ACCADEMIA NAZIONALE DEI LINCEI
FONDAZIONE «GUIDO DONEGANI»

33

Convegno nel centenario della nascita di

GIULIO NATTA

(Roma, 12-13 marzo 2003)

ROMA
ACCADEMIA NAZIONALE DEI LINCEI
2004

*Si ringrazia l'«Associazione Amici dell'Accademia dei Lincei»
per la collaborazione offerta alla edizione del presente volume*

ISSN: 0391-805X
ISBN: 88-218-0923-4

FINITO DI STAMPARE NEL MESE DI SETTEMBRE 2004

Stabilimento Tipografico Pliniana - V.le F. Nardi, 12 - 06017 Selci-Lama (PG)

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*Il Convegno è stato organizzato con il contributo
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PROGRAMMA

Mercoledì 12 marzo 2003

9.30 Saluto del Presidente dell'Accademia Nazionale dei Lincei, Edoardo Vesentini

Saluto del Rettore del Politecnico di Milano, Giulio Ballio

9.50 John A. Ewen: *Polypropylene through the Eyes of a Metallocene*

10.30 Hans-Herbert Brintzinger: *Catalyst Models and the Evolution of Olefin Polymerization Catalysis*

11.10 Intervallo

11.30 Gaetano Guerra: *Impact of Natta's Discoveries on Industry and Uses of Polypropylene in Everyday Life*

12.10 Paolo Galli: *The Polypropylene Technology: a Revolutionary Development, Unique in the History of Polymer Materials*

15.00 Luigi Resconi: *Control over the Enchainment Modes of Propylene: from Stiff Plastic to Elastomer*

15.40 Giampiero Morini: *The Role of Electron Donors in Heterogeneous Ziegler-Natta Catalysts*

16.20 Intervallo

16.40 Tavola rotonda:

PERSONAL AND/OR HISTORICAL NOTATIONS
RELATED TO NATTA'S DISCOVERY OF STEREOREGULAR POLYMERS

Interventi di

Enrico Albizzati, Giuseppe Biardi, Fausto Calderazzo, Paolo Corradini, Ferdinando Danusso, Giorgio Mazzanti, Italo Pasquon, Lido Porri, Adolfo Zambelli, Giuseppe Zerbi.

Giovedì 13 marzo 2003

9.30 GERHARD FINK: *Some Insight into Molecular Mechanistic Details of Stereospecific Working Catalysts*

10.10 WALTER KAMINSKY: *New Polymeric Materials by Metallocenic Catalysis*

10.50 Intervallo

11.10 BERNARD LOTZ: *Isotactic Polypropylene Crystal Structures: a Tale of Nightmares, Frustration and Beauty*

11.50 GIUSEPPE ALLEGRA: *Chain Mobility in Non-Stereoregular and Stereoregular Polymers*

PAOLO CORRADINI

OPENING REMARKS

Professor Vesentini, the President of the Academy, has not been able to reach Rome from Turin in time for the opening of this meeting. So he asked me to say a few words in his place.

We celebrate this year the centenary of the birth of Professor Giulio Natta, who was Professor of Industrial Chemistry at the Politecnico of Milan, Academician of the Lincei and Nobel Prize in Chemistry in 1963.

He was born in Porto Maurizio, which is now Imperia, on 26 February 1903.

The discoveries made by Professor Giulio Natta have given a strong impetus to the progress of science and have made available a whole series of new materials that we are using now to the benefit of mankind. An example is isotactic polypropylene.

Its production, which started from zero in the Fifties, amounts nowadays to more than 25-million tons per year worldwide, we have reached probably 30-million tons per year with an average consumption of the order of magnitude of 4 or even more kilograms per year per inhabitant of the earth.

Propylene may be obtained cheaply and in large quantities from oil. The possibility to obtain a crystalline polymer from propylene, the polymer that was then called isotactic polypropylene, was discovered by Giulio Natta and his collaborators in March 1954.

I have a photograph of Professor Natta to project on the screen. On the photograph that I received from Professor Natta he has written: "*Al mio caro allievo e collaboratore, Paolo Corradini, affettuosamente*". Professor Natta has a huge model of a polypropylene molecule on the back. (The photograph is displayed as fig. 1 in the report of Paolo Corradini at the "Round Table" of this meeting). Well, that may be sufficient.

In fact, the macromolecules of isotactic polypropylene are characterized by the presence of long sequences of monomeric units, which have the same configuration. In the solid state, such sequences give rise to helicoidal molecular conformation.

The first two memoirs on the subject were submitted for publication at the Accademia dei Lincei in December 1954. I have two copies here, but I see they are also being distributed outside. Of the memoirs, which Natta gave, the first was given here at the Academy.

The discovery of the stereospecific polymerization has opened an entirely new field in macromolecular chemistry. Its interest is not only scientific, but also practical. The industry of plastics, of elastomers and of fibers has been strongly influenced.

In 1963, Professor Ziegler and Professor Natta together received the Nobel Prize in Chemistry. Professor Fredga, in the presentation speech for the Nobel Prize, said that our epoch is witnessing the gradual replacement of traditional materials such as glass, porcelain, wood, metals, bones and horn with synthetic materials such as plastics, which can be obtained by polymerization of small molecules.

Professor Ziegler invented an entirely new method of polymerization, in particular of ethylene, obtaining the growth of polymeric chains completely linear through the addition on metal-carbon bonds.

This catalytic addition is much softer than the one known previously, which occurred starting from free radicals and which gives rise to side chains and other anomalies along the chain. If, instead of ethylene, we polymerize propylene, propylene may originate chains with a large side group (CH_3), every two carbon atoms. This group may be oriented on the right or on the left along the main zig-zag chain.

When the orientations of the CH_3 groups are randomly distributed, the chain has an especially irregular configuration. Professor Natta found that certain types of Ziegler catalysts led to stereoregular macromolecules. That is macromolecules with uniform structure in space.

In such chains, all the side groups point to the right or to the left of a zig-zag chain – this configuration being called isotactic. The molecular environment of the metal atom in the catalyst, at which new units are stuck on the chain (as mentioned before) is so shaped that it permits only a definite orientation of the side groups.

These statements by Fredga, and analogous statements by Professor Natta in his Nobel speech, may be considered prophetic in respect to the scientific findings and certain conclusions, which have been obtained much more recently.

In the motivation by Fredga we read more. And the more recent acquisitions we will hear in this meeting, of course. In the motivation by Fredga we read: "Isotactic polymers show very interesting characteristics."

Thus while ordinary hydrocarbon chains are zigzag in shape, isotactic chains form helices with the side groups pointing outwards. Such polymers give rise to novel synthetic products such as fabrics, which are light and strong at the same time, and ropes which float on the water – to mention only two examples.

"Nature synthesizes", says Fredga in the motivation for the Nobel Prize, "many stereoregular polymers: for example cellulose and rubber.

This ability has so far been thought to be a monopoly of nature, operating with biocatalysts known as enzymes. But now Professor Natta has broken this monopoly".

The discovery of stereoregular polymers has produced and is still producing important consequences in the field of pure and applied science. During this meeting for the "*Celebrazione del Centenario della nascita del Professor Natta*", which we are holding now, we are going to hear (as in the program) many well-known professors and researchers, Italian and foreign, who have been recent "*primi attori*" (as we say in Italian) in the comprehension of the mechanisms of the stereoselective catalysis of polymerization and the discovery and exploitation of new catalytic processes and their technologies and in the study of the structure and use properties of the polymer.

In the round table of recollection, this afternoon, some moments will be dedicated to the discovery of isotactic polypropylene and numerous other stereoregular polymers by Professor Natta and his direct collaborators, as well as the impact of research which has been conducted also in other fields of chemistry and more generally in science, technology and teaching.

We are pleased and honored by the presence of so many distinguished participants in the meeting, and also of so many distinguished scientists.

We are going to hear first Dr. Ewen, who will give a report on "Polypropylene through the eyes of a metallocene". As you may know, Ewen made the fundamental discovery of homogeneous catalysts for the stereospecific polymerization of propylene. Professor Brintzinger then, who made and prepared the chiral catalytic molecules and studied them.

The chiral molecules which are such important catalysts for homogeneous polymerization and which have cleared up the mechanisms of stereospecificity, in a sense.

And then we will hear Guerra and Galli, speaking on polypropylene. And Resconi and Morini. We will have the round table and then we will have, from the laboratory of Professor Ziegler, Gerhard Fink. And then Walter Kaminsky, who discovered the very important cocatalyst, methylaluminoxane, MAO. And we will hear of many other polymers. Professor Lotz for the structure and Professor Allegra. And we will finish tomorrow at about half past noon, I believe.

So, now I will give the word to Professor Pasquon, who was an important co-worker of Professor Natta and who, together with me, established the helical structure, of many polymers different from polypropylene, but isotactic also, in the Fifties, soon after their discovery.

ITALO PASQUON

I am from Politecnico di Milano and an unforeseen commitment has prevented the Rector of our Politecnico from participating in today's meeting dedicated to Giulio Natta. And Professor Giulio Ballio has asked me to bring you his apologies and his salutes. I bring, too, the salute of the President of Istituto Lombardo, Accademia delle Scienze, Professor Emilio Gatti.

Giulio Natta has worked in the Politecnico di Milano as Professor of Industrial Chemistry and as Chairman of the Institute (nowadays Department) of Industrial Chemistry for thirty-five years (from 1938 to 1973). But Giulio Natta's association with Politecnico di Milano has even deeper roots. In fact, he graduated in Industrial Chemical Engineering from Politecnico in 1924, when he was only twenty-one.

At the same Institution, he continued also his activity as a researcher. His first scientific publication on the stability of alkaline chloride solutions dates to 1923. He was a student at that moment. He started his career as a Professor in the Institute of General Chemistry in Milano, which he left in 1933 after winning the Chair of General Chemistry of the University of Pavia at only thirty years of age. In 1935 he proceeded to the Chair of Physical Chemistry in Rome and then in 1937 to that of Industrial Chemistry in Torino, before returning to Milano in 1938. Here, thanks to the facilities of Politecnico and to the support of the Montecatini Company (support in money and researchers), he developed researches which made one of the most eminent chemists of our age.

Hans-Herbert Brintzinger (a)

CATALYST MODELS AND THE EVOLUTION OF *ANSA*-METALLOCENE CATALYSTS FOR THE STEREOSELECTIVE POLYMERISATION OF α-OLEFINS

1. Early studies on metallocene catalysts

Shortly after Natta, Pino and coworkers [1] and Breslow and Long [2] had independently reported in 1957 that soluble, titanocene-based catalyst systems polymerise ethylene in a manner similar to that of solid-state Ziegler catalysts [3], a series of in-depth investigations led to plausible and largely correct descriptions of the course of homogeneous olefin polymerisation catalysis [4-7]. Essential parts of the Cossee model for solid Ziegler catalysts, which are still considered valid today, are based on these early studies on homogeneous catalysts [8].

The discovery of stereospecific polyolefin formation by Natta and Corradini [9], on the other hand, did not find an early counterpart in homogeneously dissolved catalyst systems, from which plausible stereochemical models could have been derived. While a remarkable vision – that an asymmetric metallocene catalyst might stereoselectively interact with a prochiral olefin so as to favour concatenation by one particular enantioface (Fig. 1) – was proposed already in 1958 by Patat and Sinn [10], this proposal remained buried in the literature for more than two decades, since metallocene catalysts capable of polymerising olefins other than ethene were not known at that time.

Possibly for this reason, it took about twenty five years until a convincing model for stereocontrolled polyolefin formation – chain-segment mediated catalytic-site control – was advanced by Corradini and experimentally verified by Zambelli and their respective coworkers [11, 12].

(a) Fachbereich Chemie – Universität Konstanz – D-78457 Konstanz (Germany).

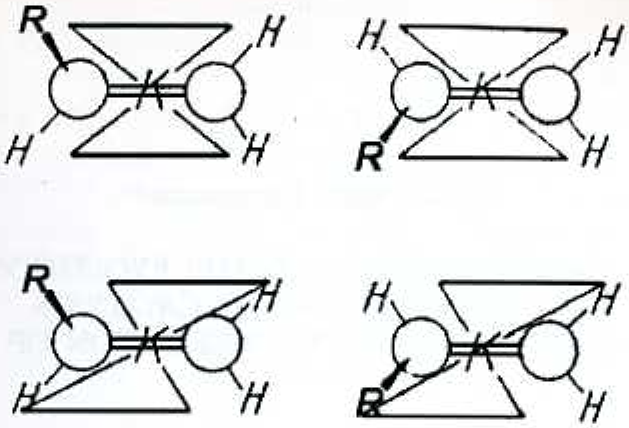


Fig. 1 – Enantiofacial preference for coordination of an α-olefin to an unsymmetrical catalyst, proposed by Patat and Sinn in 1958 [10].

2. CHIRAL ANSA-METALLOCENE CATALYSTS

Stereoselective olefin polymerisation by homogeneous catalyst sytems became known as a research topic to the author of this report in the early seventies by discussions with Charles Overberger, then at the University of Michigan. Overberger, who had investigated the polymerisation of styrene by titanocene-based catalysts without obtaining definitive stereochemical results [13], was acutely aware of stereochemical problems in polymerisation catalysis and, through his former association with Herrmann Marks at Brooklyn Polytechnic, possibly even of the proposal by Patat and Sinn. In 1974 the author received from Overberger an unpublished manuscript "Ziegler-Natta Catalysts and Polymerizations", written by the just-deceased John Boor, and was impressed by the concluding paragraphs of this posthumously published and frequently quoted book [14], which expounded the necessity to find homogeneous catalyst systems capable of inducing stereocontrolled α-olefin polymerisation.

Shortly thereafter, the author submitted to Deutsche Forschungsgemeinschaft, for a special programme supporting research in homogeneous catalysis from 1974 to 1979, a proposal to prepare chiral, configurationally stable metallocene complexes with substituted ring ligands linked by interanullar bridges for use as stereoselective catalysts. In a workshop hearing on the programme projects, Sinn, one of the programme coordinators, made the author aware of his and Patat's early proposal and cautioned that it might not be possible to activate titanocene complexes for the polymerisation of α-olefins. Walter Kaminsky, one of the programme participants, expressed optimism, however, that this obstacle might eventually be overcome.

While preparations of the first ring-bridged [15], chiral *ansa*-titanocenes were still beset by the formation of regio- and stereoisomers [16, 17], reliable and relatively short synthetic routes to the *rac*-isomers of C_2H_4-bridged bis-indenyl and bis-tetrahydro-indenyl titanium dichlorides, *rac*-$C_2H_4(ind)_2TiCl_2$ and *rac*-$C_2H_4(thind)_2TiCl_2$, were found in 1982 by Ferdinand Wild [18], who then set out to prepare also the analogous zirconocenes [19], since reports of α-olefin-polymerisation by methylalumoxane-activated zirconocene complexes had just appeared in the literature [20, 21].

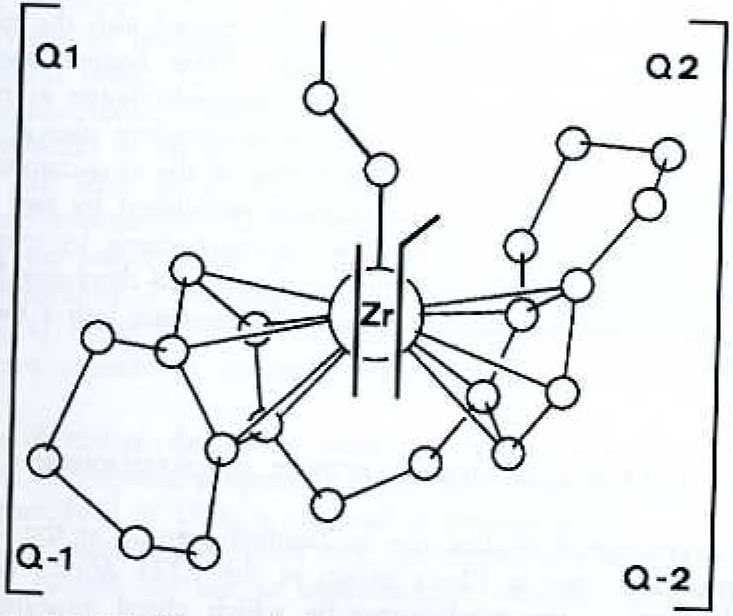
In the fall of 1982, we discussed possible uses for chiral *ansa*-titanocenes with visitors from the United States and suggested to them to make the availability of these complexes known to colleagues interested in potential applications. This information may thus have reached the Exxon laboratories by diffusion through the American scientific network or directly from our publication in *J. Organomet. Chem.* At any rate, the ability of MAO-activated *rac*-$C_2H_4(thind)_2TiCl_2$ to produce isotactic polypropene under catalytic-site control at sub-ambient temperatures was observed there already during 1983 by John Ewen and reported soon thereafter [22].

In the meantime, Ferdinand Wild had prepared also the analogous *ansa*-zirconocenes and successfully persuaded Klaus Külper, one of Kaminsky's graduate students, to study their stereoselectivities as polymerisation catalysts, which was thus found to be excellent also at ambient temperatures [23]. With the stereoselectivities of the *ansa*-titanocene and -zirconocene catalyst systems independently established by two research groups, the scene was set to elucidate the mechanisms by which these and many other *ansa*-metallocene complexes prepared thereafter [24] control the enantiofacial orientation of an olefin inserting into a metal-polymer bond.

3. ORIGINS OF STEREOSELECTIVITY AND STEREOERRORS

Two experimental studies, one in Zambelli's group at the University of Salerno [25], one in Pino's group at the ETH Zürich [26], gave essential clues on the mechanisms by which chiral *ansa*-metallocene catalysts control the stereochemistry of growing polyolefin chains. By a ^{13}C-labelling strategy analogous to that employed to study solid-state polymerisation catalysts [11], Zambelli and coworkers showed that insertion of an α-olefin into a *rac*-$C_2H_4(thind)_2Ti$-alkyl bond is stereo-selective only for Ti-bound alkyl units with at least two C atoms and concluded that the chirality of the coordination site is transmitted to the incoming olefin by way of the orientation of the C(α)-C(ß) alkyl segment, as had been proposed before for solid-state polymerisation catalysts [12].

This proposal was supported by studies in Pino's group, which made use of resolved *ansa*-metallocene enantiomers. After several common meetings of Pino's research group with ours, Ferdinand Wild went to Pino's laboratory in 1986 to prepare isolated enantiomers of $C_2H_4(thind)_2ZrCl_2$ for this purpose. When MAO-activated C_2H_4(1,1'-*R*-thind)$_2ZrCl_2$ was used to catalyse the hydrotrimerisation of propene in the presence of H_2, the preponderantly formed stereoisomer was found to be that expected from a 1,2-insertion, where the olefin substituent is oriented away from the C(α)-C(ß) chain segment, while the latter is placed into the open quadrant Q_1 of the metallocene ligand framework (Fig. 2).



ig. 2 – Preferred enantiofacial approach of an α-olefin controlled by the orientation of the last-nserted polymer chain segment in the least-crowded quadrant Q_1 of 1,1'-R-$C_2H_4(thind)_2Zr$-pol$^+$, as derived from the absolute configuration of a hydrotrimerisation product by Pino *et al.* [26].

This qualitative picture was corroborated through molecular-modelling studies by Corradini, Guerra and coworkers (Fig. 3) [27, 28], who showed that the concept of chain-segment mediated catalytic-site control applies to isospecific polymerisations with C_2-symmetric *ansa*-metallocenes as well as to syndiospecific polymerisations with the C_S-symmetric complexes prepared and studied by Razavi and Ewen [29].

Even though correct in its predictions, this model was further modified by the concept of α-agostic interaction [30, 31]. Following a tripartite discussion session with Malcolm Green in Oxford, hydrocyclisation experiments in John Bercaw's group at Caltec and hydrodimerisation studies in the author's group at Konstanz were done in parallel with deuterated dienes and alkenes, respectively [32, 33]. Significant stereokinetic isotope effects gave first evidence [34] that agostic interaction of

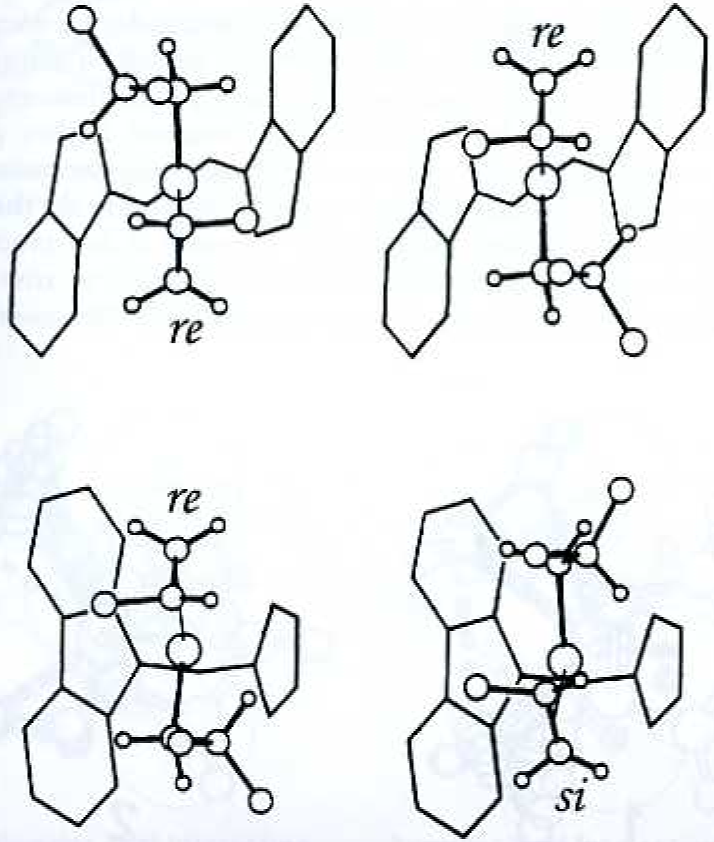


Fig. 3 – Enantiofacial preference for α-olefin coordination to homotopic (top) and enantiotopic (bottom) catalyst sites, mediated by the orientation of the last-inserted chain segment, from molecular-model calculations by Corradini, Guerra *et al.* [27, 28].

one of the α-C-H bonds of the growing chain with the metal centre facilitates insertion of an α-olefin into a Zr-alkyl bond. This notion, that a tilting of the Zr-bound alkyl group must precede insertion of the olefin into the Zr-C(α) bond, was portrayed by simple Extended-Hückel calculations with astonishing clarity (Fig. 4) [35], which was reached much later also by high-level molecular-dynamics calculations [36].

That actual polymerisations with *ansa*-metallocene catalysts are likewise stereocontrolled by α-agostic interactions was shown by Margarete Leclerc by use of deuterium-labelled propene isotopomers (Fig. 5) [37]. The requirement to lock the C(α)-C(ß) chain segment into an orientation which is compatible with the extension of the ligand framework thus reduces the conformational analysis required for the model shown in figure 3 to a choice between two possible Zr-H(α) interactions (Fig. 6), which clearly discriminates between stereoregular and -irregular insertions.

In addition to explaining the high stereoselectivity of metallocene-catalysed olefin polymerisations, this study also helped to clarify the origins of stereoerrors in metallocene-catalysed polymerisations. At the STEPOL Symposium held 1994 in Milano, Margarete Leclerc presented a poster on her results with propene isotopomer polymerisations, while Vincenzo Busico and Luigi Resconi reported independently that stereoerror frequencies in isotactic polypropene increased at low propene concentrations [38, 39]; a phenomenon that was proposed to arise from an isomerisation of the last-inserted chain segment [38]. Discussions in the

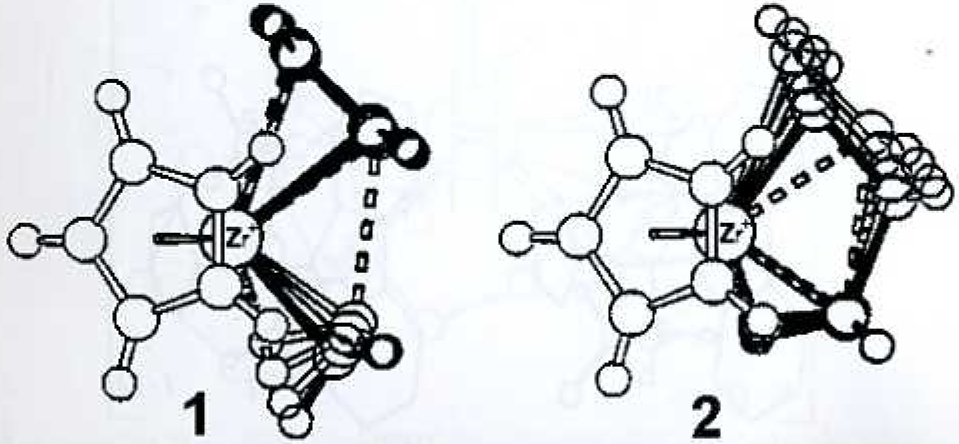


Fig. 4 – Insertion of ethene into a Zr-CH$_3$ bond under α-agostic assistence. **Phase 1**: tilting of the CH$_3$ group by formation of a Zr-H(α) agostic bond; **Phase 2**: formation of the new C-C bond, Extended-Hückel MO calculations by Prosenc *et al.* [35].

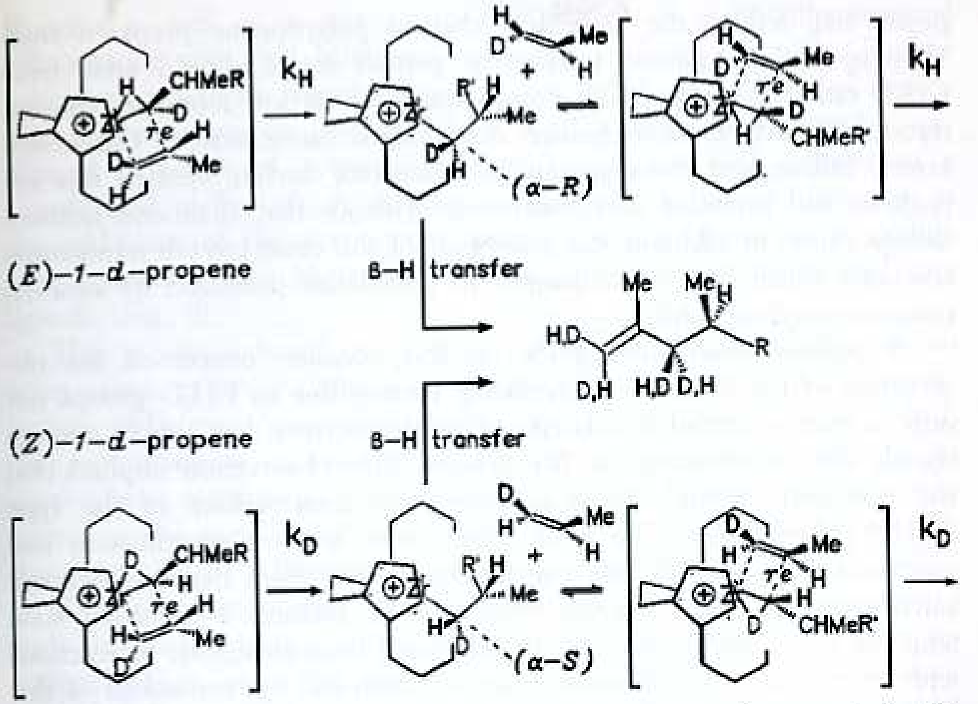
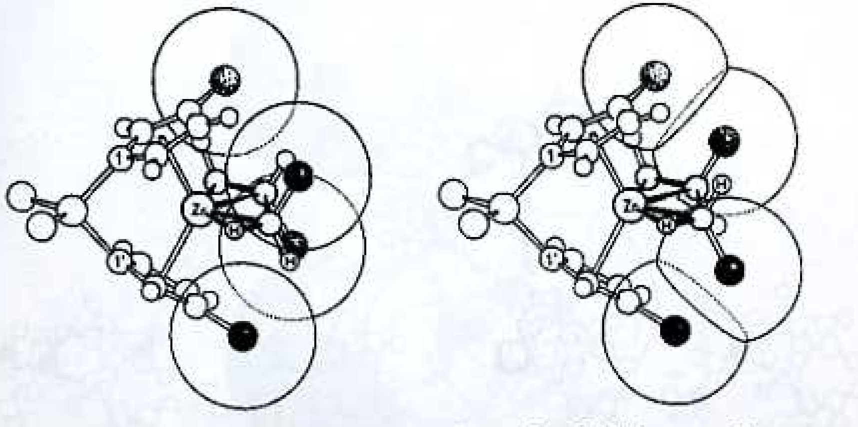


Fig. 5 – Stereokinetic isotope effects, due to α-agostic interactions, on the rates of polyolefin chain growth, determined by use of propene isotopomers by Leclerc *et al.* [37].



Regular Zr-H Interaction **Irregular Zr-H Interaction**

Fig. 6 – Zr-H(α) agostic bonds reinforce the orientation of the Zr-bound chain segment (in front) and thereby the stereochemistry of the olefin insertion (in rear) [35].

poster hall led to the agreement that in polypropene prepared from 1D-propene, the mmmr stereoerror pentad signal should arise from CH$_2$D rather than from CH$_3$ groups, especially at low monomer concentrations, if such an isomerisation does indeed cause most of the stereoerrors. Subsequent investigations by Margarete Leclerc verified this hypothesis and provided also convincing evidence that chain-end isomerisations cause, in addition, the main part of the chain-growth termination reactions which limit chain lengths in polyolefins produced by *ansa*-zirconocene-catalysts [40].

A curious observation made on this occasion concerned the observation of the characteristic splitting pattern due to CH$_2$D groups not only in mmmr pentad signals caused by stereoerrors, but also in mmmm signals due to stereoregular Me groups. This observation implied that the polyolefin ligand in an isomerisation intermediate of the type Zr(H)$^+$···polyolefin can flip a the easily from *si* to *re* coordination and vice-versa. A model for this conversion, derived from density-functional calculations by Marc-Heinrich Prosenc [41], pictures a transition state with the polyolefin ligand held by the metal through agostic interactions with its terminal C(1)-H bonds (Fig. 7). Chain-end epimerisations of this kind were recently verified by double-labelling experiments in John Bercaw's group [42], and by direct NMR studies on "working" catalyst systems in the group of Clark Landis [43].

In another development, aimed at an extension of the range of accessible polymer chain lengths, effects of substituents in 2-position of the indenyl ring, i. e. of a lateral extension of the *ansa*-zirconocene complex, were studied at the same time in Walter Spaleck's group at Hoechst as well as in our group at Konstanz in a BMBF-sponsored collaboration with Rolf Mülhaupt's group at Freiburg and with Günther Schweier's polyolefin-research group at BASF [44, 45]. Effects of monomer concentration on polymer chain lengths were most plausibly explained in terms of a transition state model for ß-H transfer to a coordinated olefin, which extends substantially in lateral direction in the mid-plane of the zirconocene complex and is hence apt to collide with laterally placed Me substituents in 2-position of the indenyl ring ligands (Fig. 8).

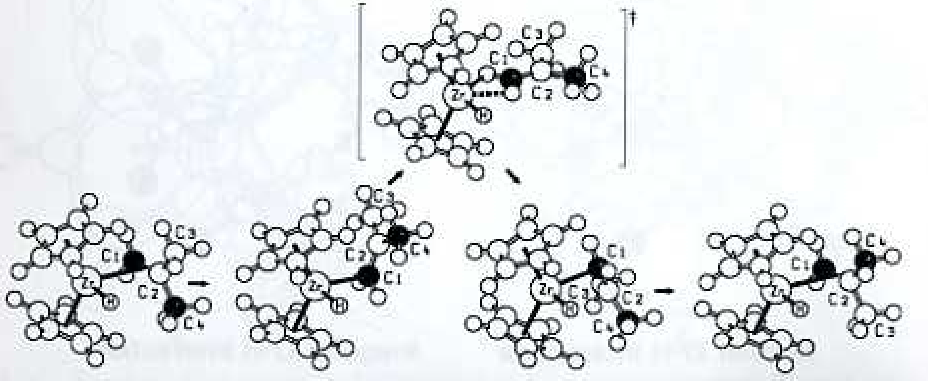


Fig. 7 – Transition state for the enantioface interchange of a polyolefin chain end bound to a zirconocene hydride cation, from DFT calculations by Prosenc *et al.* [41].

This picture induced us to study the effects of ring substituents on other reactions which require an uptake of extra ligands in the metallocene mid-plane. Anion-displacement reactions in particular, by which the counter-anions of reactive metallocene cations are relegated to an outer-sphere association, were found to be greatly retarded by substitutents at the metallocene ring ligands which interfere with the associative formation of a five-coordinate reaction intermediate (Fig. 9) [46].

The anion-displacement model represented in figure 9 is in accord with the stereoselective course observed for these ligand exchange reactions, which leaves the alkyl group in its original coordination position [46]. It would thus explain why the growing polymer chain bound to a syndiospecific ansa-zirconocene catalyst might remain at the same catalyst site even if re-coordination and renewed displacement of the anion by the olefin substrate would occur before each successive insertion step.

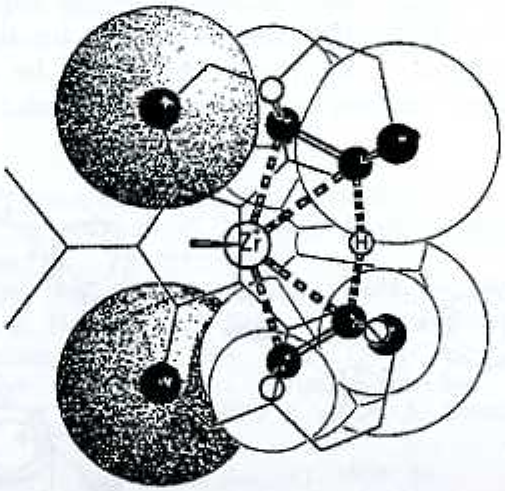


Fig. 8 – Steric hindrance for ß-H transfer from a growing polyolefin chain to a coordinated monomer by CH$_3$ substituents in 2-position of the indenyl ligands [45].

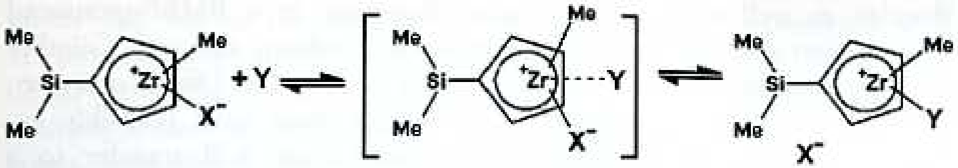


Fig. 9 – Five-coordinate intermediate for the displacement of an anion X^- by a neutral ligand Y, derived from kinetics of outer-sphere ion-pair formation by Schaper *et al.* [48].

To which degree of completion an anion displacement has to proceed before an olefin can insert into the metal-polymer bond [47], how frequently displacement and re-coordination of the anion does in fact occur – in a fast pre-equilibrium, after each olefin insertion [48], or as the terminal event in the growth of each polymer-chain – and which role ion quadruples and higher-order ion aggregates (Fig. 10) [49, 50] play with regard to anion and/or polymeryl exchange between individual cationic species as well as to catalyst degradation reactions remain open questions at this time.

For ion pairs of the type $Cp_2Zr(\mu\text{-}Me)_2AlMe_2^+$ $MeMAO^-$, formed in zirconocene catalyst systems at high Al(MAO):Zr ratios [51,52], diffusion rate measurements by pulsed field-gradient NMR indicate huge dimensions of the anion (Fig. 11) [53]. This would suggest that the metal centre of a cationic metallocene species cannot approach the surface of the $MeMAO^-$ anion directly and that this circumstance might contribute to the particularly useful properties of MAO as an activator.

Similarly challenging, in view of great practical implications, remains the task to develop appropriate model pictures for the structures and typical reaction patterns of reactive species formed by MAO^- or borate-activated metallocene catalysts on the surface of solid supports. In regard to these and related questions, great advances can be expected to materialise within the next few years.

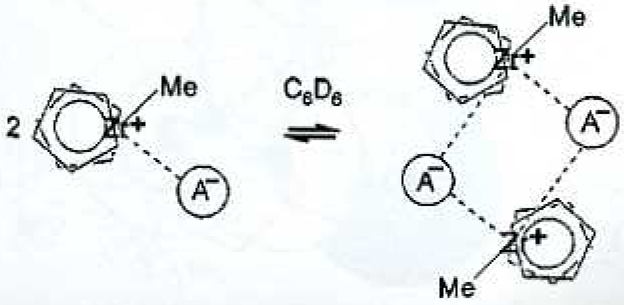


Fig. 10 – Ion quadruples as intermediates for anion exchange between zirconocene contact ion pairs, from pulsed-field gradient NMR diffusion rate studies by Beck *et al.* [49].

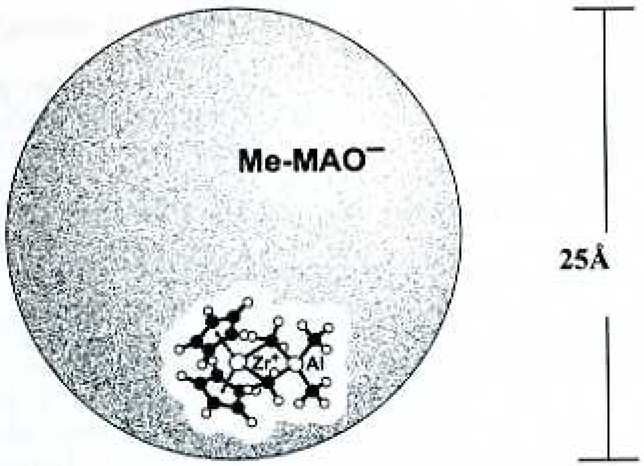


Fig. 11 – Size relation between $(C_5H_5)_2Zr(m\text{-}CH_3)_2Al(CH_3)_2^+$ cation and its $Me\text{-}MAO^-$ counteranion, from pulsed-field gradient NMR diffusion rate studies by Babushkin *et al.* [53].

ACKNOWLEDGEMENTS

The author expresses his thanks to the collaborators and colleagues whose names appear in the text or in the references of this article as well as to the many students in his and in other research groups who have laid essential foundations for the catalyst models referred to in this article.

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Gaetano Guerra[a]

IMPACT OF NATTA'S DISCOVERIES ON INDUSTRY AND USES OF PP IN EVERY DAY'S LIFE

This presentation is aimed to describe the major impact of the Natta's discoveries on the polymer industry and more in general to the chemical industry. Of course, a substantial part of this contribution will be devoted to isotactic polypropylene (i-PP), which is presently the highest volume industrial polymer product.

For centuries mankind has used *natural polymers* for clothing and shelter. Manufacturers used these polymers as bases for new materials in the nineteenth century. Generally these polymeric materials obtained from chemical modification of natural polymers are defined as *artificial polymers*.

A first milestone of artificial polymers is the discovery in 1839 by Charles Goodyear of the process of vulcanization of the natural rubber. In fact, he discovered that by treatments of natural rubber with varying amounts of sulfur it is possible to control its toughness and elasticity. The natural rubber, which till then was only used to produce minor products, like e.g. erasers, became extremely relevant for several technical applications. Frederick Schoenbein in 1846 discovered cellulose nitrate by procedures involving treatment of cellulose with nitric acid. However, this material was marketed as celluloid only in 1870 when John Hyatt discovered that cellulose nitrate combined with camphor can be shaped and hardened by the application of heat and pressure. The production of the first artificial fiber (Rayon), obtained by dissolution and spinning of cellulose, started in France in 1889. In 1905 begins marketing of cellulose acetate, obtained by reaction of cellulose with acetic acid. This artificial material fully replaced celluloid for production of plastic films as well as for several other applications.

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The industrial history of wholly *synthetic polymers*, that is of materials obtained from polymerization of small molecules, begins on 1909, when following the discovery by the Belgian scientist Leo Baekeland, in the United States starts the production of Bakelite, a thermoset resin obtained by reaction of phenol and formaldehyde. This kind of industrial product, presently named as phenolic resin, remains at the beginning of this new millennium the mostly produced thermoset material.

The first industrial production of a synthetic rubber begins in Germany in 1915 with the poly(2,3-dimethyl-butadiene). However this kind of rubber was soon replaced by polybutadiene, whose production began in USSR in 1932 and mainly by copolymers of butadiene and styrene (Buna-S was the name at that time, presently this kind of rubber is known as SBR, which means Styrene-Butadiene Rubber), whose production began in Germany in 1934. As for fully synthetic rubbers, it is quite interesting the impressive increase of production due to the needs of the second world war. For instance the USA production which in 1942 was close to 20 thousand tons increased up to nearly 600 thousand tons in 1945. For the sake of comparison, the US production of SBR, which is also presently the mostly used synthetic rubber, has been in 2001 of 1.165 thousand tons.

The first industrial production of a synthetic thermoplastic, in particular of polyvinylacetate, was in Canada in 1925. However, the industrial production of thermoplastics which presently are high volume commodities starts in Germany in 1927 with polyvinylchloride and in 1932 with polystyrene. An other important event is the start of production of polyethylene by using radical initiators and high pressure plants, which was in Great Britain in 1939. By this kind of process an highly branched and poorly crystalline polyethylene was achieved, which presently is named Low Density PolyEthylene (LDPE, scheme 1).

The history of fully synthetic fibers begins in USA after the discovery by Wallace Carothers of polyesters and polyamides (nylons). In particular, in 1939 the industrial production of Nylon 6,6 obtained by polycondensation of adipoyl chloride and hexamethylene diamine, starts. The production of polyester fibers (polyethyleneterephtalate) starts in 1949 in Great Britain. These two kinds of fibers remain, at the beginning of this new millennium, the mostly used synthetic fibers.

The decade between 1920 and 1930 saw also the birth of the macromolecular science. In fact, in that period the same concept of macromolecule was defined and a quite important contribution was given by the definition of the crystal structure of a macromolecular compound (cellulose) by Meyer and Mark in 1928. An outstanding contribution to the field was also given by Hermann Staudinger, which received a Nobel price in 1953 [1].

Possibly the most accurate synthetic description of the polymer industry, before the discovery by Ziegler and Natta of organometallic polymerization catalysis, is just included in the Nobel Price lecture of Prof. Staudinger (Table 1).

TABLE 1

Classification of macromolecular substances.

I. Substances occurring in nature

1. Hydrocarbons - rubber, guttapercha, balata.
2. Polysaccharides - celluloses, starches, glycogens, mannans, pectins, polyuronic acids, chitines.
3. Polynucleotides (nucleic acids).
4. Proteins and enzymes.
5. Lignins and tans (transition from low- to macromolecular substances).

II. Conversion products of natural substances

Vulcanized rubber, rayon, cellophane, cellulose nitrate, leather, galalith etc.

III. Synthetic materials

Plastics formed by

polymerization	- buna, polystyrene, polymethacrylic ester.
polycondensation	- bakelite, nylon, Perlon, Terylene.
polyaddition	- polyurethane.

In order to understand the relevance of the Ziegler's and Natta's discoveries, it is also worth recalling that after the 2nd world war a major change was occurring in Chemistry. In fact while until that time the main source of raw materials was coal, a gradual shift toward oil occurred, making available large quantities of aliphatic hydrocarbons, mainly ethene, propene, butene and butadiene.

In this framework, in 1953 there was the discovery by Prof. Karl Ziegler, in Mulheim (Germany), of organometallic catalysts which are able to polymerize ethene at low pressure and low temperatures to a linear high crystalline polymer, which presently is named High Density PolyEthylene (HDPE, scheme 1) [2]. Only one year later there was the discovery by Prof. Giulio Natta in Milan that this kind of catalysts is also able to polymerize 1-alkenes to isotactic polyolefins [3]. For these discoveries both scientists got a joint Nobel Price for Chemistry in 1963.

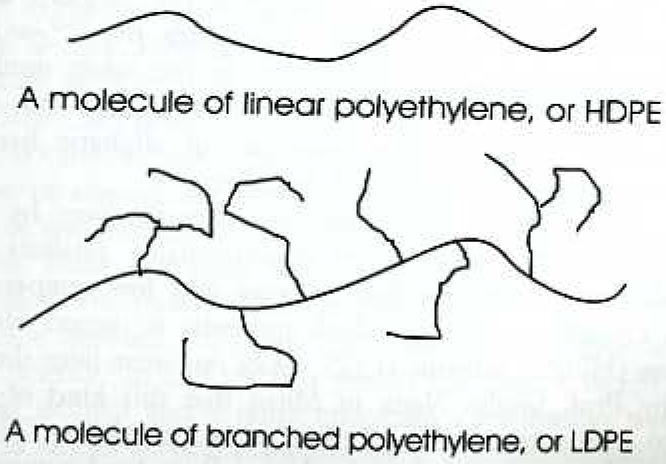
In order to describe the impact of Ziegler's and Natta's discoveries on Industry, five different classes of new polymers from transition metal catalyzed polymerization of hydrocarbon monomers will be considered in the following: linear polyethylenes, stereoregular polyolefins, stereoregular polydienes, ethene/propene copolymers and polyacetylenes.

As for new polymers from ethene, beside the linear HDPE (Scheme 1), also a new linear copolymer of ethene with minor amounts of 1-alkenes, the so called Linear Low Density PolyEthylene (LLDPE), was discovered.

LLDPE presents physical properties and application fields very similar to those of the classical LDPE from radical polymerization, however it has the advantage to be produced in low pressure swing capacity plants, alternatively producing HDPE. In fact, LLDPE has gradually assumed a growth rate faster than LDPE. In fact, since 1995 the production growth has been for LLDPE larger than five percent per year while it has been nearly null for LDPE.

The discovery of the Natta's school which has given the highest impact on the industry has certainly been the discovery of stereoregular polyolefins and mostly of isotactic polypropylene. The original figure which defined the new concepts of atactic, isotactic and syndiotactic vinyl polymers, taken by the Nobel Price lecture of Prof. Natta is shown in Fig. 1.

Two models representing the ternary helix which is present in the crystal structures of isotactic polypropylene are shown in Fig. 2. In particular, on the left side there is the old-style but highly accurate representation, taken from a paper published by Prof. Natta with Prof. Corradini on the "Memorie" of the "Accademia Nazionale dei Lincei" in 1955 [4]. On the right there is the same helix as shown by a computed aided picture.



Scheme 1.

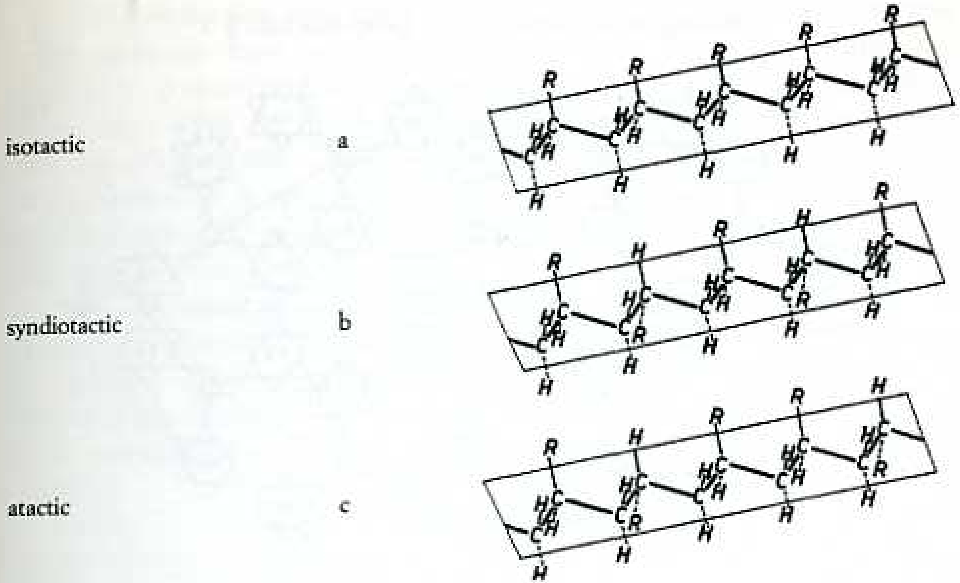


Fig. 1 – Models of chains of head-to-tail vinyl polymers supposed arbitrarily stretched on a plane, having, respectively, isotactic (a), syndiotactic (b), and atactic (c), successions of the monomenic units.

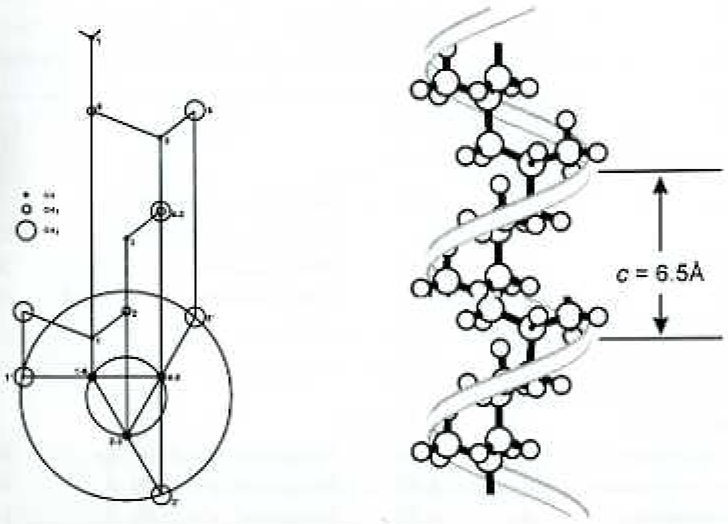


Fig. 2 – Models representing the ternary helix of the crystal structures of isotactic polypropylene.

Also taken by the Natta's Nobel lecture, in the following are shown the first crystal structure of an isotactic polymer (isotactic polystyrene) [5] (Fig. 3) and a Table 2, including an impressive list of X-ray data on newly achieved isotactic polymers.

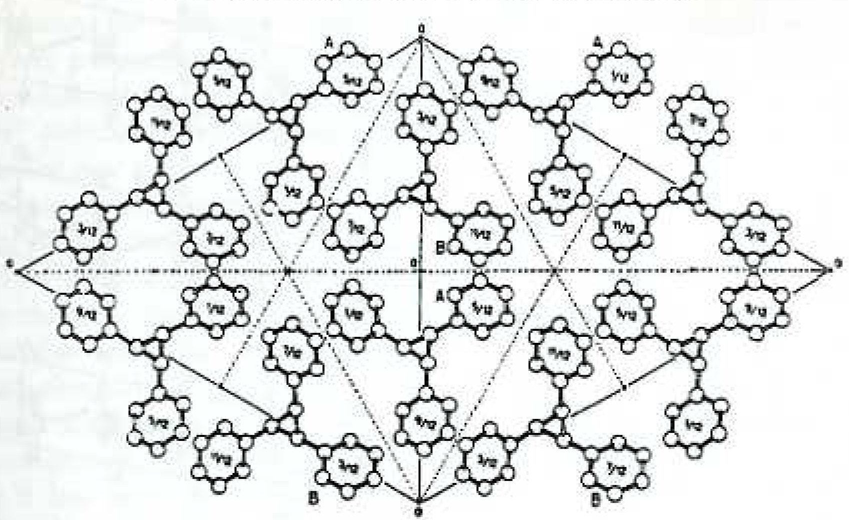


Fig. 3 – Model of packing of isotactic polystyrene in the crystalline state, projected on the (001) plane.

TABLE 2

X-ray data on some typical isotactic polymers with different chain conformations.

Polymers	*Helix type* [(a)]	*Chain azis (Å)*	*Unit cell*	*Space group*
Polypropylene	3_1	6.50	Monoclinic, $a = 6.65$ Å; b = 20.96 Å; b = 99°20′	C2/4
Poly-α-butene [(b)]	3_1	6.50	Rhombohedral, a = 17.70 Å	R3c or R$\bar{3}$$c$
Polystyrene	3_1	6.63	Rhombohedral, a = 21.90 Å	R3c or R$\bar{3}$$c$
Poly-5-methylhexene-1	3_1	6.50		
Poly-5-methylheptene-1	3_1	6.40		
Poly-3-phenylpropene-1	3_1	~6.40		
Poly-4-phenylbutene	3_1	6.55		
Poly-o-methylstyrene	4_1	8.10	Tetragonal, $a = 19.01$ Å	I4_1cd
Poly-α-vinylnaphthalene	4_1	8.10	Tetragonal, $a = 21.20$ Å	I4_1cd
Polyvinylcyclohexane	4_1	6.50	Tetragonal, $a = 21.70$ Å	I4_1a
Poly-3-methylbutene-1	4_1	6.84		
Poly-4-methylpentene-1	7_2	13.85	Tetragonal, $a = 18.60$ Å	P$\bar{4}$
Poly-4-methylhexene-1	7_2	14.00	Tetragonal, $a = 19.64$ Å	
Poly-m-methylstyrene	11_3	21.74	Tetragonal, $a = 19.81$ Å	

(a) It is to be understood that, besides the right-handed Xn helix, the left-handed X_{X-n} helix also esists.

(b) Modification 1.

USA production data from 1960 to 2000 of the highest volume polymeric materials have been collected in Table 3. These data clearly show that i-PP presently is the highest production commodity resin. Moreover, since 1996 the production growth has been for i-PP larger than five percent per year. Closely similar behaviors is observed for the European market. It is also worth adding that, according to market specialized journals, i-PP should remain for the next future the world's fastest-growing polymer.

The principal reasons of i-PP industrial strength are the very low density associated with high stiffness and good tensile strength, but also the inertness toward acids, alkalis and solvent and mainly good injection-molding characteristics and cost advantage. All these properties make i-PP particularly suitable for the large-volume cost- and weight-conscious markets.

A list of principal i-PP uses, as reported by the *Chemical Profiles* of the *Chemical Market Reporter*, is shown in Table 4. The main use of

TABLE 3

USA production (1960-2000) (thousand of metric tons).

	Year				
	1960	1970	1980	1990	2000
LDPE	560	1923	3307	5069	7042
HDPE	70	728	1998	3780	6333
PP	—	468	1655	3773	7139
PS	450	1075	1597	2273	3104
PVC	590	1413	2481	4122	6551
Total:	1700	5600	11000	19000	30100

TABLE 4

Uses of isotactic polypropylene taken from Chemical Profiles of Chemical Market Reporter *(2001).*

Injection molding	31%
fiber and filament	30%
compounders	23%
film and sheet	11%
blow molding	2%

i-PP is in injection molding applications (food containers, electrical appliance, furniture, etc.). It is particularly interesting to cite the i-PP applications in the automotive market, which is a typical large-volume cost- and weight-conscious market. 1700 components on 5000 are made with plastics, which correspond to 10% by wt. (and 60% by wt. of the interior of an average car). In particular, i-PP is used for instance for battery cases, bumpers, exterior and interior trim, fuel tanks, instrument panels, under-the-hood applications, wires and cables.

An other high volume use of i-PP is in fibers and filaments, which are mostly used for carpets, ropes and "non-woven" textiles (disposable garments, diapers). Presently, as for the market of synthetic fibers, olefinic fibers (mostly based on i-PP) are produced in amount comparable with polyamide (nylon) fibers and smaller only with respect to polyesther fibers.

Nearly one fourth of the i-PP production is used by compounders which prepare special grades of the material by adding several additives and making blends with other polymers. Quite relevant is also the production of films for packaging and for coating of other materials (mostly paper) to make them glossy or waterproof.

As for stereoregular polydienes, a quite impressive representation of the chain conformations in the crystalline phases of the four possible stereoregular polymers of butadiene, all obtained by Ziegler-Natta catalysts, also taken from the Nobel lecture of Prof. Giulio Natta, has been reported in Fig. 4.

A high impact on the industry has also been given by the discovery of stereoregular polydienes. In particular, some stereoregular polydienes obtained by Ziegler-Natta catalysts are relevant for the rubber industry. The most relevant is *cis*-1,4-Polybutadiene, but also *cis*-1,4-Polyisoprene, which presents a chemical structure equal to the natural rubber, can reach high volume productions. In the last decades the rubber industry has also produced not negligible amounts of 1,2-Syndiotactic Polybutadiene.

As for the rubber industry, Ziegler-Natta catalysts have also been relevant for production of Ethene/Propene Copolymers, which are commonly indicated as EPR, i.e. Ethene Propene Rubber, or EPDM when minor amounts of Diene Monomers are copolymerized. In fact, the production growth per year of the rubber based on ethylene-propylene copolymers has been in the last decade close to 6%, that is much higher than for the other synthetic rubbers (2%). This fast growth is primarily due to excellent performance in the automotive and roofing markets.

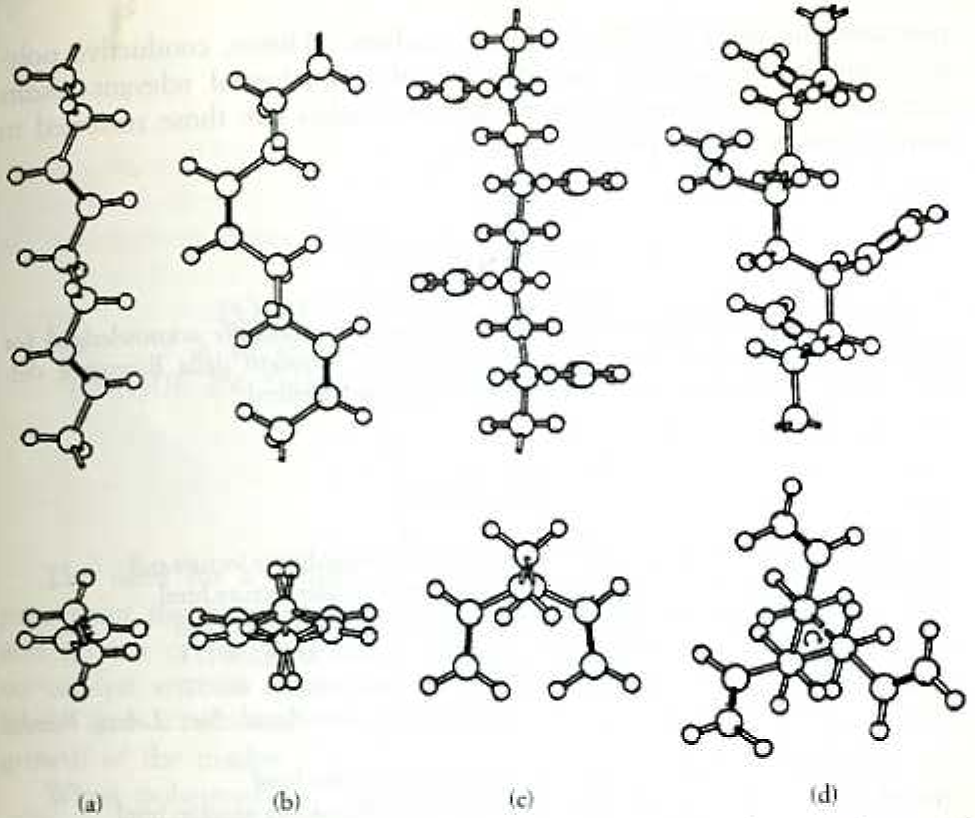


Fig. 4 – Side and end views of the chain conformations of the four stereoisomers of polybutadiene: (a) *trans*-1,4; (b) *cis*-1,4; (c) syndiotactic-1,2; (d) isotactic-1,2.

Last but not least, it is relevant to remind that polyacetylene was firstly obtained by the Natta's laboratories, again by using the Ziegler-Natta catalysts [6].

Studies on electrical conductivity on doped *cis* and *trans* polyacetylene gave to Alan Heeger, Alan MacDiarmid and Hideki Shirakawa the Nobel Prize in Chemistry 2000 [7].

As already occurred for the discovery of the Ziegler polymerization catalysts, serendipity toke his role. In fact, it is interesting to read in the Shirakawa's autobiography that the formation of a polyacetylene film, which was an extremely relevant step to the achievement of conductive polymers was obtained "through an unforeseeable experimental failure... The catalyst concentration of a thousand-fold higher than I had planned..." [8].

In the same autobiography it is possible to read that "the initial purpose of his study was to determine the polymerization mechanism of polyacetylene using the Ziegler-Natta catalysts". Hence, conductive polymers can be included in the long list of technological relevant results connected with polymerization mechanism studies like those reviewed in some chapters of the present booklet.

ACKNOWLEDGEMENTS

Prof. Paolo Corradini and Prof. Italo Pasquon are gratefully acknowledged for helpful discussions. The financial contributions of "Ministero della Ricerca e dell'Universita" (PRIN2002) and of CNR are also acknowledged.

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PAOLO GALLI[a], GIANCARLO VECELLIO[a]

POLYPROPYLENE TECHNOLOGY: A REVOLUTIONARY DEVELOPMENT, UNIQUE IN THE HISTORY OF POLYMER MATERIALS

INTRODUCTION

The need for a continuous and dramatic process and product improvement has been a main driving force behind the entire innovation and growth of polypropylene. This need has pushed scientific research on catalyst systems and material structure property relationships to new levels and is ultimately responsible for the dynamic and continuous growth of the market.

When polypropylene was born and in the early stages of commercialisation, it appeared affected by two main limitations that threatened its commercial success:

1) a complex production process that was difficult to operate consistently, produced unreliable quality and which had limited flexibility or versatility and

2) products that had almost no utility since they apparently had limited properties that were of practical use. This latter element was further complicated by a lack of knowledge on how to control and use these materials and basic structure-property relationships.

Those two critical issues are in fact strictly interconnected but they were in practice kept separated by a deep lack of understanding of the basic chemistry underlying production process technology and the relationships between process and material property requirements of the market.

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In summary, the first generation processes were complicated, expensive, and inflexible with undesirable byproducts and high pollution risks for the various operations.

Attempts to improve or to generate new product properties were barred by the process complexity, rigidity and system constraints.

However since the potential was recognised by the scientists early in its life cycle these difficulties did not get the upper hand!

On the contrary; the polypropylene story really represents a uniqueness in material development. Fueled by a tremendous commitment to understanding the basic phenomena involved in propylene polymerisation and associated polypropylene product processing technology, the problems were tackled with a spirit of innovation, creativity and a professionalism that quickly turned by-products into highly desirable materials of commerce.

At the same time the difficult challenges catalysed a reaction, no pun intended, that has become the main driving force for the development of entire families of polyolefins and which crystallized into a strong robust industry over the last half century. Polyethylene, for example, has benefited from the understanding and developments achieved by its most demanding and difficult "travelling companion", polypropylene.

REVISITING THE PAST

Let us see what has happened since the very beginning of the PP technology commercialisation and what has been the rationale for the intensive R&D developments of the following years.

The bright promises of the early period:

I remember well the very beginning and early period of the novel Ziegler-Natta technology. We were all shocked, admired, full of trust and enthusiasm for the potential of the novel, revolutionary catalysts, able to generate new materials like polyethylene (PE) and polypropylene (PP) with a new, convenient, apparently easy technology and with a new gamut of properties.

There was a lot of enthusiasm for the novelty of the catalytic system, which was able to operate in mild, easy conditions. There was also a deep curiosity for the new materials and their set of properties, a strong expectation to have good and low cost materials, driven by readily available monomers and the expected low cost processes.

The enthusiasm and the push were on the scientists' part, and also the top management of several companies. In November 1955, in Montecatini, a large-scale pilot plant for the polymerisation of ethylene and propylene started operating in the Ferrara plant in Italy.

In January 1957, a very first multipurpose BATCH polymerisation plant for the production of the first high density injection moulding PE ("*Moplen* RO") and PP started operating (Fig. 1).

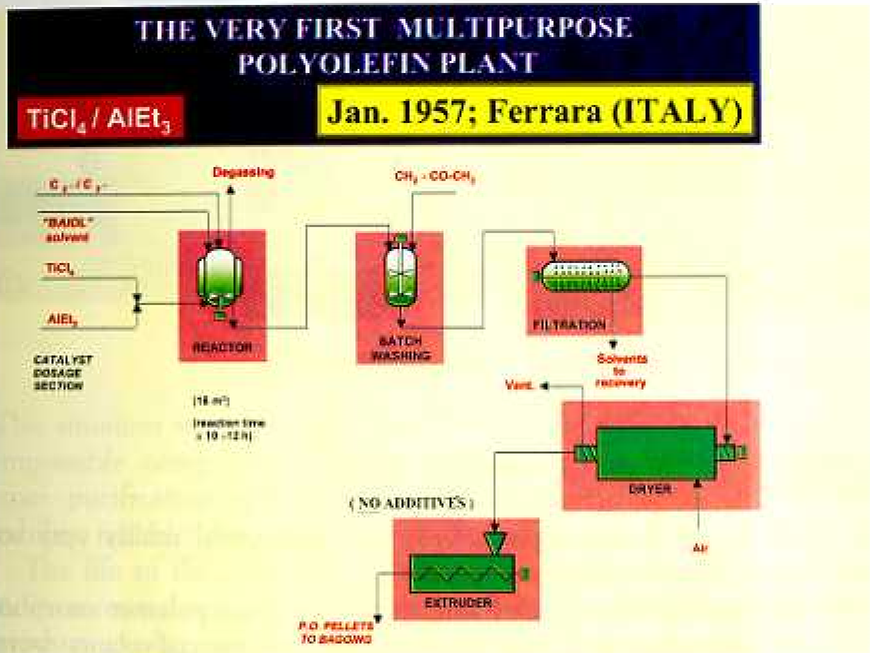


Fig. 1 – The first multipurpose P.O. plant.

It was mainly dedicated to the production of PE; a larger scale, more sophisticated plant fully dedicated to PP started operating in Ferrara in November 1957 (Fig. 2).

Those plants were projected, built and started up in an extremely short time at the cost of tremendous efforts, in terms of commitment, on the researchers' and management's part.

They all made great sacrifices, pushed and supported by the great enthusiasm based on the trust of the fluttering promises of the new family of catalysts and materials.

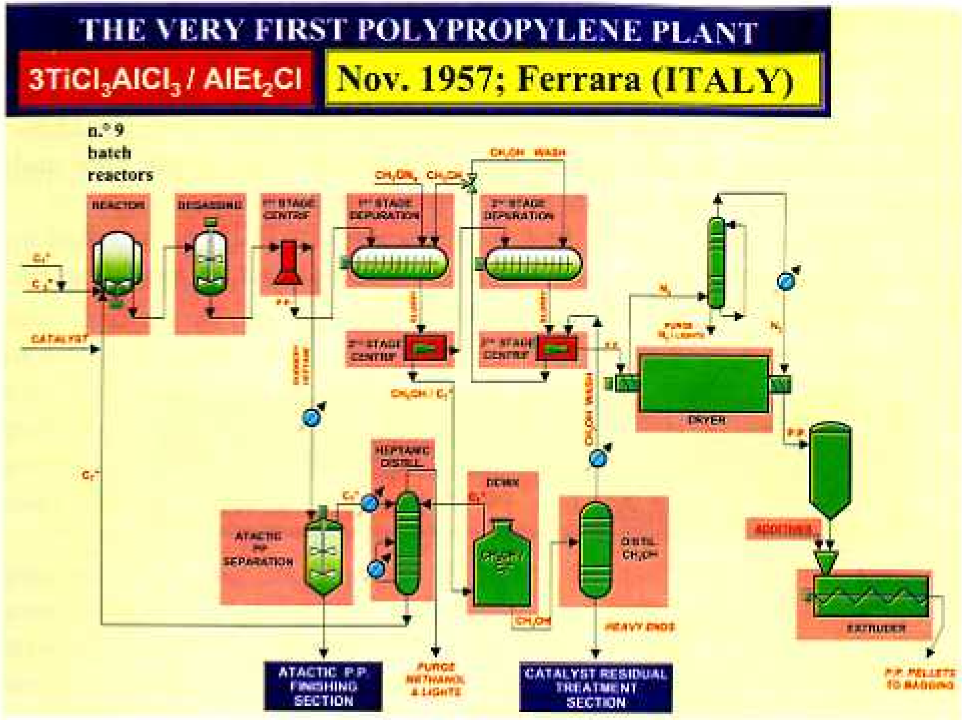


Fig. 2 – The first PP plant.

The bitter, tough commercial reality:

In spite of the bright expectations, the commercial reality very soon turned out to be completely different:

The catalyst activity and selectivity were very poor, polymer morphology did not even exist at a concept level, the commercial plants were a real nightmare to operate, the production costs very high, the properties at best simple and poor and consequently the selling price... low.

In other words, as a business it was a downright disaster!

After many efforts in several different directions to dramatically improve the process technology, it was clear that the *only* answer had to come from a fundamental scientific understanding and development approach.

In particular, we did not recognise that the key to the main commercial plant issues was a largely ignored and misunderstood principle of polymer morphology control which affected all the commercial plants, heavily spoiling all cosmetic efforts made in order to improve quality and cost.

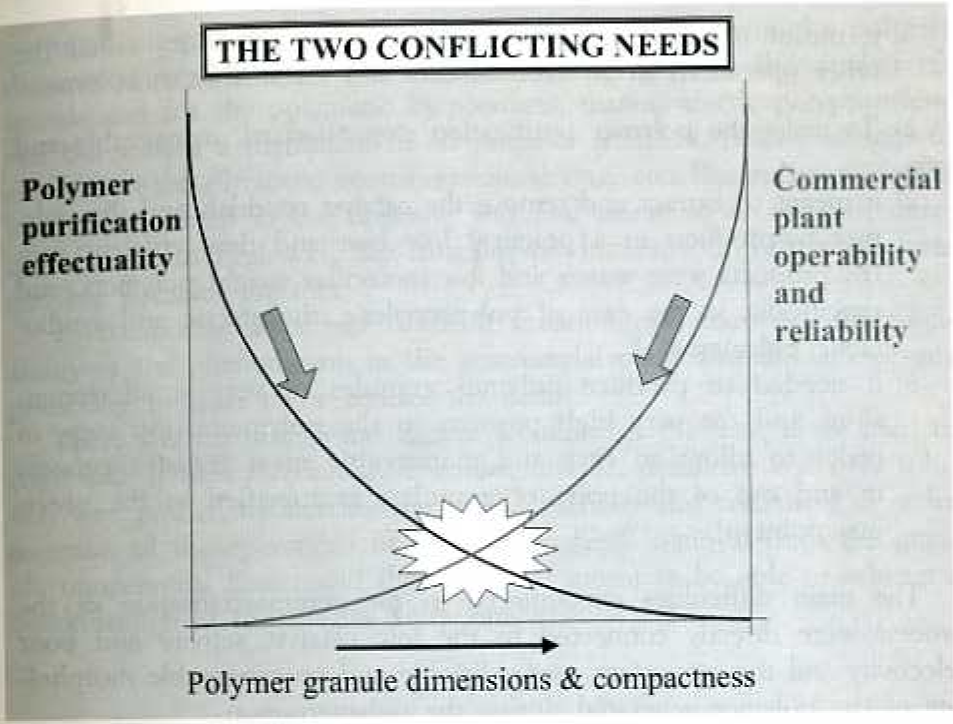


Fig. 3 – The two conflicting needs.

The situation was at a dead end because the solution had to resolve an impossible compromise between two conflicting needs to make the polymer purification step effectual and to make the commercial plant operability reliable, fast and cost efficient (Fig. 3).

The life of the industrial plant was an adventure, or better, a nightmare, in a continuous precarious balance between conflicting needs, such as product quality or plant operability. The plants always had to live under "Damocle's sword", regarding the alternative to have to shift in between a total plugging of the lines or not to be able to achieve a decent quality of the materials in terms of purification from the catalyst residual and undesired polymerisation by-products.

1) To make the overall operability of the commercial plant manageable, reliable and cost efficient:

a) it meant, and means, to obtain medium or large size and compact morphology polymer granules. The granule porosity was a big issue because it meant high polymer fragility during the plant operations, which generated large amounts of very fine and irregular polymers, creating fouling issues.

b) it meant to perform the extraction in the same way as all the other operations in an economically and sustainably short time.

2) To make the polymer purification step effectual, manageable and easy;

a) it meant to extract and remove the catalyst residuals and the polymer by-products in a practical low cost and time efficient way. (By-products were waxes and low molecular weight polymers, and specifically, in the case of polypropylene, the atactic and syndiotactic polymers).

b) it needed to produce polymer granules of very small dimensions and /or very high porosity in the polymerisation step, in order to allow an easy and manageable mass transfer process in and out of the polymer granules, as specified in the previous point a).

The main difficulties encountered in the commercialisation of the process were directly connected to the low catalyst activity and poor selectivity and the inconstant, unpredictable and unmanageable morphology of the polymer generated during the polymerisation.

Those two drawbacks were in fact the cause of the following main consequences:

The totally unpredictable, random, polymer morphology (such as fine particles, extra fines, or vice-versa, very big, porous, fibre like or pop-corn like etc.) (Fig. 4) created insurmountable obstacles to the smooth running of industrial operations, such as discharge from the reactors, slurry or powder, transportation, filtration, purification, centrifugation, drying etc.

Fig. 4 – Examples of bad polymer morphology.

Small morphology was very favourable, for example in the polymer depuration step, it made the extraction easier for both the catalyst residuals and for the polymeric by-products, waxes, atactic polypropylene etc. but it was a nightmare in all polymer transfers, from one step to another, in the filtration, centrifugation, drying, etc. Big polymer particle morphology acted in the opposite way and worst of all and not infrequently was to deal with the irregular random mix of very small fines and big particles together.

To compound an already difficult situation, was the total unpredictability of the phenomenon in the commercial plant and the lack of any possibility to react to or control the issue!

There was no simple and elegant solution for the issue if we tried to cope with it in a direct way. The real, unique, definitive and only solution was, and is, to increase the catalyst activity and selectivity in order to make all the operations of chemical material removal from the granule unnecessary. Easier said than done! It meant to be able to achieve a breakthrough in the Ziegler-Natta catalysis.

THE PROACTIVE TECHNOLOGY REACTION

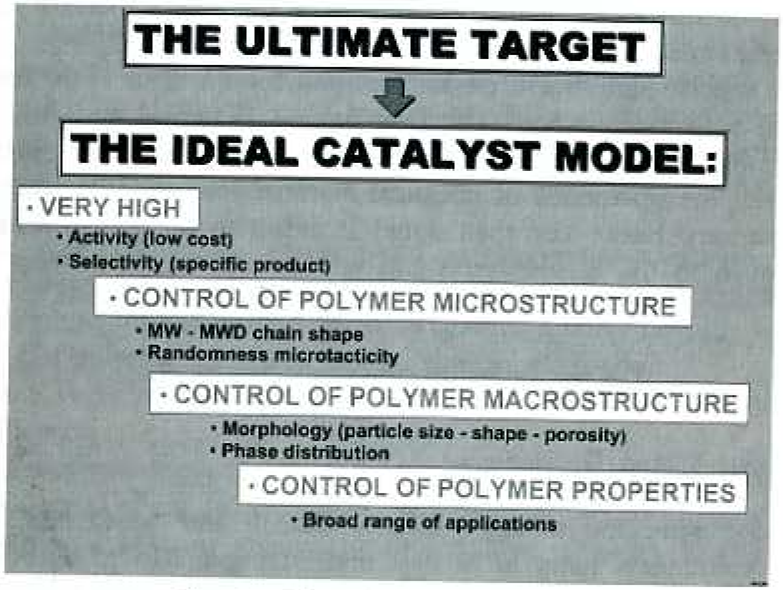
The Catalyst System Development

To cope with, and to solve such a difficult and "dead end" situation, a revolutionary jump in catalyst understanding had to be achieved in order to obtain a major breakthrough in catalyst science. The heavy commitment on the part of many companies all over the world in that field obtained the result.

The intensive efforts in basic research on the catalysts in the 70s, aimed at the understanding of the chemical and physical-mechanical phenomenon linked to polymerisation, brought about the achievement of two major breakthroughs in the catalyst activity and architecture. This had a tremendous impact on polymer quality and morphology, culminating in the discovery of the current 4th generation Ziegler-Natta catalysts. Most important, it was the beginning of a *new way* of thinking and conceiving the catalyst. It was realised that it was mandatory to look for a catalyst showing an *entire, complete, all embracing set of properties*. Just *one*, even if an outstanding property, such as activity or selectivity, was not at all enough! It appeared that it was not possible to achieve a complete success just by operating empirically, looking at the new catalyst properties, one by one.

It became necessary to elaborate and to develop the research in line with a MODEL for the catalyst to achieve.

The Model for the "new dream", the all embracing ideal catalyst, was imagined and called "the extreme target: the ideal catalyst", a catalyst, that in addition to processing a very high catalytic activity and great selectivity, would have imparted the desired proper morphological structure to the appropriate product, whether this was a polymer, a copolymer or a polymer alloy (Fig. 5).


THE ULTIMATE TARGET

THE IDEAL CATALYST MODEL:

- VERY HIGH
  - Activity (low cost)
  - Selectivity (specific product)
- CONTROL OF POLYMER MICROSTRUCTURE
  - MW - MWD chain shape
  - Randomness microtacticity
- CONTROL OF POLYMER MACROSTRUCTURE
  - Morphology (particle size - shape - porosity)
  - Phase distribution
- CONTROL OF POLYMER PROPERTIES
  - Broad range of applications

Fig. 5 – The "ideal catalyst" model.

The discovery of the high activity "d"$MgCl_2$ – supported catalyst for the olefins polymerisation in 1968, became the first of the two major breakthroughs which have revolutionised the development of the Polyolefin technologies in the following 30 years.

It brought about the elimination of the need of the removal of the catalyst residues. This resulted in a significant simplification of the polymerisation processes but did not satisfy the other parameters for an Ideal system.

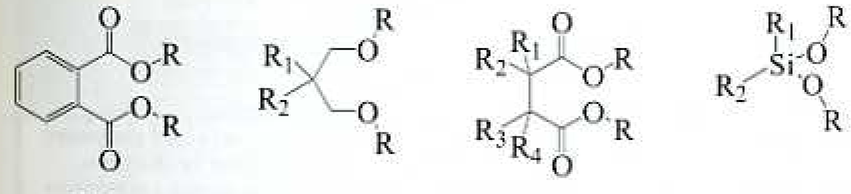
Nevertheless, in order to fully achieve the first target, eliminating all the constraints generated by the catalytic system, it soon became necessary to meanwhile also achieve a much better catalyst selectivity.

The target was achieved in 1975, with the introduction of the 3rd generation catalyst that gave for the first time high yield and high selectivity.

These high-activity Ziegler-Natta catalysts comprises $MgCl_2$ $TiCl_4$ and an "internal" electron donor and are typically used in combination with an aluminium alkyl co-catalyst such as $AlEt_3$ and an "external" electron donor added in polymerisation.

Additional and impressive progress has been made over the years to understand the function of donors and their structure has been designed accordingly. As a result, catalyst performances have been largely improved, starting first from activity and stereoselectivity, by displacing the first generation of internal/external donors (ethylbenzoate/aromatic esters) with the couple diisobutyl phthalate/alkoxysilane and, more recently, with the introduction of diethers, typically a 2,2-disubstituted-1,3-dimethoxypropane, used without or in combination with an alkoxysilane. But in addition to activity and stereo-control, other catalyst attributes exist that need fine-tuning to drive product innovation and, in particular: hydrogen response and control of polymer molecular weight distribution (MWD). In this respect, whereas phthalate-based catalysts are characterised by high isospecificity, medium hydrogen sensitivity and provide medium MWD polypropylene, diether-based catalysts are characterised by very high activity, medium-high isospecificity, high hydrogen sensitivity and are able to provide narrow MWD polymers. And the progress is not at an end!

Quite recently, a very new catalyst system has been patented, based on a particular family of internal donors, namely succinates, which looks particularly interesting since it was found to provide both high polymer stereoregularity and broad polymer MWD.



Phthalate Diether Succinate Silane

Fig. 6 – General formula of internal and external donors.

Thus, as a function of donor structure (Fig. 6), it is possible to modulate both catalyst performances and polymer structure. Actually three families of catalyst systems have been developed that are complementary to one another offering the best choices in terms of both production plant performances and final product property envelope finely tuned towards the most demanding commercial needs (Table 1).

Table 1

General performances of different electron-donor classes

Cat.	1 I.D.	2 E.D.	3 Yield (KgPP/gCat)	X.I. (%)	mmmm (%)	Mw/Mn	H_2 response
A	Phthalate	Silane	70-40	96-99	94-99	6.5-8	medium/low
B	Diether	Absent	130-100	96-98	95-97	5-5.5	excellent
B	Diether	Silane	100-70	98-99	97-99	4.5-5	excellent/high
C	Succinate	Silane	70-40	96-99	95-99	10-15	medium/low

I.D. = Internal Donor; E.D. = External Donor

The ranges are mainly function of the structure of I.D. and E.D. employed.

Bulk polymerisation at 70°C for 2 h, $[AlEt_3] = 2.5$ mM, Al/E.D. = 20 molar, $[H_2]$ = as needed to obtain an intrinsic viscosity of 2 dl/g

In conclusion, the benefits achieved eventually brought about the elimination of the need of the removal of all the catalyst residuals and the atactic fraction. This made a significant simplification of the polymerisation processes. The elimination of these constraints allowed a remarkable reduction in investment costs and brought about several new degrees of freedom (Fig. 7).

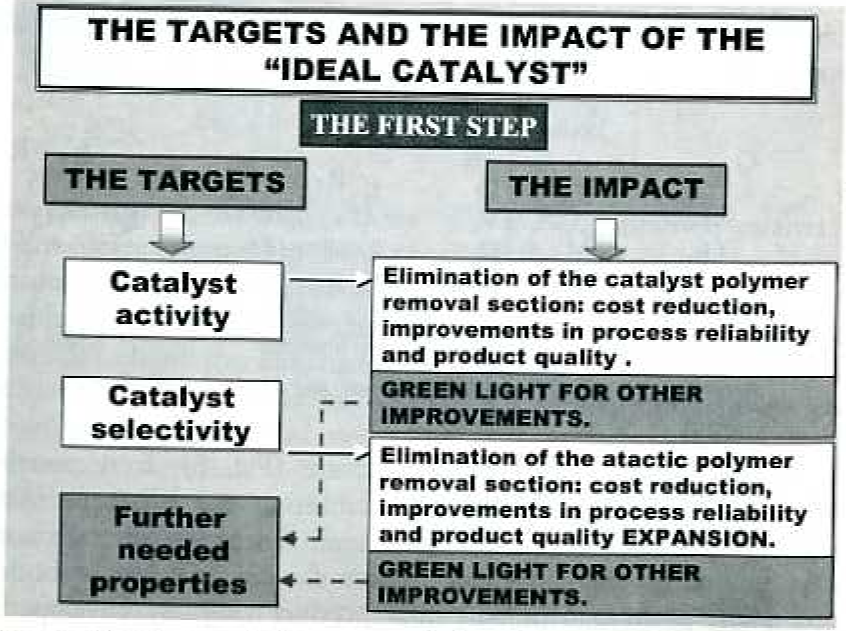


Fig. 7 – The first step in the way towards the achievement of the ideal catalyst.

From these discoveries, the "dream" of the "Ideal Catalyst" as the extreme target in the heterogeneous catalysis started appearing as an achievable reality.

The elimination of the need of the removal of the catalyst residues and to a large extent, of the atactic polymer fractions, were not such important facts in themselves, but mostly because they became the starting point and the base for all the future revolutionary developments.

As a matter of fact, the most important event for all the future scientific, technological and commercial development was not just the increase in the catalyst activity and selectivity. It was the green light to conceive, with a total freedom from any process constraints, the "IDEAL CATALYST" system.

It enabled us to maximise the technology versatility so as to have a significant expansion of the product property envelope (Fig. 8).

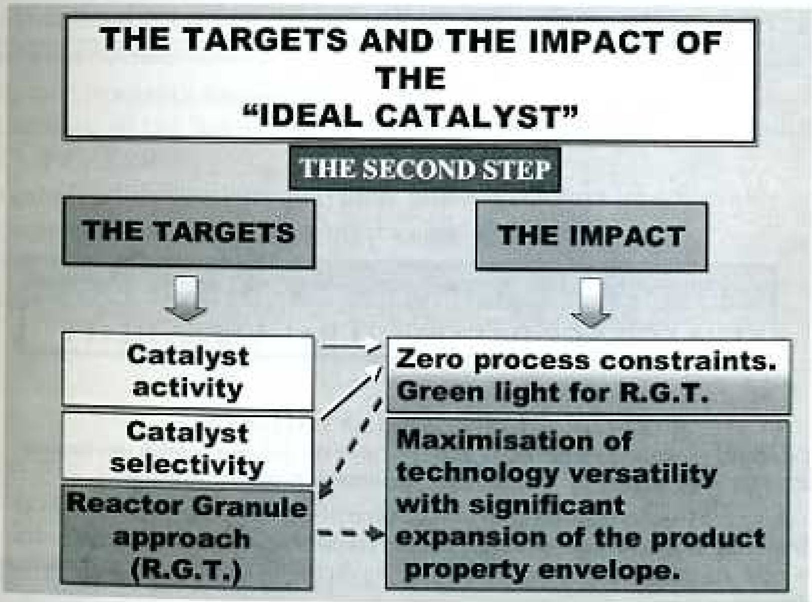
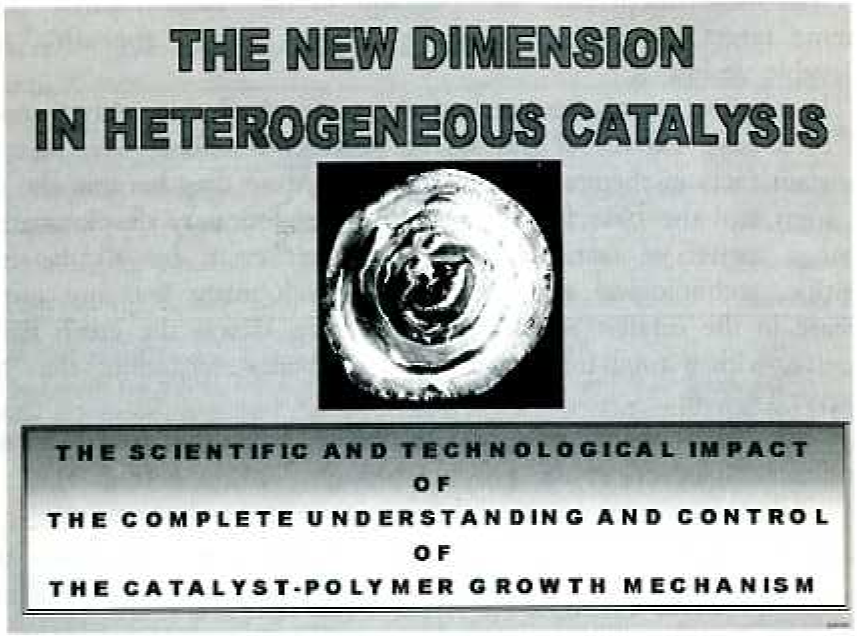


Fig. 8 – The targets and the impact of the "Ideal Catalyst".

This fundamental research led to *the second breakthrough*: discovery and development *of a new dimension* in heterogeneous catalysis and of the "Reactor Granule Technology" (R.G.T.) (Fig. 9).

Its discovery and understanding brought about the complete control of the catalyst-polymer granule genesis and growth: The R.G.T repre-

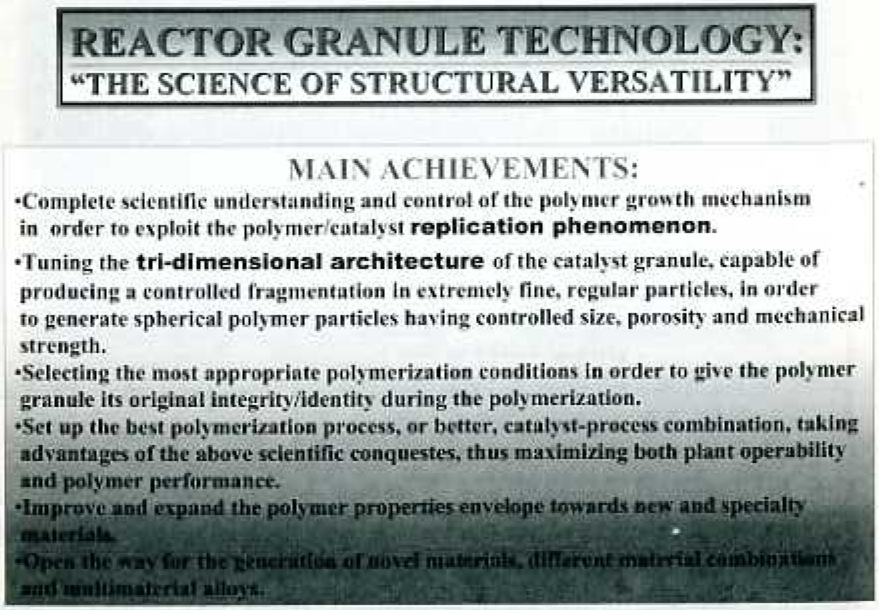


THE NEW DIMENSION

IN HETEROGENEOUS CATALYSIS

THE SCIENTIFIC AND TECHNOLOGICAL IMPACT
OF
THE COMPLETE UNDERSTANDING AND CONTROL
OF
THE CATALYST-POLYMER GROWTH MECHANISM

Fig. 9 – The new dimension in heterogeneous catalysis.



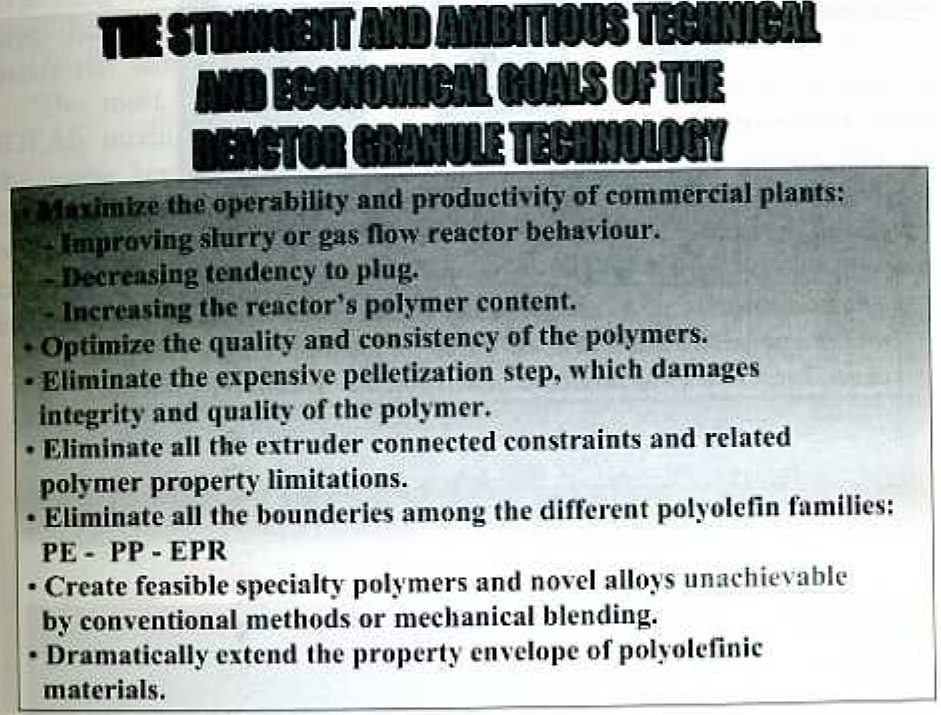
REACTOR GRANULE TECHNOLOGY:
"THE SCIENCE OF STRUCTURAL VERSATILITY"

MAIN ACHIEVEMENTS:

- Complete scientific understanding and control of the polymer growth mechanism in order to exploit the polymer/catalyst **replication phenomenon.**
- Tuning the **tri-dimensional architecture** of the catalyst granule, capable of producing a controlled fragmentation in extremely fine, regular particles, in order to generate spherical polymer particles having controlled size, porosity and mechanical strength.
- Selecting the most appropriate polymerization conditions in order to give the polymer granule its original integrity/identity during the polymerization.
- Set up the best polymerization process, or better, catalyst-process combination, taking advantages of the above scientific conquestes, thus maximizing both plant operability and polymer performance.
- Improve and expand the polymer properties envelope towards new and specialty materials.
- Open the way for the generation of novel materials, different material combinations and multimaterial alloys.

Fig. 10 – Reactor Granule Technology, the main achievements.

sents a key breakthrough result in the Science of structural versatility in the polymerisation technology (Fig. 10) and a fundamental milestone in the entire history of the *process* and *product* development (Fig. 11).



THE STRINGENT AND AMBITIOUS TECHNICAL
AND ECONOMICAL GOALS OF THE
REACTOR GRANULE TECHNOLOGY

- **Maximize the operability and productivity of commercial plants:**
  - **Improving slurry or gas flow reactor behaviour.**
  - **Decreasing tendency to plug.**
  - **Increasing the reactor's polymer content.**
- **Optimize the quality and consistency of the polymers.**
- **Eliminate the expensive pelletization step, which damages integrity and quality of the polymer.**
- **Eliminate all the extruder connected constraints and related polymer property limitations.**
- **Eliminate all the bounderies among the different polyolefin families: PE - PP - EPR**
- **Create feasible specialty polymers and novel alloys unachievable by conventional methods or mechanical blending.**
- **Dramatically extend the property envelope of polyolefinic materials.**

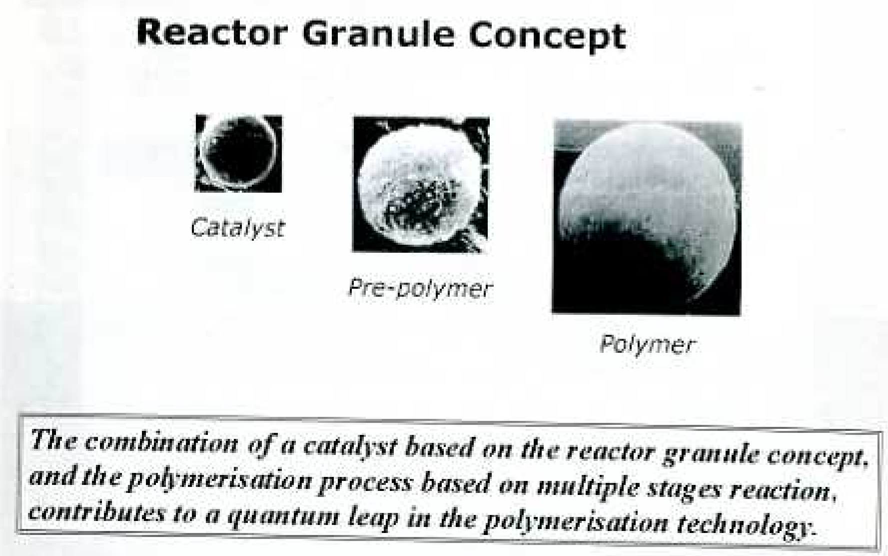
Fig. 11 – Reactor Granule Technology, technical an economic achievements.

The role of the CATALYST THREE DIMENTIONAL ARCHITECTURE in the controlled expansion of the polymer granule was deeply explored, so as to reach an optimum equilibrium between the mechanical strength of the growing granule and the catalyst polymerisation activity.

In the first step the catalyst has been combined and optimised with a unique process designed to capitalise and exploit the full potential of the catalyst.

Catalysts with controlled spherical morphology were developed allowing the full control of particle size and compactness of the related spherical form polymers (Fig. 12).

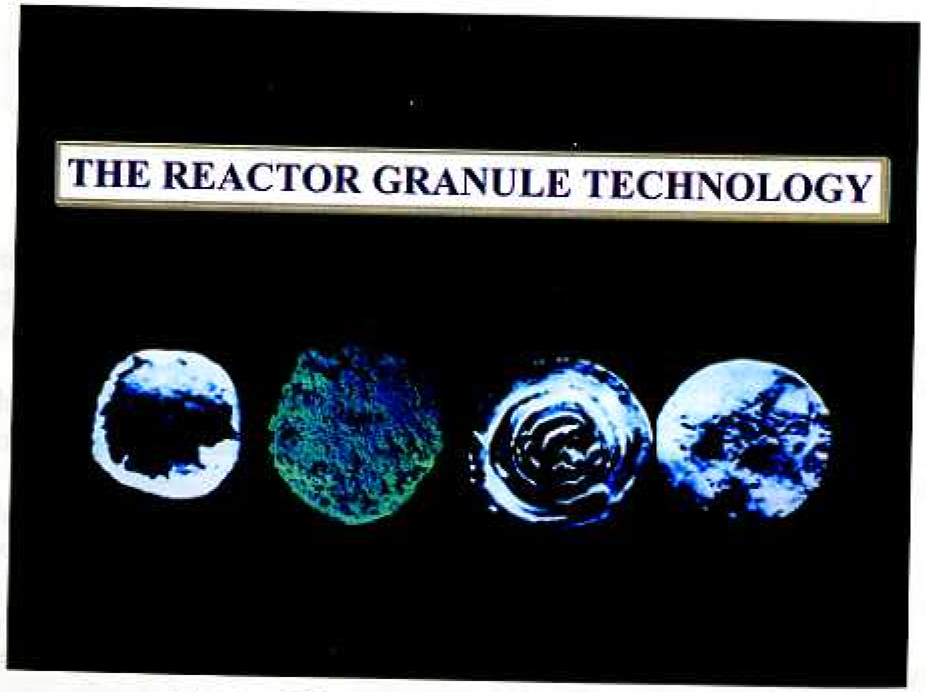
As a second step, under appropriate polymerisation conditions, polymer particles with an internal morphology ranging from compact to porous can be obtained (Fig. 13).



Reactor Granule Concept

The combination of a catalyst based on the reactor granule concept, and the polymerisation process based on multiple stages reaction, contributes to a quantum leap in the polymerisation technology.

Fig. 12 – "Replication" phenomenon during the polymerisation.

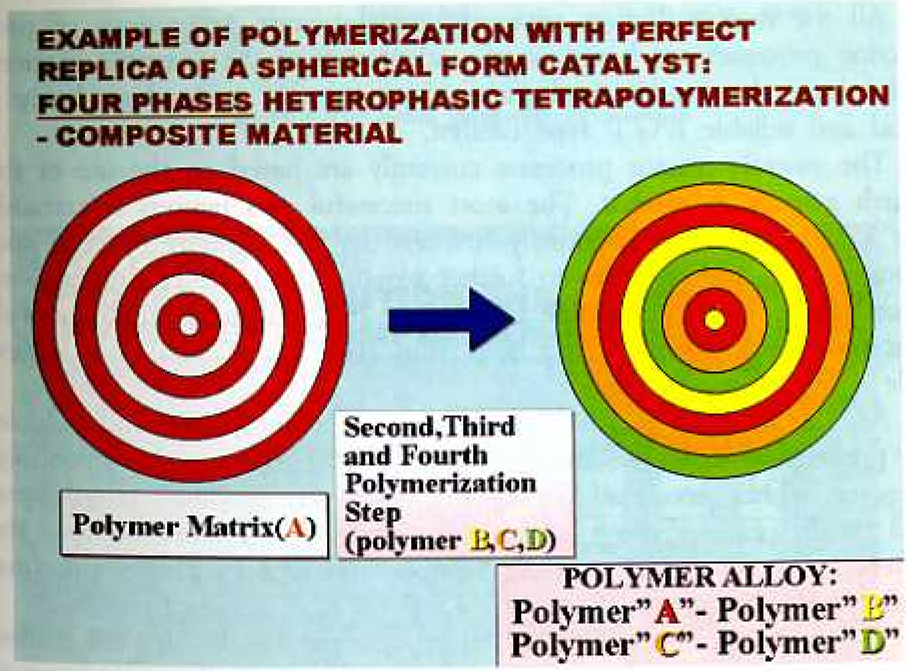


THE REACTOR GRANULE TECHNOLOGY

Fig. 13 – Different polymer morphologies from R.G.T.

The polymer particle becomes the reactor itself in which polymerisation occurs, and by changing monomer it is possible to obtain another polymer intimately dispersed within the mass of the solid granule of the matrix. It became the basis to the "Reactor Granule Technology" fully exploiting the potential of the Spherical Form Catalyst to generate alloys, thanks to the capability of building different polymers components *inside* the same granule.

The most important fact is that now it is possible to achieve an IDEAL mixing of *different* and even *very different* components *inside* the same granule, overcoming the difficulties of their mixing via the blending technology. In many cases, even the difficulty, or impossibility, of handling incompatible products, that *cannot* be processed alone because of their M.W. (either too low or too high) sticky or oily products is overcome (Fig. 14).



EXAMPLE OF POLYMERIZATION WITH PERFECT REPLICA OF A SPHERICAL FORM CATALYST:
FOUR PHASES HETEROPHASIC TETRAPOLYMERIZATION - COMPOSITE MATERIAL

Polymer Matrix(A)

Second,Third and Fourth Polymerization Step (polymer B,C,D)

POLYMER ALLOY:
Polymer"A"- Polymer"B"
Polymer"C"- Polymer"D"

Fig. 14 – Four phases polymer alloy achievement.

In this way, we have now generated a novel possibility of overcoming the difficulties of miscibility of the different polymer phases, with a degree of freedom clearly superior to the one we may have via the mechanical blending of the different polymer components and phases.

We are now approaching this new frontier, just entering the exciting future of the full exploitation of such a tremendous potential.

In the development of the polyolefin technology, the discovery and implementation of the "R.G.T." is today considered, together with the discovery of the high yield catalyst, based on active $MgCl_2$, a fundamental milestone in the Polyolefin technology development.

The process development

The different catalyst generations developed from the 1st to the current 4th have allowed, or better still, have driven the development of a family of new and novel processes taking full advantage of the new virtuosity made available by the various generations of catalyst families. This made a complete revolution in the process concept, the polymer properties and the market development.

All the new and most successful revolutionary generations of production processes are based on the adaptation of the "cascade reactor" technology; the fundamental prerequisite for that technology being a good and reliable R.G.T. type catalyst.

The cascade reactor processes currently are based on the use of the fourth generation catalyst. The most successful and famous is certainly the *Spheripol* process, eventually followed by the *Catalloy* process, specifically conceived in order to further expand the polymer property envelop. These make it possible to generate multipolymers, multiphase alloys and blends directly in synthesis, thus achieving materials not achievable with traditional technologies.

All that, made it possible to expand the polypropylene and polyolefin properties obtainable in polymerisation from the straight homopolymers or slightly modified copolymers, to highly modified copolymers, and to real polymer alloys without boundaries in the ratios between the different comonomer introduced, number and type of phases and final compositions.

The *first impact* of RGT is well represented by the implementation of the first modern technology: the *Spheripol* process (Fig. 15). We may take it as the first and very likely best example among all the PP production processes.

The *Spheripol* process, the first modern, most known and utilised PP process, has been designed to increase and exploit to the maximum the efficiency of the catalytic system in the production of PP homopolymers as well as random and heterophasic copolymers.

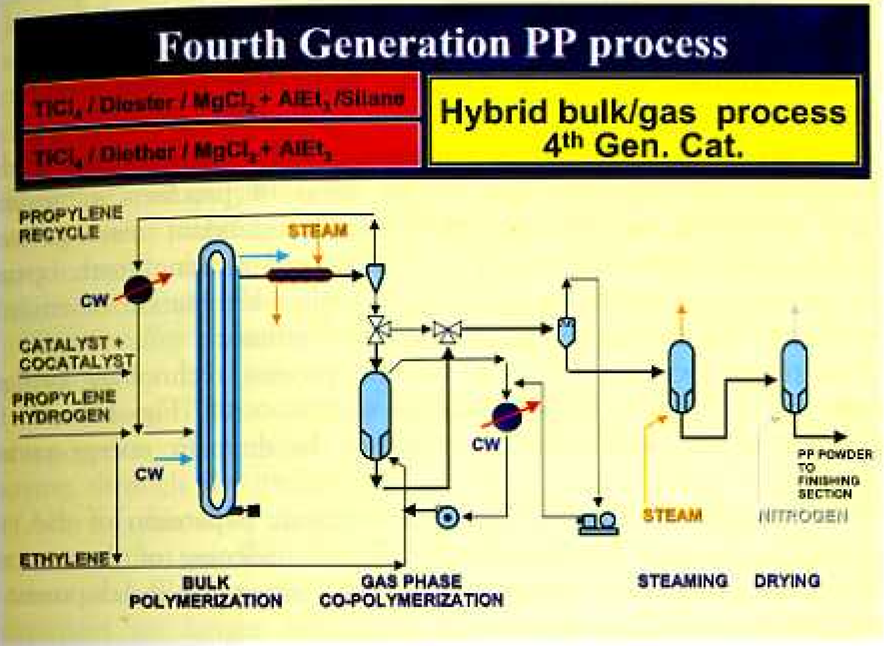
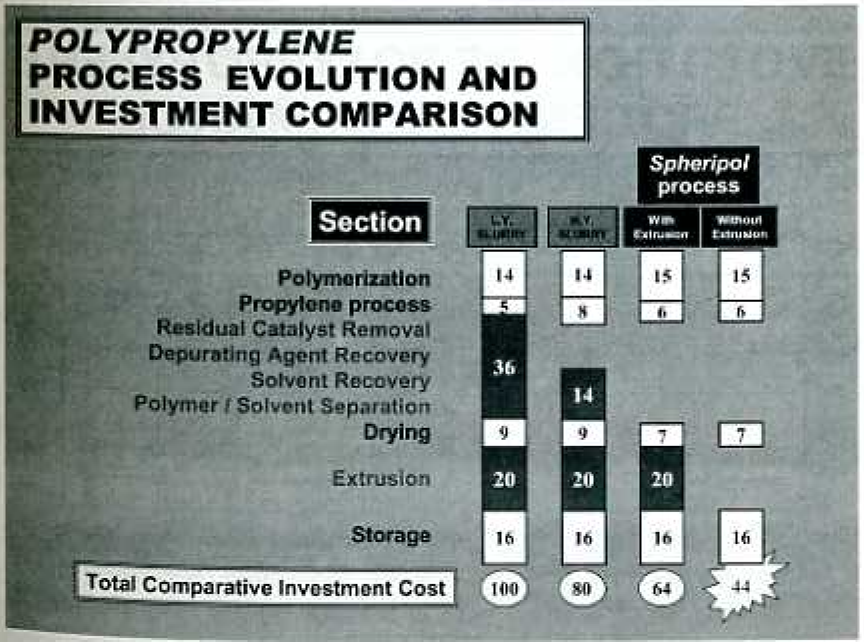


Fig. 15 – The fourth generation PP process.


POLYPROPYLENE
PROCESS EVOLUTION AND
INVESTMENT COMPARISON

			Spheripol process	
Section	L.Y. SLURRY	H.Y. SLURRY	With Extrusion	Without Extrusion
Polymerization	14	14	15	15
Propylene process	5	8	6	6
Residual Catalyst Removal	36			
Depurating Agent Recovery				
Solvent Recovery		14		
Polymer / Solvent Separation				
Drying	9	9	7	7
Extrusion	20	20	20	
Storage	16	16	16	16
Total Comparative Investment Cost	100	80	64	44

Fig. 16 – Investment cost comparison.

It is a two-stage hybrid process as it consists in the combination of the bulk technology in liquid monomer for the production of homo and random copolymers and of the gas-phase technology for the production of heterophasic copolymers.

Compared with the previous processes, the *Spheripol* process is dramatically simpler and more versatile in terms of products achievable. This is thanks to the elimination of several redundant reaction steps with the consequent reduction of investment and running costs, optimisation of economics and, above all, the complete elimination of environmental risks due to the complete absence of effluents.

The progressive simplifications of the process technology brought about a dramatic reduction of both: the CAPITAL COSTS (Fig. 16) and the PRODUCTION COSTS connected, first of all, to the dramatic energy savings (Fig. 17).

But, certainly most important, is the dynamic expansion of the PROCESS VERSATILITY with the sharp and endless broadening of the POLYMER PROPERTY ENVELOPE. This concept has brought about the development of the *Catalloy* technology.

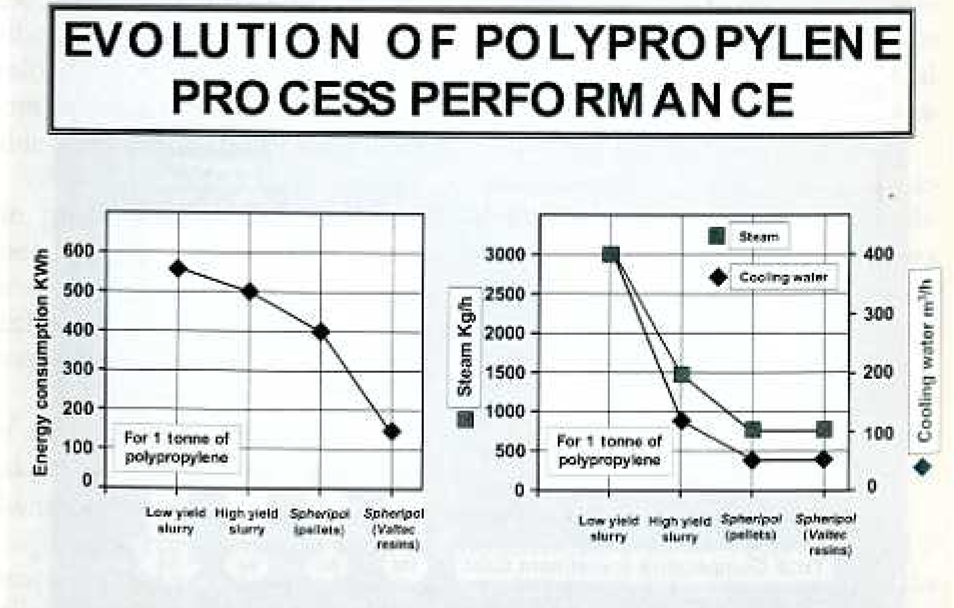


Fig. 17 - Evolution of polypropylene process in terms of energy saving.

The Catalloy *Process represents the most recent advance: in the achievement of a new family of* POLYOLEFIN ALLOYS

The *Catalloy* process was designed to make maximum use of the Reactor Granule Technology allowing the repeated introduction of different monomers during propylene polymerisation thus generating a multiphase multipolymer alloy directly in the reactor. The spherical free-flowing resins obtained are fit for the subsequent conversion and are provided with an extremely wide range of properties which cannot be obtained with any other process for polypropylene.

The *Catalloy* process is a multistage, highly flexible, mainly gas-phase technology.

The Reactor Granule based on the catalytic system used, permits the incorporation of multiple polymer structures within a single particle moving through the multistage process.

Also in this case the growing particle itself becomes the polymerisation reaction medium thus eliminating all the previous process constraints and allowing the production of unique reactor-made resins with properties no longer limited from mechanical considerations of the process.

The synthesis of polypropylene alloys directly in the reactor has demonstrated the capability of giving resins with unexpected new properties which could expand the property envelope of polyolefins and enable them to compete in properties with other non-olefinic plastic resins, such as Nylon, PET, TPU, PS, PVC, etc. (Fig. 18)

The physical-mechanical properties of products made via *Catalloy* process cover the field of elastomeric and very rigid materials significantly broadening the already rich polymer property envelope of *Spheripol* process technology.

In particular, with this process, materials, which have been obtained so far only via mechanical blends of different pre-formed polymers, can be better obtained directly in synthesis (Fig. 19).

The product development

The most impressive fact brought by the R.G.T. based cascade reactor technology, has been the revolutionary expansion of the polymer property envelope, which has not just satisfied the existing market needs, but much more widely expanded the boundaries of the existing one generated a novel wave of applications and markets.

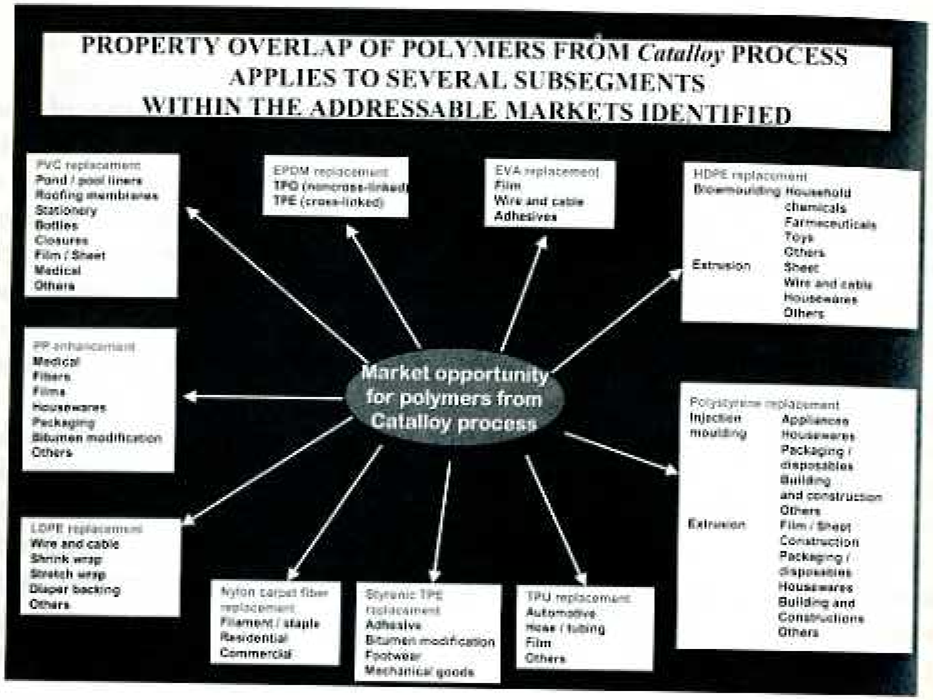


Fig. 18 – New application fields for polymers obtained from the *Catalloy* process.

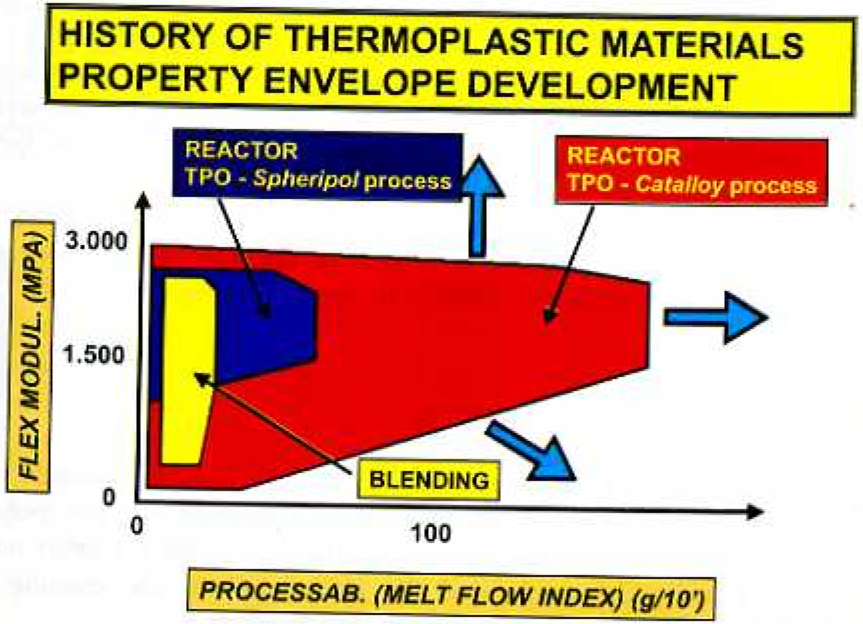


Fig. 19 – Impact Copolymer Technologies.

We would like to support this statement by quoting a third party: Peter Bins and Ken Sinclair, who say in their last interesting multi-client study on PP "ULTIMATE PP MARKET POTENTIAL": "the new technologies were not of themselves valuable, their value had to be developed through and from the market". Leaders of the 1979/83 revolution such as Himont (then Montell, now Basell) therefore devoted particular attention to the identification and satisfaction of real market needs.

The growth of polypropylene (PP) from its commercial introduction in 1957 provides one of the best examples of market response to the introduction of new technology. Demand growth expressed in kg/capita for the first 25 years of the industry from 1957/58 to about 1982/83 could be fit quite well to a logistics curve moving toward a fixed target of ultimate per-capita consumption. As illustrated in the chart below (Fig. 20), indications in 1983 were that the market was maturing – approaching an upper limit of per-capita consumption – and that future growth was trending toward growth in the economy in general. Expectations of medium term growth were in the region of 4-5% per year.

These expectations, however, failed to take into account the structural changes in PPs life cycle brought about by technological innovations,

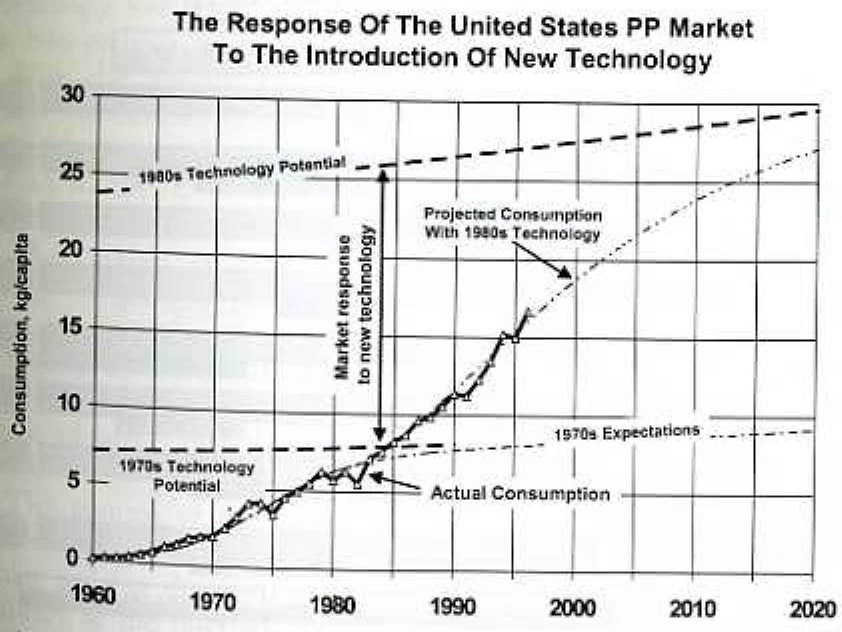


Fig. 20 – The response of U.S. PP market to a new technology introduction.

particularly the development in the *late 1970s* of high-yield, highly stereoselective (HY/HS) catalysts. This boosted PP demand in virtually all markets world-wide. This led to a global consumption growth by more than 10% per year through the 1980s. It became apparent that growth in all categories was following a new logistics curve with an ultimate per-capita consumption two to three times the previous target”.

The continuous development in the product properties has been, and will remain, the fundamental pre-requisite to the endless commercial success of PO in general and PP in particular. As a matter of fact, the commercial success of *Spheripol* process has been determined by its efficient technology, but even more, by the capability of offering the best flexibility in producing both highly crystalline or amorphous polymers, and homo-random, hetero-phasic co-polymers covering the broadest commercial range of tailor-made properties.

The broadening of the key product properties offered by *Spheripol* process technology with respect to the previous generation technology is evident (Fig. 21).

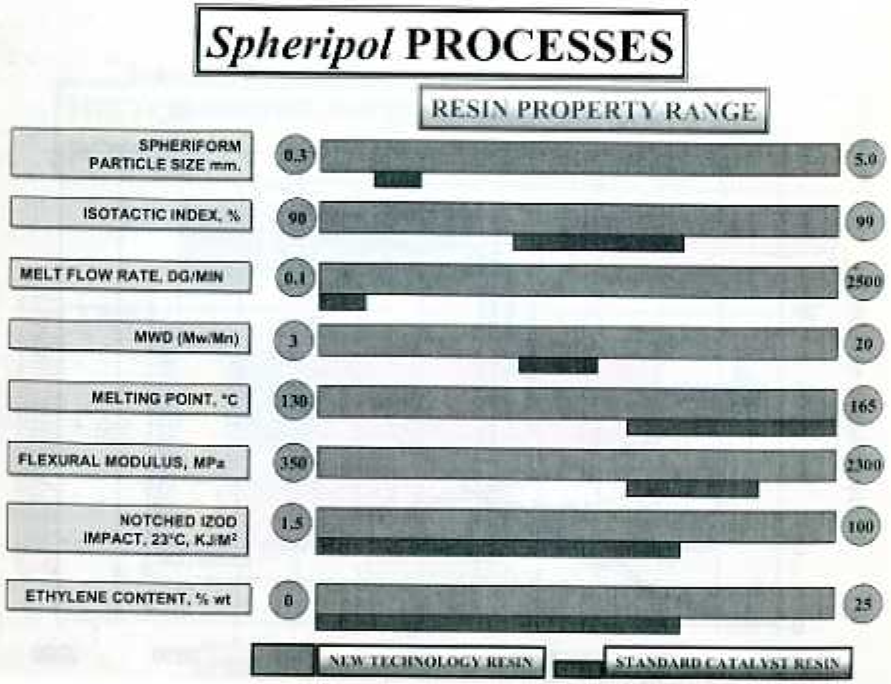


Fig. 21 – *Spheripol* process versatility vs. previous generation technology.

The process is first of all extremely versatile. It may produce three large families of materials:

- a wide range of highly crystalline homopolymers (I.I. from 90 to 99%), with a wide spectrum of molecular weights (MFR from 0.1 to 2000) and controlled molecular weight distribution (MWD from 2.7 to >30);
- random copolymers and terpolymers with a wide spectrum of co-monomers, molecular weights and a controlled molecular weight distributions;
- heterophasic copolymers with an excellent stiffness/impact balance, a wide range of ethylene content (up to 25% by weight) as rubber phase and copolymerisation not limited to ethylene.

Random copolymers represent an important class of materials particularly fit for films, needing a balance between good clarity, flexibility and mechanical resistance. Recent market trends require products with ever lower heat seal initiation temperatures.

The open porous structure or “onion structure” of the Reactor Granule allows to introduce very high levels of two co-monomers inside the granule itself, and thus to produce copolymers and terpolymers with unique properties.

In the conventional technology, heterophasic copolymers are limited to relatively low levels of the second polymer phase, particularly when it is a low melting amorphous rubber.

With the Reactor Granule Technology it is possible to produce a highly- -isotacticity homopolymeric phase in a first step and then to uniformly polymerise the desired elastomeric material within this matrix. Thanks to R.G.T. it is possible to incorporate over 50% of rubber inside the granule without any risk of reactor fouling.

The catalyst is designed to have polymerisation kinetics regular enough to allow a propylene/ethylene-propylene sequential polymerisation.

Owing to the fact that the elastomeric phase grows on the crystals previously originating the homopolymeric phase, a morphological structure is obtained directly in synthesis which is nearly ideal for the polymer alloy.

The control of the chemical structure of both the matrix and the elastomeric phase as well as their individual molecular weights and molecular weights distributions, makes it possible to even control the compatibility at the interface for the production of optimum impact properties over a wide range of temperatures. In terms of properties and applications it has brought about the continuous development of the PP property envelope.

The PP commercial situation started changing and changed dramatically starting from the years 1980s (Fig. 22), a change that is still dynamically in progress nowadays.

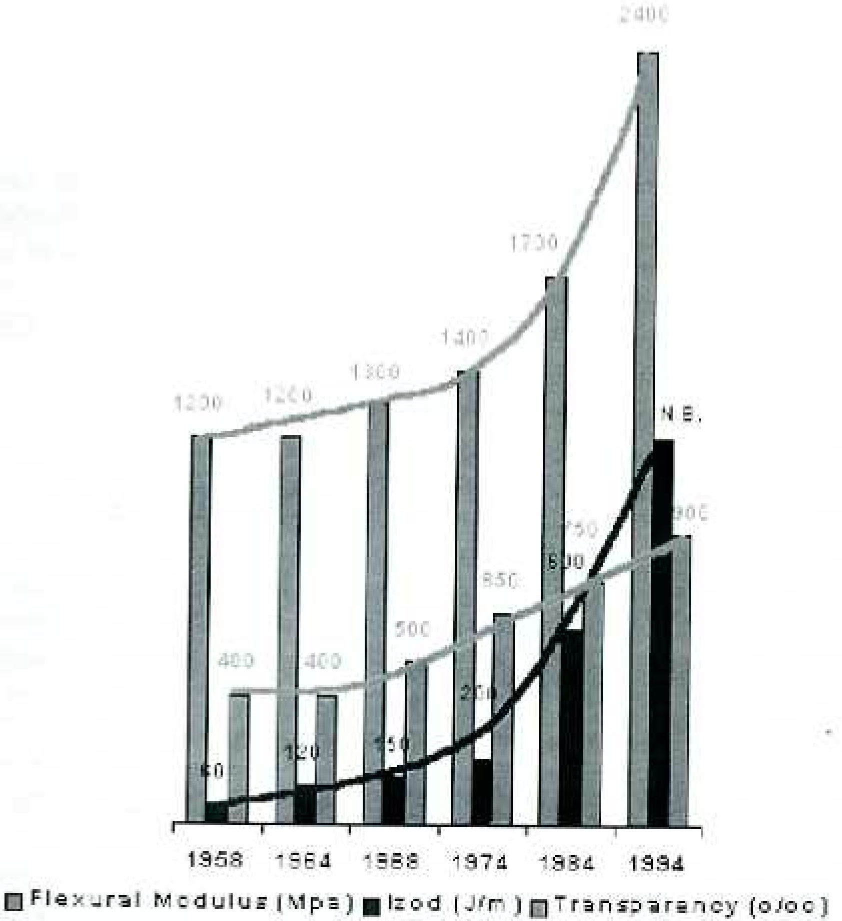


Fig. 22 – Variation of properties for polymers by different catalyst generations.

New materials previously not considered as PP conventional materials have been created. Thanks to the R.G.T., these materials containing large amount of ethylene-propylene rubber are today commercially available. They represent the best compromise between stiffness

and impact properties. However, other possibilities of further property expansion achievable thanks to the full exploitation of the R.G.T. potential are still to be exploited. The new process and product developments driven by the possibility to obtain a product directly from the reactor (PE, PP or PO alloys) that is a perfect replica of the catalyst, make it possible to offer today, several additional significant advantages to the customers. Some of them have not yet been exploited and remain an interesting potential for future technology expansion in the near future.

The key driving force behind the dynamic polymer property expansion has again been and still is, the dynamic and revolutionary catalyst development conjugated with the development of smart, tailor made processes like *Spheripol* process and *Catalloy* process. The entire effort was specifically tuned to the development of new product properties, novel materials and applications.

Figure 23 offers an example of the challenges in terms of properties, market reactors and intermaterial competition choices offered by the broad technology package available to a company, leader in the PP sector such as BASELL.

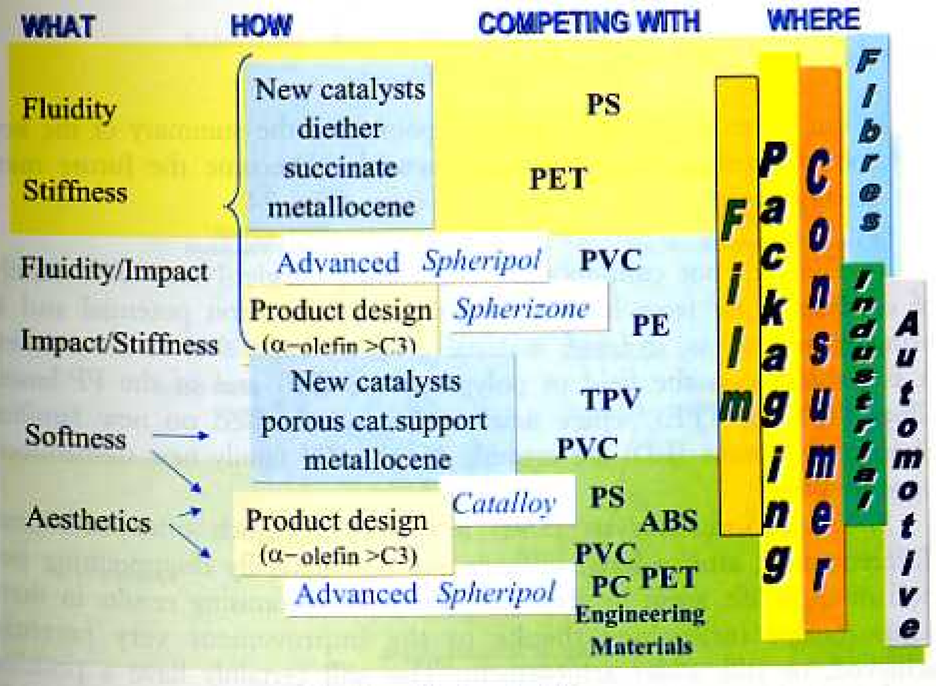


Fig. 23 – The Basell challenge.

THE LATEST, MOST PROMISING TECHNOLOGY DEVELOPMENTS

1 - The continuous ,dynamic and revolutionary Z.N. catalyst family rejuvenation

2 - The new opportunities offered by the properly supported S.S.C. in the heterogeneous processes.

3 - The new technology opportunity of utilisation of the S.S.C. in large size, solution phase process plants

4 - The new / novel opportunities offered by the R.G.T. system:
  - **the continuous polymer property expansion via the cascade multi-reactor processes**
  - **the novel properties / materials achievable with the *Spherizone* , the ultimate frontier of the R.G.T.**

5 - The technical capability of building convenient, reliable, giant polymerisation commercial plants with the continuos improvement of the material cost / performance balance

Fig. 24

The forecast for the future developments

In our opinion, the following five points are the summary of the key technology developments with the potential to become the future market driving force opportunities we envisage (Fig. 24).

1) The old, but continuously rejuvenating Ziegler-Natta (ZN) family of catalysts is far from having exhausted its innovation potential and is bringing an endless, dynamic material property expansion to the market. It is particular in the field of polypropylene (PP) and of the PP-based alloys (TPO & TPE), where new catalyst types based on new families of electron donors (ED) are creating for the ZN family new tremendous opportunities.

2) Single Site Catalysts (SSC) new families which offer additional differentiation, after a long, difficult and commercially disappointing period of their life, seem to offer interesting and promising results in their supportation technology thanks to the improvement very recently achieved, or still under achievement. This will certainly have a positive impact on the possibility of achieving new properties and new materials

in the convenient, large volume processes based on the heterogeneous catalysts such as slurry, gas-phase or hybrid processes.

3) The new technology potential coming from the use of the SSC in solution processes operating at high temperatures, is disclosing significant opportunities in terms of generation of convenient, economic, large volume commercial plants able to produce either commodity or specialty materials.

4) The Reactor Granule Technology system, in combination with the cascade multi-reactor processes, is offering and already generating an impressive new properties and new material innovation wave in the PO material family in general. The ultimate frontier of the RGT in the cascade reactor processes is represented by the novel *Spherizone* technology.

The *Spherizone* technology is today already experimentally confirming all the premises and bright expectations of a further generation leap in novel properties and materials, more in general, of the achievement of the last product cost/performance balance possible today (Fig. 25).

The further potential and hope of these new technologies based on the RGT systems, stays in the possibility of the use the SSC or mixed SSC+ ZN in the RGT itself.

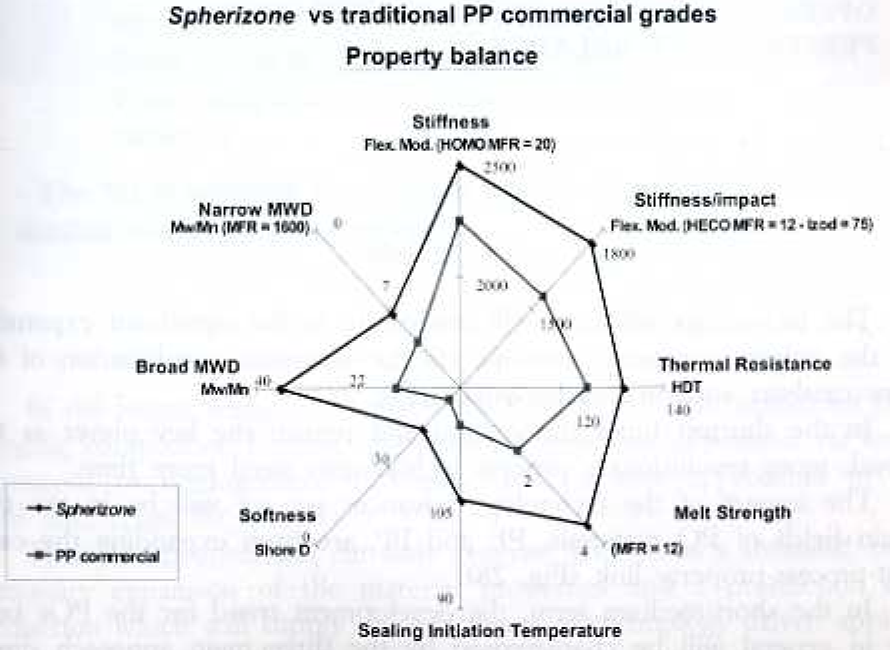


Fig. 25

5) The demonstrated technical capability to build convenient, reliable, world scale production plants, maintaining an excellent material quality standard, is offering the market expansion new challenging opportunities thanks to the significant continuous improvement in the materials cost/ performance balance (Fig. 26).

COST/PERFORMANCE BALANCE
CONTINUOUS IMPROVEMENT

- BULK, GAS, HYBRID PHASE PROCESSES: SIGNIFICANT INCREASE IN PLANT SIZE (100/200.000 T/y ⟶ > 400.000 T/y)

- BULK, GAS, HYBRID PHASE R.G.T. PROCESSES: SIGNIFICANT IMPROVEMENT IN COST/PERFORMANCE BALANCE VIA THE NEW R.G.T.

- SOLUTION PHASE PROCESSES: SIGNIFICANT NEW OPPORTUNITIES OFFERED BY NEW CATALYSTS, HIGHER OPERATIVE TEMPERATURES, BETTER COST/ PERFORMANCE BALANCE

Fig. 26

CONCLUSIONS

The technology advances will contribute to the significant expansion of the polymer property envelope via the synergetic combination of the new catalysts and process potentials (Fig. 27).

In the shortest times the catalyst will remain the key player as the novel, more revolutionary process technologies need more time.

The impact of the technology advances we see will be in the two main fields of PO materials, PE and PP, are from expanding the catalyst-process-property link (Fig. 28).

In the short-medium term, the development trend for the POs family in general will be characterised by the three main approach directions as from Figure 29.

POLYMER PROPERTY ENVELOPE EXPANSION

- NEW PROPERTIES FROM CATALYTIC SYSTEM IMPROVEMENTS /NOVEL ACHIEVEMENTS

- NEW PROPERTIES FROM PROCESSES IMPROVEMENTS / NEW TECHNOLOGIES

Fig. 27

THE CATALYST IS THE KEY PLAYER IN QUALITY IMPROVEMENT AND POLYMER PROPERTY EXPANSION

- The continuous improvements in the Ziegler-Natta based R.G.T. catalysts are driving a dynamic expansion of the PP based materials property envelope.

- The achievements of a complete family of specific, excellent "electron-donors" has generated a decisive jump ahead in Z. N. catalysts making them today even more competitive with respect to any other family of catalysts.

- The MCN catalysts are evolving but are currently limited to narrow niche markets.

Fig. 28

In the longer terms we envisage the positive effect of continued challenging competition between the main development directions: via heterogeneous or homogeneous processes, and via new approaches in ZN and SSC (Figs. 30 and 31).

Their competition will certainly generate and boost a dynamic, revolutionary expansion of the material properties and a production cost reduction which will supply the next wave of technology driven applications markets and volumes growth.

PO MATERIALS : SHORT/MEDIUM TERM GENERAL DEVELOPMENT TREND

1. IMPROVEMENTS AND OPTIMIZATION

   - The improved catalysts with higher productivity/ selectivity either of the R.G.T., Z.N. catalysts and new MCN.

   - Significant opportunity of dramatic revamping of solution processes for PE, modified PE and ethylene/propylene/higher olefins co- and ter-polymers driven by the MCN catalysts.

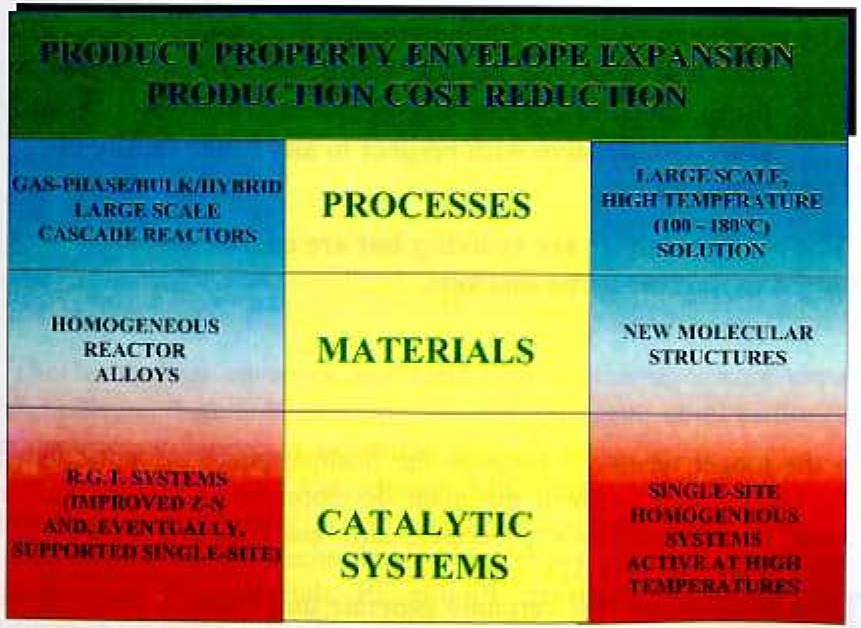
2. INCREASE IN THE SIZE

   - Gas-phase, bulk, hybrid and solution plants from 200.000 to over 400.000 mt/y.

3. NEW TECHNOLOGY

   - The R.G.T. based cascade reactor technologies and their extreme frontier, the *Spherizone* technology, making achievable new/improved materials with superior quality, new properties, better economics.

Fig. 29

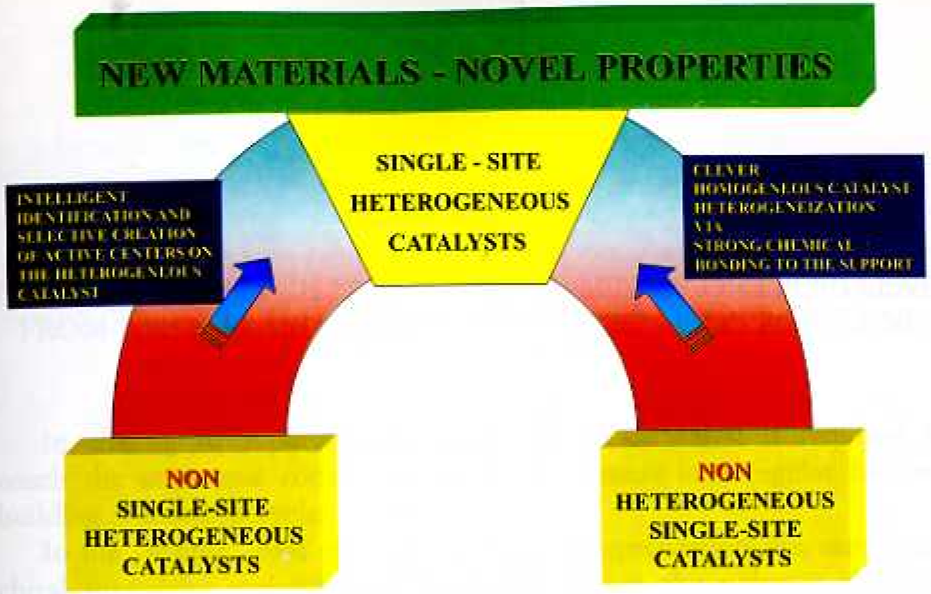


PRODUCT PROPERTY ENVELOPE EXPANSION
PRODUCTION COST REDUCTION

GAS-PHASE/BULK/HYBRID LARGE SCALE CASCADE REACTORS	PROCESSES	LARGE SCALE, HIGH TEMPFRATURE (100 - 180°C) SOLUTION
HOMOGENEOUS REACTOR ALLOYS	MATERIALS	NEW MOLECULAR STRUCTURES
R.G.T. SYSTEMS (IMPROVED Z-N AND, EVENTUALLY, SUPPORTED SINGLE-SITE)	CATALYTIC SYSTEMS	SINGLE-SITE HOMOGENEOUS SYSTEMS ACTIVE AT HIGH TEMPERATURES

The main development directions towards a new, technology driven, market expansion wave.

Fig. 30



NEW MATERIALS - NOVEL PROPERTIES

Fig. 31

Luigi Resconi[a]

CONTROL OVER THE ENCHAINMENT MODES OF PROPYLENE: FROM STIFF PLASTIC TO SOFT ELASTIC POLYPROPYLENE

In chain-growth polymerization of olefins, a catalyst is required to coach the sequential connection of the monomers in a regular fashion, building a linear polyolefin chain (Fig. 1).

In the "simple" case of propylene homopolymerization, the same prochiral propylene molecule can be placed within the polymer chain in

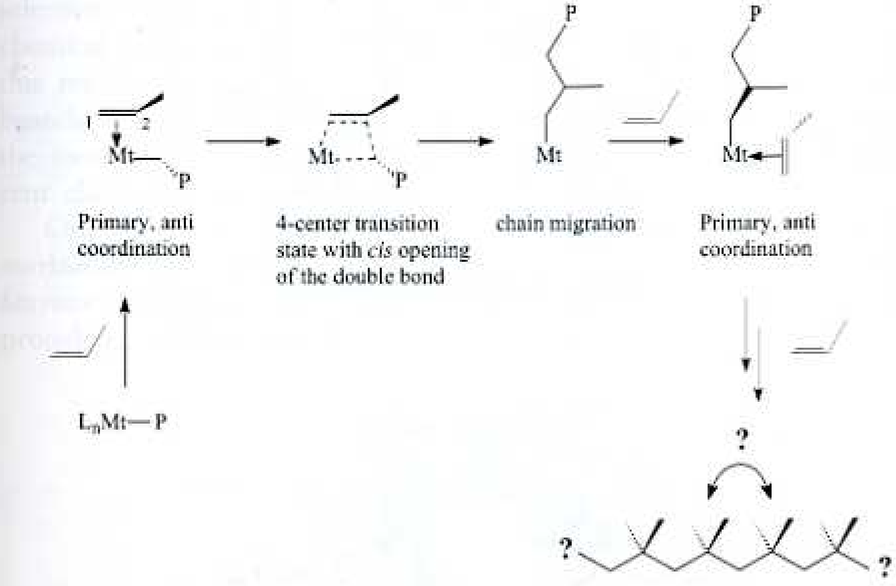


Fig. 1 – Schematic representation of chain-growth polymerization of propylene (primary monomer insertion only is shown). The question marks indicate the most important structural features of polypropylene: the structure of end groups, the average number of enchained monomer units (chain length), and the spatial relationships between neighboring side groups.

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[a] Basell Poliolefine Italia – Centro Ricerche «G. Natta» – Piazzale Donegani, 12 – 44100 Ferrara (Italy).

four different orientations (Fig. 2). This means that the catalyst reactive site has actually four building blocks to choose from, while building the polymer chain. The major achievement of Giulio Natta and his team was to develop catalysts able to connect the propylene molecules in only one and the same way – a process that led to the invention of highly isotactic polypropylene, a semicrystalline polyolefin whose material properties continue to be developed still today, 50 years after its first discovery.

The task of the catalyst chemist today is to design catalysts able to connect these building blocks in the desired sequence, and to make connection "mistakes" in a controlled way (Fig. 3), since varying the degree of chain regularity (stereoregularity) means controlling the crystallinity and melting point of polypropylene, that, together with its molecular weight,

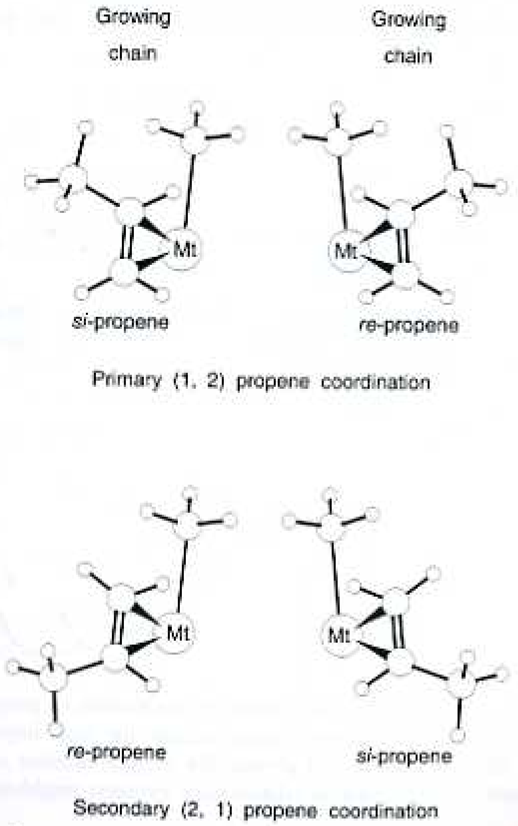


Fig. 2 – In the "simple" case of propylene homopolymerization, the catalyst can actually choose among four building blocks from the same propylene molecule. Top: The two modes of primary propylene insertion. Bottom: The two modes of secondary propylene insertion. Mt = transition metal. The Mt-CH$_3$ group represents the growing polymer chain.

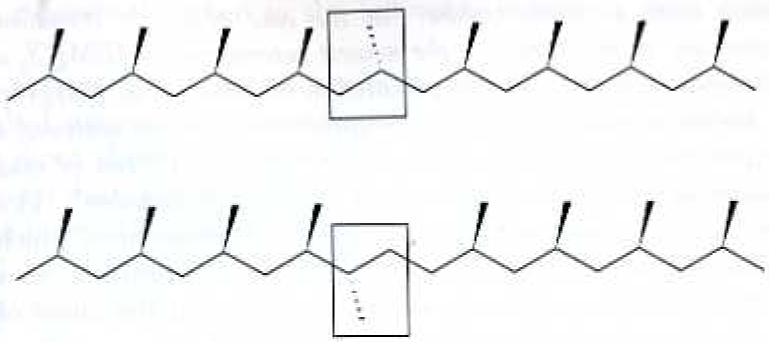


Fig. 3 – Most common propylene insertion errors in isotactic polypropylene from single-center catalysts. Top: primary insertion error: isospecific metallocene catalysts can be *less stereoselective* compared to heterogeneous Ziegler/Natta catalysts. Bottom: secondary insertion error: isospecific metallocene catalysts can be *less regiospecific* compared to heterogeneous Ziegler/Natta catalysts.

define all its physical and mechanical properties. The stereoregularity of polypropylene can be finely tuned by altering the monomer enantioface selectivity of the catalyst, which in turn can be altered by modifying the chemical environment of its reactive sites. In the case of metallocenes, this means changing the chemical structure of the two cyclopentadienyl ligands (Fig. 4). Metallocenes, and in general "single-center" catalysts, are the most versatile systems for the production of polypropylenes of different chain stereoregularity and molecular weights.

One of the many challenges facing the catalyst chemist in the polymerization of propylene with single-center catalysts, is to achieve *simultaneous* control over the stereoregularity and molecular weight of polypropylene, without having to pay a price in catalyst activity.

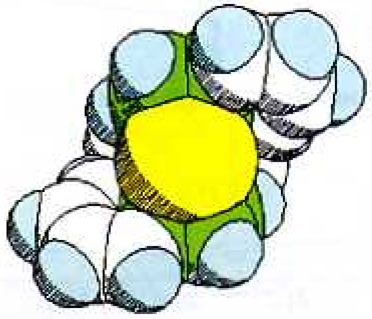


Fig. 4 – Space-filling model of the S,S enantiomer of Brintzinger's catalyst, *racemic*-ethylene-bis(1-indenyl)ZrCl$_2$. Yellow: zirconium; green: cyclopentadienyl carbons; white: benzo carbons; blue: hydrogens. The ethylene "strap" which locks the two indenyl ligands into their chiral configuration is not visible. The two chlorine atoms are removed for clarity.

Quoting from a recent review, "*in the case of highly crystalline i-PP, metallocenes are unlike to replace the newest heterogeneous Ti/MgCl$_2$ catalysts in any foreseeable future* (for the production of commodity polypropylene). *So, why use metallocenes to produce polypropylene? In one sentence, because polypropylene properties can be tailored! For example, i-PP can be made from fully amorphous to highly crystalline and anything in between*" [1].

Here, we will review some recent catalysts developments, which made possible to produce flexible and elastomeric polypropylenes of varying degrees of crystallinity, and with molecular weights in the range of industrial applications, by the use of ligand structures that control the amount of monomer insertion mistakes. The catalysts described are limited to those that produce highly regioselective polypropylenes, that is polypropylenes free from 2,1-monomer enchainments. The amount of primary insertion errors is measured by solution ^{13}C-NMR, a highly sensitive spectroscopic technique able to "see" the steric environment of propylene sequences (Fig. 5) [1].

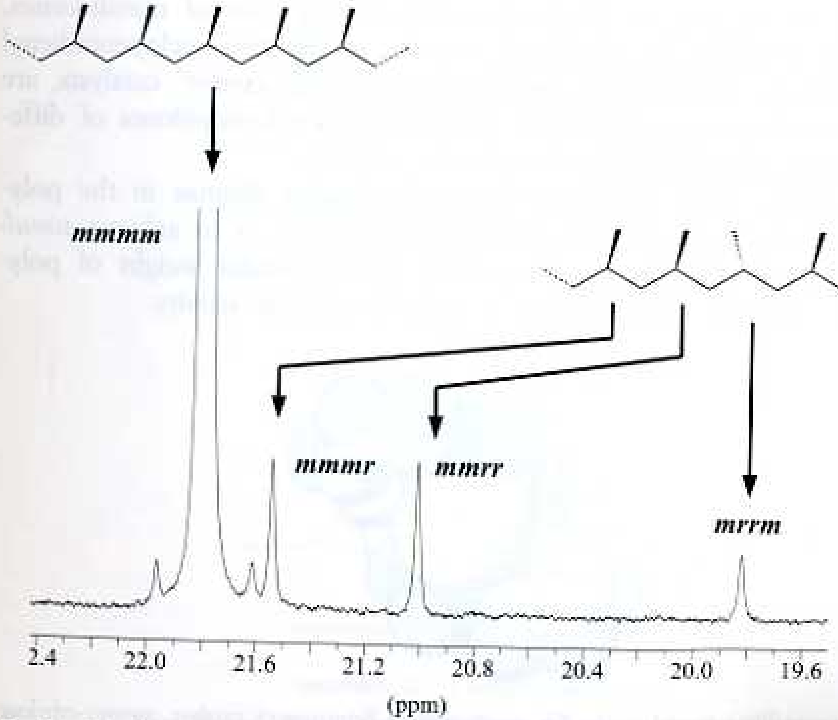


Fig. 5 – Reading polypropylene microstructure by ^{13}C NMR: regioregular polypropylene with stereoerrors. Note the relationship *mmmr* = *mmrr* = 2 *mrrm*, the "fingerprint" of stereoerrors in site controlled polymerization.

The catalysts described in the following, belong to three distinct families.

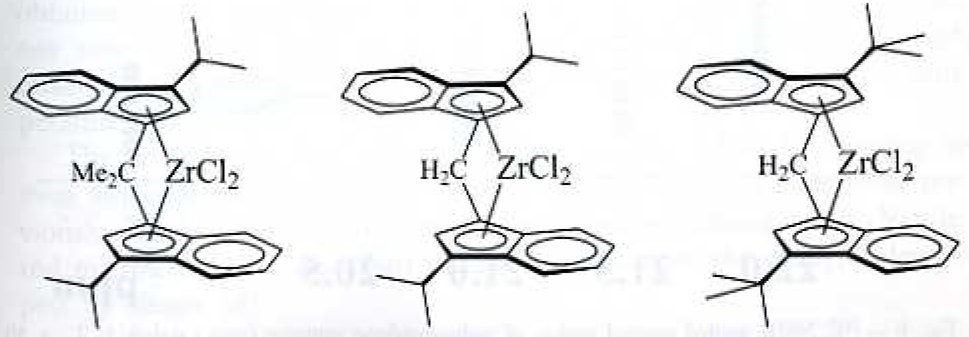
The first catalyst family is made of C$_2$-symmetric zirconocenes, bearing 3-alkyl substituted indenyl ligands linked by a single-carbon bridge, such as those shown in Chart 1.

Despite their structural similarity, catalysts **1**-**3** produce amorphous (**1**), elastomeric (**2**) and high melting, highly crystalline (**3**) polypropylenes. All have in common a very high regioselectivity, and differ widely in their enantioface selectivity (isospecificity). The ^{13}C NMR pentad region of polypropylenes from **1**-**3** are shown in Figure 6.

The properties of polypropylenes from **1**-**3** are compared to those of atactic polypropylene made with an aspecific zirconocene, Me$_2$Si(Flu)$_2$ZrCl$_2$, in Table 1.

The main drawback that prevented the development of *am*-PP from the simplest catalyst, Me$_2$Si(9-Flu)$_2$ZrCl$_2$, is the tackiness of atactic polypropylene, that precludes efficient homopolymer production in gas phase or liquid monomer. In addition, purely atactic polypropylene shows limited miscibility with *i*-PP. The solution we sought was to introduce short, crystallizable isotactic sequences into an otherwise amorphous material. This approach met with success: isotactic amorphous polypropylene (*iam*-PP), produced in liquid propylene with catalysts **1** and **2**, have *mmmm* pentad contents in the range 15 to 30%, shows elastic properties (at room temperature), is not tacky, and shows improved miscibility with *i*-PP.

These chiral C$_2$-symmetric zirconocenes were made from inexpensive and simple ligands, but have some limitations: in their synthesis, the



1 2 3

Chart 1.

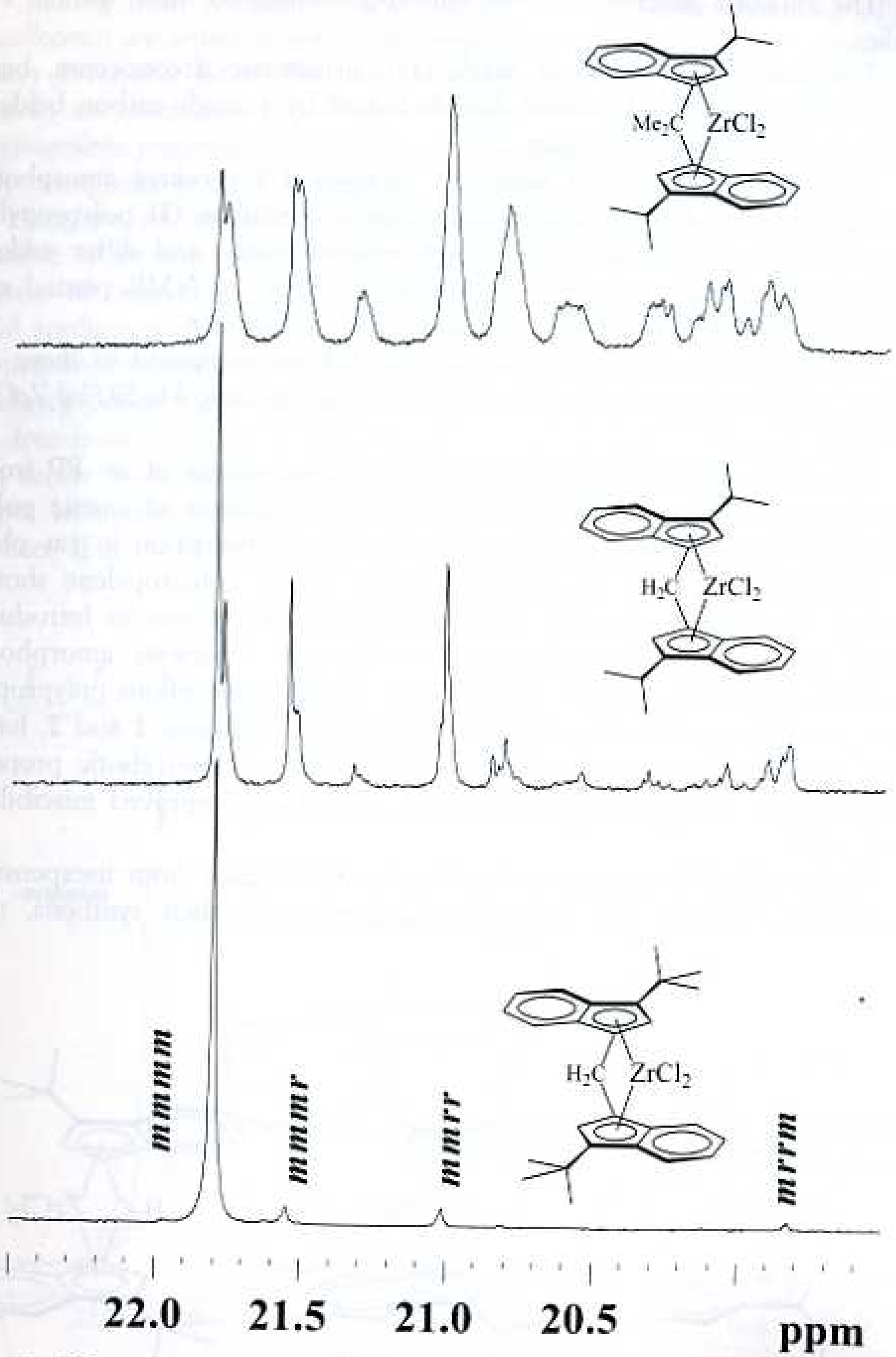
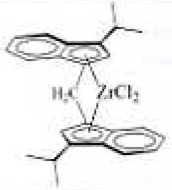
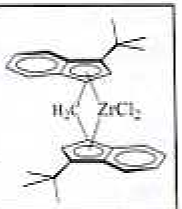


Fig. 6 – ^{13}C NMR methyl pentad region of polypropylene samples from catalyst **1**, T_p = 50 °C (top), **2**, T_p = 40 °C (middle) and **3**, T_p = 50 °C (bottom). All polymerizations were carried out in liquid propylene, and zirconocenes were activated with 1000 – 5000 equiv of methylalumoxane cocatalyst.

TABLE 1

Achiral (C_{2v}-symmetric) and Chiral (C_2-Symmetric) Zirconocenes for Amorphous, Elastomeric, or highly rigid polypropylene.

	 Me₂Si ZrCl₂	 Me₂C ZrCl₂	 H₂C ZrCl₂	 H₂C ZrCl₂
$\overline{M}_w$	425 000	160 000	145 000	120 000
T_m (°C)	none amorphous	none amorphous	about 40° after annealing (oriented γ form)	159
T_g, DSC (°C)	~0	~0	~−9	n.d.
mmmm %	~2	17	35	97
Yield Strength (MPa)	—	0.6	1.76	37.2
Elongation at Yield (%)	—	140	75	9
Tension set (%) (100%)	12	48	8	
Elongation at break (%)	1100	>1500	834	380
Elastic modulus (MPa)	5 [a]	7.8 [a]	12.5 [a]	2100 [b]

[a] tensile. [b] flexural

obtained isomer ratio is rac/meso < 1, and their catalytic activities are not very high. In addition, *iam*-PP can be made with relatively high molecular weights, but not high enough at industrial polymerization temperatures (60-80°C).

The solution to the above problems can be found by moving to even longer isotactic sequences. Several catalyst solutions have been previously demonstrated for making more crystalline, although still disordered microstructures (see Chart 2), such for example the catalysts developed by Rieger [4].

Our solution was to use zirconocenes bearing the (2-MeThieno)₂Cp – indenyl ligand system (see Chart 3), which brings us to the second

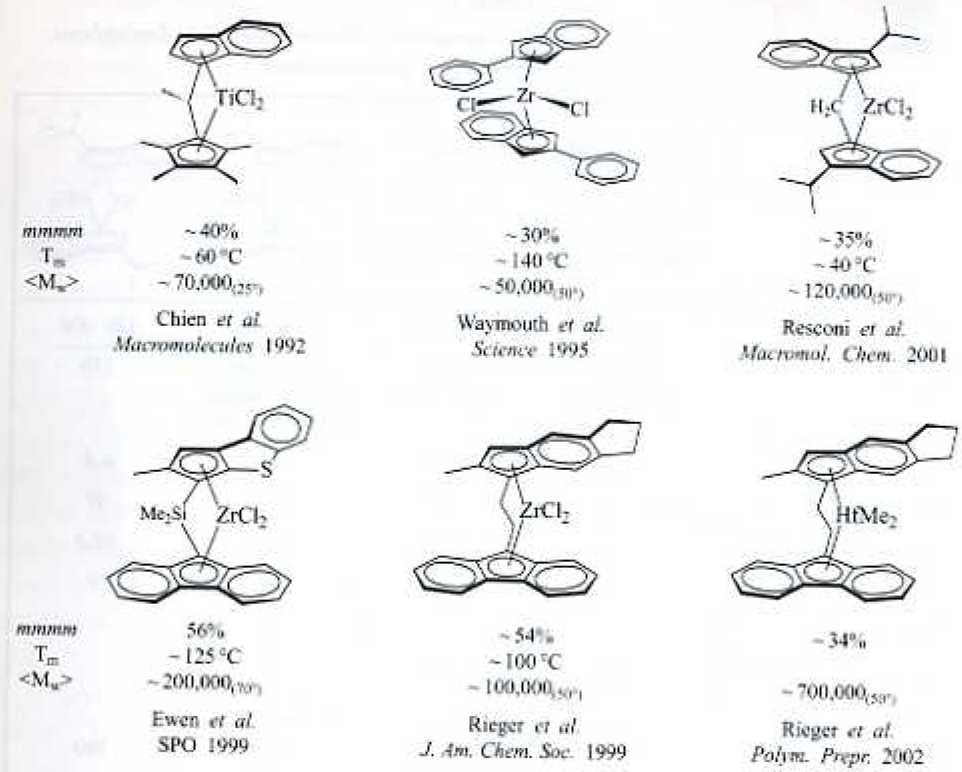


Chart 2 – Metallocene catalysts for elastomeric or flexible polypropylene.

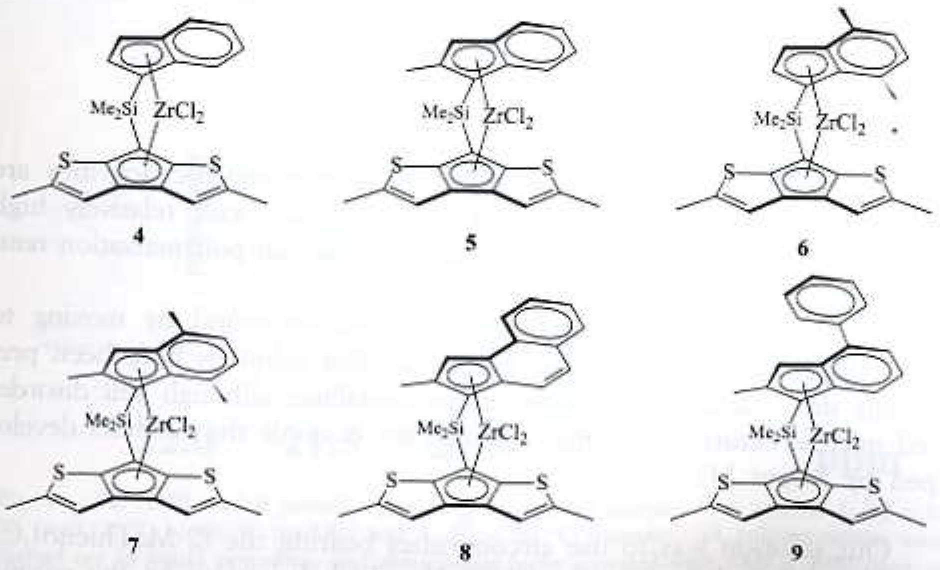


Chart 3.

of our catalyst families consisting of C_1-symmetric zirconocenes whose *ansa*-π-ligand system is based on combinations of substituted indenes linked to the 2,5-dimethyl-7H-cyclopenta[1,2-b;4,3-b']dithiophene (2-MeTh)$_2$Cp for short) ligand [2, 3]. These zirconocenes, of general structure $Me_2Si(R_nInd)[(2\text{-}MeTh)_2Cp]MtCl_2$, have been found to be highly active in propylene polymerization: in liquid propylene at $T_p = 50\text{-}70°C$, they produce highly regioregular, low melting, low elastic modulus, moderately isotactic polypropylenes with *mm* triad content in the range 78-95% and viscosity average molecular weight ranging between 100 000 and 350 000. These modified polypropylenes have melting point T_m between 80 and 145°C, enthalpy of fusion ΔH_f in the range 20-80 J/g, and are characterized by higher flexibility and transparency compared to "standard" i-PP.

Molecular weight and crystallinity are strongly dependent on the type of indenyl substituents. The microstructures of these polypropylene samples was investigated by ^{13}C NMR ($C_2D_2Cl_4$, 120°C), and defined by the *mm* triad values reported in Table 2. This microstructural analysis proved also the high regioselectivity of these catalysts, since no 2,1 units could be detected in the spectra of the polymers. Chiral induction comes mainly form a weak enantiomorphic site control, possibly coupled with occasional back-skip of the chain to the least hindered site.

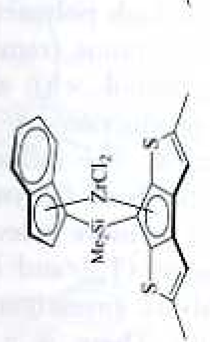
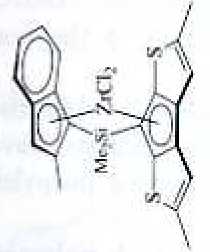
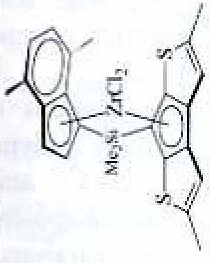
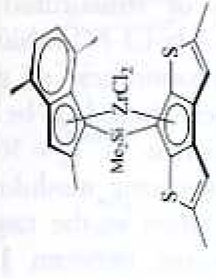
A selection of these complexes is shown in Chart 2, while the polymerization results are compared in Table 2. The catalysts have been tested under the same or very similar conditions (liquid propylene, 50-70°C, MAO cocatalyst, MAO/Zr = 300-1000).

These catalysts show in general good stability at high polymerization temperatures, and quite high activities at low Al/Zr ratios (remarkable that of **8**, at above 300 kg/(g_{cat} × h), or 2×10^5 g/($mmol_{Zr}$ × h), at 70°C and MAO/Zr of only 500 mol/mol). For the production of *flexible isotactic*-PP, the best catalyst structures are **7** and **8**. The influence of polymerization temperature on the performance of these C_1-symmetric catalysts is quite low on stereoregularity, while it is more relevant on molecular weights. The values of the melting point (T_m) and heat of fusion (ΔH_f) of polypropylenes from all catalysts investigated are plotted in Figure 7 as a function of isotacticity. There is a strong correlation between the isotacticity of the polymer and its thermal properties.

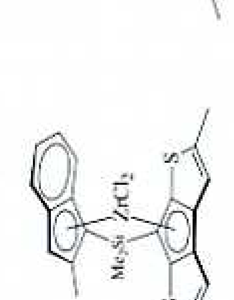
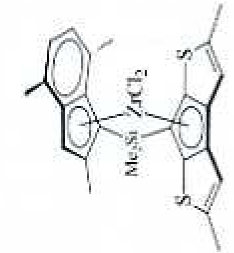
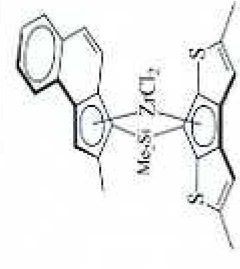
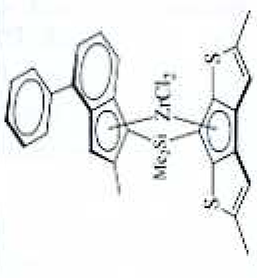
In Figure 8, the correlation between melting point and softness is shown. It is apparent that by changing the ligand structure, the whole range of elastic properties can be covered.

TABLE 2

Propylene polymerization with Indenyl-2MeTh$_2$Cp based catalysts [(a)]

				
$\overline{M}_v$ [(b)]	165 000	250 000	180 000	230 000
T$_m$ (°C)	111	116	121	137
mm %	77.8	81.5	81.8	90.4

(a) Polymerization conditions: 2.5 L reactor, 600 g propylene, 2 mmol Al(iBu)$_3$, 1 h, T$_p$ = 60°C, Al$_{MAO}$/Zr = 500 mol/mol.
(b) Average viscosity molecular weight.

								
T$_p$	60	70	60	70	60	70	60	70
T$_m$ (°C)	116	116	137	138	121	119	148	148
mm %	81.5	80.9	90.4	91.7	82.9	82.7	94.1	93.9

(a) Polymerization conditions: 2.5 L reactor, 600 g propylene, 2 mmol Al(iBu)$_3$, 1 h, Al$_{MAO}$/Zr = 500 mol/mol.

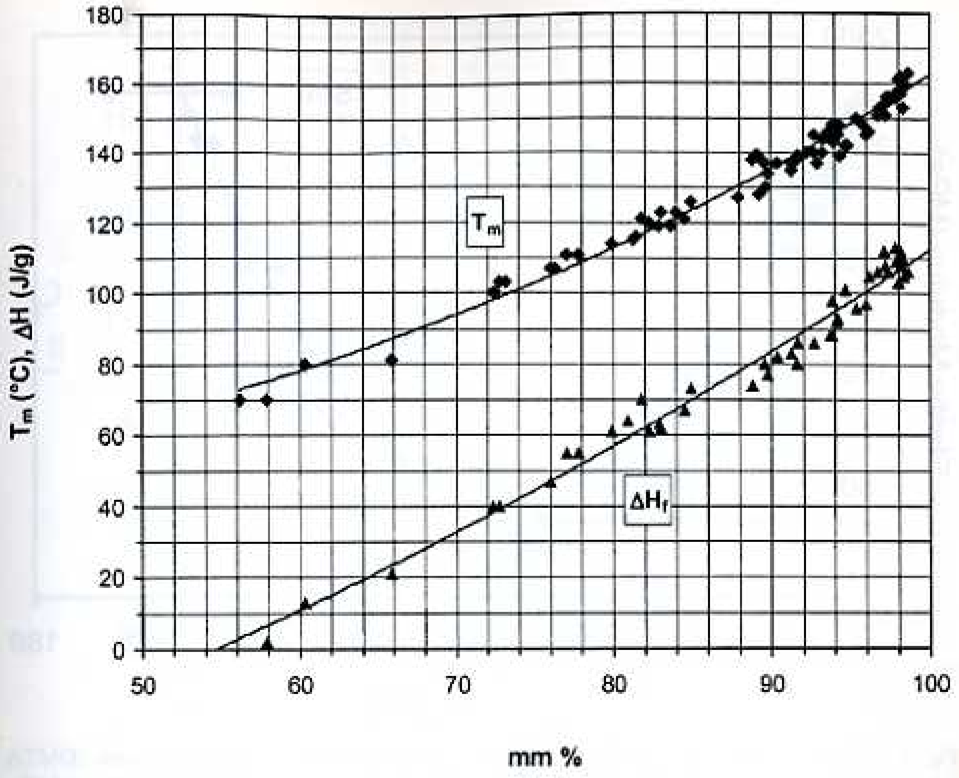


Fig. 7 – Melting point, T$_m$ (◆), and enthalpy of fusion, ΔH$_f$ (▲), of isotactic polypropylenes made with regioselective metallocene catalysts (C$_1$- and C$_2$-symmetric), as a function of their isotacticity (mm %). Empirical correlations are shown. T$_m$ of second melt, scan rate 10°/min.

The third family of single-center catalysts includes indenyl silyl amido titanium complexes based on *t*Bu-amide linked to indenoindole, indenopyrrole or 2-methylindenothiophene [5]. The indenoindole ligand precursors are especially simple to prepare in high yields by the acid-catalyzed Fischer condensation of indan-2-one and the hydrochlorides of arylhydrazines. All the Ti complexes were prepared as their dimethyl derivatives by reacting the ligand, a 2-fold excess of MeLi, and TiCl$_4$. Some examples are shown in Chart 4, and a selection of polymerization results is shown in Table 3. Figure 9 shows the correlation between melting points and stereoregularity in the syndiotactic domain, while Figure 10 shows the ^{13}C NMR methyl pentad region of three different polymers, from slightly to highly syndiotactic.

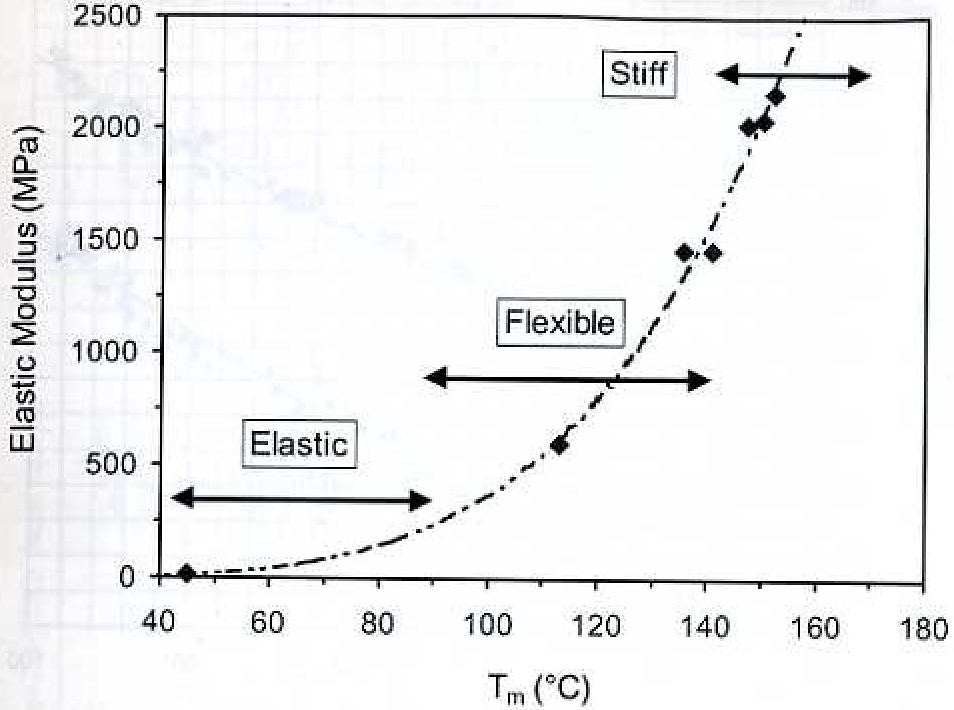


Fig. 8 – Elastic modulus of isotactic polypropylenes as a function of melting point (DMTA on compression moulded plaque, T_m of second melt, scan rate 20 °C/min, C_2- and C_1-symmetric catalysts). The subdivision into the elastic, flexible, and stiff regions is somewhat arbitrary.

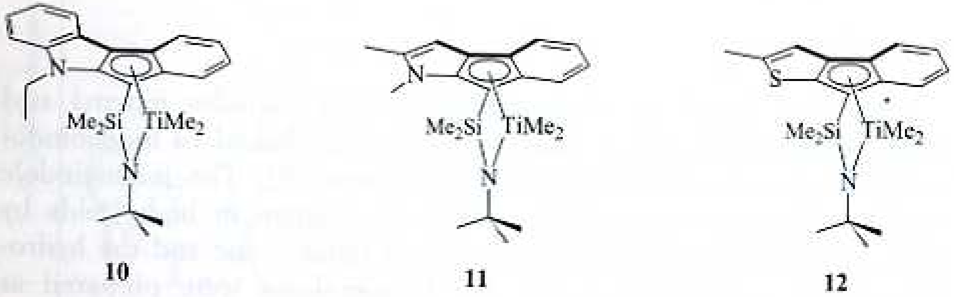


Chart 4.

Catalysts **10**, **11** and **12**, produce syndiotactic amorphous polypropylenes (*sam*-PP) of very high molecular weights, even at polymerization temperatures as high as 80°C. Syndiotactic pentad contents range between 48 and 57% *rrrr*, and regioerrors are close to or below the detection limit of the ^{13}C NMR analysis. These polypropylenes show remarkable elasticity, with tensile modulus <30 Mpa and elongation at break >600%.

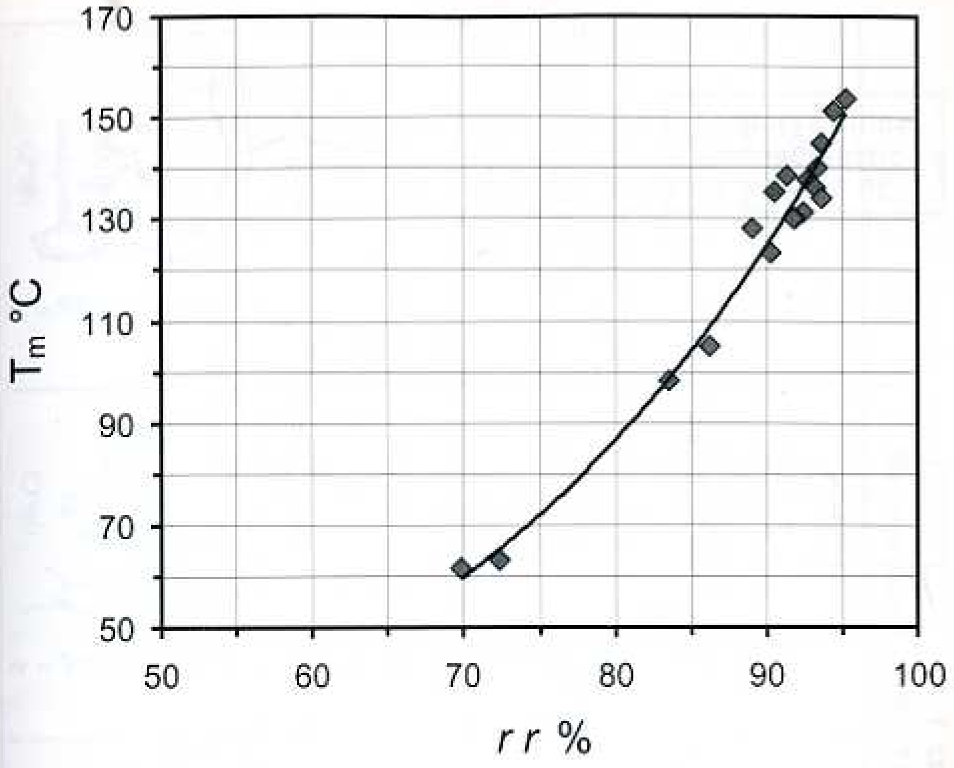


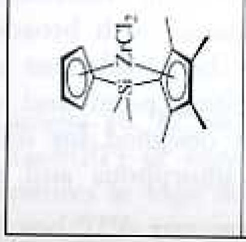
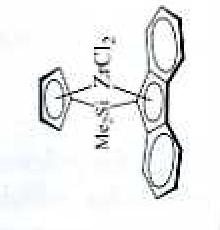
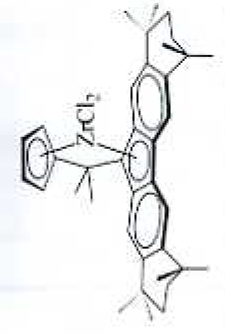
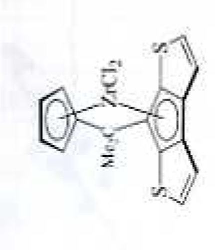
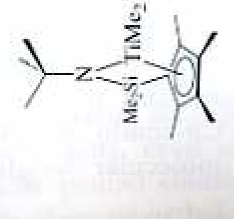
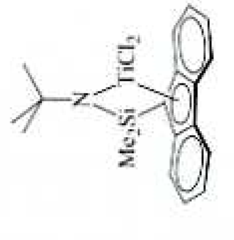
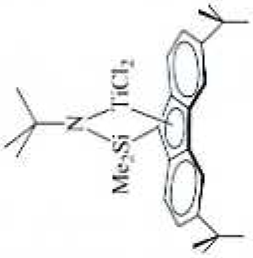
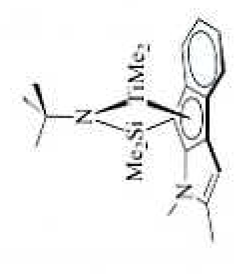
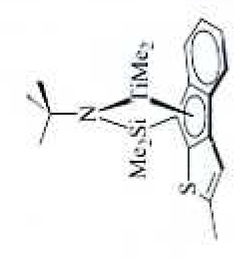
Fig. 9 – Melting point (second melt, scan rate 10°C/min) of syndiotactic polypropylenes made with C_s-symmetric catalysts, as a function of the *rr* triad content.

CONCLUSIONS

Single-center catalysts allow the synthesis of polypropylenes covering the whole range of chain stereoregularity, molecular weight, melting point, flexibility. New organic and organometallic reactions have been developed to prepare new and simpler ligands with broader catalytic tunability. We have established (for i-PP) the correlations between stereoregularity and melting point, and melting point and elastic modulus. New Cp-amido complexes have been designed for the synthesis of high molecular weight syndiotactic amorphous and elastic polypropylenes.

TABLE 3

Syndiotactic polypropylenes (T_p = 60°C, liquid propylene).

					
rrrr	14	51	82	92	74
M_w	low	300 000	100 000	> 1 000 000	100 000
T_m	amorphous	n.r.	137	154	110
(T_p)				(0°C)	(50°C)
					
rrrr	25	38	76	51	36
M_w	650 000		350 000	1 000 000	980 000
T_m	amorphous	amorphous	105	60	amorphous
(T_p)		(40°C)		(80°C)	(80°C)

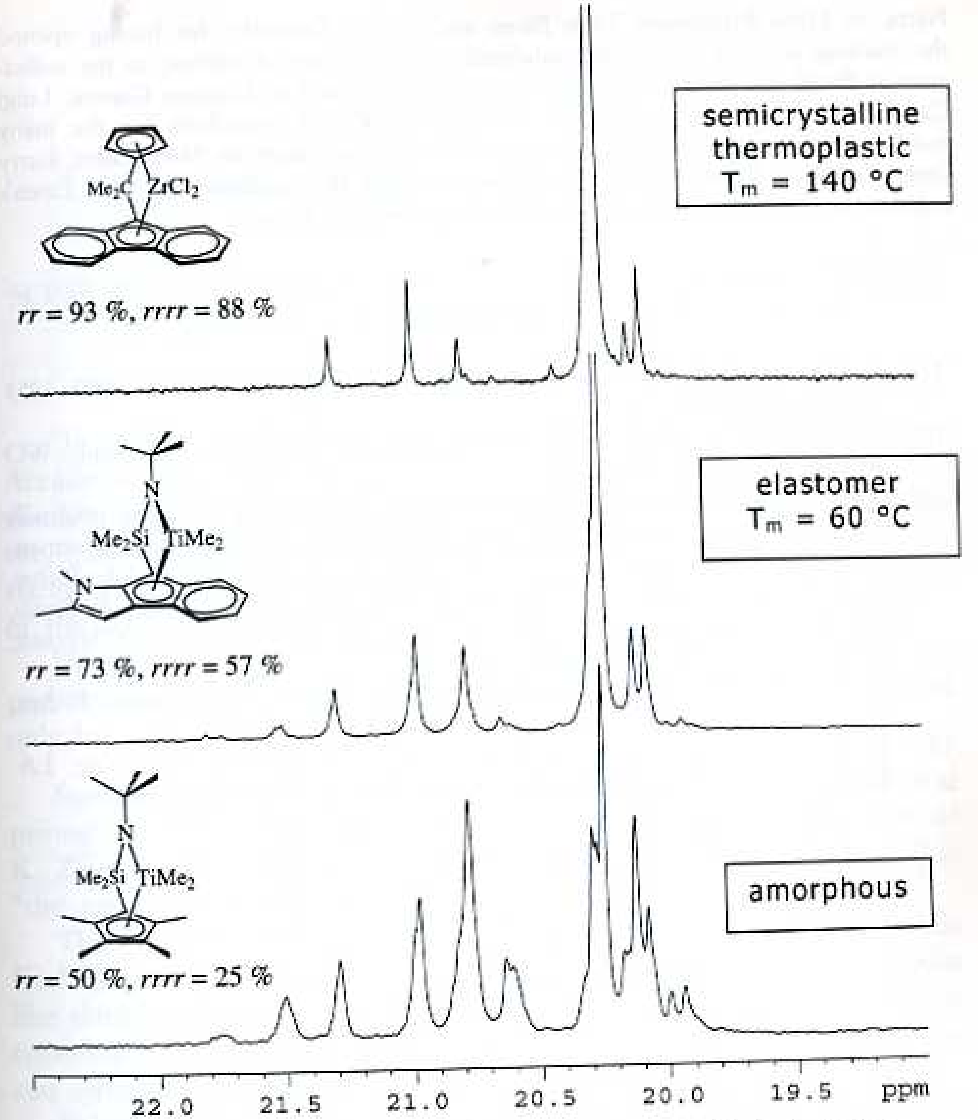


Fig. 10 – Methyl pentad region of ^{13}C NMR spectra of *s*-PP obtained from **$Me_2C(Cp)(Flu)ZrCl_2$**/MAO (top), *sam*-PP from **11**/MAO (middle) and of *am*-PP obtained from **$Me_2Si(Me_4Cp)(N\text{-}tBu)TiMe_2$**/MAO (all prepared in liquid propylene).

AKNOWLEDGEMENT

Thanks go to Basell Polyolefins, Centro Ricerche G. Natta, its present and past managers for financial support and for providing a great working environment, to Enrico Albizzati, Romano Mazzocchi, Ivo Marchetti, Adolfo Zambelli, Paolo Corradini and the late Umberto Giannini, for having propagated the teaching of Giulio

Natta, to Hans Brintzinger, John Ewen and Walter Kaminsky, for having opened the exciting field of metallocene-catalyzed polymerization of olefins, to my colleagues at Basell for providing all experimental results, and to Gaetano Guerra, Luigi Cavallo, Ilya E. Nifant'ev, Claudio De Rosa, and their coworkers for the many fruitful collaborations over the years, and, last but not least, to Mike Elder, Larry Jones and Ilya Nifant'ev for having demonstrated the feasibility of John Ewen's concept of the heterocycle condensed cyclopentadienyl ligands.

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GERHARD FINK[a]

SOME INSIGHTS INTO MOLECULAR MECHANISTIC DETAILS OF STEREOSPECIFICALLY WORKING CATALYSTS

"Il convegno nel centenario della nascita di Giulio Natta" at the Accademia Nazionale dei Lincei in Roma was for me a great event. I thank that I could contribute with may lecture. This presentation was very comprehensive because of the desire of the president to be understandable not only for the natural scientists but also for other members of the academy.

However, it is not possible in this article to deal with the full comprehensiveness of the presentation. Hence, my written contribution can only be a shortened and simple image.

Starting with figure 1 you see on the left side a stamp which was printed in 1988 reminding on the 25th anniversary of the invention of K. Ziegler and G. Natta. The spider in the stamp shall symbolize that "the nature lost a monopoly".

The photo shows G. Natta and K. Ziegler during the dinner: while Karl Ziegler is flirting with the Swedish princess, Guilio Natta looks like thinking about "the prediction of Natta". This means his prediction concerning the origin of the stereospecificity or in other words, how we can synthesize polymers with a definite microstructure.

In the middle part one can see the microstructure of a strong alternating copolymer consisting of propylene and ethylene.

Below is shown the model of a polyethylene molecule in solution. Polymers in solution form a so called statistical coil. It should be emphasized that in solution this "spaghetti coils" are in motion and permanently change the conformation.

Now the question arises: What is a (synthetic) polymer? Figure 2 demonstrates the different structures of a polypropylene polymer.

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Ziegler – Natta - Polymerization

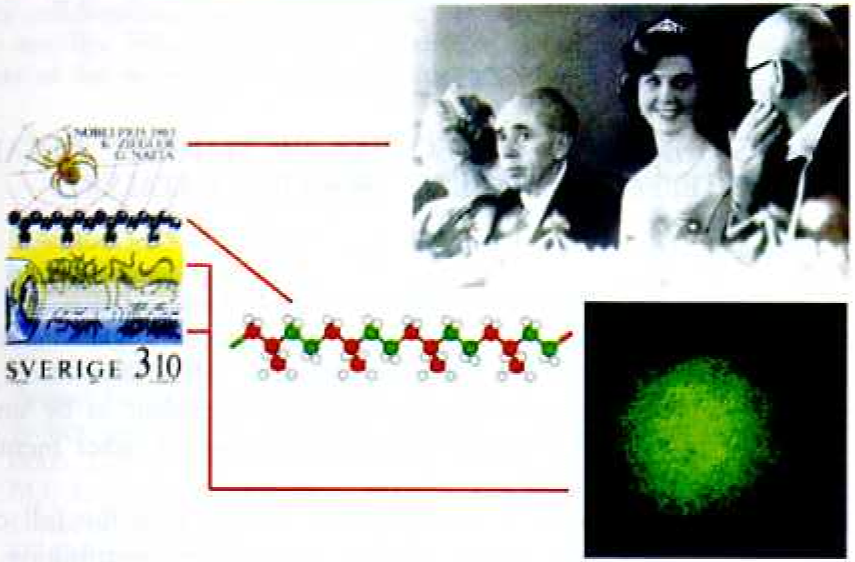
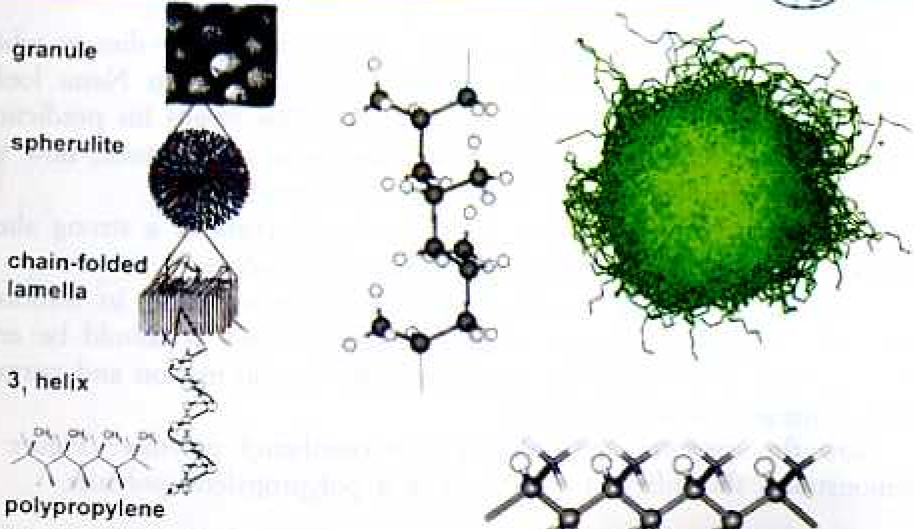


Fig. 1.

What is a (synthetic) polymer ?



P. Mülhaupt in: *Polypropylene: An A-Z Reference*, J. Karger-Kocsis (Ed.), Kluwer Publ. 1999, S. 909

Fig. 2.

On the right side below is drawn an isotactic polypropylene chain. The terminus "isotactic" means that along this propylene chain all methyl groups show in the same direction. In the crystalline state (shown in the middle part) this chain is oriented in a "helix-structure": this means the main chain (backbone) forms a spiral with the methyl groups staggered in the periphery.

The left part of figure 2 shows the possible structure sequence coming from the polypropylene chain via the 3_1-helix to the crystalline chain-folded lamella. The subsequent overstructure are globular sperulithes in which the lamellae are radial directed. Finally, the granules are the basic material – for instance – for bumpers and all the other applications.

Now, how we can generate polymer macromolecules? The term polymer comes from the old greek language and means "many parts". In a process named polymerization many, many monomers are repeatingly connected to some macromolecules. This polymerization is initiated and accomplished by a small amount of a substance, named "catalyst" and the reaction process is called "catalysis".

The terminus "Catalysis" is shown in the figures 3 and 4.

κατάλυσις – Catalysis

1836 original definition by J. J. Berzelius

old Greek dictionary:

1. dissolution, putting down, esp. of governments.
   dismissal, disbanding of a body of men, breaking up of a ship's crew, dismissal of soldiers at a review.
   pacification.
   end, termination.
   settlement of disputes.
   feebleness, impotence.
2. resting, lodging.
   restingplace, guest-chamber, quarters, lodging.
   pl., billets for troops.

Fig. 3.

κατάλυσις – Catalysis

1901 more precise definition by W. Ostwald

Oxford Minireference Science:

Catalyst: A substance that alters the rate of a chemical reaction without itself being used up. Each *catalyst* affects only certain reactions.

Webster's New World Dictionary:

Catalysis from *κατάλυσις* dissolution, *κατα* down and *λυαυ* to loose.
The causing of speeding up of a chemical reaction by the addition of some substance which itself undergoes no permanent chemical change thereby.

Fig. 4.

It is interesting, in my opinion, how in the old greek language the meaning of a word is changed, here from dissolution to resting. The more precise definition by W. Ostwald leads to a positive sense of the word catalysis.

Chemical catalysis plays an enormous role in our life and in industrial processes. And again, a small amount of catalyst (e.g. 1g of polymerization catalyst) generates a big amount of product (e.g. 5000 kg polymer per hour).

In the case of polymerization catalysts another important question is: how can the catalysts regulate the microstructure (e.g. tacticity) of the formed polymers.

Hence, in the last years the search increased considerably for new catalysts which should be capable to control better and better the properties of the formed polymers and simultaneously should have a high activity and selectivity.

The metallocene-methylaluminoxane catalyst systems e.g. meet this desires. In the case of propylene polymerization using stereorigid bridged Zirconencenes the experiments proof that the molecular structure of the catalyst determines the tacticity of the polymer (see figure 5).

Relation of catalyst structure and polymer microstructure

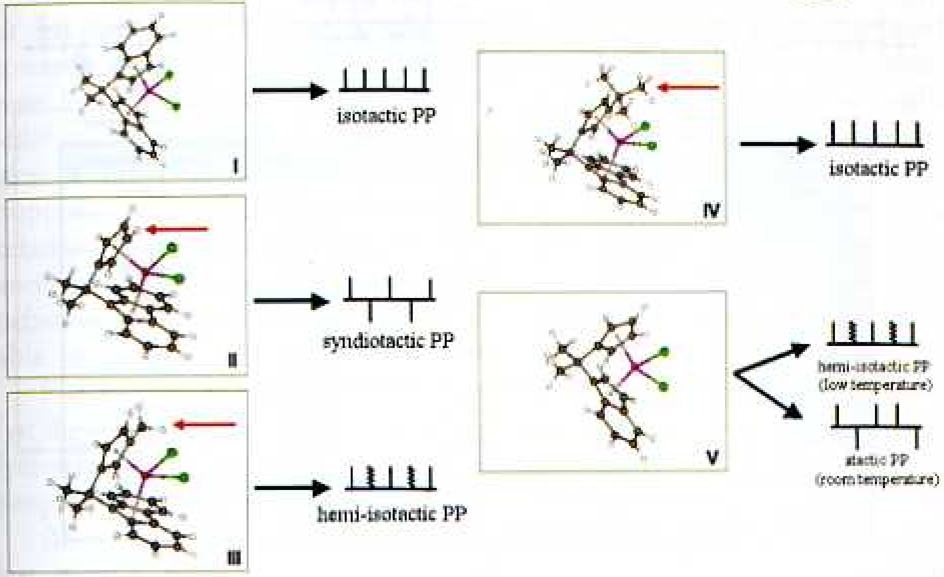
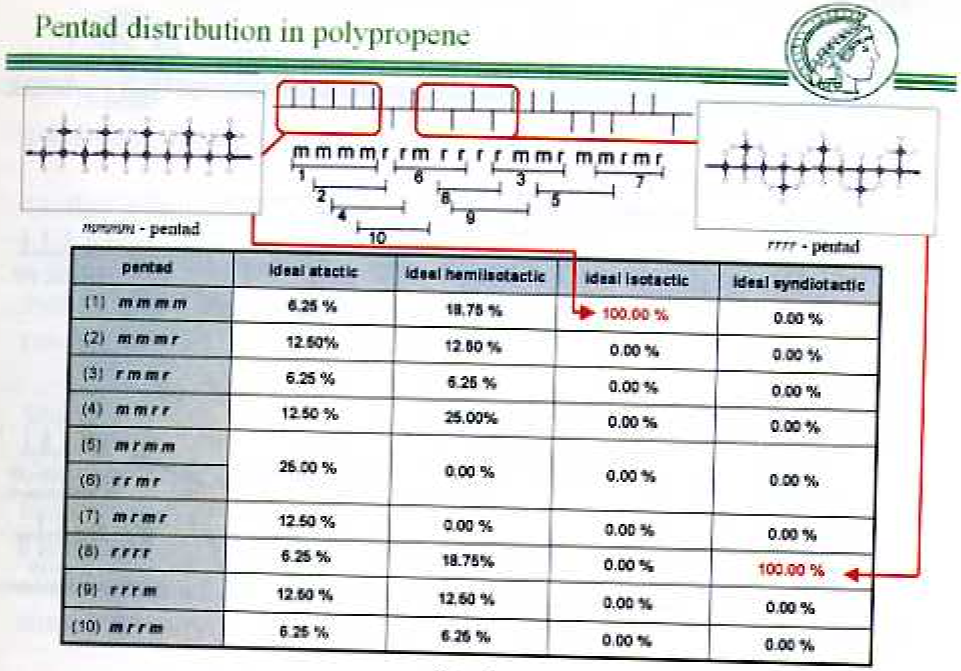


Fig. 5.

So, with catalyst I (left side top) isotactic polypropylene (all methyl groups are on the same side of the polymer chain) is formed, whereas with catalyst II (left side middle) syndiotactic propylene with alternating methyl groups is formed. So, through a small variation in the catalyst molecule (see arrows in catalyst II, III an IV) the polymer microstructure is changed from syndiotactic over hemi-isotactic (left side bottom) to isotactic (right side top). Quantitatively the tacticity is described by means of the pentad distribution (see figure 6) which is experimentally determined by ^{13}C-NMR-spectroscopy.

This pentad distribution is the relative position of the methyl groups in a sequence of five successive propylenes in the polymer chain and gives knowledge about the frequency of the different stereo errors which may occur. These stereo errors influence considerably the mechanical properties of the polymer.

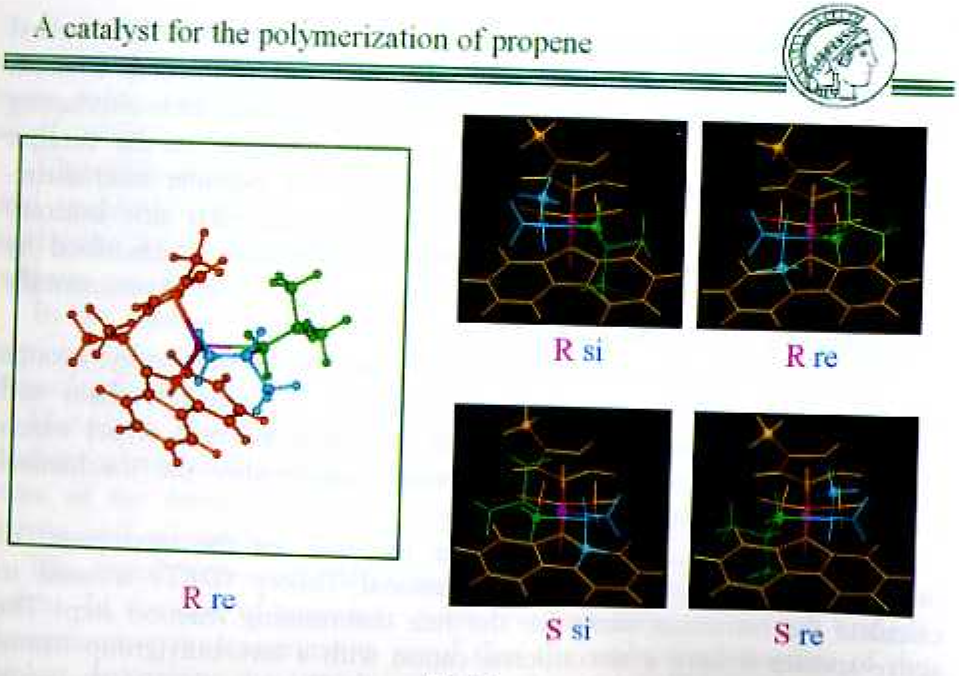
For the theoretical description (see figure 7, on the next page) of the catalysis course the Density Functional Theory (DFT) is used to calculate the transition states for the rate determining reaction step. The active species is here a zirconocene cation with a tert.-butylgroup (simulating the polymer chain) bond to the metal. The insertion of the coor-



Pentad distribution in polypropene

pentad	ideal atactic	ideal hemiisotactic	ideal isotactic	ideal syndiotactic
(1) *mmmm*	6.25 %	18.75 %	100.00 %	0.00 %
(2) *mmmr*	12.50%	12.50 %	0.00 %	0.00 %
(3) *rmmr*	6.25 %	6.25 %	0.00 %	0.00 %
(4) *mmrr*	12.50 %	25.00%	0.00 %	0.00 %
(5) *mrmm*	25.00 %	0.00 %	0.00 %	0.00 %
(6) *rrmr*				
(7) *mrmr*	12.50 %	0.00 %	0.00 %	0.00 %
(8) *rrrr*	6.25 %	18.75%	0.00 %	100.00 %
(9) *rrrm*	12.60 %	12.60 %	0.00 %	0.00 %
(10) *mrrm*	6.25 %	6.26 %	0.00 %	0.00 %

Fig. 6.



A catalyst for the polymerization of propene

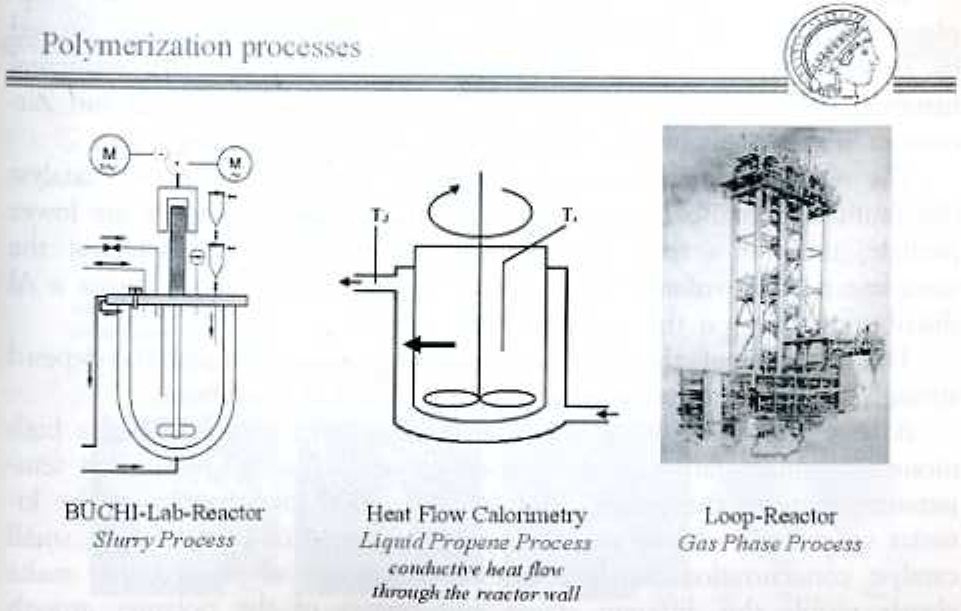
Fig. 7.

dinated propene occurs via a transition state consisting of a four membered ring (Fig. 7 left). For the exact description of the stereospecificity we need four different transition states (Fig. 7 right).

The green tert.-butylgroup bond to the metal atom can point at right or left hand side (R versus S) whereby the polymer chain can be directed towards above or below (re versus si). The blue propene then can coordinate in four different orientations (Rre, Sre, Ssi and Rsi, in figure 7 right side) and these four conformers have different energies. The relative energies of the four transition states can be calculated by means of DFT. Supposing the single insertions occur independent from each other these relative energies of the transition states can be converted via Boltzmann-average in pentad distributions. On the basis of this model for the sterechemistry of the Zirconocene catalyzed propylene polymerization we are able to predict the stereospecific behavior of new analogous catalyst.

For industrial application now, these homogeneous metallocene catalyst have to be immobilized on a heterogeneous support. Industrial polymerization processes are carried out as a slurry process, as a liquid propylene process or as a gasphase process, see figure 8.

As catalyst support mostly spherical silica gels are used. These catalyst carriers have to be relatively stable to avoid polymer fines but on the other hand they have to permit the subsequent fragmentation into



Polymerization processes

BÜCHI-Lab-Reactor
Slurry Process

Heat Flow Calorimetry
Liquid Propene Process
conductive heat flow through the reactor wall

Loop-Reactor
Gas Phase Process

Fig. 8.

sub-micrometer range primary SiO_2 particles induced by the hydraulic forces of the growing polymer. Figure 9 shows a scanning electron microscopic picture of a typical SiO_2-supported metallocene/Mao-system.

Silica / Methylaluminoxane / Metallocene

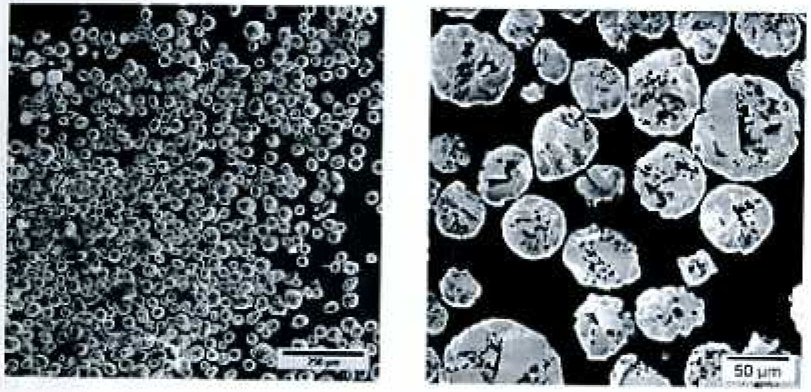


Fig. 9.

The most important condition to initiate a polymerization is the completely homogeneous distribution of the active species. This can be proved by Energy Disperse X-Ray Microanalysis (EDX-analysis). This elemental mapping concerning the elements Silicium (Si), Aluminium (Al) and Zirconium (Zr) is demonstrated in figure 10, upper series, next page.

The two linescans below are showing a "bad" and a "good" catalyst distribution. Looking on the aluminum distribution (green) in the lower particle, there is a total homogeneous Al distribution throughout the complete particle volume. The linescan of the particle above shows a Al distribution only on the surface of the particle.

The kinetics of the SiO_2-supported metallocene catalysts depend strongly on the reaction process and the reaction conditions.

A high concentration of active species on and in the support, a high monomer concentration in the suspension and high polymerization temperature increase the activity. But for a detailed investigation of the kinetics we willfully choose soft reaction conditions (low temperature, small catalyst concentration, small monomer concentration) in order to make clearly visible the different stages and phases of the polymer growth (see Fig. 11).

Catalyst system - elemental distribution

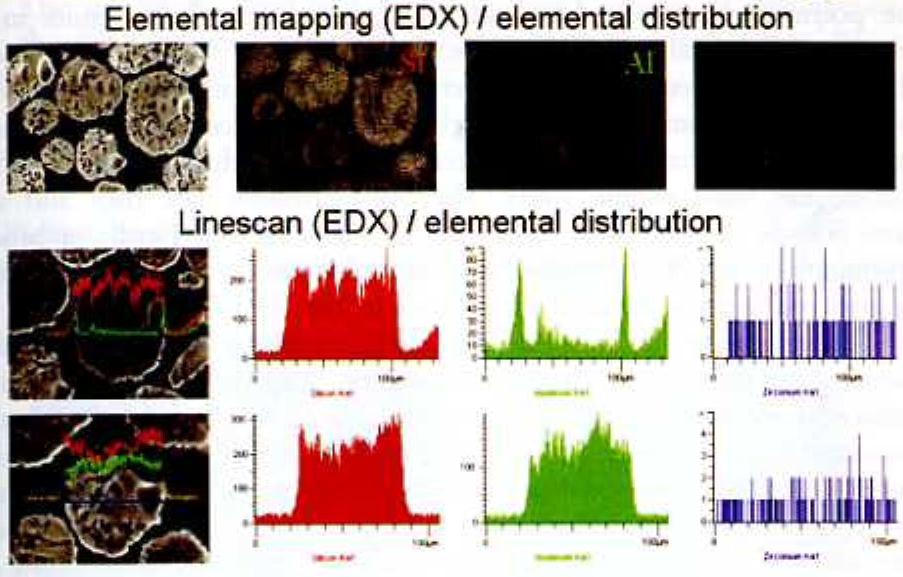


Fig. 10.

Propene polymerization with SiO_2-supported metallocenes

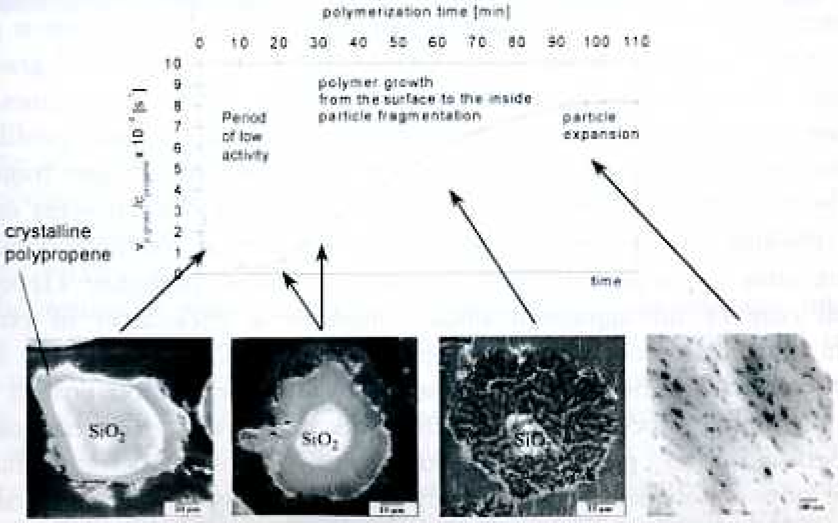


Fig. 11.

The graph of figure 11 shows the polymerization rate normalized on the propene concentration as a function of the polymerization time. The polymerization process can be divided into four different sections. First the polymerization rate shows an initial maximum which results in a coating of the catalyst particle surface with polymer. After this, a period of low activity occurs (induction period) as the coating limits the diffusion of the monomer. When enough monomer molecules have reached the inner polymerization active centers by diffusion through the polymer coating the third section starts. The polymerization rate rises and we have polymer growth with silica carrier fragmentation. Finally, a broad maximum of activity is reached and particle expansion starts. We want to give you a more detailed description in the following:

The polymerization starts at the active centers on the surface of the particle, because access to them is without hindrance. On the outer surface of the silica support and to some degree below the surface (subcutaneous) the thin polymer boundary layer is formed during this initial stage. This thin cover consists of highly crystalline polypropene with up to 75% crystallinity Corresponding to this in figure 11a lighter region represents silica, the darker region polymer. This polymer layer works as a diffusion barrier for the monomer supply, so that the diffusion of propene molecules through this layer becomes the rate determining step of the polymerization reaction. As a consequence, the high initial polymerization activity decreases sharply during the first minutes and a period of relative low polymerization activity is reached. The length of this period can vary notably and is a function of some parameters like temperature, monomer concentration and particle diameter. Polymer is growing from the outer shell towards the center of the carrier and gradually breaks down the carrier more and more (Fig. 11b). A continuous increase in polymerization activity is observable in the kinetic profile. As a consequence of the increasing activity the silica support gets fragmented by the hydraulic forces of the growing polymer. This process continues towards the center until the whole support is fragmented and all active sites are accessible for monomer molecules. In figure 11c only a small core of unfragmented silica coated by a thick layer of polymer with silica fragments is left. An interesting detail in figure 11c is the wavy surface of the polymer phase. This is a preparation artifact from the sectioning process, due to differences in the degree of hardness of embedding resin, polymer and bulk silica. This demonstrates that we have now a polymer matrix with fragmentized silica particles. Finally, in figure 11d the silica support is completely fragmentized into particles in the size range of about 50 nm and below. They are homogeneously distributed in the polymer matrix. Now, the maximum polymerization activity is achieved and a significant particle expansion starts and lasts much longer as shown in figure 11.

The size of the final SiO_2-fragments which consist of agglomeration of about 10 nm small spherical primary particles lies between 30 and 100 nm (see figure 12, top, left and the enlargement, top, right).

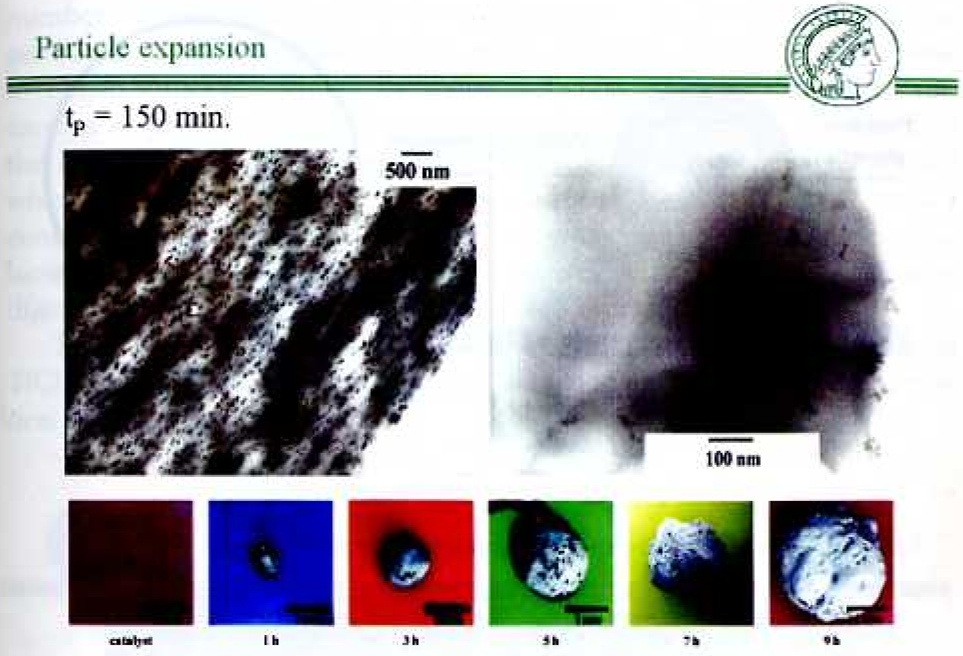


Fig. 12.

The series in figure 12 demonstrates the increase of the volume of a polymerizing catalyst particle by a factor of 40.000. The morphology of the formed polymer particle in all phases represents a replica of the starting catalyst grain.

The results of these extensive micro- and macrokinetic and microscopic investigations led to a comprehensive modeling of the total polymerization process shown in figure 13 on the next page.

By means of this polymer growth and particle expanding model we were able to design a mathematical simulation of the whole polymerization process. For this mathematical simulation (see figure 14) we developed a "shell by shell" – fragmentation of concentric shells – from the outside to the center of the particle.

Polymer growth and particle expansion model

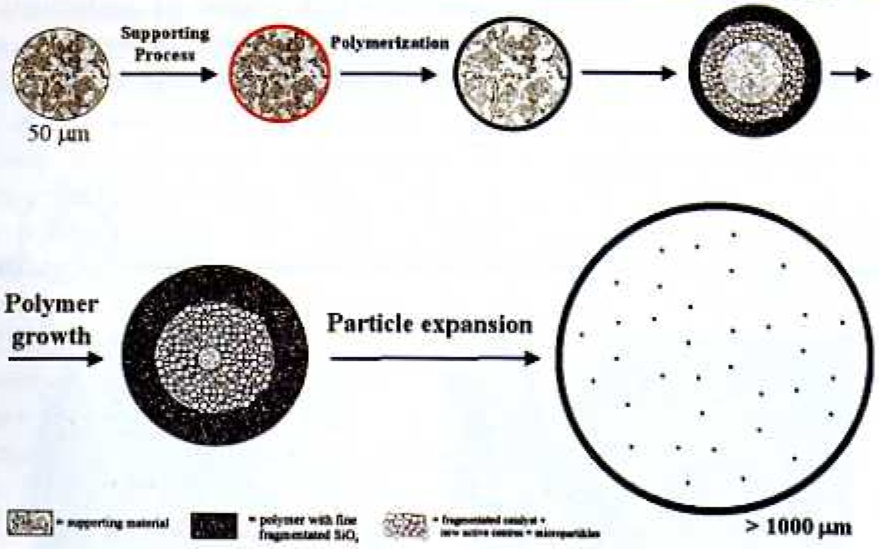


Fig. 13.

Mathematical modeling of the polymerization process

Shell-by-Shell-Fragmentation: Model of concentric shells

Mathematical rate law

$$R_i = \frac{1-\varepsilon}{\varphi^3(l)} \cdot R_p$$

[illegible]

R_i = polymerization rate per macroparticle shell unit
R_p = total polymerization rate
ε = macroparticle void fraction
$\varphi(l)$ = microparticle growth factor
$[C^*]$ = concentration of active species in the support
$[M]_s$ = monomer concentration on the particle surface
$[P^k]$ = living polymer chain concentration produced by the k-th active site
$[PH^k]$ = concentration of vacant metallocene species produced by the k-th active site

φ(l) microparticle growth factor

is the ratio of the actual microparticle radius and the radius of the catalyst fragment

is the most important factor for the breaking off of the shell and for the monomer access to the active species of the next inner shell

Fig. 14.

This has enabled us to determine the mathematical rate law and the rate constants for the activation, propagation, transfer and termination steps of the complex and multiparametric polymerization process. This complete mathematical modeling is the prerequisite for the transfer into the industrial slurry, bulk or gas phase process.

A very useful and sometimes colorful investigation tool is the videomicroscopy. This technique is a new and innovative instrument and enables the simultaneous detection of the individual growth of a large number of catalyst particles. In addition to the visualization of the growth of the polymer and of the morphology replication, it is possible to obtain detailed information about the polymerization kinetics of numerous catalyst particles. The particles act as discrete microreactors in the industrial process. For this purpose special equipment was employed which consists of an autoclave equipped with a glass window and a connection to a vacuum system and a monomer supply. The autoclave is located under a light optical microscope connected to a high resolution digital camera. This camera takes pictures every 20 seconds.

The catalyst system in study here is composed of a 4th generation $TiCl_4$ Ziegler Catalyst with $AlEt_3$ and an external donor (see polymerization start, figure 15).

4th generation Ziegler catalyst – Polymerization start

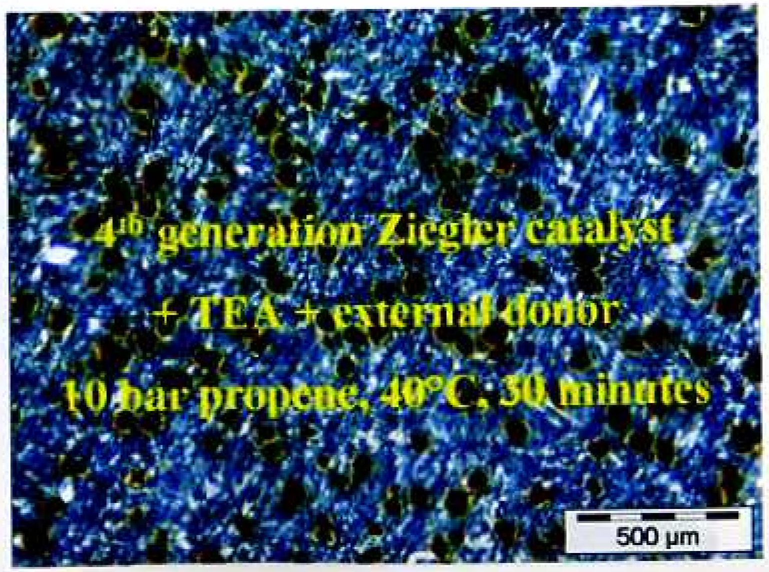


Fig. 15.

Because of the $TiCl_4$ component the starting catalyst grains are brown colored. After a few minutes of polymerization (polymerization stage 1, figure 16) these brown catalyst particles have a white circle (cover) of polypropylene indicating the begin of the polymerization on the surface. After further polymerization time (polymerization stage 2, figure 17) these covering is broadened and the particles become lighter.

4th generation Ziegler catalyst – Polymerization stage 1

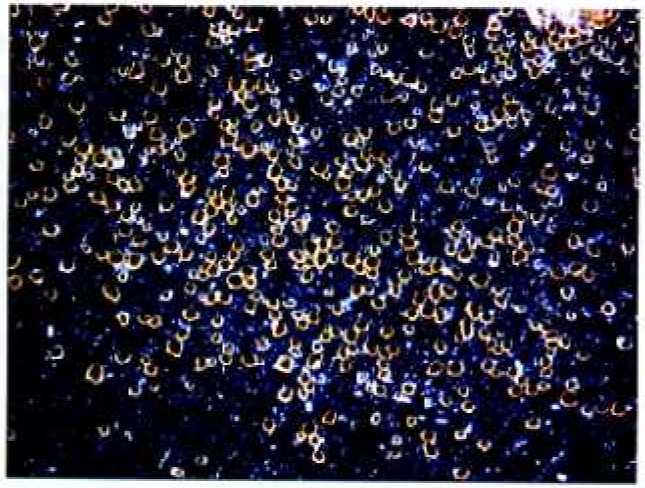


Fig. 16.

4th generation Ziegler catalyst – Polymerization stage 2

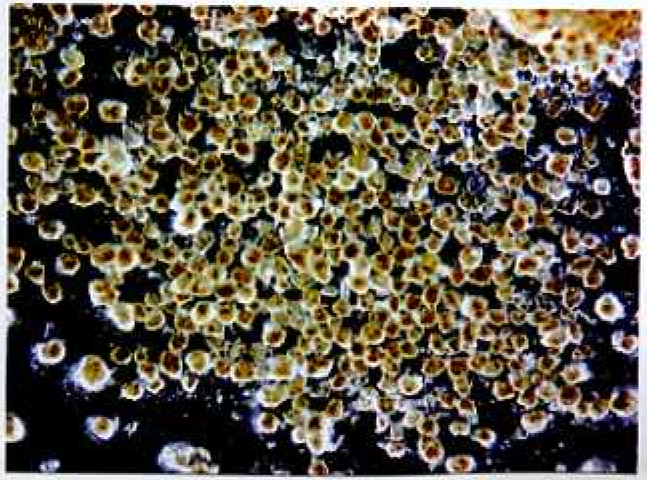


Fig. 17.

After another time of polymerization (polymerization stage 3, figure 18) this process is increased and indicates the polypropylene growth from the grain surface to the inner volume of the particle.

Hence; with this catalyst system, we could visualize directly our polymer growth and particle expansion model.

4th generation Ziegler catalyst – Polymerization stage 3

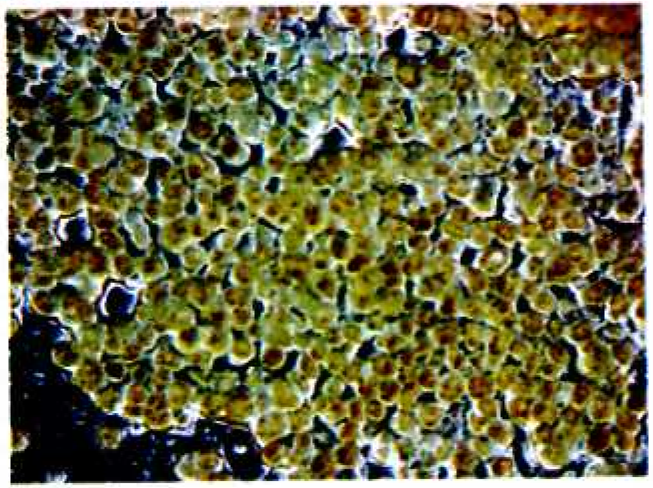


Fig. 18.

ACKNOWLEDGEMENT

This PowerPoint lecture would not have been possible to be held without the work and help of many people.

Thanks to: K. Angermund, K. Hauschild, R. Kleinschmidt, V. R. Jensen, W. Thiel, Ch. Przybyla, J. Zechlin, F. Korber, B. Steinmetz, S. Knoke, B. Tesche, B. Weimann and BASELL for fruitful cooperation and support.

Walter Kaminsky (a)

NEW POLYMERIC MATERIALS BY METALLOCENIC CATALYSIS

Introduction

Metallocene catalysts show in contrast to Ziegler-Natta systems only one type of active sites (singe site catalysts) which produces polymers with a narrow molar mass distribution [1-5]. They are soluble in hydrocarbons or liquid propene.

These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molar mass and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions.

Metallocenes, in combination with the conventional aluminumalkyl cocatalysts used by Natta [6] and Breslow are indeed capable of polymerising ethene, but only at a very low activity. Only with the discovery and application of methylaluminoxane (MAO) in our Institute in Hamburg in 1977 was it possible to enhance the activity, surprisingly, by a factor of 10 000 [7]. Therefore, MAO plays a crucial part in the catalysis with metallocenes. Methylaluminoxane is a compound in which aluminium and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents. It is gained by careful partial hydrolysis of trimethylaluminum and, according to investigations by Sinn [8], Barron *et al.* [9], Ystenes *et al.* [10], it consists mainly of units of the basic structure $[Al_4O_3Me_6]$ which contains four aluminum, three oxygen atoms and six methyl groups. As the aluminum atoms in this structure are coordinatively unsaturated, the basic units (mostly four or three) join together forming clusters and cages. These have molar masses from 1200 to 1600 and are soluble in hydrocarbons.

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If metallocenes, especially zirconocenes, are treated with MAO, then catalysts are acquired that allow the polymerisation of up to 100 tons of ethene per gram of zirconium. At such high activities the catalyst can remain in the product. The insertion time (for the insertion of one molecule of ethene into the growing chain) amounts to some 10^{-5} s only.

It is generally assumed that the function of MAO is firstly to undergo a fast ligand exchange reaction with the metallocene dichloride, thus, rendering the metallocene methyl and dimethylaluminum compounds. In a further step, either Cl^- or CH_3^- is abstracted from the metallocene compound by an Al-center in MAO, thus, forming a metallocene cation and a MAO anion [11-13]. The alkylated metallocene cation represents the active center. Meanwhile, other weakly coordinating cocatalysts, such as tetra(perfluorophenyl)borate anions $[(C_6F_5)_4B]^-$, have been successfully applied to the activation of metallocenes [14].

Polyolefins, with different microstructures and characteristics, can be custom-made just by varying the ligands of the metallocene. By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefins with tailored microstructures and of chemically uniform copolymers has not yet been achieved by conventional heterogeneous catalysts.

Using metallocene catalysts, it was possible for the first time to produce polyethenes, polypropenes and copolymers with narrow molar mass distributions [18], syndiotactic polypropene (in technical scale amounts [19], syndiotactic polystyrene [20], optically active oligomers [21] and composite materials of biomass, powdered metals with polyolefin [22]. Organic or inorganic particles (starch, cellulose, quartz sand, or powdered metal) can be coated with a hydrocarbon soluble metallocene catalyst and, in turn after polymerisation, with a polyolefin film of variable thickness [23].

Metallocenes are useful catalysts for the production of cycloolefin copolymers (COC), materials with special properties and a high potential as engineering plastics. Ethene/norbornene copolymers are of interest because of the easily available monomers. Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range independently from the used catalysts. A copolymer with 50 mol % of norbornene yields a material with a glass transition temperature of 145°C [24].

Alternating copolymers are obtained by some metallocene and other single-site complexes. The melting point of the alternating copolymer depends on the molar ratio of norbornene in the polymer while the glass transition temperature is almost independent. A maximum melting point of 320°C was reached.

Fluorinated half-sandwich titanium complexes are in combination with MAO very active catalysts for the polymerisation of styrene and butadiene. The microstructure of the polybutadiene (80% cis, 1% trans, and 19% vinyl) depends on the methyl substitution of the cyclopentadienyl ring [25, 26].

ETHENE/NORBORNENE COPOLYMERS

Copolymers of ethene/norbornene (COC) have been of great interest to industry and science because of their excellent optical, mechanical, and electrical properties. With their high transparency to blue-green laser light, they have potential application to higher-capacity CDs. Most metallocene complexes are active for the copolymerisation but the activity has to be increased. It is difficult to obtain copolymers with high molecular weights. The constrained geometry catalyst $[Me_2Si(3\text{-}^{tert}BuCp)(N^{tert}Bu)]TiCl_2$ was investigated to produce copolymers with high molecular weights (Tab. 1).

The activity rises with increasing temperature and reaches 30 000 kg copolymer/mol catalyst in one hour by 90°C. The maximum of the polymerisation rate is reached by about 50 mol% of norbornene in the starting phase. The molar masses of all copolymers are summarized in Tab. 2. The molar masses increase with increasing norbornene fraction in the feed until $c_N = 0{,}6$. At higher norbornene fractions the molar masses decrease. For COCs prepared at 30°C, the molar masses increase from 200 000 to 320 000, then decrease to 76 000 g/mol.

Recent publication describes the copolymerisation of ethene with

TABLE 1
Polymerization conditions.

Catalyst	5×10^{-6} mol/L
MAO	500 mg
Ethene	0,237 mol/L
Norbornene	0-1,13 mol/L
Solvent	toluene
Temperature	30, 60, 90 °C

TABLE 2

Ethene/norbornene copolymerizations by $[Me_2Si(3\text{-}^{tert}BuCp)(N^{tert}Bu)]TiCl_2/MAO$ *at 30, 60, and 90°C, respectively. Molar masses determined by viscosimetry and molar fraction norbornene in the feed* χ_N

c_N	30°C Mη [g/mol]	60°C Mη [g/mol]	90 °C Mη [g/mol]
0	insoluble	insoluble	insoluble
0,2	200 000	81 000	45 000
0,4	230 000	85 000	48 000
0,6	321 000	95 000	46 000
0,8	259 000	62 000	37 000
0,9	100 000	33 000	22 000
0,95	83 000	23 000	20 000
0,99	76 000	28 000	20 000

norbornene to show living or quasi-living character [27]. As shown, molecular masses up to 320 000 can be reached. With increasing temperature the molar masses decreased, for example from 230 000 to 85 000 to 48 000 g/mol with $c_N = 0{,}4$.

Obtained are random up to alternating copolymers. In contrast to other alternating COC producing catalysts the constrained geometry catalyst, $[Me_2Si(3\text{-}^{tert}BuCp)(N^{tert}Bu)]TiCl_2/MAO$ produces alternating COCs with mostly isotactic structures. The alternation is influenced by the temperature if sufficient norbornene is present in the copolymerisation. Thus, alternation up to 0,77 can be obtained with $c_N = 0{,}99$ and at a polymerisation temperature of 90°C. The norbornene incorporation, copolymerisation parameters, microstructures, and glass transition temperatures are barely influenced by the temperature, except for copolymerizations with very high molar fraction of norbornene in the feed $c_N = 0{,}99$, where with increasing temperature the norbornene incorporation increases, more alternating and NN sequences are observed and the glass transition temperature is higher than expected. As assumed, the temperature has great influence on the molar masses. Lower temperatures increase the molar masses intensely.

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BERNARD LOTZ(*)

SOLVING THE CRYSTAL STRUCTURES OF ISOTACTIC POLYPROPYLENE: A TALE OF NIGHTMARES, FRUSTRATION AND BEAUTY

1. INTRODUCTION

The first synthesis of isotactic polypropylene (iPP) in Giulio Natta's laboratory in 1954 has been the start of an extraordinary technical and economical achievement, as recounted in other contributions to this volume. It has also been, in the broad field of structural investigations, the start of a scientific adventure and intellectual challenge that is not yet ended. In this adventure, scientists from all over the world took their part – isotactic polypropylene has indeed become a part of the world's heritage. In this adventure however, the Italian school of crystallographers played a major role. Some of the founders of the field are in this audience and could give a better, first hand account of the same facts. Major contributions to the field are due to several Italian colleagues (the school in Naples and Salerno, or Valdo Meille and Sergio Brückner), who would be equally qualified to present this account. It is therefore with a great sense of humility that I will cover some aspects of the structure of iPP, underline the various contributions whenever possible in chronological sequence, and put these contributions in perspective in the broader context of structural analysis of crystalline polymers. For obvious reasons, I will emphasize the information obtained by diffraction techniques, either X-ray or electron diffraction. Needless to say, the present contribution draws on material that can be found in different reviews on the crystalline structure and polymorphism of isotactic polypropylene [1-3].

Isotactic polypropylene is not the first synthetic crystalline polymer.

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Polyethylene, polyamides, aliphatic and aromatic polyesters were synthesized in the 1930s and 40s. These polymers are *linear* polymers, with no substituant attached to the main chain. As a result, the chain conformation is essentially stretched out or extended. Isotactic polypropylene is the first *helical* synthetic polymer the crystal structure (or at least one of them!) has been solved [4]. Polypropylene is a polymer that bears a side-chain, in this case, a simple methyl group- in first approximation a sphere 4 Å in diameter. This methyl group makes all the difference, and it will be a central theme during the whole presentation. In isotactic or syndiotactic polypropylene (sPP), and contrary to atactic polymers, the position of the methyl group is *regular*, i.e. is the same (iso), or alternates (syndio) along the extended chain. Extended chain conformations are impossible for iPP, since the diameter of the methyl group exceeds the distance between the atoms of the main chain ($\approx$ 2.5 Å) to which neighbor methyl groups are linked. This steric encumbrance forces the chain to adopt a helical conformation. Three residues build up one turn of the helix [4]. Another novelty lies in the fact that since the chain has side chains, it is chiral: indeed, each carbon atom that bears a methyl group has four different substituents: one hydrogen, one methyl group and the two ends of the chain that are of different lengths. This *would* imply that iPP adopts helical conformation of only one sense – one *hand*, either right-handed or left-handed. However, on a local scale, the (usually large) lengths of the two chain-ends cannot be "measured" and "compared" by the asymmetric carbon, which has a major consequence: iPP is "chiral but racemic" [4], which means that the chain can adopt *either* right-handed *or* left-handed helical conformations.

The above elements set the stage for *all* structural studies of iPP. Isotactic polypropylene exists in only *one* helical conformation, a three-fold helix. This conformational "rigidity" is at variance with many other polyolefins [6], and the next member of the family, isotactic poly(1-Butene) most prominently among them, the three crystal structures of which rest on three *different* helix conformations. The structural challenge is therefore to identify packing schemes that rest on a single helix conformation and yet, as seen next, generate strikingly different crystal structures with different physical properties (melting point, modulus, impact resistance, transparency, etc.).

2. The alpha phase of isotactic polypropylene

2.1. *The unit-cell of isotactic polypropylene, α phase*

As recounted on several occasions [7], the first synthesis of polypropylene in an autoclave polymerization of propylene alone produced a solid material that Paolo Chini took to Paolo Corradini, located on the next floor of the Polytechnic Institute in Milano, to be investigated by X-ray diffraction. Paolo Corradini was the crystallographer who, following the advice of Alfonso Liquori, had joined the group of Giulio Natta with the assignment to investigate the structure of the heterogeneous catalysts and semi-crystalline polymers. The solid material turned out to yield X-ray reflections – actually was a *crystalline* material, the first of a long series of similar materials that, as a group, build up a new class of crystalline, stereoregular polymers, of which isotactic polypropylene remains the most prominent member.

It took only a few months to Paolo Corradini to solve the crystal structure of the most common crystal phase of isotactic polypropylene, later known as the α phase. Figure 1a represents the chain axis projection of the electron density map of αiPP, together with the same *c* axis projection of the structure (Fig. 1b) as published in 1960 in *Nuovo Cimento* [4]. The electron density map displays clearly the three-fold symmetry of the chain, and makes it possible to locate the methyl groups that "stick out" of the helix backbone. The chain axis repeat is 6.5 Å. The unit-cell is monoclinic with parameters $a = 6.65 \pm 0.05$ Å, $b = 20.96 \pm 0.15$ Å, $c = 6.50 \pm 0.05$ Å, $\beta = 99°20' \pm 1°$, space group *C2/c*. The structure is rather complex, since it is based on an intimate mixing of right- and left-handed helices, and alternation of orientations of the chains along the *b* axis (horizontal in Figure 1). Specifically, it is a *layered* structure, with layers parallel to the *a* axis (vertical in Figure 1) made of helices of one hand only, successive layers along the *b* axis being made of helices of opposite hand. This will be an important ingredient of the analysis of lamellar branching and the structure of the γ phase (cf. *infra*).

The structure of the α phase of iPP is important in the history of structural investigations of polymers. It is the third *helix conformation* of polymers that has been established, only shortly after the α helix conformation of polypeptides and proteins due to Pauling and Corey, and the double helix of DNA of Watson and Crick. More importantly, it is the first *complete* crystal structure of helical polymers that has been solved,

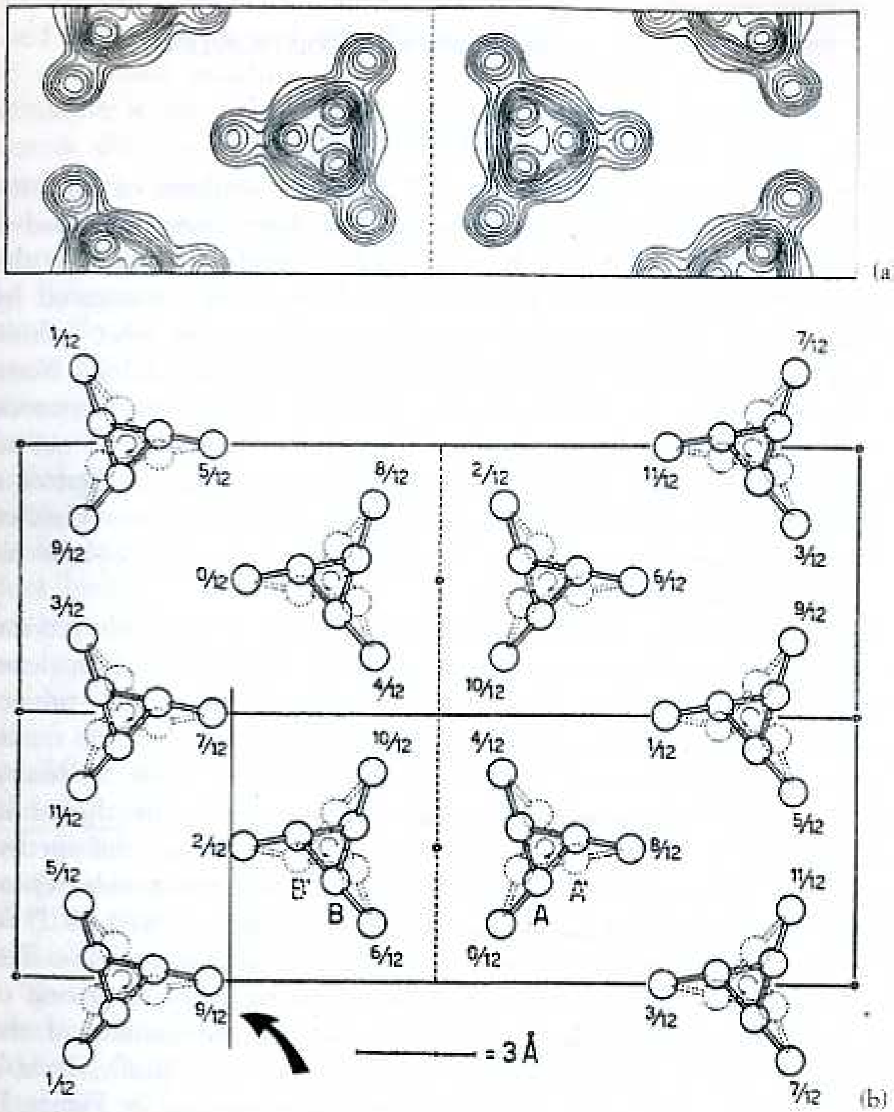
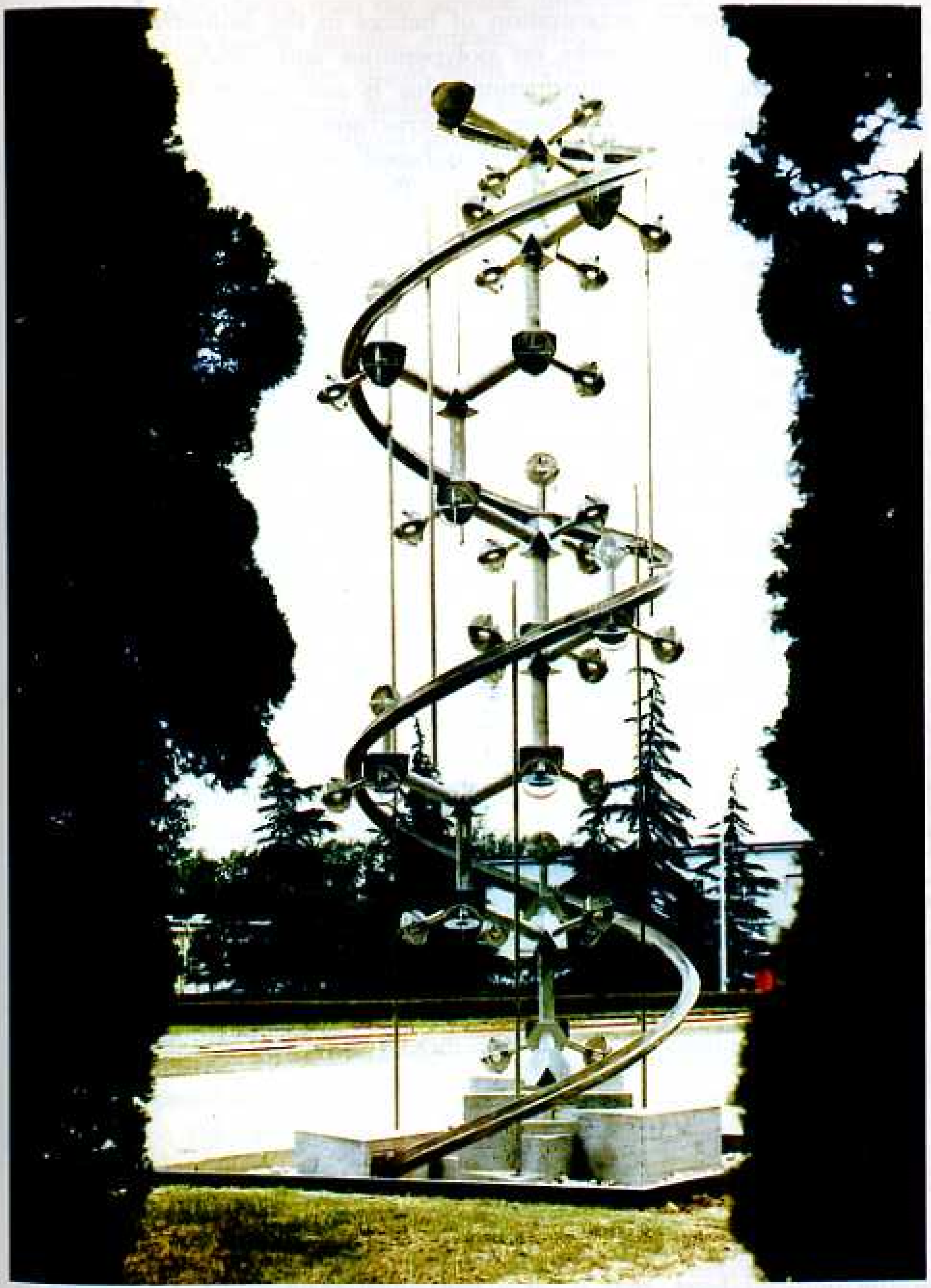


Fig. 1 – (a) The electron density map of isotactic polypropylene, α phase unit-cell, determined by Natta and Corradini [4]. Contours are drawn every 0.5 e/Å^2. The first line corresponds to the 2 e/Å^2 level. Note the clear three-fold symmetry and the location of the methyl groups that stick out of the helix main chain path. a^* axis vertical, b axis horizontal. Reprinted from reference 1 with permission of the publisher; (b) Projection parallel to the chain axis of the structure of isotactic polypropylene, α phase for the *C2/c* space group, similar to the electron density map of part (a). "Up" and "down" chains are represented in full and dashed lines, respectively. Note that the methyl group positions are maintained, but the main chain atoms have slightly different atomic coordinates. The arrowed plane is imaged by AFM in Figure 2; (c) An artist's rendering of the three-fold helix of isotactic polypropylene, located in front of the Giulio Natta Research Center in Ferrara (photograph courtesy of Pr. Galli, Basell). The bonds lengths and angles are respected. The helical path has been underlined by a continuous helix that does not exist in the structure, but underlines the right-handed helical hand of this iPP chain.



(c)

Fig. 1.

including the detailed organization of helices in the unit-cell. This is in sharp contrast to the works on polypeptides and DNA, which established only the chain conformation (this is not meant to dismiss the fundamental importance of these two structures!).

The structure shown in Figure 1 is based on a space group – *C2/c* – that supposes some structural disorder. The structural disorder rests on a distinction that has not been introduced so far: it deals with the orientation of the helices in the crystal lattice. The methyl group is linked to the main chain by a bond that is tilted to the chain axis, much like the bones in a fishbone. A given helix can be oriented "up" or "down" depending on the orientation of this bond. For both orientations, the positions of the methyl groups in the lattice can be maintained, but the positions of the "inner", main chain atoms are slightly different, as illustrated in Figure 1b by the full and dotted lines. Such a statistical presence of "up" and "down" helices at every site corresponds to a "limiting disordered structure", described as the α_1 structure, and obtained at low temperature. Later studies have shown that for well annealed samples, additional reflections appear in the diffraction pattern, which indicate an α_2 structure with lower symmetry (space group $P2_1/c$). In other words, the "up" and "down" orientation of the helices in α_2 is "not as random" as in α_1. This line of research has been actively pursued by several groups in the world (Hikosaka and Seto in Japan, the group of Corradini in Naples, etc.). It turns out that the crystal structure of αiPP can be best described as the stacking of *bilayers* made of parallel, all "up" or all "down" right-handed helices and left-handed helices. The relative orientation of the bilayers depends on a probability *p* that is controlled by the crystallization/annealing conditions (Fig. 3) [6, 8]. It is likely that with the development of polymers with improved tacticities that crystallize at higher temperatures, even "purer" forms of the α_2 phase will be obtained – and are indeed suggested by the work of Maiti *et al.* [9].

2.2. *The lamellar branching of isotactic polypropylene, α phase*

The preceding section was devoted to the crystal structure of αiPP at the unit-cell level, that is, at a very local scale. Moving now on to the next level of organization of polymers, we consider the lamellar organization. When they crystallize from the bulk or solution, polymer chains fold back and forth in a hairpin fashion, and form lamellae that are ten to several tens of nanometers thick, depending on crystallization conditions. The chains span the lamellar thickness, and are oriented more or less normal to the lamellar surface, which is less organized since it contains the folds of the chains (fold surface). Growth of the lamellae proceeds by deposition of molecular stems on the lateral, thin edges of the lamellae where the crystal structure "is apparent". During this deposition step, selection of the helical hand of each stem must take place, that will ultimately become a characteristic of the unit-cell.

Most or, for that matter, *all* polymers crystallize from solution or from the melt in the form of single lamellae, often generating screw dislocations. The simplest form of these lamellae is therefore a single, flat or tent-like lamella, several micrometers in lateral size, and only ≈10 nm thick. The shape of the lamella often reflects the symmetry of the underlying unit-cell, e.g. hexagonal for hexagonal or trigonal unit-cells. Isotactic polypropylene in its α phase has a *very* peculiar crystal morphology. It does indeed produce single lamellae that are elongated, lath-like. However, during growth, these lamellae branch repeatedly at a constant angle. When crystallized from solution, the structures are so regular that they were termed "quadrites" by Freddy Khoury [10]. Similar branching takes place in thin films (Fig. 4a), in the bulk, on spinning at relatively slow take-up rates, etc. This lamellar branching is *unique* to the α phase of iPP, and has been a puzzle for many years. Geil [11], Khoury in an extensive study [10], Keith and Padden [12, 13], all in the USA, Binsbergen and de Lange [14] in Holland, made contributions to the analysis of this lamellar branching. Khoury [10] suggested a mechanism of branching through the fold surface. Keith and Padden [12] pointed out that the branching takes place on the lateral edges of the lamellae, specifically in the *ac* face of the unit-cell, and that the chain axes orientations in mother and daughter lamellae are 100° apart – exactly the β angle of the monoclinic unit-cell. Binsbergen and de Lange [14] were very close to the correct answer. They pointed out that the pattern of methyl groups in the *ac* face is such that it is possible to create two schemes of interdigitation of these methyl groups for two successive layers. In one of them, the chain axes are parallel, and in the other the chain axes are nearly 100° apart – again the value of the β angle of the monoclinic unit-cell.

The origin of this lamellar branching is indeed purely crystallographic, and amounts to a case of self-epitaxy [15], also described, in crystallographic language, as a rotation twin. It is best established when considering the organization of the methyl groups in the *ac* face of αiPP, as revealed by epitaxial crystallization [16, 17]. Epitaxial crystallization makes it possible to deposit the chain axes of the polymer parallel to a substrate that presents topographic similarities with a given crystallographic plane [16]. Epitaxial crystallization makes it possible to orient the *ac* plane of αiPP parallel to the substrate. After dissolution of the substrate, the topography of the contact face, now exposed, can be imaged by Atomic Force Microscopy (AFM) [17]. This technical feast reveals a *lozenge shaped pattern of methyl groups* (Fig. 2) consistent with the crystal structure determined by Natta and Corradini [4]. The key of the lamellar branching lies in this lozenge shaped *ac* face, that results from the near-identity of the *a* and *c* axes dimensions. Superposition of two facing faces, one made of right-handed helices and one made of left-handed helices results in a perfect interdigitation of the facing arrays of methyl groups, which corresponds to the crystallographic packing [4]. However, a *similar interdigitation* can be made *when the facing layers are both made of helices of the same hand*. The chain axes of one layer is now oriented parallel to the *a* axis of the other layer, which creates the new chain axis orientation, and is the seed for a new lamella, in "branched" orientation relative to the parent one (Fig. 4b) [3]. This mechanism can be repeated and thus generate several generations of mother, daughter, grand-daughter, etc. lamellae [10, 17], every generation restoring the crystallographic orientation present in its *grand*-mother one (cf. Fig. 4a). In essence, the lamellar branching results from a mistake in the strict alternation of helical hands in successive *ac layers*, that is, from a "stumble" of helical hands. Clearly, the specificity of the lamel-

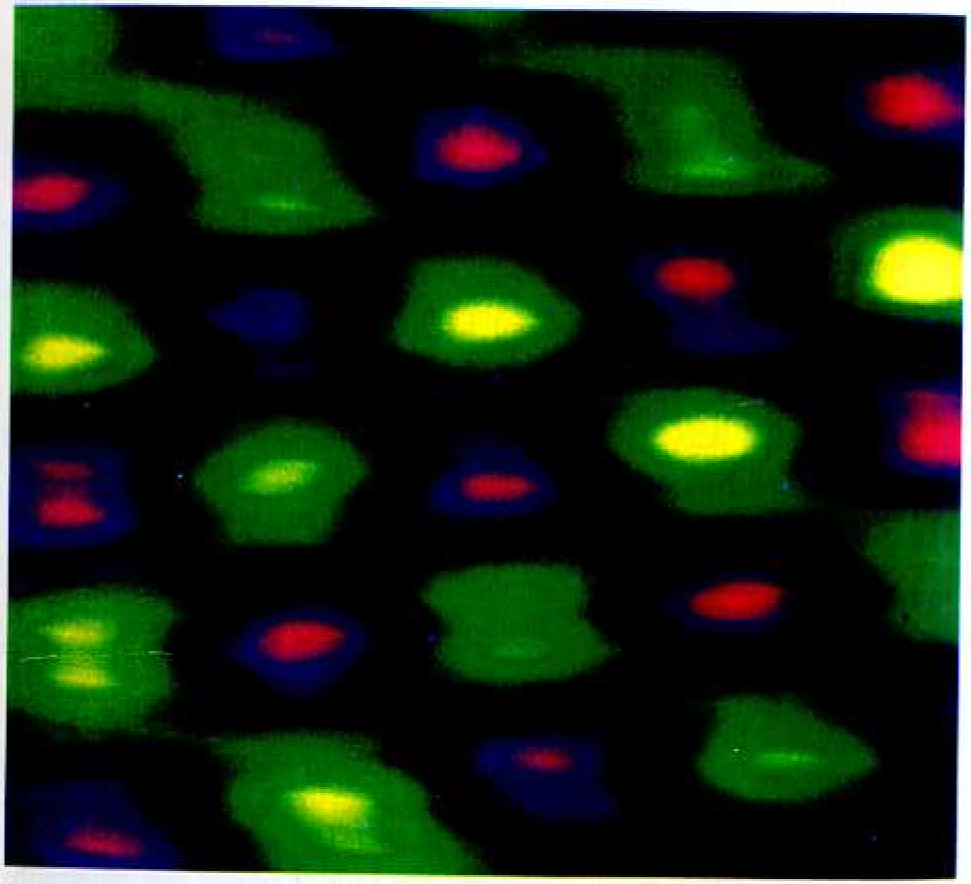


Fig. 2 – AFM image of the *ac* face of the α phase crystal structure. iPP was epitaxially crystallized on benzoic acid, which was then dissolved, leaving the *ac* contact face exposed and ready for the AFM imaging. The methyl groups 6.5 Å apart are darker and are arranged in a lozenge shaped pattern that is fully consistent with the crystal structure in Figure 1. More specifically, the face imaged here corresponds to an *ac* face with the lowest density of methyl groups, arrowed in Figure 1b. Area imaged: 2 nm by 2 nm. Reprinted from reference 17 (correction) with permission of the publisher.

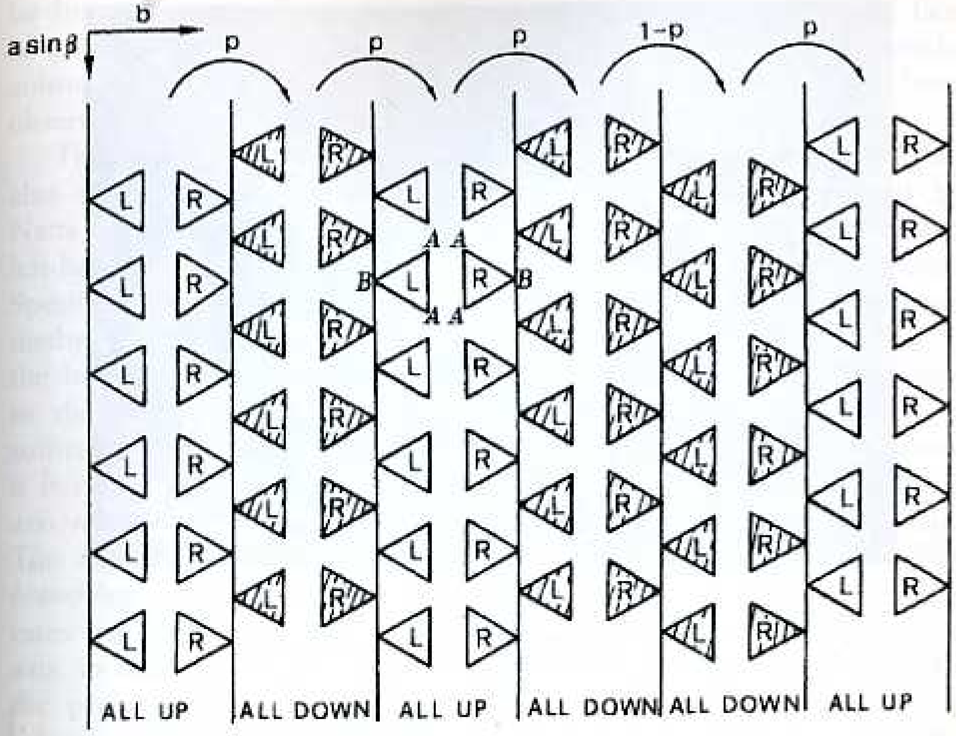


Fig. 3 – Model of the structural disorder in αiPP. The bilayers are made of isoclined right- and left-handed helices (R and L). In the next bilayer, the helices may be oppositely oriented (up-down, probability *p*) or identically oriented (up-up or down-down, probability *1-p*). A regular succession of anticlined bilayers would correspond to the more ordered α_2 structure, $p=0.5$ (statistical succession) corresponds to the less ordered α_1 structure. Reprinted from reference 1 with permission of the publisher.

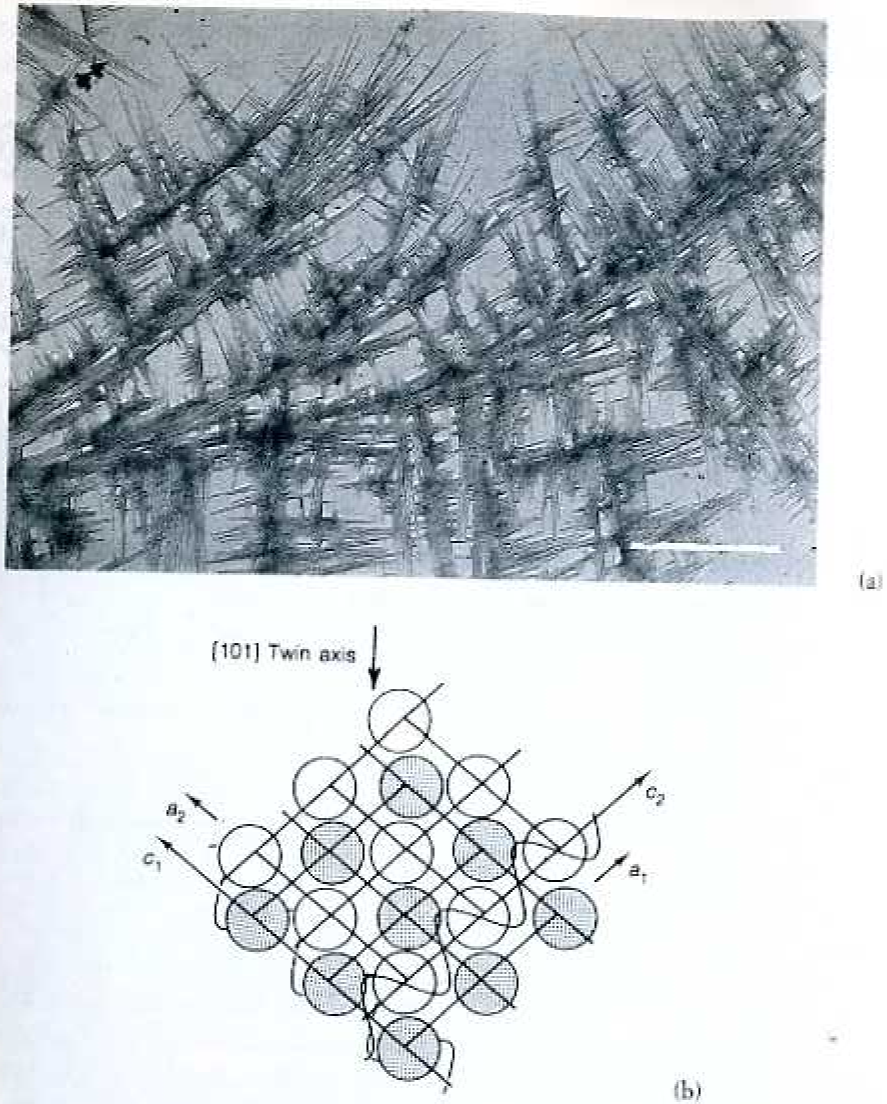


Fig. 4 – (a) Lamellar branching in the α phase of isotactic polypropylene, as revealed by thin film growth from the melt. The "spherulite" center is in the lower left corner. Due to lamellar branching, the odd (first, third, etc) generations of lamellae are radial, the even (second, fourth, etc) generations are nearly tangential. Scale bar: 2 μm. Reprinted from reference 15 with permission of the publisher; (b) Model of the interdigitation of methyl groups for the facing *ac* faces indicated in Figure 1b. The topography of the faces is that of a lozenge array of bulges (the methyl groups). Similar interdigitation is realized when the two facing layers are made of helices of opposite hand (in which case the helix axes remain parallel, and the structure corresponds to the unit-cell shown in figure 1b) or when the facing layers are made of helices of the same hand. In the latter case, represented here, the chain axis of the depositing layer is parallel to the *a* axis of the substrate layer (shaded), and a new chain orientation is generated, parallel to the *a* axis of the substrate layer. The relationship between the two layers is a rotation twin (twin axis indicated), and the interaction may be described as a self-epitaxy or homoepitaxy. Reproduced from reference 69 with permission of the publisher.

lar branching stems from the very unusual high symmetry of the *ac* face of αiPP (in the present case, of lozenge type). Similar branching mechanisms could be envisaged for other polymers, but have not yet been observed because their crystallography is less well or not adapted.

The analysis of the lamellar branching in molecular terms provides also another insight, *unique* to αiPP. In the structure determined by Natta and Corradini [4], the location and orientation of the right- and left-handed helices have a unique relationship with the unit-cell axes. Specifically, the crystal structure determination shows that when a single methyl group is exposed in the *ac* plane (as in Figure 2), the path of the helix that supports it (but which is burried in Figure 2) is parallel to the *long* diagonal of the *ac* plane or lozenge. In other words, it suffices to know what is the *c* axis orientation (easy to determine, since it is nearly normal to the lamellar surface), *and the orientation of the a axis relative to that c axis*, to "position" all the chains in the structure. *This is precisely the information provided by the self-epitaxy and lamellar branching.* Indeed, the chain axis orientation in daughter lamellae indicates the orientation of the *a* axis in the mother crystal relative to its *c* axis, in other words the "dip" to the right or the left of this *c* axis, or the position of the β angle relative to the chain axis. This piece of information is an essential one, since *it links the morphology with the crystal structure* at the unit-cell level [15, 3]. Indeed, it indicates the orientation of the unit-cell in space, and more precisely if the unit-cell has its *b* axis oriented towards or away from the observer (is seen from the +*b* or the −*b* axis sense). This information in turn helps determine the orientation of the right- and left-handed helices in the entire quadrite (or spherulite), i.e. whether the helices point the "lone" methyl group towards or away from the viewer (Fig. 5). As indicated, this possibility to determine unambiguously the helical hand and to locate and orient *each and every* helix stem in the entire crystalline entity (quadrite, spherulite) on the basis of morphological indicators *alone* has *no equivalent* in polymer science.

Finally, analysis and understanding of the lamellar branching helps explain on a clear structural basis an otherwise puzzling morphological feature of αiPP spherulites. When examined in a polarizing microscope, these spherulites have very weak, negative or positive birefringence, with the birefringence changing with crystallization temperature (cf. Figure 6). Given the standard spherulite architecture, in which radial lamellae are built up of chain-folded, tangential chains, the birefringence would be expected to be negative. The positive birefringence is simply a manifestation of the lamellar branching: the daughter lamellae have their chains

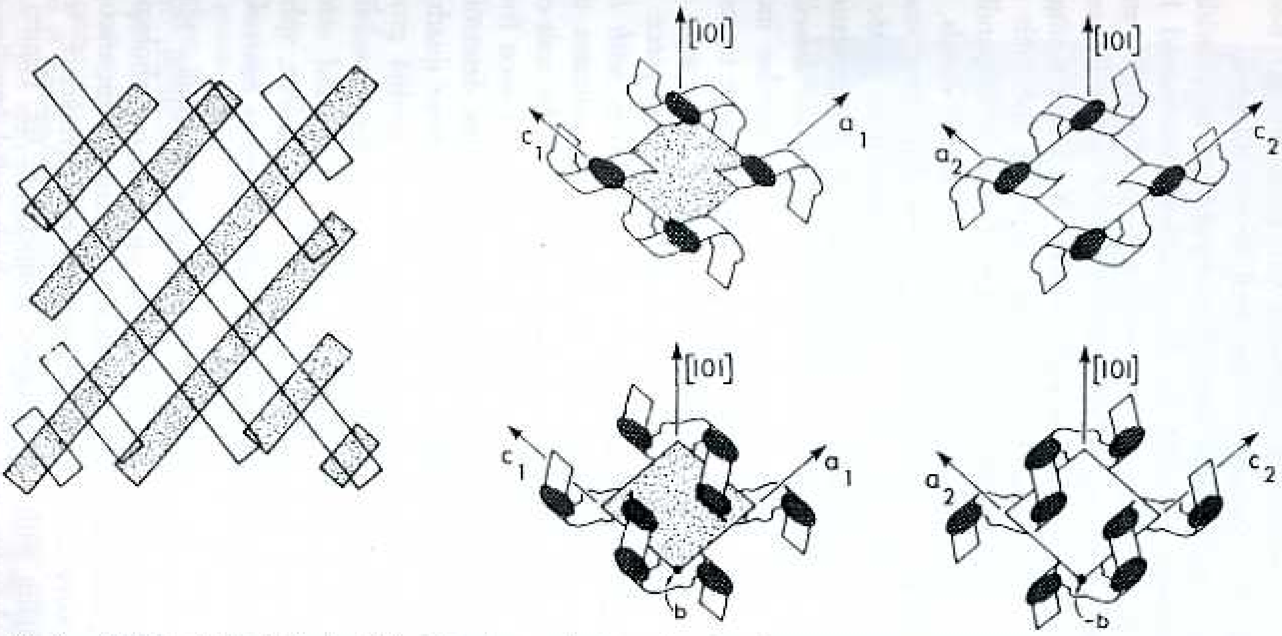


Fig. 5 – Analysis of the helix hand (spiralization) and orientation based on morphology of αiPP branched lamellae. The quadrite is schematized with its two orientations of edge-on lamellae at 80° to each other. The *c* axis in each set of lamellae is nearly at right angles to the lamellar surface. The two *c* axes position the unit-cell, with its long diagonal normal to the bisector of the acute angle, and its short diagonal parallel to it. From the unit-cell structure, it is known that the helical path is parallel to the long diagonal when one methyl group faces the observer, and to the short diagonal when two methyl groups are exposed. Combining this information with the helix axis orientation (normal to the lamellar surface) makes it possible to deduce the orientation and position of every helical stem in the quadrite, as shown on the right hand side of the figure. The heavy shading indicates the methyyl groups, the lighter shading of the unit-cell refers to that of the lamellae. Reproduced from reference 15 with permission of the publisher.

parallel to the radius of the spherulite, which means that their birefringence counteracts, or may overwhelm, the birefringence generated by the tangential chains in the primary, radial lamellae (cf. Figure 4a) [18, 19]. Also, the change from overall positive to negative birefringence of the spherulite simply reflects the decreasing frequency of lamellar branching for increasing crystallization temperatures [19-21].

To conclude this section, the crystal structure determined by Natta and Corradini for the α phase of isotactic polypropylene contains all the ingredients needed to make this phase a unique investigation material in polymer science. The fact that the structure is made of layers of isochiral chains, the alternation of antichiral layers, the near identity of *a* and *c* axes that generates a lozenge pattern of methyl groups are the structural ingredients. The latter lozenge pattern in particular explains why "mistakes" in the alternation of helical hands are possible. The lamellar branching of αiPP is a most spectacular outcome of these mistakes. This branching however comes only second to the structure of the γ phase that will be examined in a later section. First, we deal with the β phase of iPP, which happens to have its own original features.

3. THE BETA PHASE OF ISOTACTIC POLYPROPYLENE

3.1. *The experimental challenge and structural puzzle*

Immediately after its initial synthesis, isotactic polypropylene was recognized as a major industrial breakthrough, and a number of investigations were devoted to it worldwide. In 1959, Padden *et al.* in the USA reported on a new crystal modification of iPP, which they called the β phase [22]. It is easy to identify, since under the polarizing microscope, β phase spherulites are optically negative, highly birefringent spherulites, easily distinguishable from the weakly birefringent α phase ones (Fig. 6). On the basis of micro-beam X-ray diffraction on such spherulites, Padden *et al.* proposed an orthorhombic unit-cell with two chains per cell with the "standard" three-fold helix symmetry and the by then standard 6.5 Å chain axis repeat distance characteristic of the α phase [22]. Addink and Beintema [23] proposed a simple hexagonal unit-cell with one chain per cell. Turner-Jones *et al.* at ICI in England obtained samples with significantly higher proportions of this β phase, and could analyze clear *powder* patterns [24, 25]. They established that the cell must be larger, and contain either three, nine, twelve or sixteen chains. Their data were insufficient to rule out any of these possibilities, but consi-

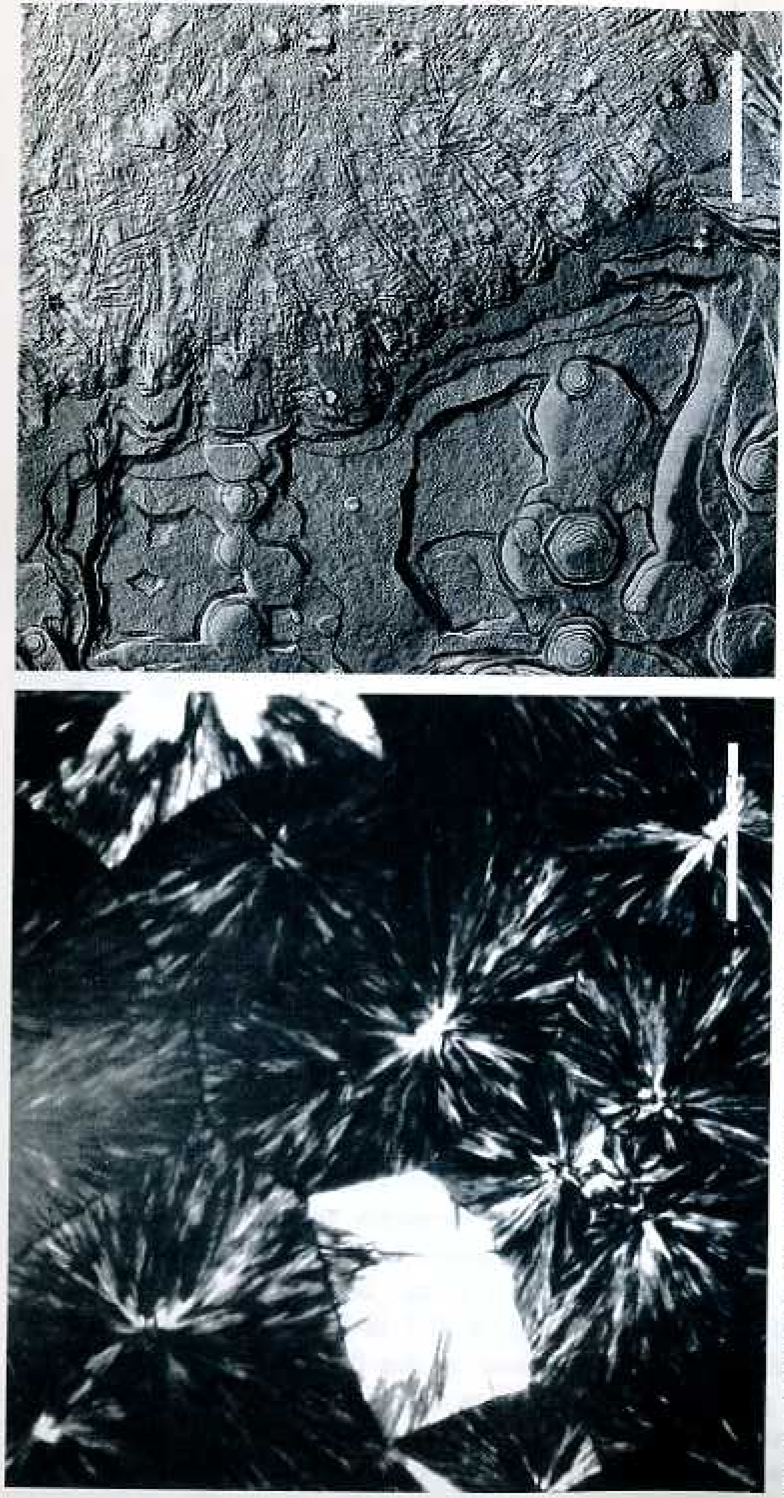


Fig. 6 – On the left side, optical micrograph of isotactic polypropylene examined in a polarizing microscope. The field shows several spherulites, which are the standard pattern of growth of crystalline polymers. αiPP spherulites are very weakly birefringent, as a result of the lamellar branching and existence of two chain orientations nearly at right angles (cf. Figure 4a and Figure 5), βiPP spherulites are highly birefringent. They are made only of radial lamellae (as in all polymer spherulites), in which all chains are tangential to the spherulite surface. Scale bar: 15 µm. The right side figure shows a replica (electron microscopy) of a similar, etched film at the frontier between an alpha (right) and a beta spherulite (left). Note the hexagonal outline of the screw dislocations in the beta spherulite, and the lamellar branching in the alpha spherulite. Scale bar: 1 µm.

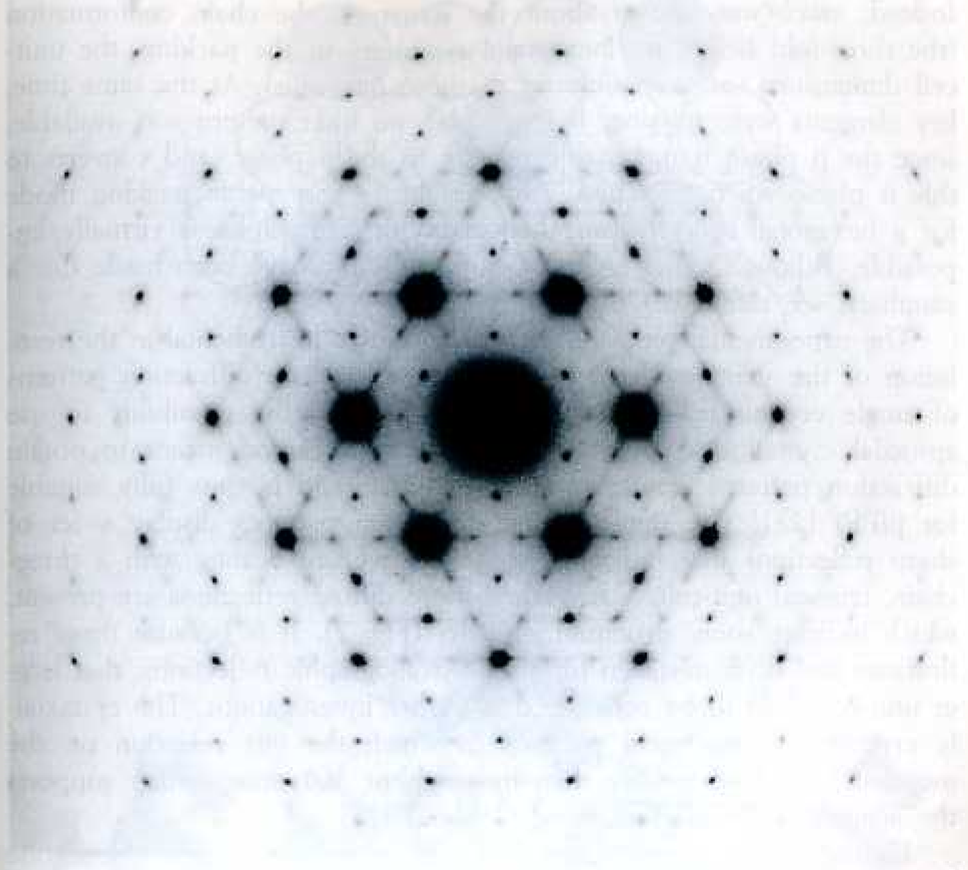


Fig. 7 – Electron diffraction pattern of a single crystal of βiPP. The electron beam is parallel to the chains, and the pattern shows only *hk*0 reflections. The hexagonal symmetry of the packing of the chains is evident. Note the presence of sharp spots corresponding to the true unit-cell, and of diffuse reflections and streaks that indicate substantial structural disorder in the packing of chains.

dered the twelve chains unit-cell as accounting best for the then available data. When a relatively poor electron diffraction pattern of βiPP became available, they opted for a *nine* chains unit-cell [25]. In addition, they had determined that the packing of the chains was a relatively complex one. In particular, they noted that the reflection labeled 003 (which, on a fiber pattern, would be meridional) was weak, which indicated that the chains in the unit-cell were at different levels along the chain axis. Were these chains at the same level (as in a one chain cell), this reflection would be strong.

Attempting to decipher the structural puzzle of the β phase of iPP has been a frustrating experience for many years – actually 35 years!

Indeed, *much* was known about the structure: the chain conformation (the three-fold helix), the hexagonal symmetry of the packing, the unit-cell dimensions (or a possible set of those unit-cells). At the same time, key elements were missing. In particular, no fiber pattern was available, since the β phase is metastable relative to the α phase, and converts to this α phase when stretched. Also, establishing a viable packing mode for a hexagonal array of *nine* helices on first principles is virtually impossible, although many attempts along this line have been made (for a summary, see reference 26).

The experimental pieces of information most instrumental in the resolution of the structure have been improved electron diffraction patterns of single crystals of the β phase [26, 27], and the possibility to use epitaxial crystallization, that is a mild, *non-mechanical* means to obtain diffraction patterns similar to fiber patterns (and is thus fully suitable for βiPP) [28]. The single crystal diffraction patterns display a set of sharp reflections that indicate clearly that we are dealing with a three-chain, trigonal unit-cell. Many other, more diffuse reflections are present, which indicate some structural disorder (Fig. 7). It is because these reflections had been mistaken for true crystallographic reflections, that larger unit-cells had to be considered in earlier investigations. The epitaxially crystallized films yield patterns in which the 003 relection on the meridian is indeed weaker than its neighbor 103 ones, which supports the analysis of Turner-Jones and Cobbold [25].

Dealing with a three chains unit-cell rather than a nine chains one makes the structural puzzle easier to solve. It turns out that the structure was solved simultaneously and independently (after 35 years!) by two teams. One of them included Italian researchers (Meille and Brückner, who had solved earlier the γ phase structure) and a group in Bell labs: Lovinger and the early discoverers of the β phase, namely Padden, with an experimental contribution from Keith [27]. We were also involved, in association with Doug Dorset in Buffalo [30, 28]. The structural answers are essentially similar, with minor variations that may reflect a physical reality. It appears easier to describe the structure by referring to its main novel characteristic, namely its *frustration* [30].

3.2. *The crystal structure of βiPP*

The structure of βiPP is original, because it rests on a frustrated packing scheme that had not been considered so far in polymer crystallography. Frustration is frequently observed in material science, and in particular in anti-ferromagnetic systems [31, 33]. Frustration is generated when a

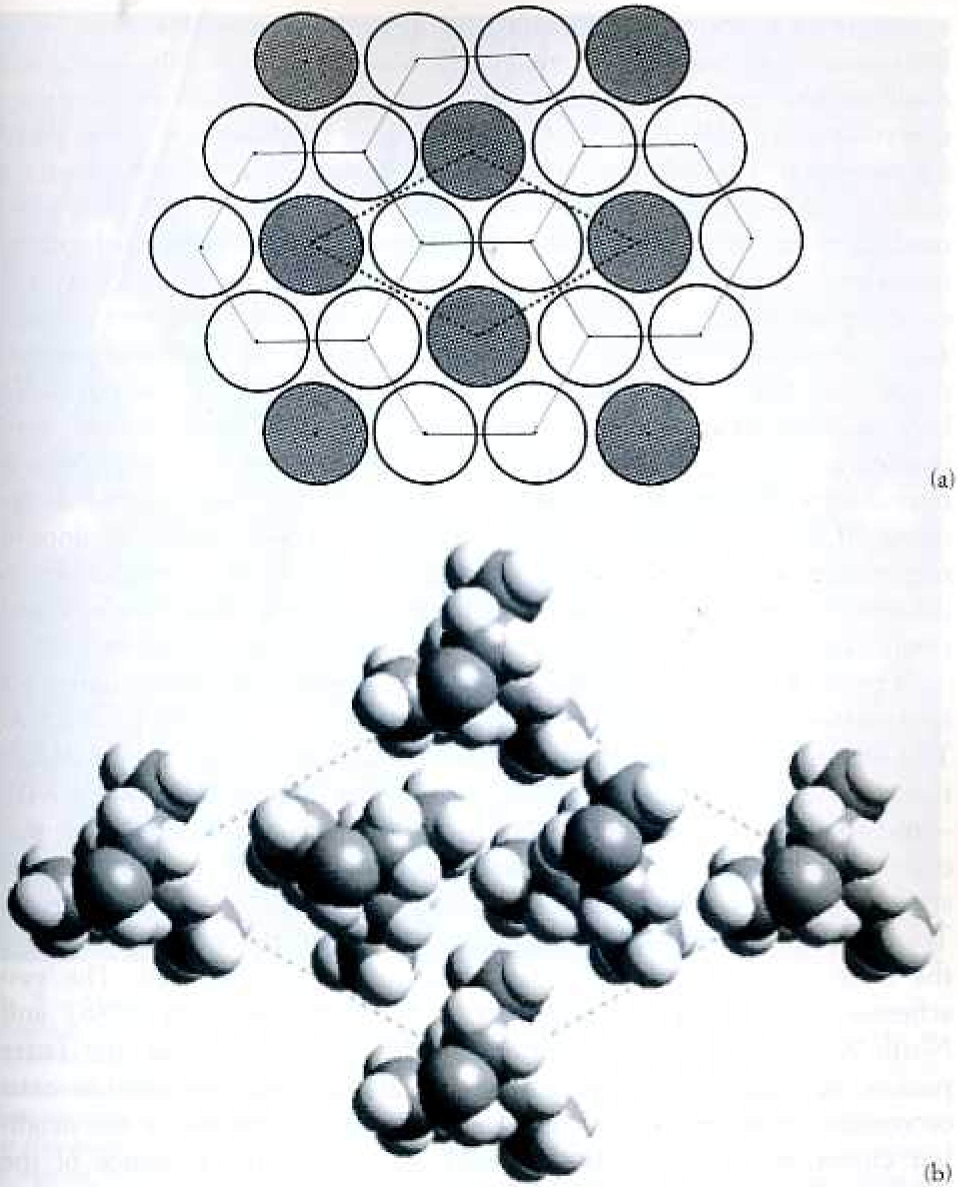


Fig. 8 – (a) Frustrated hexagonal close packing in two dimensions. Close packing of white and black balls with the additional constraint that all neighbor balls be of a different color is impossible. The model shows the smallest possible unit-cell (dashed lines) that preserves close packing, but abandons the neighbor opposite color condition for the white balls, the latter being organized in a honeycom pattern (light lines). The unit-cell is trigonal, and contains *three* balls; (b) Molecular model (in chain axis projection) of the frustrated structure of βiPP. The trigonal unit-cell contains three identical (isochiral) chains. However, the orientation on their axis differs significantly, which creates different environments for the different chains. This frustrated packing mode is preferred over a simpler one-chain unit-cell in which all the helices would have similar orientation and therefore environment [27, 28].

system must meet two incompatible conditions. It becomes evident in an hexagonal close packing of white and black balls, with the additional condition that each ball of one color be surrounded by balls of the opposite color *only*. This is impossible. Maintaining the hexagonal close packing condition, but relaxing the color condition, it is possible to create a *trigonal unit-cell that contains three balls* with one black and two white ones. This is the archetype of a frustration situation, and is of course immediately reminiscent of the structure of βiPP. In the latter case, it is equally possible to consider that a given chain establishes preferred (favorable) interactions with a neighbor chain. In view of the three-fold symmetry of the chain, these interactions can be established with three neighbors, and can be extended to two extra neighbors of these "second generation" chains, etc. This creates a *honeycomb* lattice of chains involved in favorable helix-helix interactions, but leaves aside the chain located at the center of each "cell" of the honeycomb. This chain *is frustrated* since it must adapt to a less favorable environment, which is manifested by a different azimuthal setting and/or different shift along the chain axis that create the three-chain unit-cell and establish its frustrated character.

The crystal structure of βiPP corresponds exactly to this situation. It is described as a trigonal cell with parameters $a=b=11.05$ Å, $c=6.5$ Å. The cell contains three *isochiral* helices. If the chains are right-handed, the space group is $P3_1$, and $P3_2$ if they are left-handed. The chains have – and this feature is the originality of the structure – different azimuthal orientations in the unit-cell. From investigations of different frustrated structures, two major frustrated packing schemes have been observed. They can be defined by the orientation of one of the substituants (here the methyl groups) on a compass, relative to the helix axis. The two schemes would thus be described as North-South-South (NSS) and North-West-West (NWW). Although βiPP seems closer to the latter packing scheme, it is probable that several such packing schemes exist or coexist, depending on the relative up-down orientations of the neighbor chains, etc. This variability would account for the existence of the diffuse reflections and the streaks in the diffraction pattern. Another obvious cause of structural disorder may be the coexistence of domains made of right-handed helices, and domains made of left-handed helices, a most likely structural possibility.

The frustrated packing scheme could also be brought to direct experimental check – actually to direct *visualization* by Atomic Force Microscopy [29]. The reasoning is very simple indeed. In the (110) plane of the unit-cell, the three helices have different azimuthal settings. This means that the methyl groups of one helix out of the three "stick out"

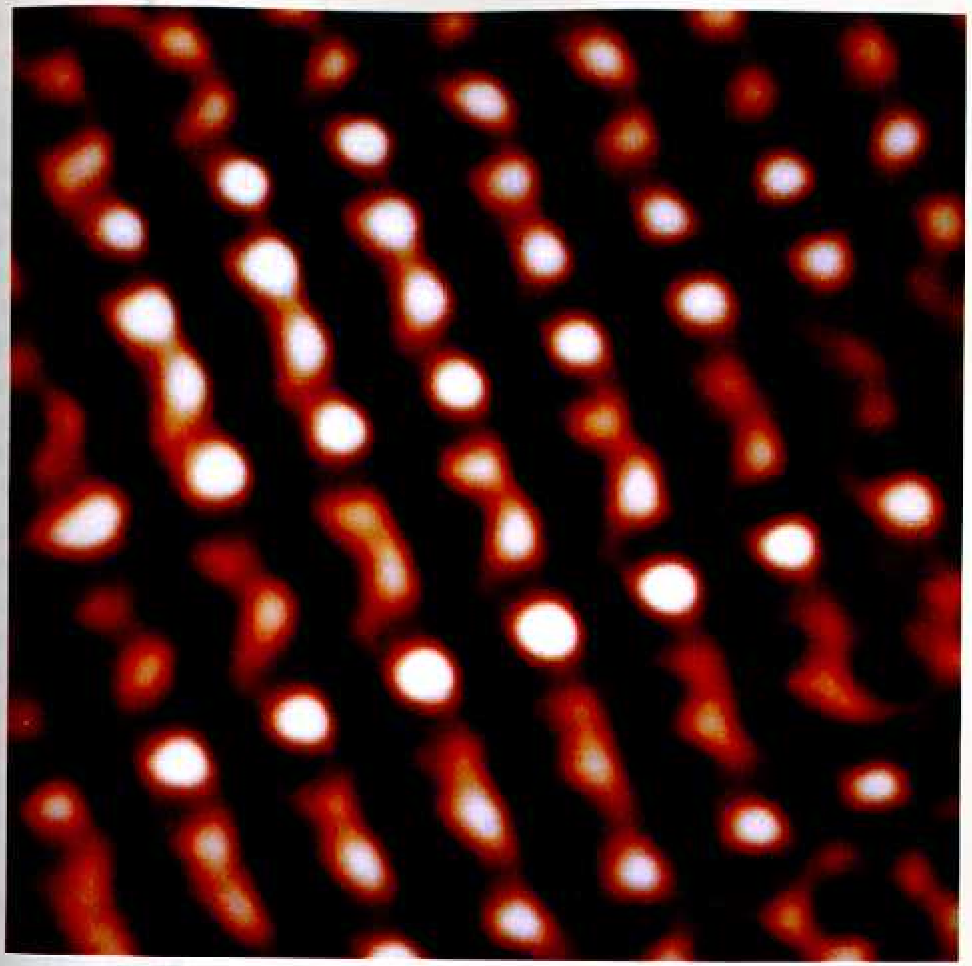


Fig. 9 – "Topographical" evidence in favor of the frustrated packing of βiPP [29]. The azimuthal setting of the three chains located in the (110) plane of the unit-cell (horizontal in Figure 8b) are different. The methyl groups of one of these chains should "stick out" more prominently from this plane than for the two other chains. This (110) plane is a contact plane in epitaxial crystallization on appropriate substrates. After dissolution of the substrate, the topography of the now exposed (110) plane can be imaged by AFM. The image shows an area of 50 nm times 50 nm. Rows of methyl groups (light) 6.5 Å apart that belong to the same helix are oriented at 2 o'clock. Prominent rows of these methyl groups are 19 Å apart, which corresponds indeed to the separation between three chains (3 times 6.35 Å), and supports the frustrated nature of the biPP crystal structure.

more prominently from the plane, in other words that the methyl groups of every *third* helix in the plane, 19.05 Å apart are more "visible" in a topographical map of the (110) plane. Epitaxial crystallization makes it possible to generate this (110) plane as a contact plane. After dissolution of the substrate in a selective solvent, this very plane becomes exposed, and is amenable to direct examination by AFM. The corresponding images (Fig. 10) display indeed rows of methyl groups 6.5 Å apart that correspond to individual chains separated by a fuzzier image: the AFM is not able to image the higher methyl groups density of the two other helices in the structure. However, and quite strikingly, the prominent rows of methyl groups, that is, the helices with different azimuthal orientation are 19 Å apart (three times the interchain distance of 6.35 Å), which is the trademark of the frustration [29].

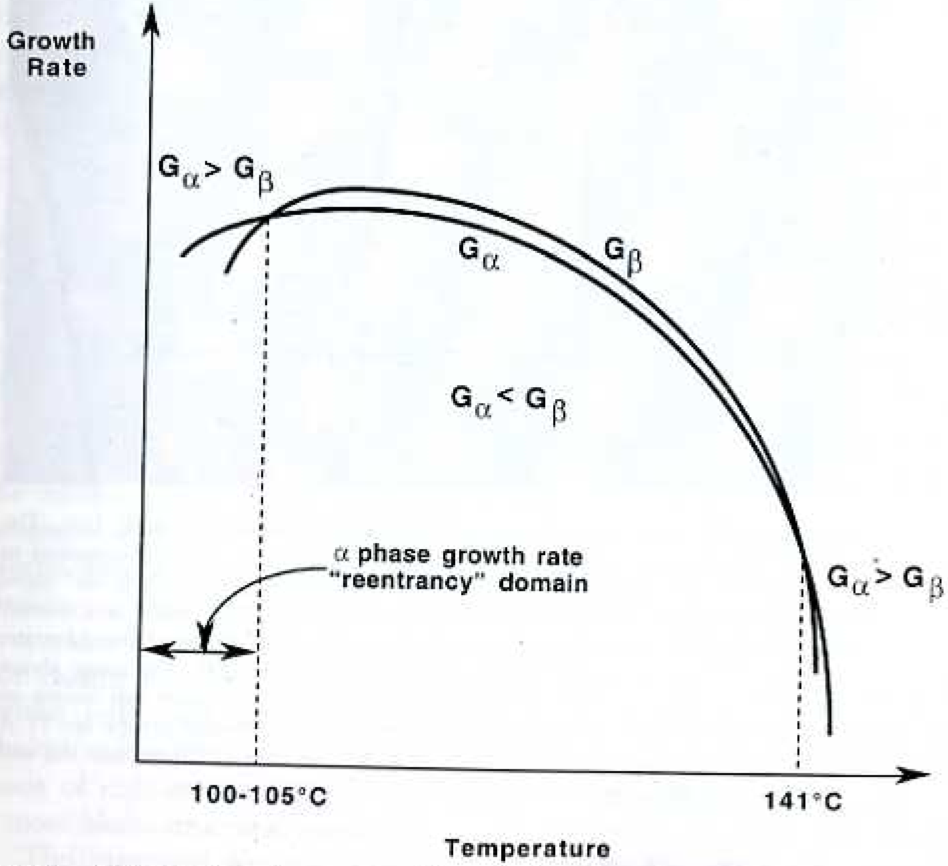


Fig. 10 – Schematic "growth rate phase diagram" for αiPP and βiPP. The growth rate of αiPP is higher (at Tc>141°C), lower (at ≈100°C<Tc<141°C) and again higher (at Tc<100°C) than that of βiPP. The latter domain corresponds to a "growth rate reentrency" of αiPP. The domain is limited at low Tc by the onset of homogeneous nucleation, at ≈80°C, which also corresponds to the production of the "mesomorphic" phase of iPP. Reproduced from reference 20 with permission of the publisher.

Recognition of the frustrated character of the βiPP crystal structure has led to a considerable work of analysis or reanalysis of crystal structures of a whole range of polymers, for which three-chain trigonal unit-cells had been determined. Only one earlier crystal structure was correctly described with helices with different azimuthal settings, but the frustration was not recognized and the packing scheme was not generalized [36]. All other structures had been determined without taking into account the notion of frustration. Reinterpretation by introducing different azimuthal settings – i.e. by introducing frustration – leads in all cases to a significant improvement of the structural models (see e.g. ref. 34 and 35). So far, frustrated crystal structures have been observed for polyolefins, a polypeptide, a derivative of cellulose, polyesters, a crystal modification of syndiotactic polystyrene, etc. It has also been observed, quite strikingly, for two biopolymers or derivatives with helical conformations that *differ* from the three-fold helix: poly-n-propyl-L-glutamate (α helix, 3.6 residues per turn) [37] and a liquid-crystalline phase of DNA, a helical structure with 10 residues per turn [38]. The structural roots at the origin of the frustrated packing of polymer helices are still somewhat unclear, and are presently under investigation. Short, round side-chains (e.g. methyl groups) seem favorable, but recent results obtained in our laboratory, in association with the group in Naples, indicate that poly(5-methylhexene-1), with a relatively long and flexible side chain, also adopts a frustrated structure [39]. It may be worth emphasizing that the elucidation of the structure of βiPP has led, in the crystallography of polymers, to the development of a new, totally unforeseen line of research.

3.3. *Correlations and interplay between αiPP and βiPP*

The formation under similar crystallization conditions and coexistence of two very different crystal phases of iPP provides an opportunity to explore the "phase diagram" of this polymer. Only a few, selected issues will be mentioned here.

βiPP is metastable relative to αiPP. The melting temperatures of βiPP and of αiPP are ≈155°C and ≈170°C, respectively. However, the growth rate of βiPP exceeds that of αiPP over a very wide portion of the crystallization range. At high T_c however (above 141°C), when the melting temperature of βiPP is approached, the growth rate of αiPP becomes again larger than that of βiPP [40]. Curiously however, the same inversion in relative growth rates is also observed at low Tc, near 100°C [41]. This situation is unique in polymer science, and may be described as a "growth rate reentrency" of the α phase at low Tcs (Fig. 11) [42].

The higher growth rate of βiPP may have a structural origin, linked with its frustrated character. Indeed, the azimuthal setting of the chains

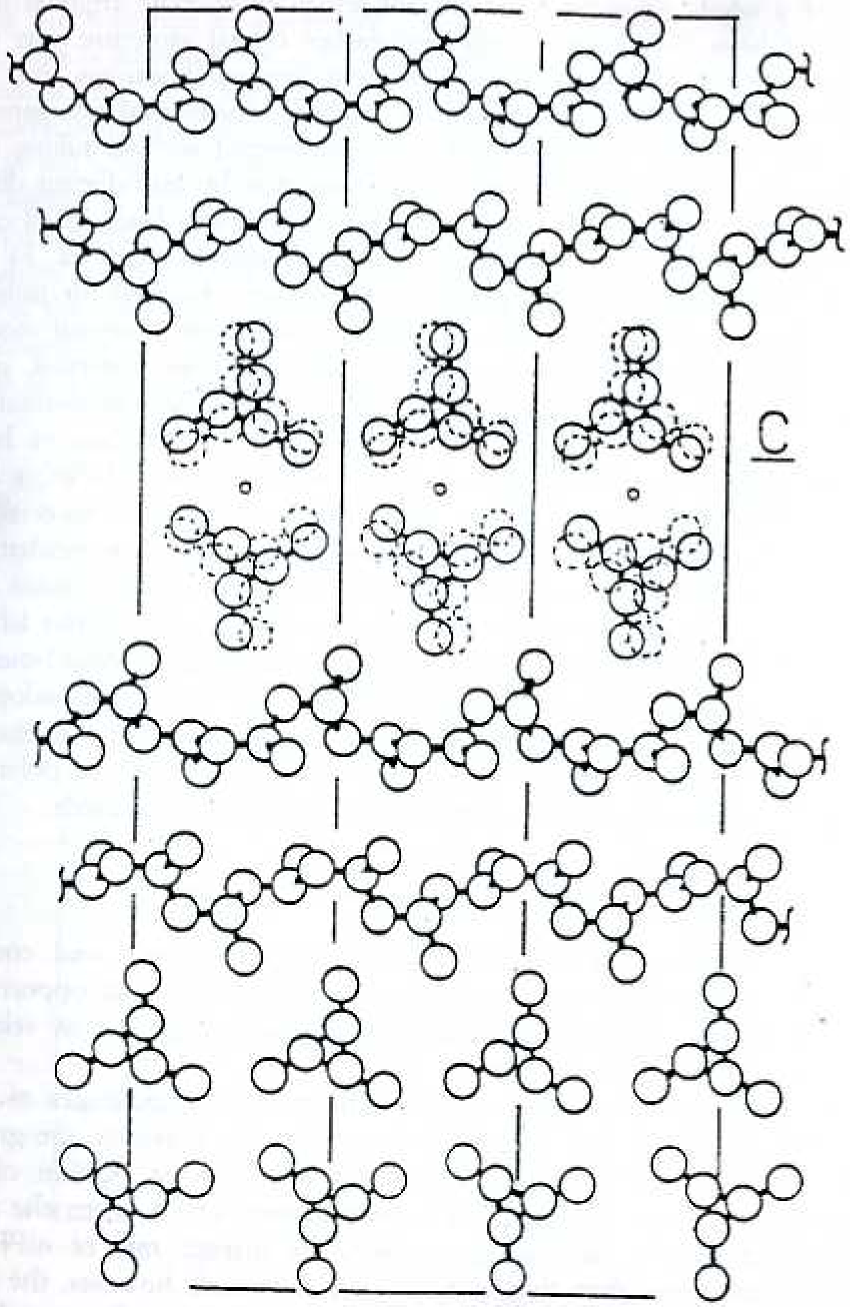


Fig. 11 – Structure of the γ phase of iPP as determined by Brückner and Meille. The structure is seen parallel to one of the two chain axes orientations that coexist in the unit-cell. These two chain orientations are parallel to the diagonals of the *ab* face of the unit-cell. The structural relationship at the transition between two chain orientations is similar in all respects to the lamellar branching of αiPP, but it is systematic in the present case. Reproduced from reference 51 with permission of the publisher.

in the unit-cell ensures that in each and every new growth layer, the layer topography is such that a notch is created, which is a very favorable nucleation site for the next layer [42].

In view of its higher growth rate, βiPP should be formed more profusely than the α crystal phase of iPP. This is not so, because "spontaneous" nucleation of the α phase is much more profuse than that of the β phase. However, nucleating agents that are "β phase specific" have been reported early on [43], and are still actively developed [44]. Similarly, nucleating agents for the α phase that help achieve faster overall crystallization rates are also the topic of much academic – and industrial! – research [45]. These are relatively easy means to generate materials with distinctly different properties (in particular, better impact resistance of the β phase) starting with the same base polymer.

As will be seen now, the situation is more complex for the third crystal modification of iPP, the γ phase, for which the molecular characteristics of iPP play a significant role.

4. THE GAMMA PHASE OF ISOTACTIC POLYPROPYLENE

4.1. *The experimental challenge and structural puzzle*

Interestingly, an account of the resolution of the γ phase structure can use the same headings as for the β phase. After all, it took only slightly less (28 years!) to solve this crystal structure. It seems therefore adequate to present first the experimental and interpretive challenges that had to be faced.

Existence of a structure different from both α and β phases was pointed out by Addink and Beintema in 1961 [46]. They obtained powder diffraction patterns very similar to that of αiPP, but with an additional reflection at 4.45 Å, that indicated a new phase. For a long time, the γ phase was obtained in sufficient proportions only under very specific conditions. The conditions relate to the polymer itself: low or very low molecular weight samples, such as fractions obtained by pyrolysis of higher M.w. materials and soluble in e.g. ether. They relate to crystallization conditions: for higher M.w. materials, crystallization under high pressure and temperature [47, 48]. More recently, and this has been part of the ultimate successful resolution of the structure, very high yields of γ phase have been obtained with high M.w. polypropylene *copolymerized with 5 to 10% ethylene or butene-1*, or even pure iPP synthesized using the newly developed homogeneous catalytic systems [49, 1].

All the available experimental evidence indicates that *the γ phase is intimately linked with the α phase.* As indicated, the diffraction patterns are very similar (except for the tale-telling reflection at 4.45 Å). Moreover, the γ phase crystallizes epitaxially on the α phase. Actually, spherulites of α phase iPP contain more or less unavoidably a small proportion of γ phase that corresponds to the crystallization, in the later stages, of the lower molecular weight tail of the polymer [1].

Diffraction evidence has been difficult to collect. It is not possible to obtain fiber patterns of the γ phase (the structural reason will become clear with the model). Single crystal electron diffraction patterns could be obtained, that led Morrow and Newman [50] to propose a triclinic unit-cell derived from the α phase monoclinic cell by a shearing along *a*. The layer structure of the α phase was maintained in the model. However, the unit-cell geometry and structure turn out to be incorrect, since the structure of γiPP has features that are definitely unprecedented in the crystallography of polymers.

4.2. *The unique crystal structure of γiPP*

In a ground-breaking paper in 1991, Brückner and Meille proposed a stunning new model for the crystal structure of γiPP [51]. The intellectual breakthrough was to consider, and accept, the possibility that chain axes are not parallel in a polymer structure. This break of a dogma is comparable in importance (even if of lesser consequence) to the proposal by Pauling and Corey, some 40 years earlier, of the α helix conformation with 3.6 residues per turn, that broke at that time accepted rules of crystallographic symmetry.

It is difficult to detail the essentially "crystallographic" reasoning that led Brückner and Meille to this revolutionary structure of γiPP [51, 52]. It is easier to describe the structure starting from the α phase structure, and the molecular mechanism of lamellar branching described earlier (*vide supra*) [15]. As indicated, the α phase structure is essentially the packing along the *b* axis of the unit-cell of *bilayers*, one layer made of right-handed helices, and one layer made of left-handed helices. Furthermore the outer faces of the bilayers are made of the lozenge pattern of methyl groups illustrated e.g. in Figure 2. The "normal" crystal structure of the α phase requires a strict alternation of the layers with different helical hands: *LRLRLRLR*, etc. Lamellar branching, and homoepitaxy with an 80° (or 100°) change in the chain orientation takes place when this alternation is not respected, as e.g. *LRLRRLRLR* [15]. *When this "accident" of the α phase growth process becomes systematic, the γ phase is generated.* The crystal structure of the γ phase thus corresponds, as for the α phase to a (bi)layered structure but with a different sequence of helical hands: *LRRLLRRLLRRLLRR* etc. For reasons of symmetry, the cell is quite large. It is orthorhombic with parameters $a=8.54$ Å, $b=9.93$ Å, $c=42.41$ Å, space group *Fddd* or, if statistical substitution of "up" and "down" (anticline) helices is absent, *F2dd* or *Fd2d* [51, 52]. It should be noted that the chain axis repeat distance (6.5 Å) of the iPP three-fold helix has "disappeared" in the unit-cell parameters, since the helices are now oriented parallel to the two *diagonals* of the rectangular *ab* face (Fig. 12) [51].

The structure is revolutionary, since for the first time, the chain axes in a polymer structure are not parallel. At the same time it is logical, since it accounts for many features that appeared puzzling. It explains the structural similarity between the α and γ phases suspected early on [24] and the fact that the γ phase crystallizes epitaxially on the α phase [13]. It also explains some morphological features that appeared puzzling. In particular, the lamellae of γiPP have their fold surfaces parallel to one bisector of the angle between the chains axes: this is logical since the two sets of chains play a similar role (Fig. 13) [52]. The structure is also logical on a local level, since it rests on very plausible and well established interdigitation of methyl groups. Indeed, packing energy calculations confirm that the two structures do have very similar packing energies [53]. It turns out that the inter-layer distance in γiPP is even a little shorter than for αiPP, which would explain that γiPP is the most stable phase when crystallization is carried out under high pressure [48, 54].

The non-parallelism of the chains could be submitted to an experimental test [55]. Single crystals of the γ phase were mounted on a electron microscope specimen tilting stage. They were tilted by + and −40°, in order to bring the two diagonals of the *ab* face (the two chain axes) parallel to the electron beam. The resulting diffraction patterns are strictly identical, thus supporting the major novelty of the structure, the non-parallelism of the chain axes [5]. Also, these patterns confirm the indexing of the reflection specific to γiPP, at 4.45 Å, as 118, in full agreement with the model of Brückner and Meille [51].

4.3. *The crystal structure of γiPP: some open questions*

The crystal structure of γiPP was proposed already over ten years ago. It has gained more and more interest in the polymer community. As indicated, many of the most recent iPPs and copolymers produced

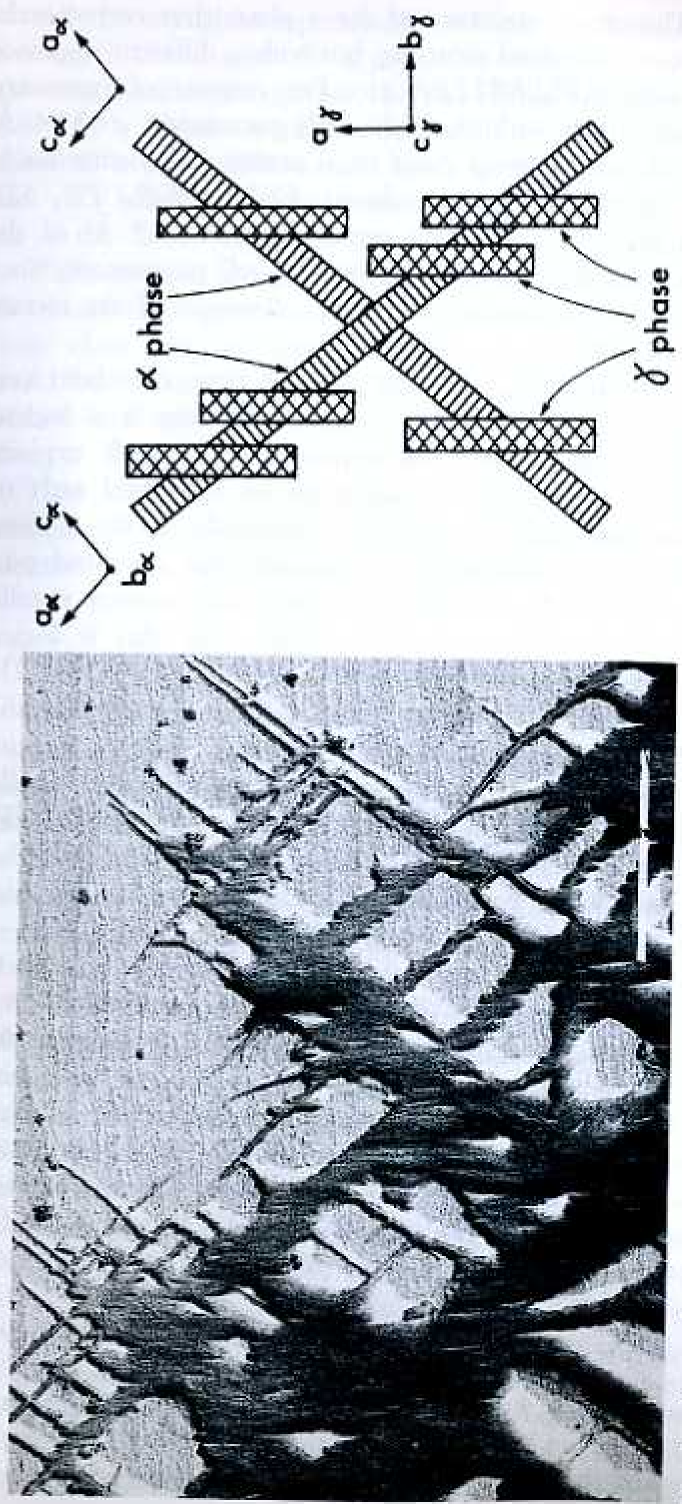


Fig. 12 – Structural relationship between αiPP and γiPP. On the left, electron micrograph of a thin film of iPP that was grown epitaxially on a polyamide substrate. αiPP quadrites developed (two sets of oblique lamellae). Later growth of γiPP took place on these αiPP lamellae. (Scale bar: 1 μm). The two chain axis orientations within *each* γiPP lamella are parallel to those existing in the two (different) sets of αiPP lamellae. Since the two chain orientations within the γiPP lamellae play similar roles, the fold surface of these lamellae must be parallel to a bisector of these two orientations. Indeed, the γiPP overgrowth is vertical, and parallel to such a bisector.

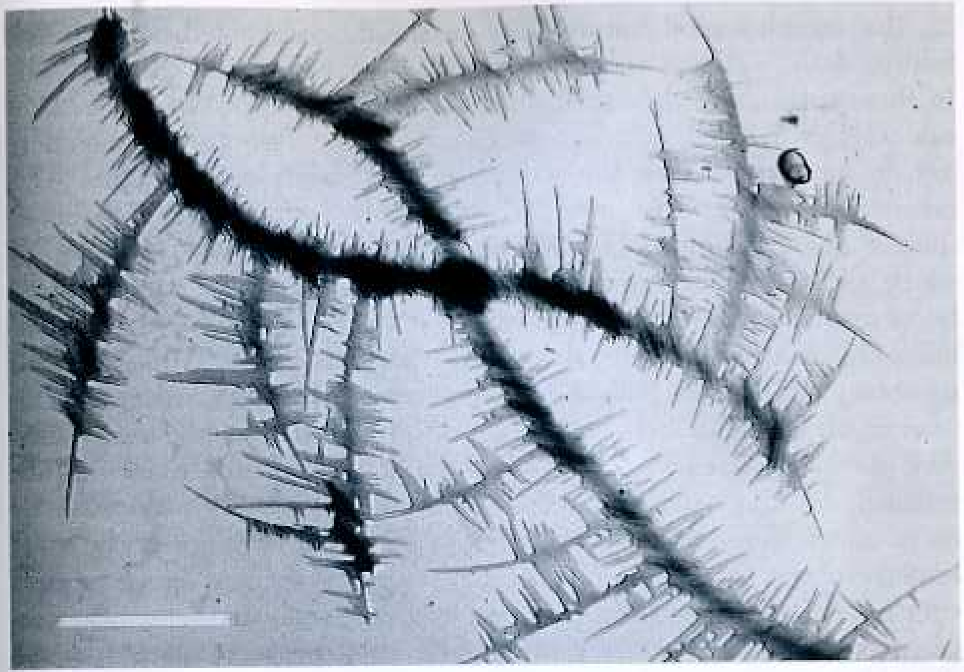


Fig. 13 – Curved crystals of αiPP overgrown with γiPP. The crystallization took place in thin film, on a mica sheet, and was not constrained by epitaxy as in Figure 12. The curvature of edge-on αiPP lamellae is associated with the γiPP overgrowth, and leads to spectacular overall curvatures. The origin of this curvature is still unknown. Scale bar: 3 μm. Reproduced from reference 54 with permission of the publisher.

with metallocene catalysts can be obtained, by proper adjustment of the crystallization conditions, in very high γiPP yields [56]. Also, with its two chain orientations nearly at right angles, γiPP is intrinsically "less anisotropic" than αiPP, which explains (at least in part) that these copolymers are intrinsically more transparent than conventional iPPs.

At the same time, the very original features of the γiPP structure raises a number of fundamental questions that have not yet been fully answered. From a structural standpoint, the most troublesome one is the problem of the growth of crystals with non-parallel chains that furthermore are linked by chain folds. It is intuitively understandable that completion of these folds is more difficult than for parallel stems. Indeed, the fact that γiPP was "traditionally" obtained from very low M.w. material that presumably forms extended stems in the lamellae (with no folds) supports this view [54]. It may be argued that the presence of ethylene units in the chains of the copolymers confers some flexibility to the chain that may be beneficial when folds are made.

Two morphological features may be shortly commented on. The first feature deals with the spherulite structure of presumably "pure" γiPP. In these spherulites, the radial direction would be expected to be the *c* axis of the unit-cell, which corresponds to the fast growth direction. Yet, in most spherulites, this axis is at right angles to the radius. This orientation suggests that even in presumably "pure" γiPP spherulites, some α phase is formed first and sets a "spherulitic frame" on (and in) which γiPP crystallizes epitaxially. In that case, the c_γ axis would indeed be tangential (as a result of the epitaxy) rather than radial, as is experimentally observed. In turn, this analysis suggests that it is very difficult to obtain γiPP devoid of αiPP "contaminant" (Note in passing the inversion of the roles between αiPP and γiPP, since in the early days, γiPP was considered as the contaminant!). The second feature is best revealed during crystallization in thin films. It deals with a systematic curvature of edge-on lamellae of αiPP when they are overgrown by γiPP, leading to spectacular morphologies (Fig. 14) [57]. The origin of this curvature is not known at present. It may be speculated, and it is suggested here, that this curvature may result from stresses induced by the slight dimensional mismatch between the 6.50 Å chain axis repeat distance of the chain in epitaxial register, and the 6.55 Å *a* axis of the parent α phase lamella to which it is parallel. The chain axis repeat distance is less prone to dimensional adjustment than the inter-chain dimensions, since the latter are determined by van der Waals forces. The resulting strain of the αiPP lattice would result in the observed curvature. However, it remains to investigate and understand why the curvature is systematically oriented towards the bisector of the acute angle of the quadrite.

Two final remarks about the duality αiPP-γiPP may be in order. The first remark deals with the fact that the two crystal phases have similar "building blocks" (the layers, or bilayers parallel to *ac* in the α phase). It is therefore conceivable that the sequence of these layers is not as "rigid" as usually assumed, in other words, that *mixed crystals of α and γ phase* can exist. Evidence in favor of such mixed crystals has been presented and analyzed recently [58]. The second remark deals with the "crystal phase ubiquity" of iPP. Recent investigations on iPPs produced by metallocene catalysts [56] have demonstrated that the same sample can crystallize, depending on crystallization conditions, with high γ or α phase yields. It is not therefore the chemical constitution of the chain that determines *solely* the fact that α or γiPP is produced, but rather the crystallization (processing) conditions. Since in addition the β phase can be produced when using appropriate nucleating agents under the

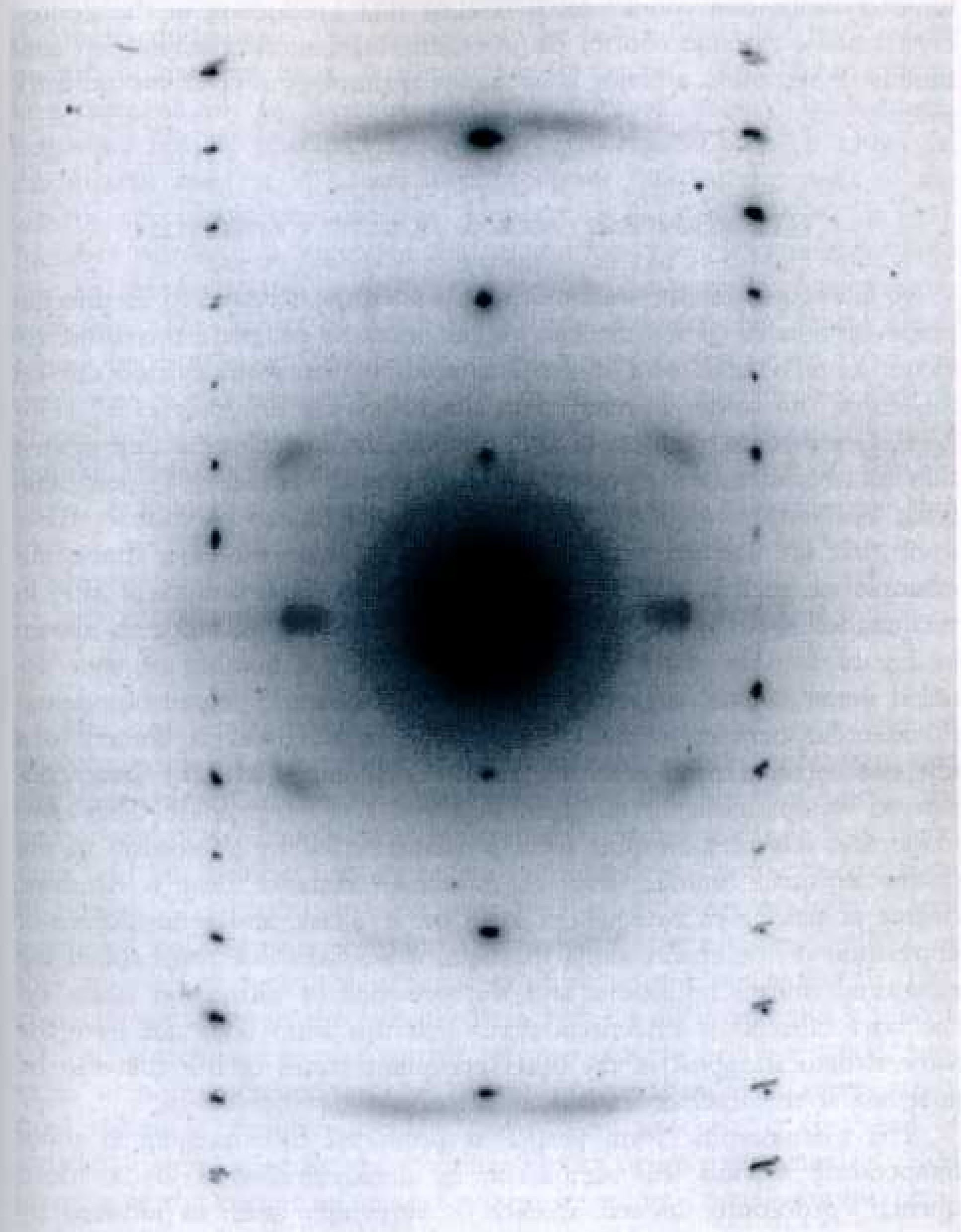


Fig. 14 – Electron diffraction pattern of a thin film of iPP produced by vaporization of an iPP sample under vacuum and deposition on a cold, orienting substrate (sharp spots). The deep quench associated with this procedure yields essentially a mesomorphic phase of iPP (more diffuse arcs). Note the three-fold helix symmetry indicated by the organization of layer lines, and the overall diffuse reflections on all layer lines. The center, dark spot corresponds to the primary beam.

same crystallization conditions, it is clear that production of the desired crystal phase through control of processing/nucleation/crystallization conditions is becoming a major issue in the technology of isotactic polypropylene.

5. THE MESOMORPHIC FORM OF ISOTACTIC POLYPROPYLENE

A few words on the mesomorphic (sometimes referred to as smectic) phase of isotactic polypropylene are in order to complete this short review. For a detailed and in-depth analysis of the work carried out on this form, the reader is referred to the review by Brückner *et al.* [1].

A "less ordered " form of iPP, obtained by quenching a thin molten film to ice water was reported by Slichter and Mandell [59], and analyzed by Natta *et al.* [60]. This form is characterized by diffuse reflections that are located on the equator as well as the layer lines. An example of such a pattern, obtained here by vaporization of iPP in vacuum followed by deposition on a cold, orienting substrate, is shown in Figure 15. The early analyses, confirmed by a number of later detailed investigations, suggest that this form has some degree of orientational order between chains, but that the lateral order is limited to a few nanometers. In an extensive study, Corradini *et al.* [26], have considered various models reminiscent of the α and the β phase. They conclude that this mesomorphic form is characterized by parallelism of the chains in small bundles, average interchain distance near 6 Å, some degree of pairing of two helices as in the α phase, and some degree of correlation of the chains along the helix axis. These features explain the equatorial diffuse reflections and the presence of diffraction peaks on the layer lines. It is evident however that this form does not have the same structural appeal as the other crystalline forms of iPP that can be analyzed at the level of individual stems.

The mesomorphic form of iPP is produced by stretching at room temperature a solid iPP sample or, as already indicated, by a "deep quench" procedure. Indeed, quench at very high rates, as induced by Piccarolo [61], make it possible to obtain (relatively thin) films that are almost purely in the mesomorphic form. These films are characterized by the fact that they are non-birefringent under the polarizing microscope, which is consistent with the small size of the "crystallites" and their random orientation. This absence of texture is typical of a so-called *homogeneous nucleation* process, which is known to take place, in iPP, at 80°C [62]. At this temperature, some 100°C below the melting

temperature, nuclei are profusely generated by random fluctuations in the undercooled melt. This process can be better illustrated by a *milder* quench of the thin films. It shows that the growth of α phase spherulites (recognizable by their lamellar branching) is arrested by homogeneous nucleation when the temperature reaches 80°C [41]. However, the growth rates at 80°C are already slower than at the peak of the growth rate versus crystallization temperature (located near 90°C) [63]. In other words, it is suggested that *production of the mesomorphic form can be strictly equated with and ascribed to the onset of homogeneous nucleation*. The impact of (fast) growth rates explains that helical hands cannot be "sorted out" to induce a well-defined crystal phase. If so, the small size of the crystallites and the fact that they contain antichiral (α phase-like) and chiral (β phase-like) patches of helices appears quite natural. However, it must be stressed again that this form can be obtained only under relatively fast cooling conditions, which imply thin films.

CONCLUSION

The structural analysis of isotactic polypropylene and its different crystal modifications has been an extraordinary scientific adventure and challenge. Indeed, the three crystal phases combine very inventively the two possible helix chiralities and even helix axis orientations. They blend right and left helix chiralities (α and γ phases) or they segregate them (β phase). They maintain helix axes parallel, as expected from a well mannered polymer (but introduce a novelty, the frustration of βiPP), or they manage to orient these axes at a significant angle (80 or 100° characteristic of both the lamellar branching in αiPP, and the γ phase).

This structural complexity, that took so long to be understood, provides an unprecedented, and so far still unique, handle to access structural details at a sub-molecular level – very precisely at the level of individual stems that are the building blocks of polymer lamellae. AFM imaging of the pattern of methyl groups in the *ac* crystallographic plane of the α phase, and analysis *from the morphology* (α phase and α-γ lamellar branching) of the helical hand of individual stems illustrate these insights.

On a more fundamental level, this understanding provides also insights that help analyze polymer crystallization processes. Recent proposals have suggested that the crystallization process is "assisted" by a spinodal decomposition that could take place in the melt prior to crystallization [64, 65], or that the melt pre-orders in small "paracrystals" prior to deposition and reorganization [66]. The conformational freedom and variety of different crystal structures of iPP provides however a critical test to evaluate the validity of these assumed processes. Indeed, from a conformational energy standpoint, the "chiral but racemic" iPP can form left-handed or right-handed helices with an equal probability. The *very* drastic selection of helical hands implied by the racemic (α, γ), or chiral (β) structures of iPP suggests that the growth process is highly controlled by the topography of the *growth front*. In other words, crystal growth in polymers is best described by a classical "nucleation and growth" process rather than by these recent more elaborate crystallization schemes. In short, the "pre-organized" melt assumed by the latter theories cannot foresee the final crystal structure of isotactic polypropylene (racemic or chiral) that will be adopted [67].

As a final remark, it may be worth insisting on the fact that the "basic" crystal structures of iPP are by now reasonably well understood. This is definitely not the end of the story. As detailed in several other contributions to this book, our colleagues chemists are now able to play with the tacticity within individual chains or use an "oscillating stereocontrol" to produce thermoplastic elastomeric polypropylenes made of alternating sequences of isotactic and atactic PP [68]. More generally, new materials or new variants of isotactic and/or stereotactic polypropylenes become available. They need to be investigated, if only to establish the complex relationships between chemical structure, processing conditions and crystal structure and morphology. The emphasis in structural investigations will unavoidably shift from the crystal structure (at the unit-cell level) considered in this presentation to the analysis of the morphology, in its broadest understanding. Indeed, the properties of these materials are most probably mainly dependent on the morphology (size, distribution, and connectivity of the crystallites). It is to be feared that the problems ahead of us are as challenging as those encountered during the resolution of the crystal structures described in this account.

ACKNOWLEDGEMENTS

The author is indebted to many colleagues for fruitful discussions that helped shape the present paper. Hervé Marand deserves special thanks for suggesting the title of this presentation. Assistance of A. Thierry, C. Straupé and A. Buono has been most useful in preparing this contribution.

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Giuseppe Allegra[a]

CHAIN MOBILITY IN NON-STEREOREGULAR AND STEREOREGULAR POLYMERS

Polymer dynamics

Any deformation of a polymer chain propagates via chain rotations. The rotational propagation is controlled by *internal viscosity*, i.e., the dissipation effect produced by the energy barriers hindering the rotations (Figs. 1-2). In particular, Figure 2 (lower part) shows that deformation waves propagate along the chain. Each wave consists of compressed and extended chain portions, where *gauche* and *trans* rotations respectively prevail.

In the Langevin equation of motion, each chain atom experiences (at least) three forces, namely:

1) the elastic force

$$K[\mathbf{R}(k+1,\ t)-2\mathbf{R}(k,\ t)+\mathbf{R}(k-1,\ t)] \cong K\frac{\partial^2\mathbf{R}(k,\ t)}{\partial k^2}; \qquad \left(K=\frac{3k_BT}{C_\infty l^2}\right)$$

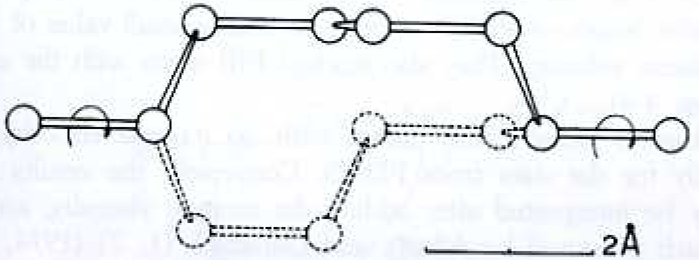

Fig. 1.

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where C_∞ is the polymer characteristic ratio, l is the C-C bond lenght, k_B is Boltzmann's constant, T is the temperature and $\mathbf{R}(k, t)$ is the position vector of the k/th chain atom ($k=1, 2, \ldots N$) at time t (see Fig. 3);

2) the friction force

$$-\zeta\frac{\partial\mathbf{R}(k, t)}{\partial t}$$

3) the Brownian force $\mathbf{X}(k, t)$, purely stochastic.

The polymer *internal viscosity* may be identified with an additional force (4^{th} force) proportional to [1, 2]

$$\pm\frac{4}{3}K\tau_0\frac{\partial^2\mathbf{R}(k, t)}{\partial k\,\partial t}; \qquad \left(K=\frac{3k_BT}{C_\infty l^2}\right)$$

The sign ambiguity is related with the direction of propagation of the deformation. It has no effect on the final results.

The rotational characteristic time τ_0 is

$$\tau_0=A\cdot\exp\left(-\frac{\Delta E}{k_BT}\right)$$

(ΔE is the average value of the energy barriers, see Fig. 2).

RECENT EXPERIMENTAL INVESTIGATIONS

Recently D. Richter, A. Arbe and coworkers [3, 4] carried out careful neutron spin-echo investigations on the dynamics of monodisperse chains with a similar length of PDMS (a polymer with a small value of τ_0) and of PIB in toluene solution. They also studied PIB melts with the same technique (Figs. 4-6).

The classical Rouse-Zimm theory, with no internal viscosity, accounts satisfactorily for the data from PDMS. Conversely, the results from PIB could only be interpreted after adding the internal viscosity, according to the approach proposed by Allegra and Ganazzoli [1, 2] (1974, 1981).

In the case of PIB in a toluene dilute solution, the numerical results for τ_0 were ($30<T<100$°C, see Figure 7)

$$\tau_0=1.27\times10^{-12}\exp\left[\frac{3\cdot1}{RT}\right]\ [\mathrm{s}]; \qquad (RT\ \text{in kcal/mol})$$

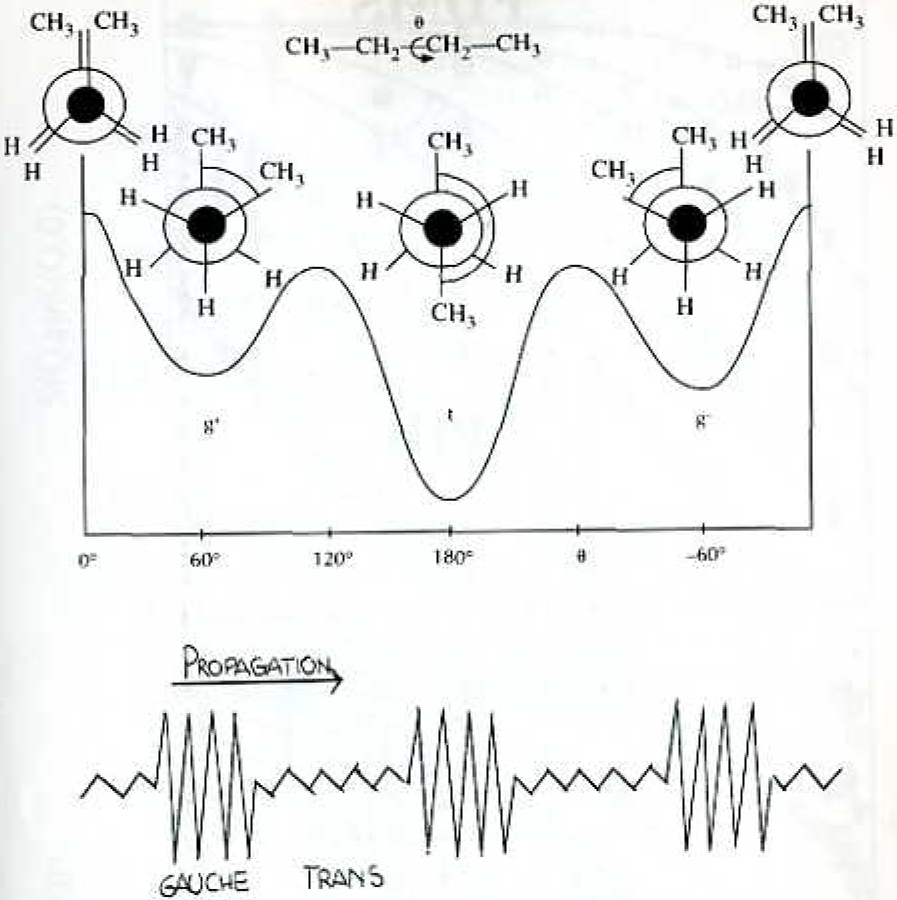

Fig. 2.

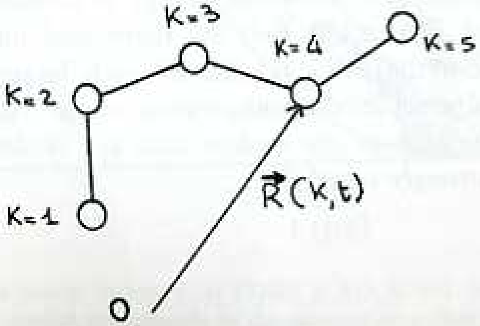

Fig. 3.

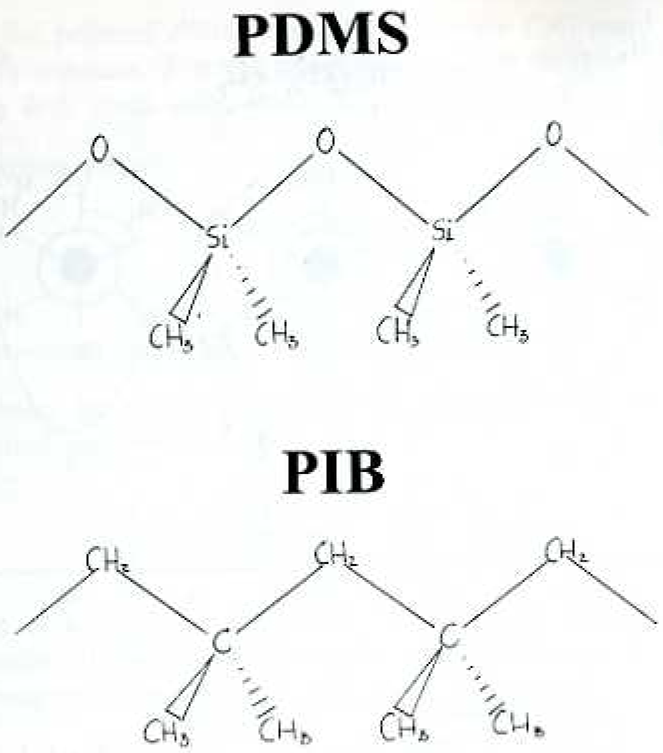

Fig. 4.

The result for ΔE (=3.1 kcal/mol) is in a reasonable agreement with the current value of the rotational barrier for alkyl polymers. The pre-factor is consistent with the rotational frequency around C-C bonds, in one of the limiting cases considered by Kramers, 1940 [5] (i.e., *the natural oscillation frequency*, whereby the medium viscosity produces a negligible friction, but is sufficient to provide the Brownian energy at constant temperature).

In the case of *PIB in the melt* the theoretical interpretation is qualitatively similar but the value od ΔE is much larger (~10 kcal/mol instead of ~3 kcal/mol, in the temperature range 100-200°C). It is reasonable to assume that *in the molten state the skeletal rotations of adjacent chains are strongly coupled.*

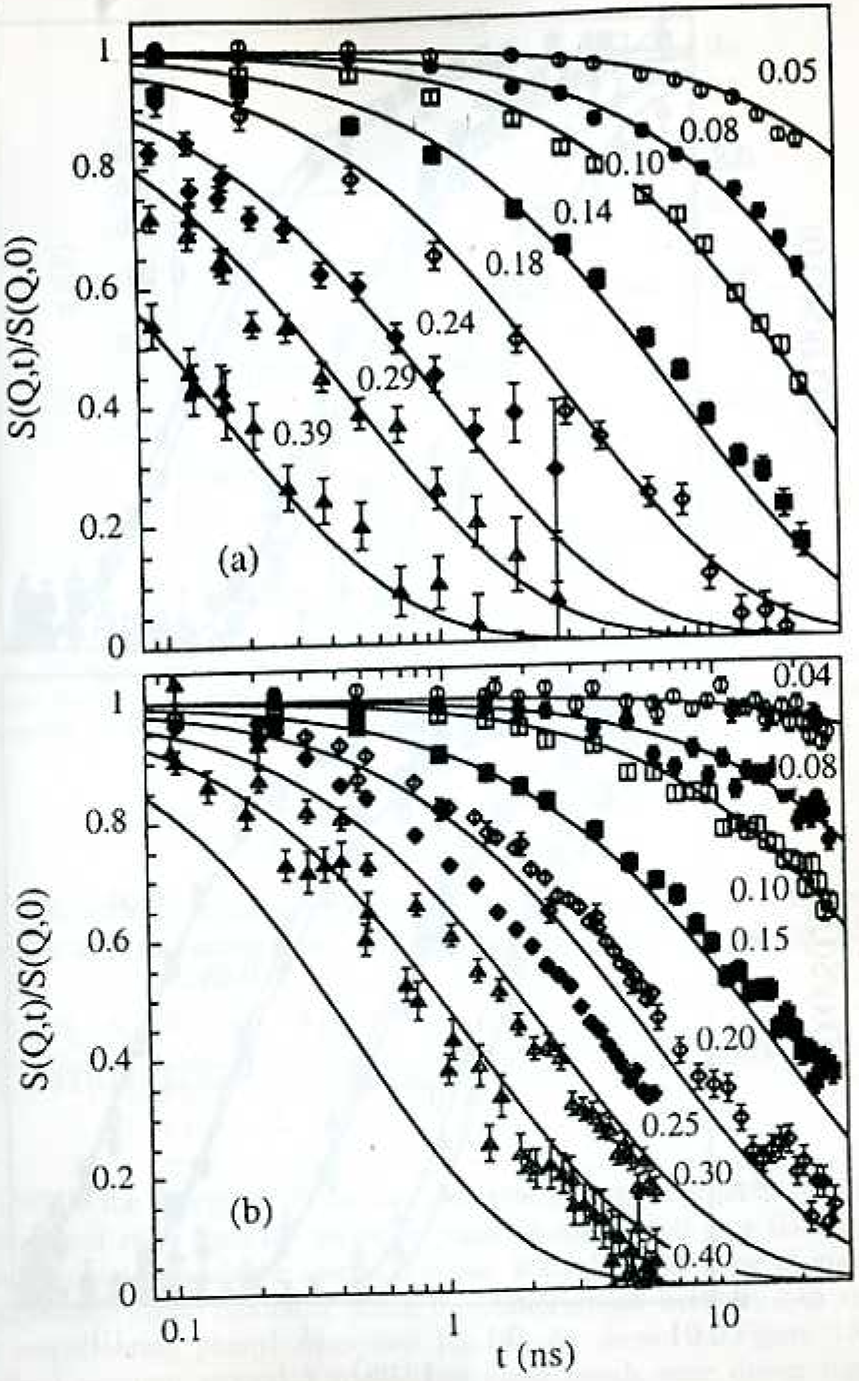

Fig. 5 – Chain dynamics structe factor of (a) PDMS at 373 K and (b) PIB at 417 K measured in the melt. Each symbol corresponds to the same or very close values of Q for both polymers, which are indicated in the figures. Solid lines show the Rouse prediction.

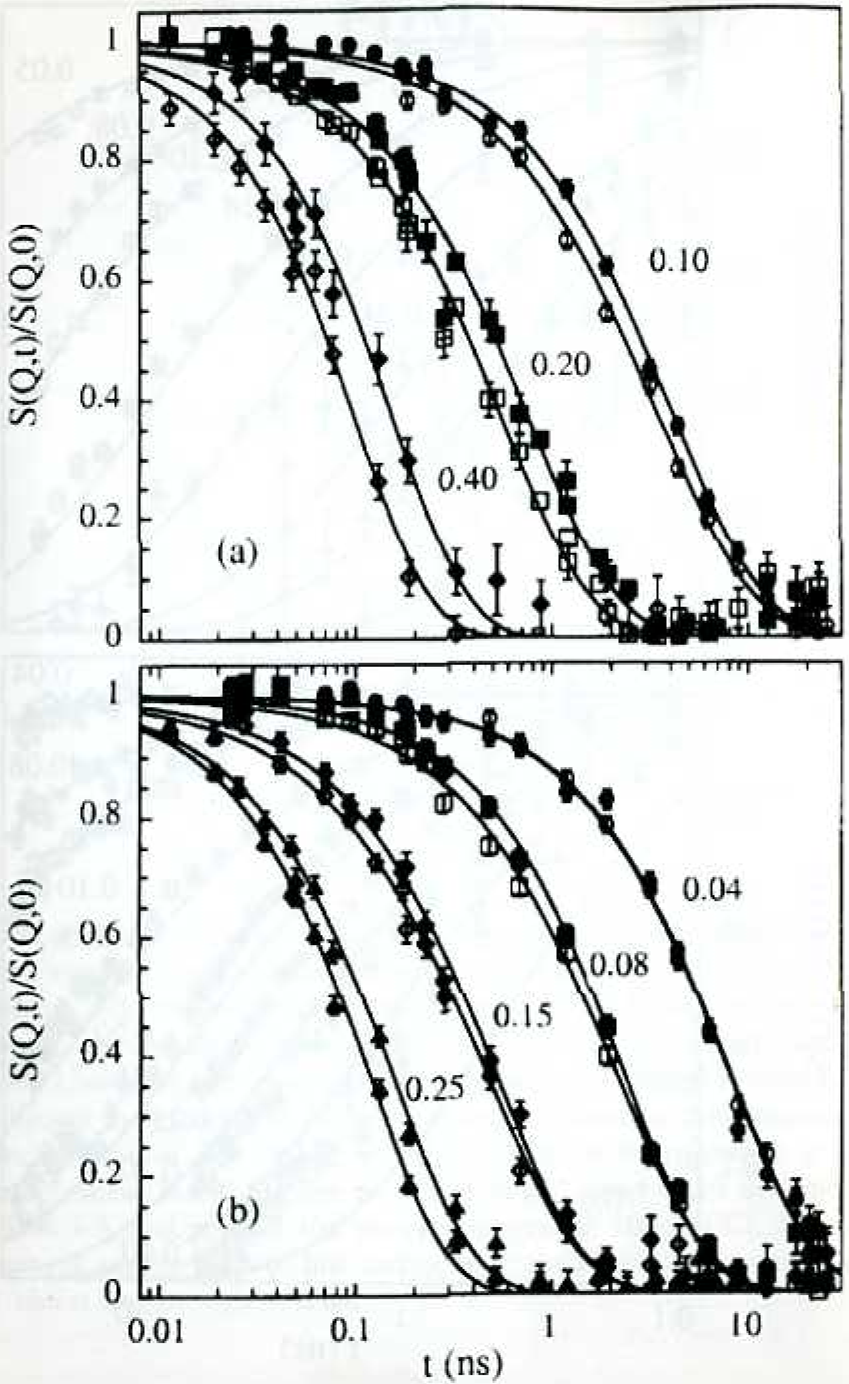

Fig. 6 – Chain dynamic structure factor of PDMS (empty symbols) and PIB (full symbols) in toluene solution at 300 K (a) and 378 K (b). The corresponding Q values are indicated. Lines through the points are guides to eye.

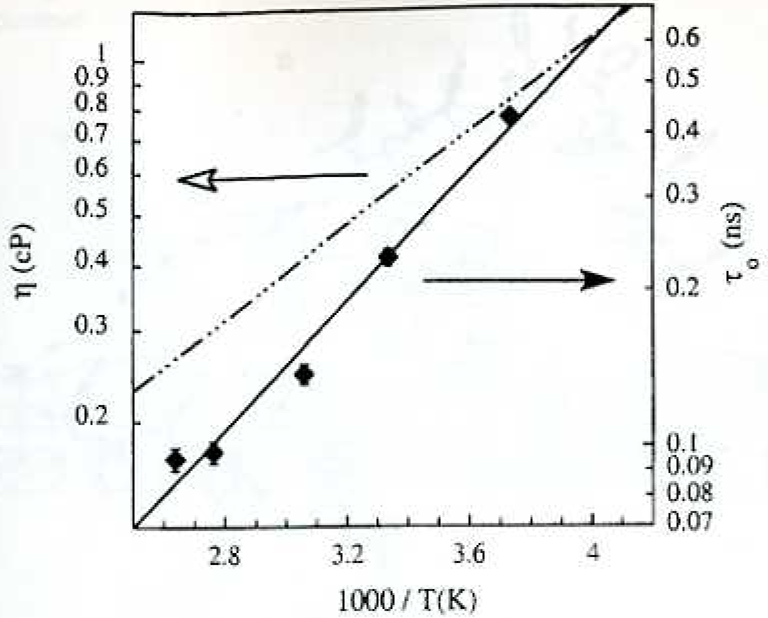

Fig. 7 – T dependence of the solvent viscosity (dashed line) and the characteristic time τ_0 deduced for the conformational transition in PIB (◆). The solid line through the points corresponds to the fit to an Arrhenius law.

STERIC HINDRANCE TO ROTATIONAL PROPAGATION: ISOTACTIC POLYSTYRENE [6]

With isotactic polystyrene, left- and right-handed chain strands follow one another with alternating types of conformational inversions (see Fig. 8).

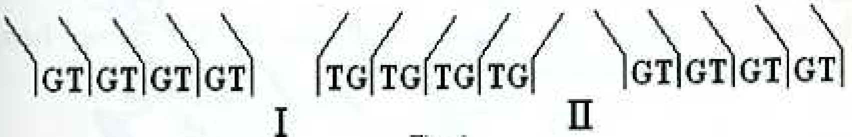

Fig. 8.

While the first type (I) implies that side groups of adjacent monomer units point *away* from the inversion point, in the second type (II) the side groups point *towards* the inversion point. With the latter type of inversion a significant steric hindrance arises from interactions between 4-th and 5-th neighbouring phenyl rings (see Fig. 9). As shown in Figure 10, the skeletal rotations around 5 consecutive chain bonds were driven together in the search for the lowest-energy path that shifts the inversion point to the next monomer unit. The energy barrier turns of out to be about 15 kcal/mol; it effectively increases the natural barrier yielding τ_0.

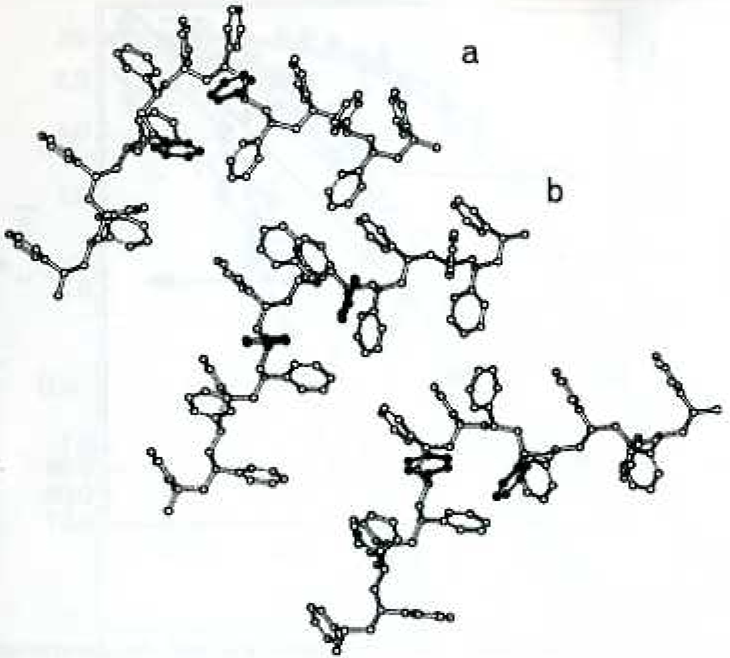

Fig. 9.

Syndiotactic Polystyrene [6]

In this case the transition shown in Figure 11 was investigated. The transition does not involve strong conflicts among side groups, and it was performed by driving four chain bonds one at a time without co-operative changes of other bonds.

The resulting energy plot is given in Figure 12. The energy barrier is in the vicinity of 6 kcal/mol.

Some comcluding remarks

The polymer crystallisation rate is controlled by strain-rate propagation. It is interesting that isotactic polystyrene (*i*-PS) crystallises more slowly and to a lower degree than *s*-PS, in qualitative agreement with the results reported, showing a much lower energy barrier in the latter case.

With a polymer chain in a low-viscosity solvent, strain propagation takes place via rotational rearrangements and its velocity cannot exceed the limiting value τ_{eff}^{-1} (bonds/s along the chain contour), where τ_{eff} is the characteristic time of the *effective* rotational barriers.

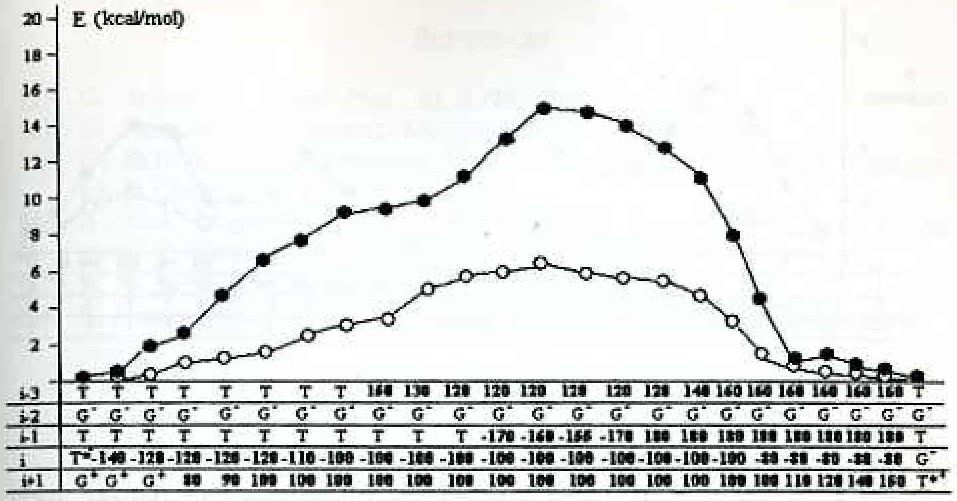

Fig. 10.

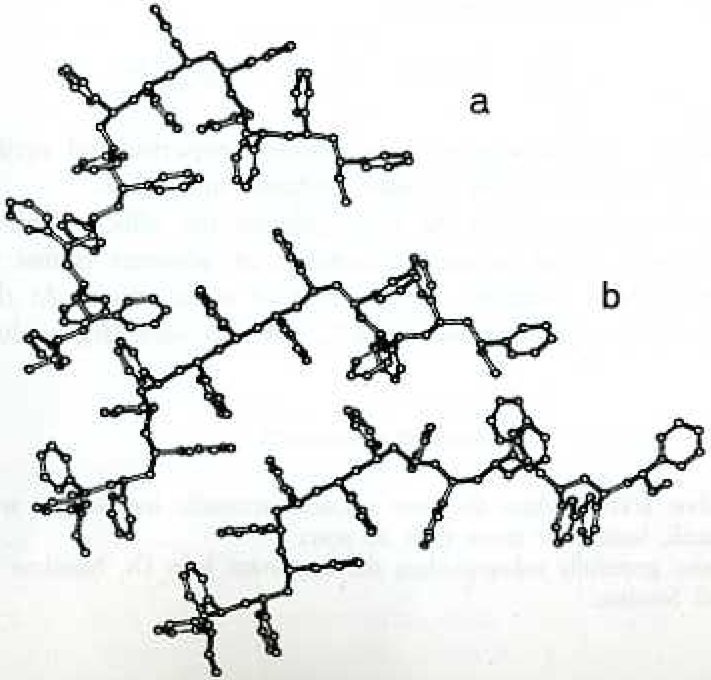

Fig. 11.

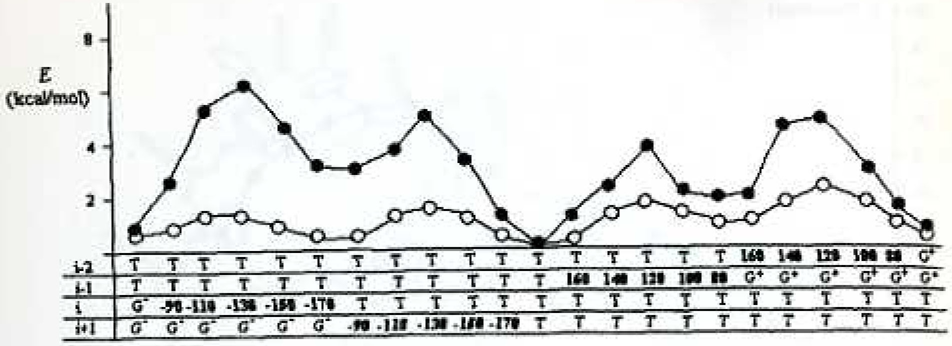

Fig. 12.

In a polymer like PIB, with a small steric hindrance to skeletal rotations, $\tau_{\text{eff}} = \tau_0$, or the characteristic time due to the *intrinsic* energy barrier (mainly due to electron-pair interactions). The resulting linear rate is around 1 cm/s, for coiled chain with $N = 10^4$ skeletal atoms at 300K. The same limiting rate of strain propagation should hold in a highly swollen polymer network.

In the presence of steric hindrance as with *i*-PS in solution, the rate may be approximately expressed as

$$\tau_{\text{eff}}^{-1} (< \tau_0^{-1}), \quad \text{where} \quad \tau_{\text{eff}} = \tau_0 + \Delta\tau_{\text{steric}}.(^*).$$

These considerations suggest new possible experimental verifications of internal viscosity in highly swollen polymer networks.

At lower temperatures, in the bulk polymer the effective energy barrier ΔE increases, as an increasing number of adjacent chains tend to couple their skeletal rotations, with a sort of steric effect. At the glass temperature T_g the effective barrier ΔE_{eff} goes to very large values.

AKNOWLEDGEMENTS

The Author acknowledges the very valuable scientific interactions with Prof. Fabio Ganazzoli, lasting for more than 20 years.

Author also gratefully acknowledges the important help Dr. Massimo Scotti in preparing this Seminar.

(*) In a bulk-polymer sample, strain propagation takes place via direct interatomic contacts, at a much larger rate. In solution, hydrodynamic interaction must be accounted for.

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PAOLO CORRADINI

CONCLUDING REMARKS

We have come to the end of this meeting. The President of the Accademia was not able to come and has asked me to close it.

I would like to thank all those who have collaborated, I believe, to the success of this meeting. And I would like also to thank the President of the Accademia, who is temporarily absent, and the personnel of the Accademia dei Lincei, and all the participants.

I was particularly glad to learn of the presence yesterday of Professor Natta's daughter, Signora Franca, who attended the meeting all the day yesterday. And I want to thank and congratulate the brilliant lecturers that we heard yesterday and today.

They have given a vivid contribution to the success of this meeting, which was held to celebrate the centennial of the birth of Giulio Natta, Professor of Industrial Chemistry, Nobel Prize for Chemistry and Academician of the Accademia dei Lincei - the Academy of Galileo Galilei and we are proud to have had Nobel Prize in Chemistry with us.

Thanks to you all and goodbye. Thank you.

PANEL DISCUSSION

PERSONAL AND/OR HISTORICAL NOTATIONS RELATED TO NATTA'S DISCOVERY OF STEREOREGULAR POLYMERS

FRANCESCO MINISCI

Before going into specific theme, I would like to present a brief personal testimony, which covers more Natta man than Natta scientist.

I have met a few times Natta, even if at the time of the discovery polypropylene was a trainee of Montecatini, at the Polytechnic, but I was one of the few trainees who did not work in the Natta Institute, I was located in the Institute of Quilico; Mazzanti was the head of all the trainees at that time, then became a head much many other important institutions.

I felt a little fervour that was in my fellow trainees, who worked in the Institute of Natta, but I did not participate directly in this atmosphere of interest. My testimony dates back to about a dozen years later, when it was already Natta Nobel Prize. In the second half of the '60s, I attended a competition for the professorship at the University of Florence and Natta was the Commissioner by far the most authoritative of the Commission, not only because it was the Nobel Prize, but because it was a contest of industrial chemistry.

Another Commissioner was Pino, who was in Pisa, where he was particularly dear to Piacenti, his close associate, but was also supported by Speroni of the Florence University.

Two other competitors were Zambelli and Farina, which were two direct students of Natta and that led to important contributions, as all you know, to the stereospecific polymerization.

In this situation, my hope was to get to the top as a third, because at that time there was the system allow to have a the winner and two suitable. The pleasant surprise was the fact of being the first one. The thing I was surprised very much because I thought a decision of this kind could not have been taken against Natta will. But in Florence was Piacenti requested and he continued to call me, day and night, for asking me to giving up the place, even Pino and Speroni pleaded me in this direction; the second one in the rank was Piacenti, the third one Farina, Zambelli was the youngest and was out in that circumstance.

Even Quilico himself, politely, with discretion and kindness, let me understand that my resignation was opportune.

I did not want to be impolite to a commission which had been so generous with me, but also I feared that giving up to Florence I could end up in some place not very comfortable.

So I decided to go to Natta to ask for an advice. To tell the truth, that I had much fear of bothering Natta for such a silly question, also because I was unfamiliar with him and I had no idea of what could be his reaction, then I took courage and I went to see him, I explained my situation, my worries and Natta said to me: "You have won the competition, it is your right to go Florence. If deemed appropriate, you can go there without problem, because it does not bother me at all".

Natta was the only one in the Commission that made a speech of this kind.

At the time I had the impression that Natta was completely outside of this university things, on the other hand I thought the quality of the person was in line with the quality of the scientist; it is a lesson that I tried not to forget over time.

Then the situation was resolved in the most satisfactory because in the meanwhile, a chair in Parma was opened, where I went with pleasure for a number of reasons, and the situation of Florence has resolved; this lesson for me was very important and I will never forget it what Natta taught me.

This is a testimony that I wanted to do to give a little measure of the man, while about the scientist you who have been more closer collaborator will be provided by you.

This list of speakers that has been done by Corradini, coincides with what I tought, however I'd still like to speak Dean Biardi as representative of the institution, as Dean of the Faculty of Chemical Engineering of the Polytechnic, in order to tell what impact this has had the great work that you have done in the Faculty and on Chemical Engineering.

GIUSEPPE BIARDI

As already said by Minisci, my presence in this roundtable, to some extent is improper because, although it was one of the last students who had signed the thesis by Professor Natta, nor in that thesis, nor in my the whole science curriculum I have dealt with Macromolecular Chemistry, but rather of Chemical Engineering, in strictu sensu ,strictly speaking, in particular of chemical reactor engineering, transport phenomena, of "unit operations", simulation, process control and so on.

However, since the will of the organizers refers closely to historical or personal connotations, I remember that "istoria" means testimony in Greek, at least originally, so I can bring the testimony of how the man of whom we speak, has left its mark in a School of Engineering as the Polytechnic, even beyond of what was his work as a scientist who has received the highest recognition.

In the Institute of Industrial Chemistry, who was directing, with a stay of 37 years, if I remember correctly, inevitably left a direct footprint with his pupils, the most recent and older, and on the whole school in the strict sense, since that institution, now the Department, was central to the formation of Chemical Engineering beside the one of Chemical Physics and Chemistry which gave to the fundamentals.

In retrospect, thinking now of what we did then and what has been the evolution, I will say two things mainly relating to changes of Chemical Engineering of the last 30, 40 years to give you an idea of what, in my opinion, was his ability to see the perspective of what would had been the problems in the future.

Now, the era in which he worked Natta is widely prior to that the use of computers, but, in retrospect, one can recognize that the systemic approach, one that takes a complex problem, examines separately the individual aspects, dissects them up at the bottom and then resyntetize the for the purpose of study or calculation or project, it is still recognizable.

His own way of working, which I happen to known only in part, and that he used many collaborators with high efficiency and that is looking for the right person to the right task, it saw him govern conceptually, as a director, all the research lines that were covered at the same time, with a clear understanding of the objectives, both the tactical and strategic research to itself.

Such a "modus operandi", and do not forget that the focus constant profess Natta was directed to the industrial realization, is a feature that I have learned by reflection from this person, and corresponds to an attitude of systems engineering even before this word has been used, because that use was born from the mathematical models, by the use of computers, from the decomposition of a problem which was necessary to be dominated by calculation.

The other issue, which is perhaps even more important, and more directly linked to its research activities such as the one in which had such a great success, although start from other reasons, it has become only recently important and, I dare to say, has not yet fully developed in the Engineering schools, and the Chemical Engineering in particular, and that is based on a more scientific approach over the technical problems, which notes that the problems are existing over different scales of description, the so-called multiscale approach.

If I can give an example, perhaps clear to everyone, even if not are all engineers, may be the following: if, we has to handle a problem of fluid mechanics, is always a good time to decide whether it is enough to operate the theorem Bernoulli or if you need to write and solve the Navier-Stokes equations.

In a scientific activity there is always need, especially in the chemical field, to refer to a molecular level or at the level where matter is considered as continuous, but also to a microscopic level, where the general equations of transport are used, or to the turbulent aggregates, of the human scale, the macroscale.

In those cases it is necessary to have a perfect knowledge of the criteria by which it is said:

"I choose this level rather than that other", and above all of the criteria of scale change, so with averaging operations you switch from lower level to an higher than that and you decide when the ability of description are consistent with the level of description. This is related, on the one side, at the level of description that is configurable in terms of sizes, from nanometers to angstroms, up to meters or kilometres and, secondly, inevitably at the level of formal complication or the mathematic.

By far before they speak, in the proper sense and meaningful mathematical modeling and / or of the multiscale approach, he had a clear perception of these problems.

I take a personal example: I did not have direct knowledge, very long, with the professor Natta, because even though I was a student with him, his health conditions were not the brightest, at those times. I graduated in '65 and I was part of that generation of students who entered in the fifth year and has attended the Industrial Chemistry 2, in 1963/64, so the first lesson in the classroom we found not only Professor Natta and all the classmates, but all the academic faculty of the Polytechnic of Milan and many other authorities at the municipal, regional or national level to pay tribute to professor who won the Nobel Prize a few months earlier. Also when he was not well, however, sometimes we called for knowing what we were doing.

In the early years of assistant I dealt with reactor modelling for steam reforming, in other words of head systems for the production of synthesis gas for ammonia and methanol, and I took care of both characterization of the effluent gas, according to the operative conditions, both in terms of the furnace, the reaction tubes, but also for the thermal and mechanical aspects.

I remember, after talking with him about the thermodynamics of those reactions, to discover that the professor Natta had dealt with the steam reforming reactions also from the numerical point of view with professor Piontelli, then he already knew much of that problem, even if he had never developed a program to do the calculations. At this point he said, "Look”, he was always speaking in third person to everyone, "be careful because it may be possible that the azimuthal distribution of radiant heat flux on the tubes of the reactor could constitute the most important mechanical stress for the tubes themselves". The scientist who was in charge of macromolecules, and catalysis at the level of the Nobel Prize, he was able to grasp, however, which could be at the core of a problem of structural static for the reaction tubes in which the level of outside temperature was in the order of 900 ° C, wherein the specific flow heat could be from 40 to 90 kW/m2, within which there were about 30 bar pressure, whose effluent contained 50% hydrogen, where then a clique would have created a dart can cut any thing, including refractory, over30 meters.

This was the person. The next time, a month later, I went by the teacher to say, "Teacher, he was right, according to his advice I was able to put the problem in formal terms and calculate the deflection of the tube due to the uneven lighting in azimuthal direction".

For me, this has meant many things, a side from the specific problem, in other words that a responsible person, and at that time the teachers role were covered very few person, in a School of Engineering must have a view capacity of 360°, as they say now, but I prefer to say 4D steraradiants, so also in the steric sense, able to perceive everything and to have a perspective of everything, to evaluate all the things for what they value: those in small scale, those that require to be examined under the light of the characteristic equations and the elementary requiring simply common sense engineering, because all things have value that you deserve and can find the correct collocation. The ability to control simultaneously all these aspects, scientific or technical ones, I dare to say even the industrial and economic - because I've always heard from Prof. Natta, "The things you need to realize that they must find an economical use in the field, so they must be viable in the strict sense "- was one of the characteristics of the man and one of the signs that left several people who knew him, and hope that this school, which protempore I have the honor to preside as President, can continue to do in the next thousand years.

GIORGIO MAZZANTI

l. I will try to tell the story of research carried out at the Institute of Industrial Chemistry of the Polytechnic of Milan in the field of polymerization stereospecific α-olefins from March to December 1954, believing that in those ten months results that had been obtained, for many years on had a major impact both on the research conducted in many laboratories in different countries, both on the development of petrochemicals in the world.
On the whole story stands the figure of prof. Giulio Natta.
One can not fail to remember that in those years and for several years follow, all the Italian chemical industry was very committed to the development and innovation, both with its own Research and Development, both with the acquisition of licenses for new products or new processes.
In that context we find the confidence and commitment of the 'Chief Director of Montecatini, engineer Piero Giustiniani, to base research and, especially, to Giulio Natta and his school.

2. As a premise, it must be remembered that as soon as published by Karl Ziegler's early work on the possibility of adding ethylene in Al-C bonds, Giulio Natta and Piero Pino sensed that this could lead to several important developments.
Under Natta pushing, Montecatini acquired a license (exclusive for Italy) on all research Ziegler in that field. Around March 1953 two chemists, Roberto Magri and and Paolo Chini and a chemical engineer, Giovanni Crespi, Montecatini went to work in the Institute of Ziegler in Mulheim.

3. Having said that we can get to the heart of our history.
Around the beginning of 1954 came to Montecatini and the Polytechnic the news that Ziegler was able to obtain polymers of ethylene at high molecular weight with a reaction based on the use at low pressure, as catalyst, of a mixture of triethyl aluminum and tetrachloride titanium.
Giulio Natta had the idea, certainly his and his alone, to try to polymerize propylene with the same catalyst. This constitutes a confirmation of his ability to think also of the outside the box based on previous knowledge.
It was known that the behaviours of ethylene, respectively, and the propylene against the ability to originate polymers were absolutely different.
On March 13th Paolo Chini using a catalyst prepared from aluminum triethyl and titanium tetrachloride in a molar ratio 10:1, obtained a polymer of propylene semi-solid consistency.
Immediately after this first result Giulio Natta and Piero Pino believed that it was appropriate to devote more forces to this line of research and so I, which I was working in the Institute for two years, stopped all other activities and I was going to dedicate myself entirely to research on these new catalysts and polymerization of propylene.
I was collaborating with two recent graduates, Paolo Longi and Umberto Giannini, who were part of a postgraduate course funded by Montecatini.
After a few weeks Paolo Chini was transferred to the Research Center Montecatini of Ferrara with the task of creating the first pilot plant for the production of aluminum triethyl. Meanwhile Roberto Magri had returned to Ferrara also with the task of developing the polymerization of ethylene.

4. I know that what I am about to say may seem now, especially today in 2003, a little debatable, but in my opinion, great importance should be attributed to the fact that from the beginning the polymer obtained from propylene was fractionated by exhaustive extraction with boiling solvents, using in the order acetone, ethyl ether and n-heptane.
In this way were isolated fractions completely amorphous (extracted by acetone and ether) of approximately 40% of the total polymer, a fraction medium crystallinity (extracted by heptane) equal to about 15-20% and a residual high crystallinity. No molecular weight fractions of the different growing significantly in passing from one to another, reaching maximum high for the extraction residue. I would say that if he had not proceeded since the beginning with the

fractionation by solvent extraction (technique quite unusual at that time in macromolecular chemistry) there would be no subsequent developments both in the interpretation of differences in the molecular structure of the different fractions, both in investigations on catalysts that led, as we will see shortly, in selectively obtain the "good part", in specific the residue of the heptane extraction, the polypropylene.

5. On 6 June 1954, Montecatini filed a patent, the inventor Giulio Natta, in which it claimed new polymers of propylene, in particular that high crystallinity constituting the residue of the extraction with boiling heptane and the process for producing such polymers. At that time there was still some doubt as to whether the crystallinity found was in some way related to the growing molecular weight. This uncertainty was then totally eliminated thanks the work of structural chemistry conducted by Paolo Corradini, but also from the analysis founding high crystallinity in the samples prepared by us by thrust de-polimerization of the heptane residue extraction, which had molecular weight also by far lower than that of amorphous fractions isolated from raw polymer by extraction with ether.

6. In May-June of 1954, however, we were rather depressed and worried because it was found a marked non-reproducibility in evidence of polymerization of propylene, and even by some time, any attempt to polymerization was completely failed. We keep saying that if they had obtained some evidence of the high polymer propylene, obviously it had to be possible obtaining them again. But it was true that at the time, when you opened the autoclaves we were not finding any polymer. Clearly something was getting to our control.

7. With the idea of being able to get a more regular polypropylene was prepared, with a reaction rather laborious, aluminum tripropile. However even with the use of the latter the polymerization tests went all failed. It was on the polymerization test in which was taking the last amount that remained of aluminum tripropile. Me and Paolo Longi, several hours after not seeing any mention of polymerization, we were very disturbed by the prospect of having to prepare another aluminium tripropile. We decided to give it a try a little "'desperate" and we injected in the autoclave a certain amount the titanium tetrachloride.
Instantly a sharp increase in temperature indicated that the polymerization had started, and after a short time, opening the autoclave we found a large amount of polypropylene. This led us to think it was important to prepare the catalyst in the presence of the monomer and increase the ratio of titanium tetrachloride and triethyl aluminum. All polymerizations of propylene carried out immediately after with these founding provided (without failures) positive and reproducible results.
Not only that, but with these tips, you also managed to get polymers of 1-butene (fractions containing high crystallinity), crystalline polymers of styrene and poly butadiene 1-4 trans crystalline.
Based on these results July 27 Montecatini filed a second patent, inventors Giulio Natta, Pino Piero and Giorgio Mazzani, in which was claimed the process based on the preparation of the catalyst in the presence of the monomer and, as already done in the previous patent, solid polymers crystallizable of propylene, adding that, in such polymers, at least for long stretches of the molecule, the carbon atoms were identical with asymmetric steric arrangement. It was claimed, crystalline polymers of α-olefins in general, and, in particular, the crystalline polybutene and polystyrene.
Systematic studies carried out by us after 1954 showed that for catalysts prepared from triethyl aluminum and TiCl4 from the maximum activity corresponds to the Al / Ti ratio equal to 2.5 (very different from that adopted in the first trials equal to 10:1), and that in any case the catalyst quickly loses its activity with time.

8. The holiday of all of us in August 1954 were limited to a few days and I well remember that Giulio Natta greeting me said that it was worthwhile to make a little sacrifice because - in his words

"research of this type may also lead to the Nobel Prize".

9. The fractionation by solvent extraction had allowed isolating polypropylenes different not only in molecular weight, but especially by structure. This led us to think that the catalysts employed could actually contain active centres, or better initiators of polymer chains, of a different type. We began to isolate the solid part which was obtained by the reaction of triethyl aluminum + titanium tetrachloride against the part that was not retained by a porous septum which had pores with diameter between 5 and 15 microns.
The filtrate phase provided a polypropylene almost completely amorphous, while the solid part (after addition of triethyl aluminum) provided a polymer with a bit richer residue with heptane extraction. It remained, however, around 50% -55% of the total (compared to 40% obtained with the original catalyst), which still far from yields that could allow an industrial development.

10. In October and November I had the opportunity to listen to a Milan conference of a very general, it seems to me given by Professor Mark in which, speaking of the 1-4 trans polybutadiene obtained with catalysts ALFIN type, was attributed to the fact the regularity of chaining of the molecules of butadiene monomer were due because those were adsorbed in all same way on the surface of the crystalline phase present in the catalyst. Reached then by free radical that triggered the polymerization and the concatenation of the monomeric units. We did not think at all that the polymerization of propylene happened with radical mechanism, but that interpretation which attributed a fundamental role in the crystalline phase present in the catalysts ALFIN, however, made me think of trying to employ, instead of the liquid titanium tetrachloride, a titanium halide and solid crystalline as the trichloride.
I immediately asked to Umberto Giannini to prepare and purify by sublimation TiCl3. Since the first test for the polymerization carried out using TiCl3 it was realized, already opening the autoclave, the raw polymer it appeared in a different way, as a solid mass of powder consistency. The idea had worked! In fact, the residual extracted with heptane of the polypropylene thus obtained was around 85/90%.
Conversely, by catalytic mixtures highly dispersed got then almost completely amorphous polypropylenes.
Montecatini then filed other two patents on 3 and 16 December, 1954, having as inventors Giulio Natta, Piero Pino and Giorgio Mazzanti, in which the claimed methods for the polymerization of a highly stereospecific of a-olefin demonstrating that:
- Catalysts obtained from crystalline solids halides of transition metals such as TiCl3, TiCl2 or VCl3 provided very high percentages of crystalline polymer, in particular isotactic polypropylene;
- Highly dispersed catalysts obtained from liquid halides such as TiCl4, the VCl4 or 3 ITEMS provided rather high percentage of amorphous polymer.

This opened the way for the industrial production of polypropylene isotactic.
It is important to remember that until the end of the 70 for the next 25 years from the filing of the patent, the catalysts based on TiCl 3 were used in all installations for the industrial production of polypropylene isotactic.
With the use of highly dispersed catalysts managed to prepare amorphous ethylene-propylene copolymers, free from crystalline fractions, which gave rise to new synthetic rubbers.
Immediately after the deposit of the two aforementioned patents Professor Natta presented a communication on new polymers at the Academy of Lincei. The December 10, 1954 signed by Giulio Natta and his collaborators, was sent a Letter to the Editor of the Journal of the American Chemical Society.

11. By December 1954, he closes the story that I wanted here today summarize. Actually, more than a story you would rather speak as the first chapter of a long story.
In fact, as everyone knows, there was then an enormous development of research in the field of polymerization of olefins and diolefins. In the latter field the group of researchers coordinated by Lido Porri has achieved results of great importance, which I imagine will be by himself remembered in this roundtable.
The research in the field of stereospecific polymerization, after almost fifty years is still very active, as is also shown from papers presented at this conference.

12. Let us ask ourselves at this point what happened after 1954 in industrial sector.
Mention must be made at about the Italian chemical industry that within of only three or four years after the first patent, in fact by 1958 to Montecatini Ferrara went ahead with the development of the process in pilot plants and then to the first industrial production of isotactic polypropylene which entered the Italian market with the trade name MOPLEN. So the first response was the deed of trust, provided, virtually limitless, a few years earlier by engineer Piero Giustiniani.
A few years later began, in Ferrara industrial production of new synthetic rubbers based on ethylene-propylene copolymers, entering the Italian market with the trade name Dutral.
Many patents have been granted licenses by Montecatini in almost all industrialized countries. The subsequent intake of royalty has covered for many, many years the cost of all the research Group Montecatini and then for all the Montedison Group.
I believe that the isotactic polypropylene represents today, from the point of view of production volumes, the second plastic material in the world. I believe that the ethylene-propylene rubber represent the second synthetic.
But I can not omit to mention that the polypropylene years longer enshrined in the Italian chemical industry products. Through some changes of ownership began in the first half of the '90s, the polypropylene existing in our country belong to a European Group, not Italian. The ethylene-propylene rubbers are still part of the productions of an Group Italian, but often we read that the industry elastomers could be sold to third parties.
I do not know if this evolution can be seen as something the inevitable. Whilst it may be that it is, equally inevitable and that I will mention it with some bitterness.

PAOLO CORRADINI

I will project some transparent for remembering some fact of that time. Giorgio Mazzanti open me the way, because he said about the collaboration that there was in place at that time with Ziegler and with the Ziegler laboratory and what happened with regard to the synthesis.

I have a set of transparencies that I project in order: this is the photograph that Prof. Natta gave me, which I keep in my studio, in where you see Prof. Natta and there is a dedication, “to my dear pupil and collaborator Paolo Corradini, affectionately "(Fig. 1). In the background is
a big model Natta isotactic polypropylene that had in the study at the time and I think it was done for a show somewhere.

Fig. 1.

the next clear that I would like to see is the first spectra of polypropylene isotactic (in red in Fig. 2): according to my memory polypropylene is born within the framework of the research that took place at the technical on polymers of ethylene and you knew that, at a certain moment from the reaction of "Aufbau" discovered by Ziegler, Ziegler as well had found a way of polymerizing ethylene - and I remember quickly only points -.

There is always a moment of serendipity in the discovery and a time happy intuition, intelligence to understand things. In the laboratories Ziegler had happened that in a autoclave the ethylene oligomerization had stopped at the dimer, butene-1, in large quantities. Ziegler and co-workers went to see what had happened and never will discovered that an autoclave had been stained with nickel, so it was discovered first the so-called "nickel effect".

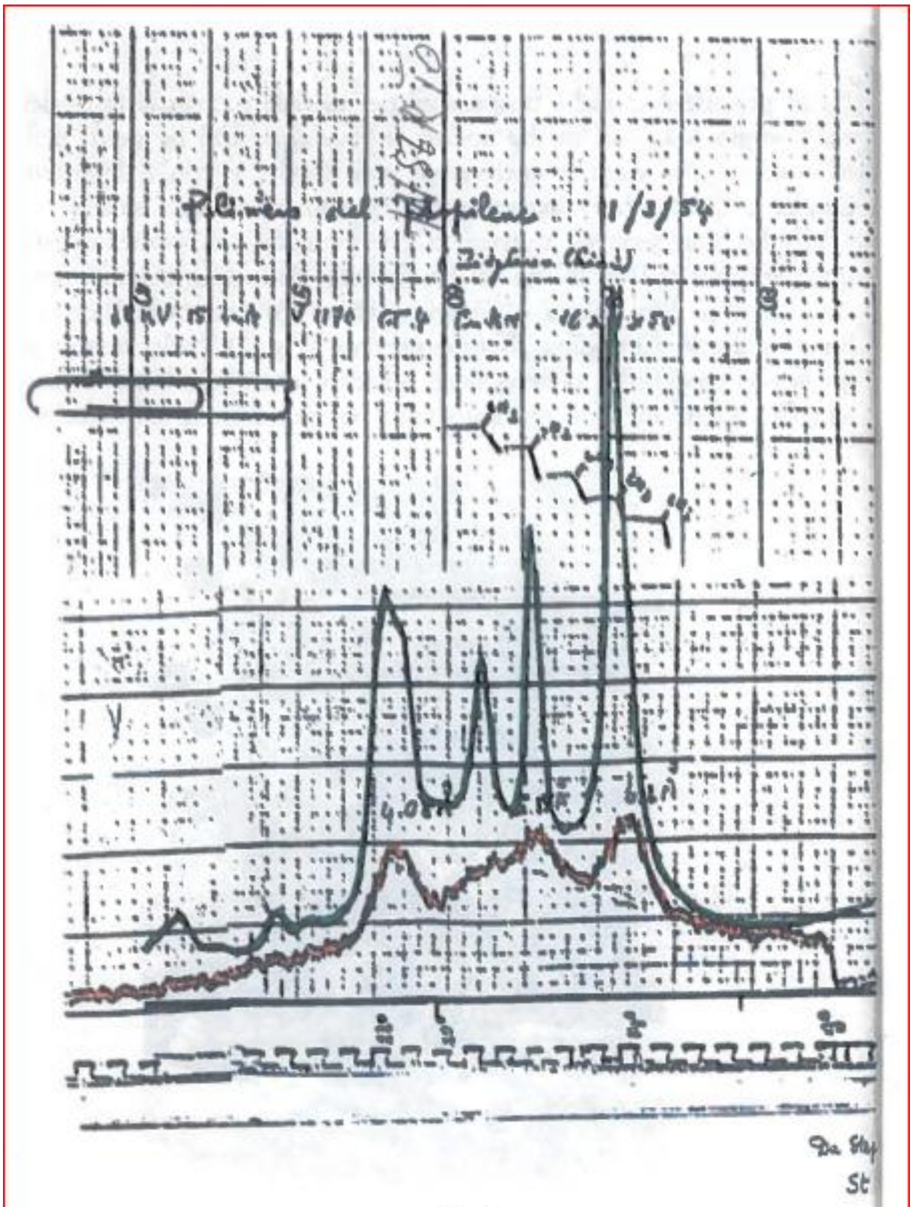


Fig. 2.

The nickel, added to aluminum triethyl, causes the polymerization ethylene monomer unit stops at the first entry and is formed butene in a quantitative way.
In a similar manner, in other way, the reaction of oligomerizazion of the ethylene in the case of propylene knew that would stop the dimer of propylene, then the propylene to Ziegler was a bad entity to polymerize, because the reaction is stopped always, quantitatively, to the dimer (which was very specific, the 2-methylpentene!).
Ziegler gave orders to his staff to try as catalysts all the elements of the periodic table, therefore, systematically, since the nickel was a certain effect, the whole system was tested with all the other element. When it came to zirconium, zirconium filled the autoclave of a polymer: the polyethylene. It was born on low-pressure polyethylene who had a good destiny, now he make millions of tons in the world that way.
They began to try this even at the Politecnico di Milano, through agreements with laboratories Ziegler Muelheim. It was polymerized the ethylene and, according to my recollection, Prof. Natta wanted to try to copolymerize ethylene with propylene. Those appointed to Paolo Chini and Chini made a blank test, and as first step did a test "in vitro". The reaction in the flask of glass not happened. Chini took the mixture in glass, TiCl4, aluminium triethyl and propylene, poured into an

autoclave, increased pressure and temperature (Certainly did not make the reaction at atmospheric pressure as had tried at the beginning, or at least is solvent as done in the beginning).
- and the autoclave was filled with a spongy material of a gray-green material. He came with this spongy material greenish to me that I was doing the X-rays - I was commissioned to make X-rays of all the polymers of ethylene which were prepared in the laboratory - and figure 2 is the spectrum was obtained, is shown in red.

There are records, where you can read: "propylene polymer" there is the date, "March 11, 1954, Ziegler, Chini, "and then there are data on x-ray and the evidence that this should be a polymer, there is no hint of a structure that is isotactic yet, for heaven's sake, because we do not thought about the isotacticity, but regular, because in my opinion, rightly, it could not be otherwise crystalline.

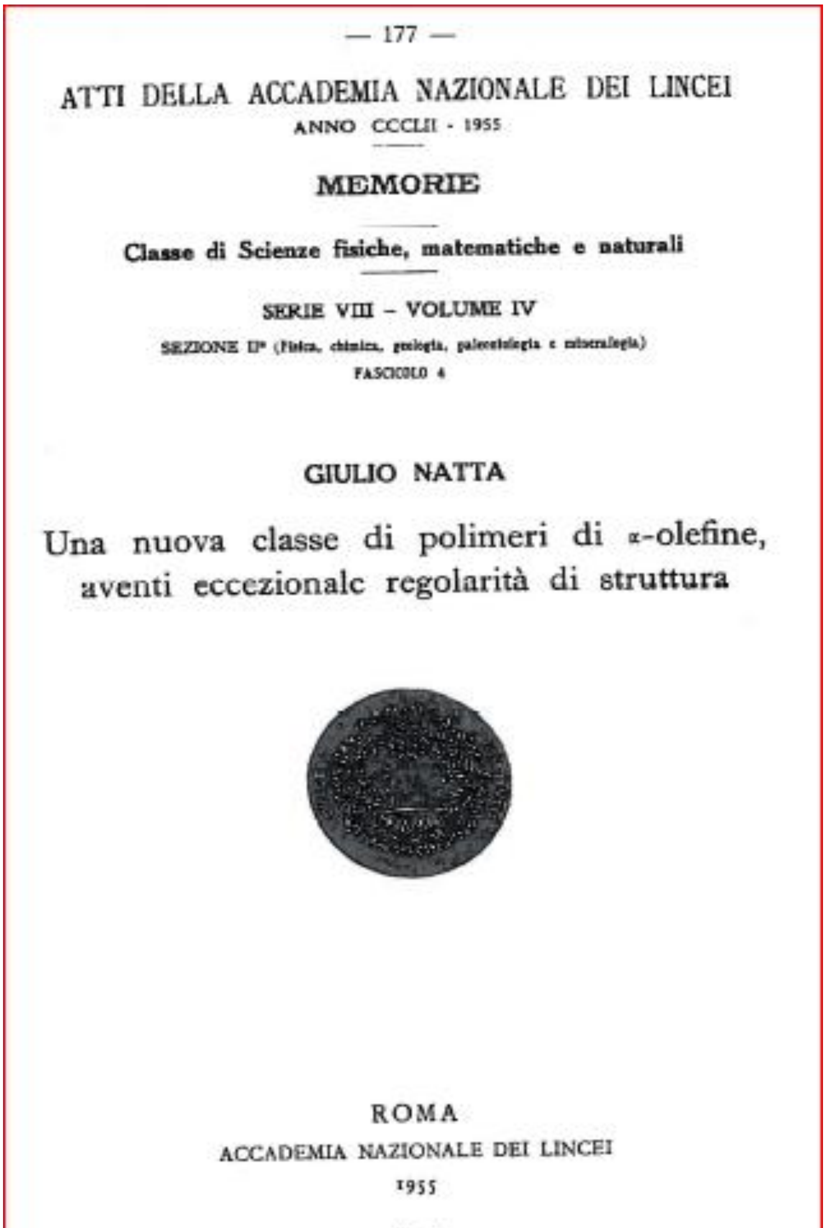
For comparison we can see, in green, the spectrum of a polymer of today and it is seen that all the peaks are in the same location, but much higher. For this there is a specific reason: the polymer was brought us was full of chlorine and titanium, just 1 -2% of these elements to lower the spectra, those are strong absorbent, regarding the X-rays, these elements like chlorine and titanium, I think especially chlorine. The spectrum in red, then, is very low, but it is (for angular positions) identical to the spectrum of our days.

I'll show you two or three transparent regarding our activity. Figures 3 and 4 represent the cover pages of two Memories of Lincei. Prof. Natta presented two memories the Accademia of Lincei, one is in its name: A new class of polymers a-olefin with exceptional regularity of structure (Fig. 3), which already introduces the term "Isotactic". The other is to Natta and Corradini and is entitled: On the structure of a new type of crystalline polypropylene (Fig. 4).

I remember, because in those days there were written so easily work with the typewriter, it had to make a run: Prof. Natta was able came to Rome a little before I took a train, I do not remember who were the secretaries of Prof. Natta at the time, but someone was typing with typewriter until the last moment and I took a train to bring these two manuscripts to be deposited at the Academy and, in fact, made themselves two memoirs, took place at the same time sending the work that has Giorgio Mazzanti quoted the American Chemical Society based on numerous data and also including the polymerization of butene and styrene, the data showed that the structure roentgenographic which was highlighting the helix structure of isotactic polymers.

In figure 5a is shown the structure of polypropylene, as is reported in Lincei memory, you see the chain, the projection along the axis of the chain and, then, as repeating units along the chain. The Figure 5b is a somewhat more modern, where you see the ternary helix and the repetition of the groups along the chain in isotactic manner, is right helix.

Figure 5c involves a comparison. At the time, the helix were the trend, Pauling had just then presented its alpha-helix for…



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ATTI DELLA ACCADEMIA NAZIONALE DEI LINCEI
ANNO CCCLII - 1955

MEMORIE

Classe di Scienze fisiche, matematiche e naturali

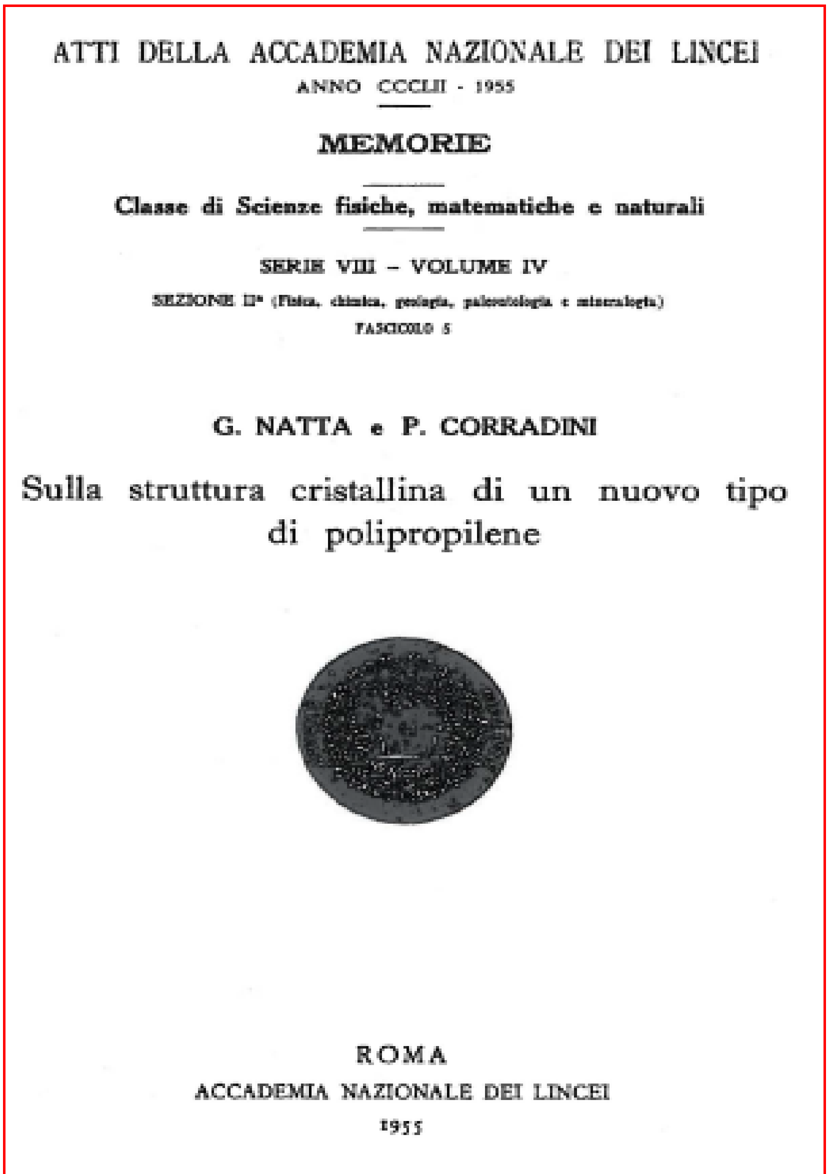
SERIE VIII – VOLUME IV
SEZIONE IIª (Fisica, chimica, geologia, paleontologia e mineralogia)
FASCICOLO 4

GIULIO NATTA

Una nuova classe di polimeri di α-olefine,
aventi eccezionale regolarità di struttura

ROMA
ACCADEMIA NAZIONALE DEI LINCEI
1955

Fig. 3.



ATTI DELLA ACCADEMIA NAZIONALE DEI LINCEI
ANNO CCCLII - 1955

MEMORIE

Classe di Scienze fisiche, matematiche e naturali

SERIE VIII – VOLUME IV
SEZIONE IIª (Fisica, chimica, geologia, paleontologia e mineralogia)
FASCICOLO 5

G. NATTA e P. CORRADINI

Sulla struttura cristallina di un nuovo tipo di polipropilene

ROMA
ACCADEMIA NAZIONALE DEI LINCEI
1955

Fig. 4.

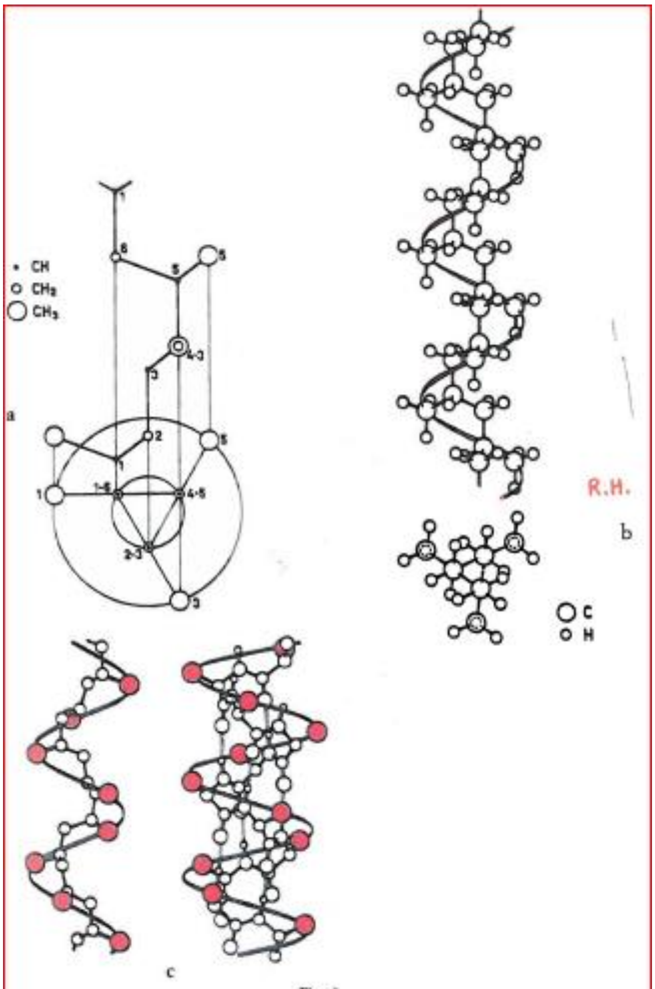


Fig. 5.

…the polypeptides and was proposed by Crick and Watson for a structure DNA, almost simultaneously, they were all helical structures. The comparison concerns a polymer that I studied with Italo Pasquon, which has worked a little on these helices with me - he says for a year, but has worked with me on it -. It is a polyolefin isotactic helix with 3.5 monomeric units by-step, side roups are in red. The alpha-helix Pauling, shown on the right, is very much similar in the side groups disposition and it has 3.7 monomer units per step.

Figure 6 is an improved presentation of the helix, always with the projection and development of the propeller of polypropylene. The propeller has become a monument to Ferrara and stands before the research laboratory of Basell (Fig. 7).

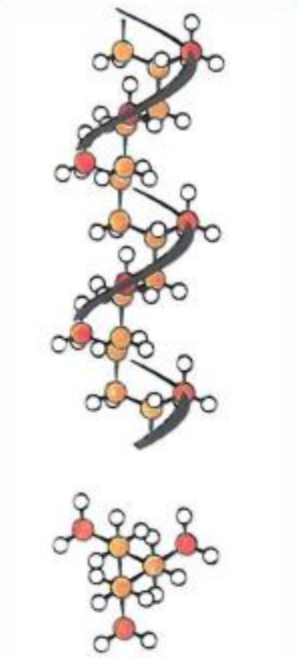


Fig. 6.

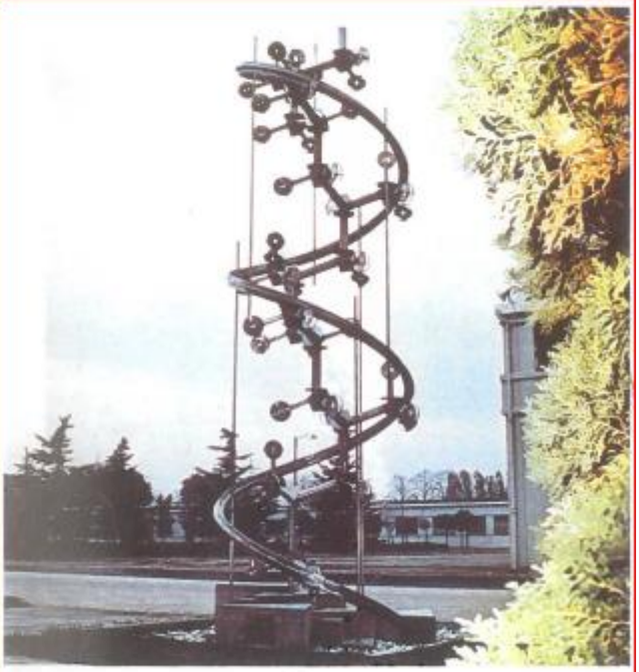


Fig. 7.

In Figure 8 we have another view of the helix, in which has been recognized atom by atom, with AFM image (this is a right helix).

I finish adding another helix (Fig. 9), that the polypropylene syndiotactic, this always choosing the right helix.

I add, for last, Figures 10 and 11 which relate to the more recent work we are doing.

Prof. Natta had the intuition that the chirality of the site should be, in some way, to promote the polymerization in a certain way and, in fact, in the book he wrote with Farina, "Molecules in 3-D", it is clearly seen the $TiCl_3$, with the presentation of the chirality of the site, as has been pointed out by Prof. Brintzinger…

Fig. 8 – AFM image of a 2.7 nm × 2.7 nm area diplaying methyl groups, and right-and left-handed helices of polypropylene.

…this morning, just in that way that the metal atoms can be right or left. Prof. TI Brintzinger seems to me that it has highlighted very well (Fig. 10).

The models in Figure 11, as we are seeing them, are taken from a work that we have recently(*) on the occasion of centenary of the birth of Prof. Natta.

Here we see the surface of solid TiCl3 and as you can imagine who are willing atoms: these are transition states with bond alpha-agostico hydrogen to metal, then represent states of tran-

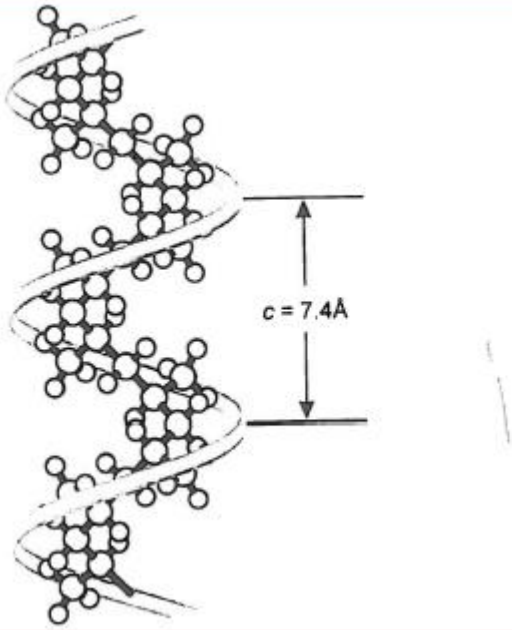


Fig. 9 - Right-handed Helix of Syndiotactic Polypropylene (4 Monomeric Units in the Repeat Period).

(*) P. Corradini, L. Cavallo, G. Guerra, Stereoselectivity in Ziegler-Natta Catalysis, La chimica e l'Industria, 85, 2003: 41-44 see also: P. Corradini, L. Cavallo, G. Guerra,
Do New Century Catalysts Unravel the Mechanism of Stereocontrol of Old Ziegler-Natta Catalysts?, Acc. Chem. Res, 2004, 37, 231-241

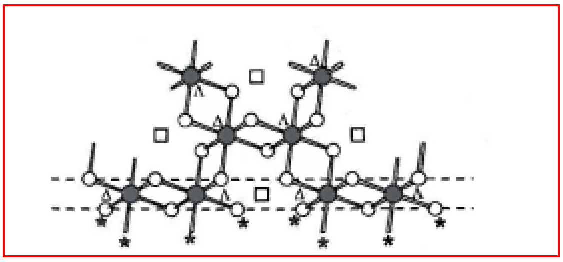
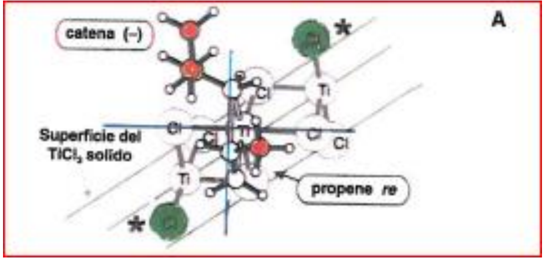
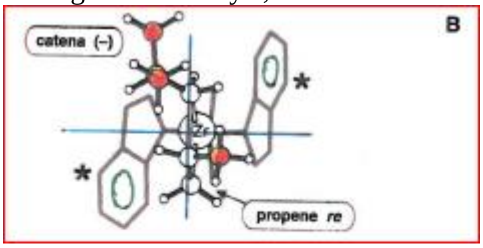


Fig 10 - Possible lateral sheet with a layer of TiC13. The positions of non-equivalent coordination, which may become available for a monomer molecule or a growing chain of polymer, are indicated with an asterisk.

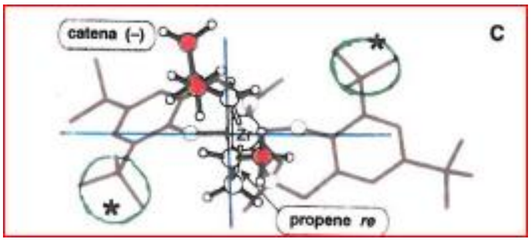
Model for isospecific systems



1979 - molecular model of heterogeneous catalyst, local situation on the surface of TICI3, solid.



1988 – molecular model of homogeneous metallo cene catalyst



2003 - molecular model of homogeneous ottaedric catalyst

Fig 11

-sition for the polymerization and it is seen that the steric hindrance of two chlorine atoms on the surface of the catalyst affects the chain: on outgoing from the atom of titanium chain comes out a CH2. In the state of transition, one of the hydrogen atoms of the CH2 must form a bond alpha-agostic, there are only two ways, but one way is prevalent for the overall dimensions of the chlorine atoms. If the chain goes from a certain part, is mandatory for the methyl of the propylene entering to go on the other way.

It is now known that in systems of this kind approximately 1000 monomeric units all put themselves in one way before to make a mistake: looks amazing, it's a really great thing. You see now with NMR, we would never have imagined at the time, even Professor Natta could not imagine it, a stereo regularity so great, which is in the order of thousand units that connect all in a way. This is a model originally presented with Guerra, we presented it when Prof. Guerra was a student with us, but I think today retains all its validity.

Always in the same figure there are catalysts homogenous of today. The model is of type catalysts Ewen or type Brintzinger, metallocene.

The groups with asterisk are arranged so chiral and force on the zirconium atom the chain, which is now redesigned in orange, out of this part, it can not go on the other way, because it would impact here, against this phenyl group and if the chain is forced to go this other way, the methyl goes elsewhere.

The stereoregularity is a bit lower, you bring a hundred monomeric units before you make a mistake or even less, so less stereospecific catalysts than the heterogeneous catalysts. How said before in heterogeneous catalysts are the sites in which 1000 groups are put themselves in a way and the wrong, each 1000.

Now other catalysts are proposed, even octahedral once, with a neighborhood, so while the zirconium has a neighbourhood similar tetraedrical, which resembles even more the catalyst of Prof. Natta where titanium is octahedral - as was shown by Prof. Brintzinger at the beginning of his lecture -. The groups are signed with asterisk and the chain is forced to orient them in chiral way due to those conditioning groups. The methyl of the propylene must go to the opposite side.

I just wanted to mention it, because they are the more recent developments in polymerization catalysis, of which Professor Natta would have been, of course, very happy, because that was the way in which reasoned and tried to carry on the scientific research.

LIDO PORRI

At the beginning of my speech I would like to submit two photographs. The first (Fig. l) is of 1957 and portrays Prof. Natta with three collaborators, Mario Farina, Giorgio Mazzanti and myself.
The second one (Fig. 2) is on October 1963 and was taken when the Academy of Sciences in Stockholm required to Prof. Natta some photographs of himself and his group. It portrays Natta with various collaborators in a laboratory of the Polytechnic.

Figure l - Natta with three collaborators (from left: Mario Farina, Giorgio Mazzanti, Lido Porri)

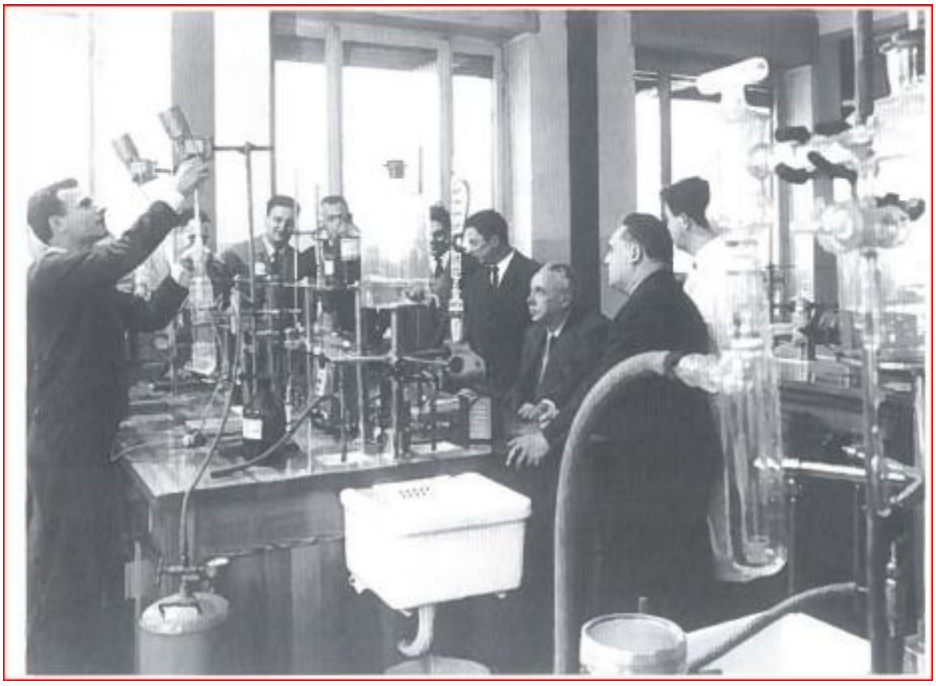


Figure 2 - Giulio Natta with some co-workers in a laboratory of Politecnico (from left: Lido Porri, Mario Pegoraro, Piero Pino, Raffaele Ercoli, Enrico Mantica, Ferdinando Danusso, Prof. Natta, Gino Dall'Asta, Mario Farina)

I started to work with the group Polytechnic Natta August 19th 1954. No Prof. Natta instructed me to take care of copolymerization of propylene with butadiene. The professor was fascinated by elastomers and he wanted to get with the new catalysts discovered by Ziegler, a propylene copolymer or propylene-butadiene-isoprene containing approximately 3-5% diolefin. This had the butyl rubber, which is a copolymer isobutene-isoprene containing 3-4% of isoprene, and considered that a propylene-butadiene copolymer or propylene-isoprene could be of considerable interest as elastomer.

The results were not exciting, on the other hand still copolymers of this type are difficult to prepare, because the two classes of monomers, olefins and diolefins, are not very compatible.

From the end of November '54 I started working on the homopolymerization of the diolefins and this opened for me a time of great satisfaction from the point of view of work. 15-month period, from December 1954 to March-April 1956 (about 13 months of actual work, if we consider holidays) were synthesized all 4 stereoregular polymers of butadiene theoretically predicted (Fig. 3). These syntheses opened the chapter of stereospecific polymerization diolefins, which led to results of great scientific interest.

From isoprene two stereoregular polymers were obtained, one consisting of practically only by the unit ,4-cis, the other only by units l, 4 - trans, respectively equal to the two naturally occurring polymers, natural rubber and gutta-percha or balata. Stereoregular polymers were also obtained from monomers more complex as the pentadiene l, 3, CH2 = CH-CH = CH-CH3. The polymers of this monomer are characterized by the fact that contain two sites for steric isomerism for each monomeric unit: a double bond, which can have configuration cis or trans, and an asymmetric carbon atom, which may get two opposite configurations. They were therefore called di-tattical.

he polymers obtained from the stereo regular pentadiene-1, 3 are reported in figure 4.

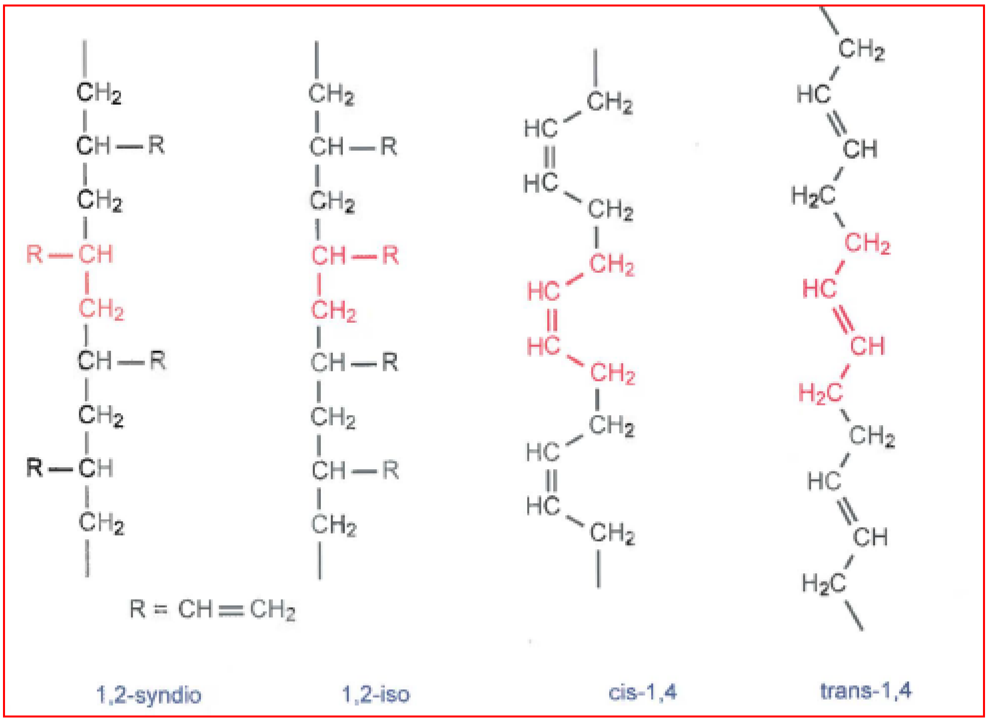


Figure 3 – four steroregular butadiene polymers

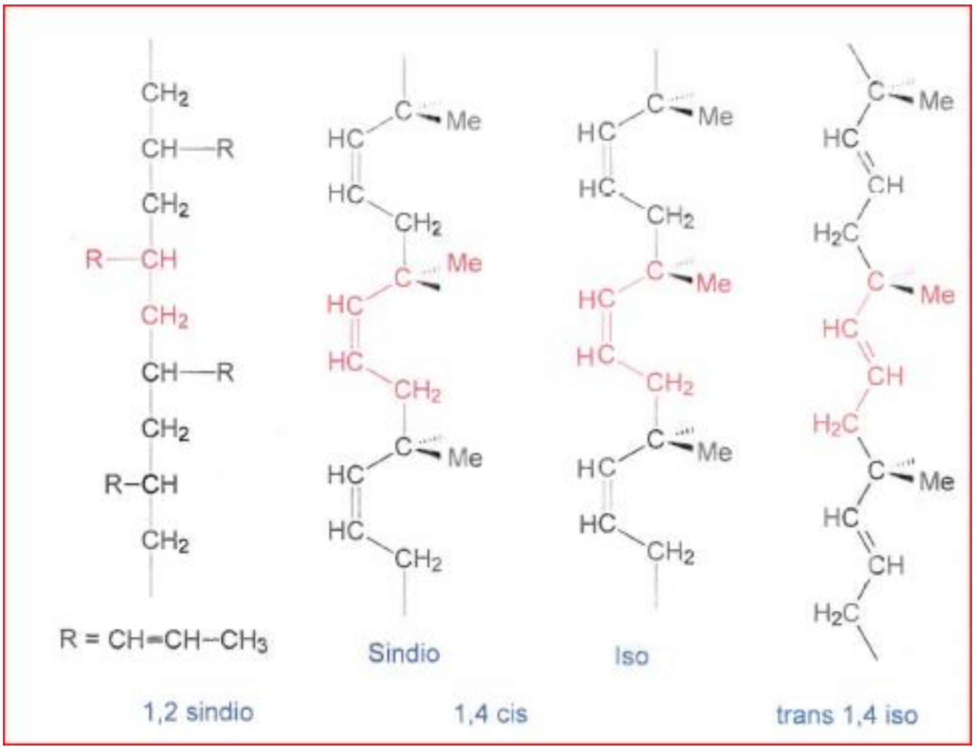


Figure 4 – steroregular 1,3-pentadiene polymers

I will not dwell further on the synthesis of stereoregular polymers of diolefins, which continued even after 1963 and has provided a large class of crystalline polymers. The polymerization of diolefins, for fact that these monomers can give monomeric units of different type, certainly has shown, more than that of mono-olefins, as great is the ability of catalysts based on transition metals stereocontrol the polymerization. The synthesis of crystalline polymers structure respectively 1,4-cis, 1,4-trans and 1,2 represented a giant leap forward compared to the methods polymerization before known.

Let me now turn to some personal memory. The polybutadiene l, 2 syndiotactic was for the first time synthesized April 7, 1955. I took the polymer to my friend Paolo Corradini, who after examining the spectrum Dust said, "Purify and then take it back, because this polymer probably contains many mineral impurities". We must then keep in mind that all the attention was given to isotactic polymers and there was some difficulty in accepting the idea that there could existing polymers having a different type of stereoregularity.

In reality, the polymer did not contain mineral residues (was soluble in hot heptane), and showed good crystallinity was formed in large prevalence by 1.2 units, according to the IR spectrum.

My friend Corradini was convinced that he could be a stereoregular polymer of new type and the value of the identity period calculated from the spectrum of fiber (about 5.1 À.) attributed to him the kind of structure that was then called syndiotactic.

I remember the discussions with Prof. Natta on this polybutadiene 1,2, talks taking place usually while you were waling in the corridor in front of the autoclaves room. The professor had realized that the new polymer constituted the first example of a new class of stereoregular polymers and he was looking for a greek name that meant "every 2" or "two by two", to indicate that the same steric situation is repeated every 2 monomer units. The right name was found with the aid of Ms. Rosita and the professor's daughter Greek teacher, Mrs. Franca, a the time an high school student. These experts suggested syndiotactic from the greek "synduo", which means "two by two". It was born the first polymer with stereoregular syndiotactic structure.

After the synthesis of polybutadiene l, 2 syndiotactic, the Politecnico began to think that some monomers (for example, alpha-olefins) could provide isotactic polymers, while other monomers (for example the diolefins) could provide syndiotactic polymers. However, a few months after the synthesis of syndiotactic 1,2 polybutadiene, butadiene was obtained from a new crystalline polymer consists of 1.2 units, but having isotactic structure. It was October of 1955.

This synthesis was a surprise, because for the first time, it became clear that the same monomer could give an isotactic polymer or syndiotactic, according to the type of catalyst used. Today, this seems obvious, but then it was not.

The synthesis, in 1955, of isotactic and syndiotactic 1,2 polybutadiene has certainly facilitated the identification of the syndiotactic polypropylene, which was characterized in 1959. I have a personal memory on this point. The Prof. Natta called me one day in his studio (can not remember exactly when, perhaps in 1958, nor I remember for what reason) and found that was examining with Ivano Bassi the spectra of powdered samples of polypropylene which, in addition to the typical diffractions of polypropylene isotactic, also showed new bands, much weaker and difficult to interpret.

I attended only the last few minutes of the discussion and I remember that at the end of the Professor began to smile and said, "These new diffractions could be attributed to syndiotactic polypropylene. After all we know that the butadiene can be polymerized as polymer l,2-isotactic, or 1,2-syndiotactic and I can’t see why even the propylene can not give a syndiotactic polymer".

The Professor Natta was right. The diffraction observed in some samples of polypropylene were indeed due to the presence of small amounts of syndiotactic polypropylene, which was then isolated for chromatography and characterized. Syndiotactic polypropylene was patented in 1959 and I think we can say that his identification was facilitated from the synthesis of syndiotactic 1,2-polybutadiene 1955.

This episode shows how the polymerization of diolefins had some influence on the polymerization of alpha-olefins.

I should add that in the case of polymerization of diolefins we came relatively early to clarify some aspects of the nature of the catalysts and the mechanism of stereospecificity. The interpretation process was faster than in the case of the polymerization of mono-olefins for the fact that the stereospecific catalysts for the polymerization of diolefins were basically all homogeneous. I bring few examples.

It was known since '64 that the catalysts based on cobalt and nickel used for the polymerization of dienes had ionic nature (G. Natta, L. Porri, Polymer Preprints, 5, 1964: 1163). In the case of the catalysts for the polymerization of 1-alkenes has come to the same conclusionvonly after they have been identified soluble catalysts for this class of monomers, so the catalysts based on metallocenes.

In the first half of the '60s was clarified that the formation units of 1,4-cis and 1,4-trans was to be put in relation with the structure “anti” and “sin” in the allylic units respectively. In addition, since '64 it was proposed a mechanism for the formation of polipentadiene 1,4-cis syndiotactic, still substantially valid, based on what oday is called "migratory insertion mechanism" (G. Natta, L. Porri, cited work).

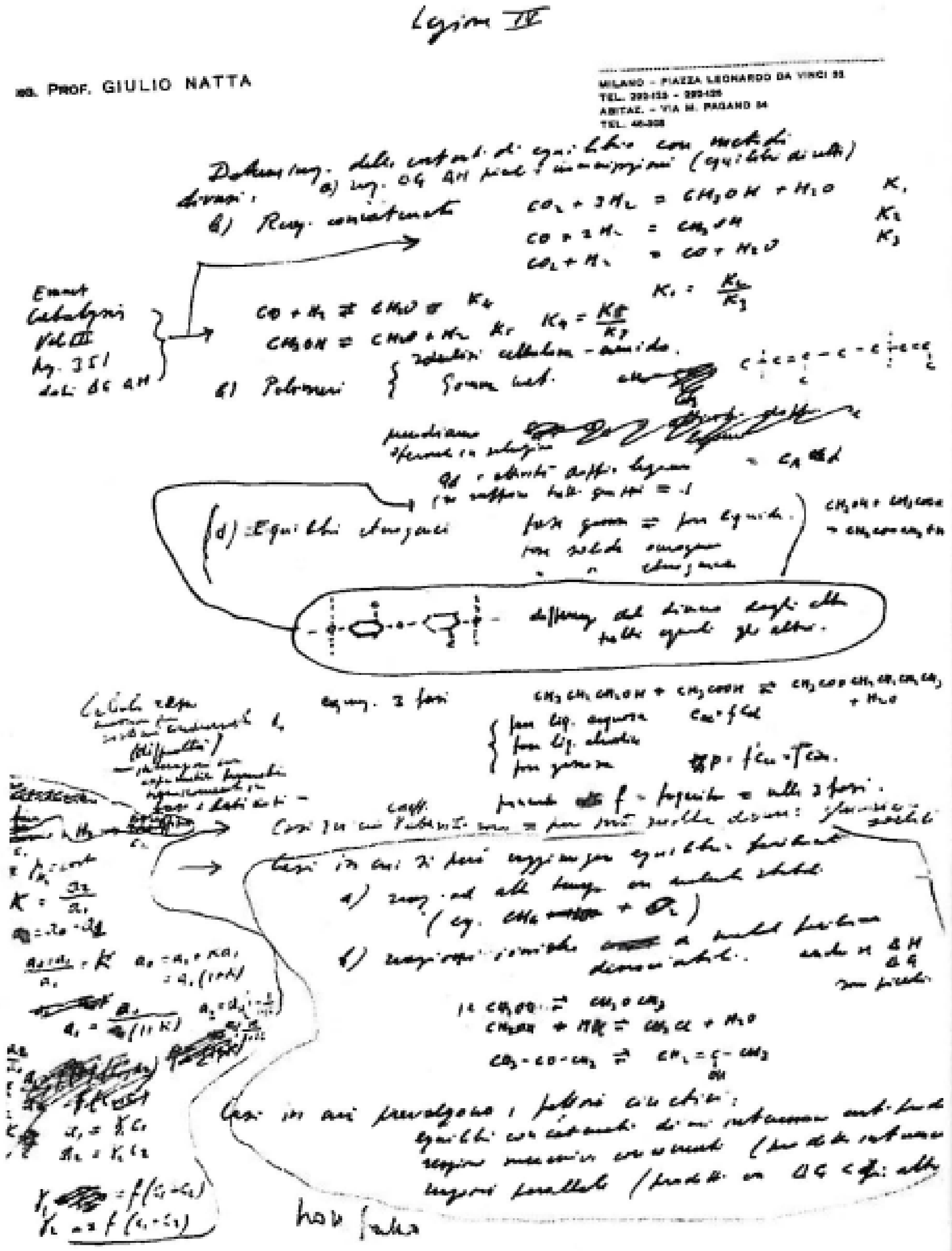
Finally, let me cite the case of metilalluminoxane, from 1979 used as cocatalysts for systems based on metallocenes. Few people know that the aluminoxanes generally (even if the metilalluminossani in particular) were already used in the 60s for homogeneous catalysts for diolefins, because significantly more active than aluminum alkyls containing no Al-0-Al bonds. Work of the group over the diolefins in Milan on these catalysts based aluminoxanes have appeared since 1967, but in these work was being paid little attention on the part of those who worked on the polymerization of mono-olefins, at that time primarily interested into heterogeneous catalysts.

ITALO PASQUON

I started to work - if I may say so - with Prof. Natta student in the fall of 1952. He assigned me an experimental thesis that I finished with Giorgio Mazzanti and Piero Pino, with good results, enough that the work was published before I graduated in December 1953.
In '55, after the military service, I returned to the Politecnico, where Professor Natta made me immediately appoint temporary assistant. Then I went to full-time assistant.
In '56 I was given the responsibility of Industrial Chemistry Course I.
After this brief presentation I would like to first point out that Giulio Natta was not only a great scientist, but also a great master. As noted by Prof. Biardi, Prof. Natta has been able to make Italy one of the most beautiful and prestigious Schools of Modern Chemical Engineering. On his return to Milan, in 1938, the Chair of Industrial Chemistry, he imposed the course on radically new bases: rather than merely to illustrate the processes of the chemical industry, as it was the tradition, he based the teaching on submission and application fundamentals of chemical, physical-chemical and technology necessary to understand the logic, I would say the philosophy to be followed in the implementation process, of production and the chemical plants. Thus he gave the young students the training and tools necessary to address the many activities in the chemical industry and its evolution.
As long as his health allowed him Prof. Natta personally always kept his lessons, carefully preparing, much to ask not to be disturbed before entering the classroom. But when his health would not permit more asked me to replace it and to hold, in addition to mine, also its course of Industrial Chemistry II and handed me the notes prepared for each lesson. I would like displays some of them, although difficult to read, as they say much more than any word.
In a transparent see data of thermodynamics, in another is illustrated Eyring's theory, we find problems in other heterogeneous catalysis subsequent reactions, a topic on which he had made original studies already published.
With this I think I have given you an idea eloquently of Giulio Natta master and teacher.
In 1955 he asked me to take care of diffraction of electrons with Paolo Corradini, with which I stayed just the time required to complete a work of structural chemistry.

PAOLO CORRADINI - A fundamental work, unfortunately in Italian.

PASQUON - You can judge it better than me. However, this work was amusing. But Prof. Natta asked me to take care of polymerization catalysis, with Ettore Giachetti, a chemical of great value and a friend, who died prematurely.



Lezione IV

ING. PROF. GIULIO NATTA

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b) Reaz. concatenate

$CO_2 + 3H_2 = CH_3OH + H_2O$ K_1

$CO + 2H_2 = CH_3OH$ K_2

$CO_2 + H_2 = CO + H_2O$ K_3

$CO + H_2 \rightleftharpoons CH_2O$ K_4

$CH_3OH \rightleftharpoons CH_2O + H_2$ K_5

Emmet Catalysis Vol III pag. 351 dati ΔG ΔH

c) Polimeri

d) Equilibri

$CH_3CH_2CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_2CH_3 + H_2O$

$CH_3OH \rightleftharpoons CH_3OCH_3$

$CH_3OH + HCl \rightleftharpoons CH_3Cl + H_2O$

$CH_3{-}CO{-}CH_3 \rightleftharpoons CH_2{=}C(OH){-}CH_3$

non fatto

Fig. 1.

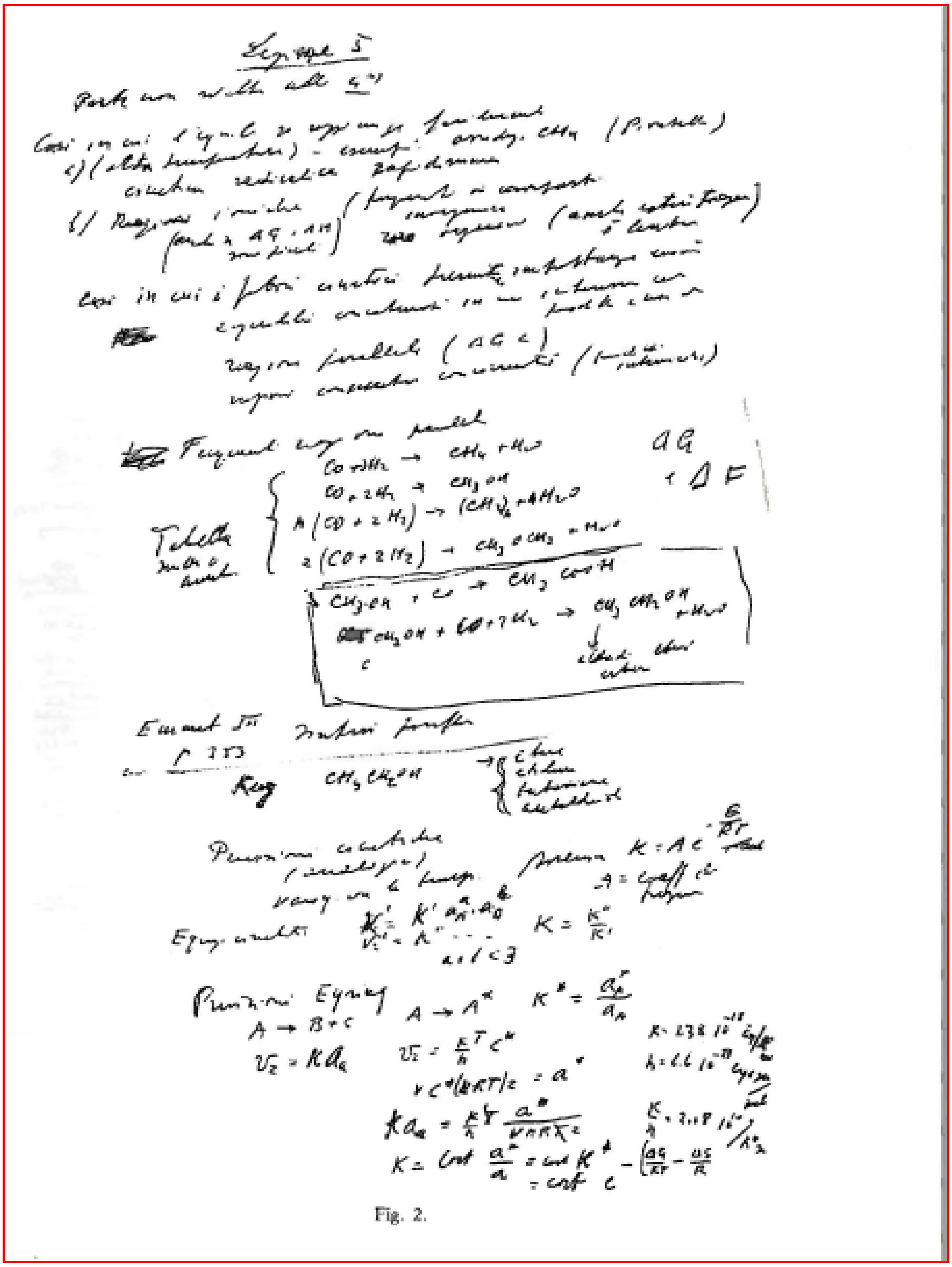

Fig. 2.

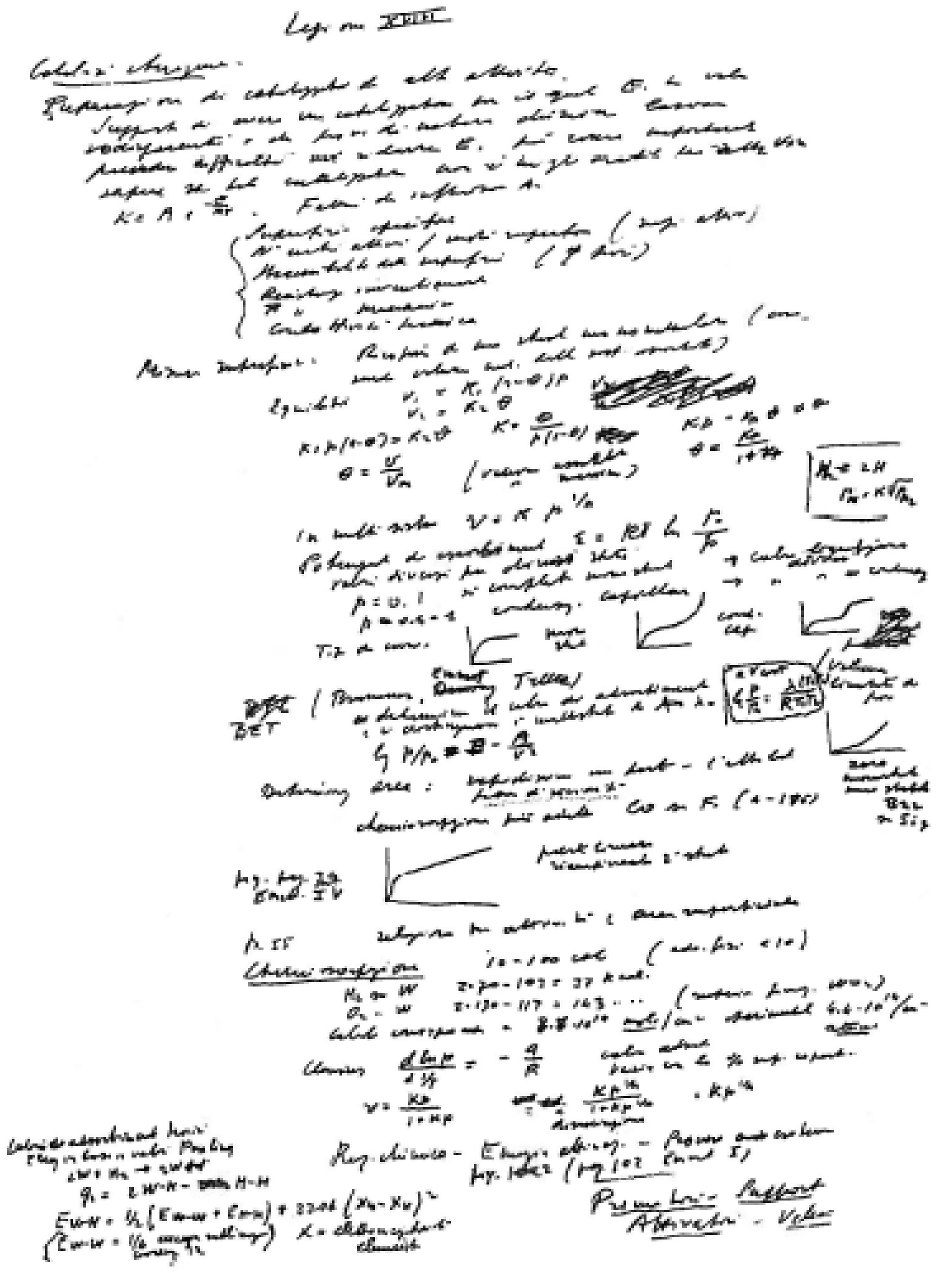

Fig. 3.

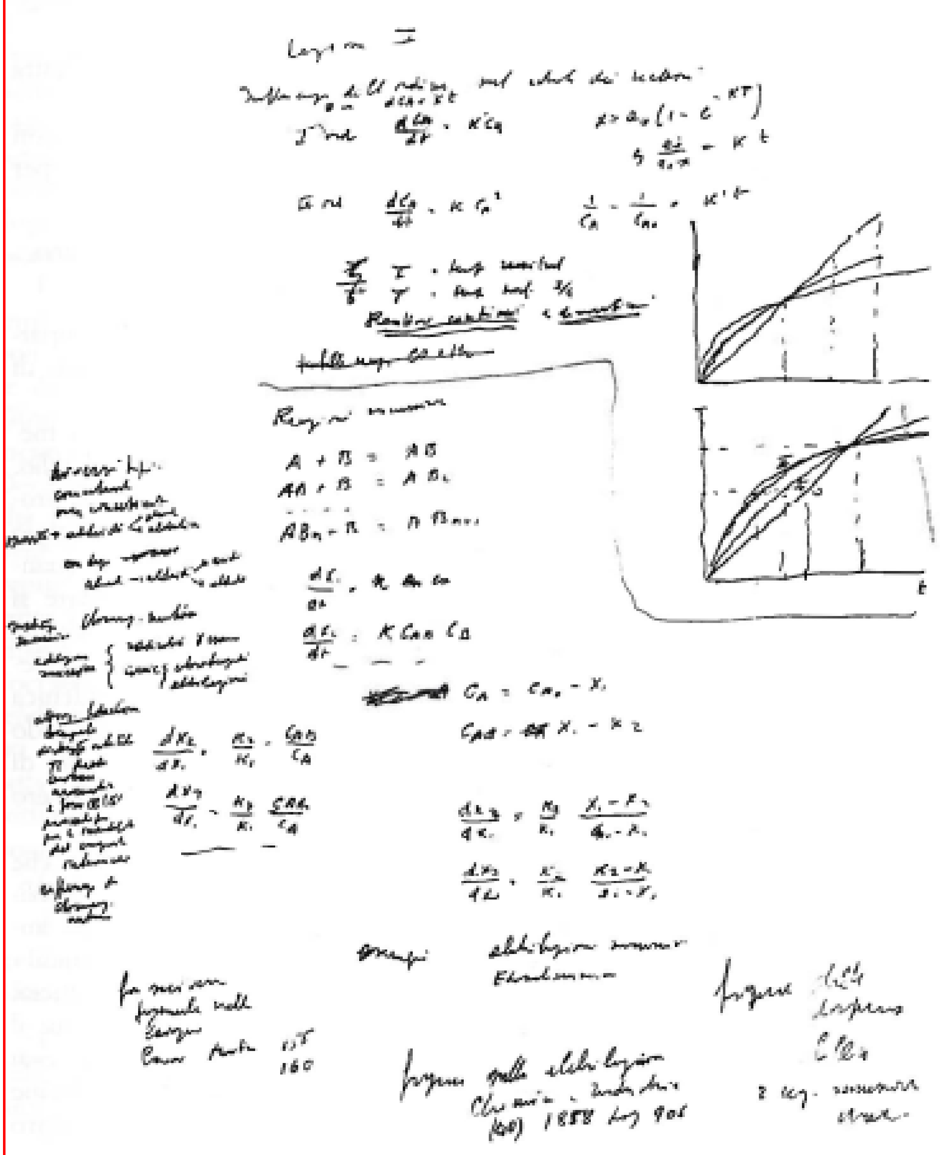

Fig. 4.

I want to remember the episodes that stucked in my memory: the friends and colleagues today present will correct me if I'm wrong.

Shortly after the discovery of stereospecific polymerization of propylene he called in his study some of us definitely Giorgio Mazzanti, Alberto Valvassori and Paolo Chini. He said, more or less, as follows: "If you disturb the attitude of polyethylene to crystallize it will be possible to obtain a good elastomer because the rotation around the bond carbon-carbon is not hindered and allows for wide swings. This result can be obtained by introducing into the polyethylene chain propylene units randomly distributed and copolymerizing ethylene with propylene; since we know polymerize each of these two monomers with the same type of catalyst, the copolymer should be easy to be prepared".

This insight that seems trivial in these terms, the fact is that few days later Giorgio Mazzanti, with his group prepared the copolymer ethylene-propylene. In '58, less than three years later, the first plant to produce ethylene-propylene copolymers was launched in Ferrara.

On another occasion - I think in 1960 - called us into his office Ettore Giacchetti and Adolfo Zambelli, to tell us: 'We have to find out the syndiotattic polypropylene, for patent protection reasons". I dare to say: “if exist we have already done it": at that time we had tried dozens catalyst and for each polypropylene prepared we had the RX spectrum provided by Paolo Corradini.
On the spectra of a series of polymers obtained, if remember well with dietilmonofluoruro aluminum and titanium trichloride, there was a small peaks that Paolo Corradini called "fly shit". This was happening on a Thursday or a Friday, the following Monday Paolo Corradini had already defined the structure of syndiotactic polypropylene.
In the raw material we had prepared syndiotactic polypropylene has been present perhaps even at l% dosages. We had to separate it. I remember that the Prof. Natta said to us: "Take a column, fill polypropylene isotactic very pure, solve your polymer in hot toluene and pass the solution column: the iso must remain retained by the filler in the column while the “syndio” will pass. And so it was: we got a fraction rich in syndiotactic polypropylene. Shortly after Adolfo Zambelli managed to find catalysts that gave almost exclusively syndiotactic polypropylene.
One last episode that I want to remember dates back at the beginning of sixties. As is known, ethylene-propylene copolymers being saturated are not directly vulcanizable with sulfur. It was important to prepare of curable copolymers. Prof. Natta called some of us, with Giorgio Mazzanti, Lido Porri and someone else to talk about how to obtain such polymer, or better a curable terpolymer. We decided to use the norbornene as termonomer, monomer which was provided to us by Lido Porri. So we got a terpolymer containing unsaturations and Giovanni Crespi vulcanizes it. All of this happened within three days. The singular fact of this episode it is not the result, because it turned out that it was anticipated a few weeks by U.S. patents, but the fact that in this occasion, I do not remember if on Saturday or Sunday, Prof. Natta telephoned me to know the outcome of the tests. So far still nothing strange, but the fact, I would say moving, is that the phone call I received was made after a delicate surgery which he had been subjected. At the hospital I found him he was walking with his head bandaged, arm in arm with Mrs. Rosita. This was Giulio Natta.

FRANCESCO MINISCI - I wanted to tell you that these notes of Natta may be useful for the Library of the Academy of the Lincei and the Science Museum.

PASQUON - I have about twenty of these notes Natta and is the first time I show them: they are of course available to the family, I have promised to Mrs. Franca and Giuseppe Natta.
If you want some of these originals are deposited somewhere, let us know.

ADOLFO ZAMBELLI

I arrived at the Politecnico in 1956 as a graduate student in Chemistry (I was from the University of Pavia) of Professor Natta. In 1957, graduated, I was hired by Montecatini and destined to stay with Natta. I had arrived, as often happens to me, a little late, when the fundamental contributions had already been given, although recently (isotactic polymerization-specification of propylene and other a-olefins, saturated and unsaturated elastomers and many other things).

Sure, there were still many things to do and so many things to understand and, I would just like to mention the curiosity of Natta, typical of the born researchers, and his attitude towards beginners (as I was), telling a small episode in which I was involved years later.

In 1965, Flory and co-workers published a series of work (eg J. Amer. Chem. Soc, 88, 1966 2873) where it was argued that the viscoelastic properties of highly crystalline isotactic polypropylene were interpretable only by admitting that the macromolecules in reality were not highly stereoregular, but containing at least the 5% stere-irregularity (syndiotactic dyads) randomly distributed. The argument was not only of academic interest, but also for the patenting because, by implication, questioned the definition of polypropylene reported in the patent Natta-Montecatini and would compromise the grant. Since I had worked on the characterization at the molecular level of polypropylene via 1H NMR (were not still available techniques of 13C NMR nor even high-field spectrographs), Natta called me, along with two senior colleagues and more experts to discuss the matter. I sustained that the only spectroscopic technique that could quantitatively clarify definitively the macromolecular structure of isotactic polypropylene was the nuclear magnetic resonance and I proposed a program of crucial experiments (for the truth very expensive) which, in short, consisted in the synthesis of a series of propylene selectively deuterated in their polymerization with isospecific catalysts and the comparison of the 1H NMR spectra of related polymers. I was very convinced of what I said and therefore I was very surprised and annoyed when colleagues participating in the meeting heavily criticized the approach I proposed, according to them, it almost certainly would not come to fruition because:

l) The synthesis of the monomers selectively deuterated was not described, it was very expensive and probably would have failed, and 2) supposed to have the deuterated monomers, during polymerization were possible “scrambling" H-D which would have invalidated the results.

I replied hardly reiterating that what I had proposed had no alternative that the risk of not getting nowhere was ran by me and Montecatini, which otherwise was only riscking to pay me for six months without conclude anything. The meeting ended without Natta saying anything. A few days later I met him at the entrance of the Institute, I greeted him and he said only, "Zambelli, do your best". It did not take more, because I was determined to come anyway in charge of the matter.

Looking back at a distance, I think I understand the dissenting opinions and the risks. The real risk was not that the experiment fails (sore little), but he could fully giving reason to Flory. I brought forward the work (I was fanatically convinced in what I was doing and it did not pass in my mind this possibility) and fortunately we could demonstrate that the highly isotactic polypropylene was containing at the most 2% of syndiotactic dyads (this was the sensitivity limit of the spectra) and we published the results (Makromol. Chem., 110, 1967).

Then I discovered that, as a true researcher, Natta was curious till the imprudence and he was also brought to trust in the enthusiasm all its employees, even the youngest.

ENRICO ALBIZZATI

I cannot say I have a deep knowledge of prof. Natta exclusively for personal or age reasons. I should note though, even though I met him a few times, I had a truly "vital" relationship with him because he signed me the authorization to use the canteen of the Polytechnic.

Extremely deep was instead my interaction with the scientist of his school: one of between all of them prof. Umberto Giannini recently disappeared.

I had the fortune to work with him for about 30 years and of had him as a consultant when I moved in Pirelli.

Umberto Giannini really taught me a lot, resulting to me and his collaborators not only a model of scientific rigor, but also an interpreter of the moral stature that hovered in the group of Natta.

I would like to mention some of the most important achievements of the prof. Giannini.

For example the synthesis of benzyl derivatives of Zirconium and Titanium, the first example of organometallic compounds with binding transition metal-carbon stable.

These compounds have been employed as monometallic catalysts in the synthesis of polyolefin. In particular in the case of propylene this foundings represented the first synthesis of an isotactic polymer in homogeneous solution.

As a second example I can say that the contribution of prof. Giannini to the knowledge and the industrial development of Ziegler-Natta catalysis were highly significant as evidenced by the numerous journals and as author in numerous patents.

Indeed, after the discovery of high yield catalysts based on $TiCl_3$ and $TiCl_4$ supported on $MgCl_2$ carried out in Ferrara by the group of Dr. Adolfo Mayr (which died recently) extremely active in the synthesis of poorly stereoregular polyethylene and polypropylene, prof. Giannini, with brilliant idea, discovered that it was possible to increase the stereospecificity of the catalytic systems using electrondonor compounds.

In previous intervention Giampiero Marini showed the evolution of these high yield catalysts occurred through the work of more than 30 years of scientific research conducted by the group of Giannini which I am honoured to have been part.

This journey started with the use of esters of aromatic acids, continued with the phthalate-silane coupled to the latest combined diethers with polymerization processes that become more sophisticated, has allowed Montedison and its subsequent developments (Himont, Montell now Basell) to hold an indisputable leadership in the production of polypropylene for almost half a century to present day.

I wanted to underline another dimension to this bright period of research collaboration between the School of Prof. Natta and Montedison, the birth of a new professional family: the men of the Patent Office.

Of all I would like to remind Dr. Lido Zambon who taught us how important it was invented but also important to protect the discovery with a proper patent coverage.

Truly genius was his intuition to claim in many patents the X-ray spectrum dell'MgC_2 "activated" as essential part of the catalysts. This has been and continues to be an insurmountable obstacle to competing companies.

I worked 29 years in the frame of the Ziegler-Natta catalysis, today I take care of others things, I’m CEO of Pirelli Labs, what I have acquired by the School of prof. Natta and I tried to transfer in this new activity is the will continue to be even in a new field the frontrunner in terms of knowledge and therefore to have the ambition “to get copied and not to copy others."

FAUSTO CALDERAZZO

In my time I will try to highlight some important scientific results arising from the School of Prof. Natta, who have not yet been mentioned in the course of the interesting discussions of this conference, particularly centred on the results of all innovative obtained in the field of stereospecific polymerization. Prof. Natta, I had the privilege of knowing in my role of collaborator, in the years 1954-1962 at the Institute of Industrial Chemistry the Polytechnic of Milan, was also active in different fields than only the polymerization, obtaining also here innovative results at the international level. In particular, he has faced fundamental problems in the field of chemistry of carbon monoxide and in the hydroformylation (the process by which olefins are converted to aldehydes with carbon monoxide and di-hydrogen).
The first point a) here below highlights the fact that at constant pressure of CO (Pco), the speed of the hydroformylation reaction increases as the pressure of di-hydrogen increases. While this first step is also quite intuitive and consistent with the composition of the reagent, the second point b), indicates that, on the basis of experimental data, a constant pressure of-hydrogen the speed of the reaction increases with the Pco up to a maximum located in the neighbourhood of 10 atm, and then decreased with a further increase.

The Hydroformylation Reaction

[Olefin + CO + H2 → aldehydes]
a) At constant CO pressure, rate increases at increasing di-hydrogen pressure;
b) at constant di-hydrogen pressure, rate increases with increasing CO pressure up to about 10 atm, and decreases at higher CO pressures.

(G. NATTA, R. ERCOLI , S. CASTELLANO, F. H. BARBIERI, J. Am. Chem. Soc., 76, 1954: 4049)

The data presented here derived from a work that Prof. Natta and his collaborators, Ercoli, Castellano and Barbieri published in 1954, where you communicate the discovery of a phenomenon, still do not fully clarified, called the actual negative pressure carbon monoxide on the rate of hydroformylation. Similar effects have subsequently been identified for other catalytic reactions involving systems olefin/CO/Co2(CO)8.
This effect has been published substantially in contemporary by two other research groups. No work of Prof. Natta and his collaborators appeared in the "Journal of the American Chemical Society" in 1954.
Almost simultaneously appeared a note of "Chemistry and Industry", while the announcement of the same effect also occurred at the 126th Meeting American Chemical Society in September 1954 by Irving Wender and co-workers, operating at the Bureau of Mines in Pittsburgh.

The Hydroformylation Reaction (effect of CO *pressure on rate)*

- G. NATTA, R. ERCOLI, S. CASTELLANO, F.H. BARBIERI, *].* Am. Chem.Soc., 76, 1954: 4049.
- A.R MARTIN, Chem. Ind. (London), 1954: 1536.
- H. GREENFIELD, S. MELIN, I. WENDER, !26th ACS Meeting, New York,Sept. 12-17, 1954.

In a subsequent article on "Chemistry and Industry" [G. Natta, R. Ercoli, S. Castellano, Chim. Ind. (Milano), 37, 1955: 6], G. Natta and his collaborators present the details of the kinetic study of the hydroformylation reaction of cyclohexene. It is always difficult to identify the critical points of scientific development. There is however to be considered that these data, obtained in the laboratory of Prof. Natta, have led to the opening of other fields of research, some of which are still very present in the field of Inorganic Chemistry. Indeed, in connection with the so-called negative effect mentioned above, Ercoli and co-workers had already studied in the fifties balance between

Co2(CO)8 and Co4(CO)12, hence with the species having a ratio CO/Co of 3, lower than the precursor Co2 (C0) 8.

At that time, was found that the formation of the derivative tetranuclear is endothermic, data later confirmed by studies carried out by Gyorgy Bor in the Laboratories of the ETH in Zurich, at the time headed by Prof. Piero Pino.

The release of bonded carbon monoxide determines the formation of metal-metal bonds, being generally more weak than the metal-CO bond determines the endothermic nature of the process.

Endothermic formation of metal clusters

2 Co2(C0)8 ↔ Co4(C0)12 + 4 CO
a) ΔH0 = + 138 ± 2 kJ mol-1
b) ΔH0 = + 123.3 ± 2 kJ mol-1
ΔS0 = + 564 ± 12 *]* mol-1 K-•

a) R. ERCOLI, F. BARBIERI-HERMIITE, Ace. Naz. Lincei. Cl. Sci. Fis. Mat. Nat. Rend., 16, 1954: 249; Chem. Abstr., 48, 1954: 10408i.
b) G. BoR, K. DIE1LER, *]*. Organometal. Chem., 191, 1980: 295.

2 Rh2 (C0)8 ↔ Rh4(C0) 12 + 4 CO
ΔH0 = + 58.6 ± 10 kJ mol-1
ΔS0 = + 305 ± *25* J mol-1 K-1

F. OLDANI, G. BOR, *]*. Organometal. Chem., 246, 1983: 309.

Paolo Chini, who, after a period spent in Ferrara, he returned to the Polytechnic of Milan, began to study metal system in cluster, getting the results of high international level. It must consider, as the rest Chini himself declares in his article summarizing, that the interests in respect of the systems in the pluri-metal cluster were derived from studies of Natta and co-workers on the effect of CO on the speed of the hydroformylation reaction. We cannot finish this topic without mentioning the fact that at the end of the fifties, Corradini and his team had solved the structure of the compound tetranuclear Co4(CO)12. The conclusions reached were then fully confirmed, for this compound, by a follow-up study some years later by F. A. Cotton.

Piero Pino began his scientific career at the Polytechnic of Milan, and then, before you even move at ETH of Zurich, has spent many years of intense scientific activity at the University of Pisa, where he created a school of Macromolecular Chemistry very robust, and of which Professor F. Ciardelli is certainly one of most authoritative representatives.

I’m obliged to thank Prof. Natta for the initial years of my training at the Polytechnic of Milan, where we learned a methodology of work, soaking up the atmosphere of scientific innovation, and absorbed forever attachment to scientific research Giulio Natta was able to instill in your staff.

LUIGI CASSAR

It is an honour for me to close this meeting, even if undeserved.
I barely touched the Ziegler-Natta catalysis at the beginning of my career, when in 1961 I was at the "Donegani" Novara and I deposited a patent on the isotactic polymerization of styrene, in special solvents, which allowed to obtain important technological advantages.
It is, therefore, certainly undeserved opportunity offered to me and thank you too, because for me it is a great pleasure to find myself together with you after more than 40 years working in the industry.
We have talked about a man who was a great scientist, who was a great manager because he knew how to choose men, and he knew how to let them together and make them work. Who knows how many quarrels he had to overcome surely you had be confronted with different ideas and he had to activated himself in an smart way to find constructive solutions.
It was, therefore, a great man, a great manager, a great teacher, because it was also able to be a manager and these are conditions not easily repeatable: you can't find every day a scientist of that level.
The chemistry evolves, it is important today hydroformylation, tomorrow is important to the polymerization, the day after tomorrow are important other things, Biology, which then it is still chemistry, materials.
In the sixties, arguably, the presence of Chemistry in Italy was much stronger than today, Italy, little by little, lost and today there is a European Chemicals where Italy can do his part if plays cards correctly and whether it promotes adequate schools.
Natta was a great figure and I think that you will prove that: you demonstrated that it was a great and that is not easily repeatable what he did. I say no more, thank you very much for had me invited.

Courtesy of Accademia Nazionale dei Lincei – Fondazione Guido Donegani

INDICE

TAVOLA ROTONDA

PERSONAL AND/OR HISTORICAL NOTATIONS RELATED TO NATTA'S DISCOVERY OF STEREOREGULAR POLYMERS

Interventi di