cascade for the production of "heterophasic" PP; (adapted from http://www.borouge.com/aboutus/Pages/ProcessOverview.aspx)

serendipity is only one part in a cocktail [51] that also includes the ability to recognize the importance and the possible implications of an unexpected result, the availability of adequate human and material resources to elaborate on such implications, and a chain-of-knowledge approach spanning all elements from initial discovery to practical application.

In my opinion, the progress of technology will greatly speed up the process of discovery [16], but is not likely to change its mechanisms in the short or medium term. If I am correct, then Natta's success story is not only of purely historical concern and should rather be looked at by scientists and managers in industry and academia as a valid model and source of inspiration for a brighter future.

Acknowledgements I am grateful to Prof. Walter Kaminsky, editor of this book, for the invitation to write the present chapter. For me, it was an opportunity to take a pause and look back, enjoying many nice memories of a time vibrant with passion and expectations. I like to thank my coworkers, and in particular Roberta Cipullo and Luca Rongo, for helping me to assemble the material and compose parts of the chapter.

Appendix: Some Biographic Notes on Giulio Natta

Whoever goes through the numerous biographies (see for example [52]) of Giulio Natta (Fig. 14) cannot but realize that the discovery of iPP and stereoselective olefin polymerization was diligently prepared by Fate. Born in 1903 in a family of judges and lawyers, Natta developed a passion for chemistry that made him build, during his studies in chemical engineering at the Milan Polytechnic, a small laboratory in his apartment to carry out "private" experiments in his spare time. The Milan Poly was in the 1920s a world-leading center in X-ray diffraction, which set the stage for Natta's interest in the still-young chemical crystallography (key to interpretation of the events of March 1954). Subsequently, he worked on electron diffraction in Freiburg; that Hermann Staudinger was a professor there was certainly more than influential on Natta's formation. Back in Italy, he went through a rapid academic career that saw him Professor of General Chemistry in Pavia, of Physical Chemistry in Rome, and of

Fig. 14 Giulio Natta (1903–1979)

Industrial Chemistry, at Turin Polytechnic first and at Milan Polytechnic from 1938 until his retirement in 1973. As for many academic chemists in Europe at that time, the forthcoming war prompted Natta to move the focus of his research to the synthesis of strategic materials. In particular, he expanded his studies in catalysis, which were pre-existing and had already led him to important achievements in oxosynthesis in the early 1930s, to the production of synthetic rubber. The interest in polymers with elastomeric properties never faded, and is another key part of the puzzle. After the war, Italy entered the most vital and productive period of its recent history, and the Italian chemical industry began an impressive growth. At that point Fate played a wild card and made the young Natta meet Piero Giustiniani, on the way to becoming CEO of Montecatini, one of the largest and most advanced Italian chemical companies. The two began a collaboration that in 1947 led them to travel to the USA, where they discovered the modern organization of the American chemical companies, employing hundreds of researchers and well ahead in the transition from coal to oil chemistry. That journey imprinted both of them and resulted in a strategic alliance that made Montecatini associate Natta as a consultant and establish at the Milan Polytechnic an “Advanced School in Aliphatic Chemistry,” where brilliant chemistry and chemical engineering graduates from all over Italy received hands-on research training in chemical syntheses and characterizations. They joined the academic staff on fundamental and applied projects under Natta’s leadership, in most cases in preparation to a career in Montecatini. The modernity of this organization, with a strong multidisciplinary character and a simple albeit efficient structure, amazes me when I compare it with the present painful situation of Italian chemical research. When in 1952 Natta attended the Achema Conference in Frankfurt, where Karl Ziegler gave an account of his work on the “Aufbau-Reaktion,” all parts of the puzzle could perfectly fit together. Natta had no difficulty in convincing Giustiniani and Montecatini to contract Ziegler as a consultant and to take a license on the developments of Al-mediated ethene oligomerization, even though the real industrial interest of that process was not yet clearly established. What came afterwards is told in the previous sections of this chapter.

A precocious Parkinson disease forced Natta to a rather early retirement, which makes me feel sad for him, and in a way for me too, because I dare to look at him as a grandfather that I never met. When I read that he was a reserved, almost shy man I have no difficulties in believing that. In my 20 years of collaboration with Paolo Corradini and, for a much shorter but highly fascinating period, with Adolfo Zambelli, I seldom heard them mention “Il Professore” or tell anecdotes about him. They had been working under Natta for many years, and shared with him the most heart-shaking experience a scientist could dream about, and yet “Il Professore” seemed to me, through them, to be a silent presence in the background. Some of his comments, of course, surfaced to their memories, and these were all modest, humble even: “we have been lucky” was a recurrent one. On the other hand, Natta was of course well-aware of the importance of his discoveries. I have been especially impressed by a recollection of Lido Porri, another well-known Natta coworker, in a recent article for a special issue of the Italian Chemical Society journal celebrating the 50th anniversary of Natta’s Nobel Prize [53]. Porri recalls that Natta used to say: “I believe that research in this field will continue until the next century.” Well, “Professore,” here we are indeed!

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