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UNIVERSITY AND LARGE INDUSTRY FOR SUCCESSFUL TECHNOLOGY TRANSFER

PART 2: STEREOREGULAR POLYMERS

In 1954, a revolution began in the polymer world: Giulio Natta and his coworkers at Politecnico di Milano prepared, isolated and identified stereoregular polymers. Nature’s monopoly was broken. The collaboration with Montecatini resulted in the industrial development of isotactic polypropylene and polyolefin elastomers within a few years. The model of cooperation between a university and a large industry, which nowadays would be called open innovation, was indeed successful for the technology transfer.

The historical context

In the late 1940s, in a Europe devastated by the Second World War, there was a profound need to build a better world, one that could also provide for its population. During the war, people had suffered great hardship and now needed everything. Materials were a fundamental part of these needs: from fibres to make clothes to lightweight, resistant materials for a wide range of applications. At home, most objects were still made of wood, iron and steel. In the States, immediately after the end of the war, thousands of people queued up to buy nylon stockings.

The 1950s were the years of the petrochemical boom. The chemical industry needed fuel to power its engine.

The conditions were thus ideal for welcoming the arrival of synthetic polymer materials.

How it all began

Germany, 1952. The Achema Fair in Frankfurt, dedicated to the world of chemistry, also saw the presence of university institutes for the first time. Prof. Karl Ziegler of the Max-Planck-Institut für Kohlenforschung presented the novel results coming from the so called Aufbau reaction. Indeed, he was studying the addition reaction of ethylene with lithium alkyls and then with lithium aluminum hydride - a newly discovered, more soluble compound - obtaining an addition product with 4 ethylene units. But when he switched to the more soluble and active aluminum triethyl, he discovered the metallorganic synthesis of paraffins (as shown in Fig. 1). With the same organometallic compound, it was possible to prepare dimers of propylene. Ziegler wrote: “The new results open up new possibilities for pre-

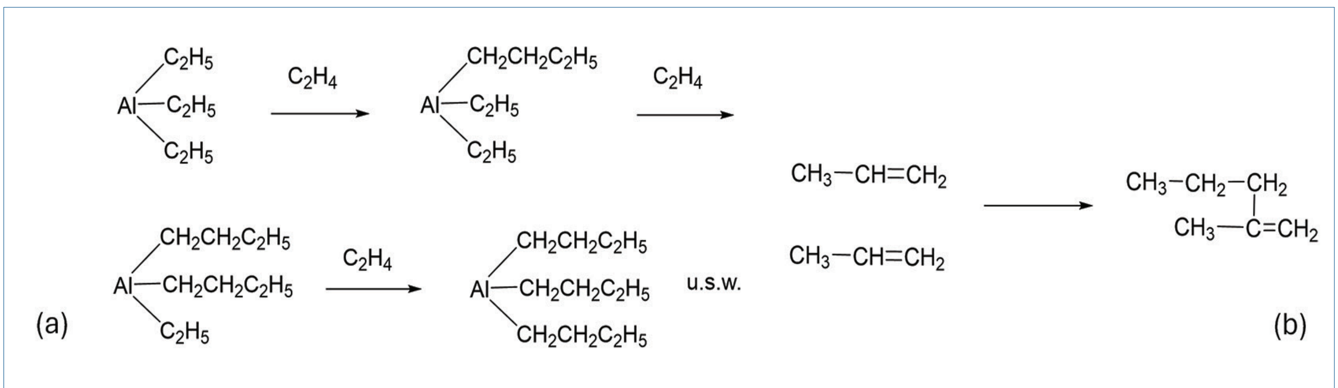

Fig. 1 - a) The Aufbau reaction; b) and the dimerization of propylene presented by Karl Ziegler in 1952. Scheme elaborated from [1]

parative organic chemistry and its technology" **[1]**. Giulio Natta attended the Achema Fair, saw Prof. Ziegler's presentation and could appreciate the novelty and the relevance of the Aufbaureaktion. He had experience with olefins, namely ethylene and propylene. However, working with cationic catalysts, he had obtained completely different results. Natta brought Prof. Ziegler's results to Politecnico di Milano, to the Institute of Industrial Chemistry, and discussed them with Pier Candiano Giustiniani, the CEO of Montecatini.

Giulio Natta and Montecatini

Natta's collaboration with Montecatini dated back to the 1930s, to the years of research into methanol synthesis, and resumed in the final phase of the project for the industrial production of synthetic rubber **[2]**. The collaboration between Natta and Giustiniani went beyond Montecatini and began in the 1940s in the Terni plant to produce butadiene from calcium carbide **[2]**. In 1947, Natta and Giustiniani visited the chemical plants in the United States. Giustiniani wrote: "We saw the olefin plants: it was already petrochemicals. In 1950, I moved to Montecatini. Natta followed me as a consultant. We had our first cracking plant in Ferrara. Acetylene chemistry had given way to ethylene chemistry" **[3]**. The Montecatini's transition from acetylene to ethylene and from coal to petroleum as the raw material for organic chemistry was characterized by the cooperation of Natta and Giustiniani.
In 1952, Natta was the director of the Institute for Industrial Chemistry of Politecnico di Milano. Montecatini financed, every year, a three-month School of specialization, sending about ten students to complete their training, with the agreement that the most promising ones would be guided towards an academic career. Around ten of Natta's professors received what nowadays would be the equivalent of 450 euros per month, while students' research was financed with approximately 280 euros per month. The total investment, for three months and every year, was more than 20 thousand euros.
Natta asked Giustiniani to acquire exclusive license for Italy of Ziegler's patent on the *Aufbaureaktion* and the right to be informed of any new development in Ziegler's research. However, the results were preliminary, $AlEt_3$ was a dangerous chemical, not commercially available, and the industrial development was very uncertain. A polite refusal would have been expected. Instead, Giustiniani and Montecatini accepted. Natta and Giustiniani also agreed on a research program for the industrial development of $AlEt_3$, and young researchers, Paolo Chini, Roberto Magri and Giovanni Crespi, were sent to Mülheim.
And the developments came, in a serendipitous way. Prof. Ziegler discovered the nickel effect. Only a dimer of ethylene was collected from an autoclave accidentally containing traces of nickel. By investigating other transition metals, a new polyethylene, linear and with high molecular mass, was obtained at normal pressure. The best results were achieved with the combination of $TiCl_4$ and $AlEt_3$ **[4]**.

The beginning of a revolution. The birth of isotactic polypropylene

These results were known at Politecnico. As Natta reported in his Nobel Lecture: "I then decided to focus attention on the polymerization of monomers other than ethylene; in particular, I studied the α-olefins" **[5]**. This was not a trivial decision, because ethylene and propylene behaved differently in polymerisation and because there was no mention of this polymerisation in the German documents.
This decision marked the beginning of a revolutionary phase. In 10 months, from March to December, an important part of the history of polymers was written. The research was conducted under the direct or indirect guidance of Giulio Natta. "At the beginning of 1954 we succeeded in polymerizing propylene, other α-olefins, and styrene" **[5]**. Probably, the most famous picture of those years, to be seen in Fig. 2, is Giulio Natta's diary, with 'polypropylene: done' written on it, to report the result of the experiment performed by Paolo Chini.
But was it true? "The crude polymer was a mixture of different products" **[5]**, a semi-solid, sticky material. Giulio Natta's main coworker was Piero Pino, an organic chemist. He decided with Natta to fractionate the product obtained by Chini, using solvents with

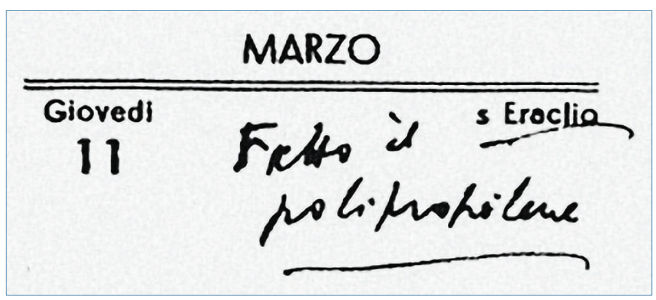

Fig. 2 - March, 11^{th} 1954: the entry in Giulio Natta's diary **[6]**

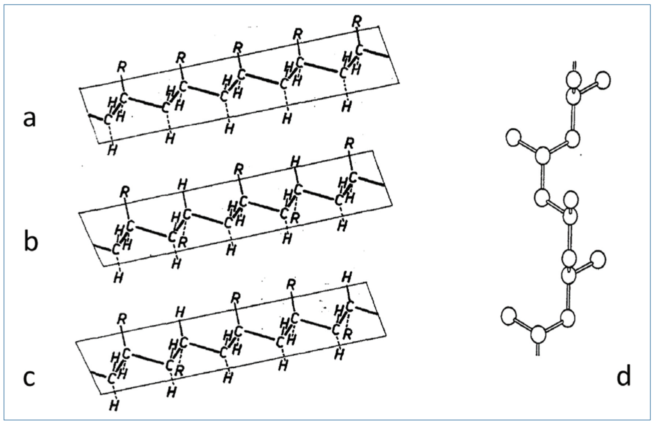

Fig. 3 - Chains of head-to-tail vinyl polymers arbitrarily sketched on a plane: a) isotactic, b) syndiotactic, c) atactic, d) side view of the chain structure of isotactic polypropylene. Taken from **[5]**

increasing boiling points. Although the fractionation technique had been reported in the literature since the late 1930s and was familiar to organic chemists, it had never before been applied to polymers. Propylene polymers were isolated from the different fractions: amorphous, slightly crystalline, and more crystalline. By increasing the boiling point of the solvents, the molecular weight and the crystallinity of the polymer increased. But the molecular weight increased gently, whereas only the fraction residual to the extraction with n-heptane was highly crystalline. "*Natura non facit saltus*" (Nature does not make leaps) **[5]**. So, crystallinity was not caused by the molecular weight; there was another explanation: the polymer's stereoregularity. In a polypropylene chain with finite length, all the asymmetric carbon atoms had the same relative configuration, *i.e.* the methyl groups were on the same side of the polymer chain. The work done by Paolo Corradini, a brilliant young coworker with education on structural investigation, led to decrypt the structure of these new polymers, called isotactic: "By accurate examination of the structure of isotactic polymers on fiber spectra, we could establish that all crystalline isotactic polymers have a helical structure" **[5]**. The sketch on a plane of the chains of vinyl polymers and the side view of the chain of isotactic polypropyene are in Fig. 3.

The industrial development

However, the isotactic polymer was only 20% of the total product. Hard to imagine an industrial development. Giorgio Mazzanti, discussing with Piero Pino, proposed to use a crystalline titanium compound, in order to possibly promote a regular propylene arrangement **[7]**. Titanium trichloride was prepared via sublimation by Umberto Giannini. The combination of $TiCl_3$ and $AlEt_3$ was used and the autoclave was found filled with a white crystalline powder of polypropylene, with isotacticity equal to 85-90%.
The catalyst was then ready for industrial development. $TiCl_3$ was used at the industrial level up to end of the 1970s.
In those days, much work still had to be done to get at the industrial scale and to find real applications for the isotactic polymers, rather than just as a decoration on a Christmas card, shown in Fig. 4. Montecatini's CEO, Giustiniani, firmly believed that a chemical company should develop its own technologies, yet he relied on the Professor's research. He did not hesitate and generously financed all the research and development activities necessary to achieve the industrial production of isotactic polypropylene. Between 1952 and 1962, Giustiniani financed Natta's research group with approximately 7.5 million euro, in salaries for Natta and collaborators and labora-

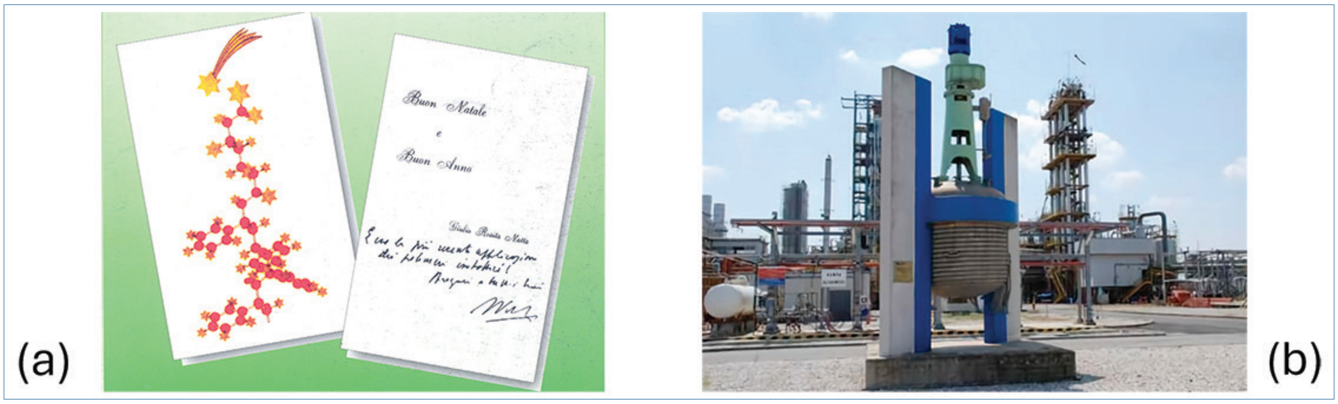

Fig. 4 - a) Christmas card from Giulio Natta and his wife, Rosita Beati: "here is the latest application of isotatcic polymers"; b) Ferrara: the first plant for the production of iso-PP

tory expenses. The significance lies not so much in the absolute value of the funding but in having the certainty of being able to count on a substantial sum and a good number of coworkers, more or less constant, over the years. The importance of achieving a critical mass was clearly recognized.
Natta closely followed all industrial developments. As recalled by Mazzanti **[7]**: “Natta, accompanied by some of his closest collaborators, visited Ferrara twice a month and Terni once a month for scientific exchanges rich in new ideas.” The Montecatini Research Centre in Ferrara, which is still dedicated to Giulio Natta, made a fundamental contribution: the yield of isotactic polypropylene increased significantly and the polymer isolation process was perfected to eliminate the catalyst and amorphous polymer. Four pilot plants were installed for aluminum compounds, polyethylene, polypropylene, and rubbery copolymers.
The Ferrara plant for the polymerisation to isotactic polypropylene, shown in Fig. 4, began operating within four years from Natta’s note in his diary.
In the competition with ANIC and AGIP, Montecatini was the company with the least capital available. Despite that, huge efforts were made to develop plants in Ferrara, Terni, Novara, and Brindisi. This led to the dramatic economic crisis of the early 1960s and the subsequent merger with Edison.

Stereoregular polymers

But not only polypropylene. Many other olefins were polymerized to isotactic polymers, all with helical structures, but with different pitch: 1-butene, 5-methyl-1-hexene, 5-methyl-1-heptene, allylbenzene, 4-phenyl-1-butene, 4-methyl-1-pentene, 4-methyl-1-hexene, vinylcyclohexane, styrene, 2-methylstyrene.
Natta moved his research onto a different family of monomers: the diolefins, and 1,3-butadiene was selected as the first candidate. Natta had experience with butadiene, due to the work on the preparation of rubber from butadiene and styrene in the 1940s, already in cooperation with a large company, Pirelli, at that time **[2]**. Butadiene is a very interesting monomer, because it gives rise to different microstructures. However, Natta was sceptical, because, in his previous experience, he obtained only the 1,4-structure, mainly 1,4-*trans*. The research of another young coworker, Lido Porri, led to new stereoregular poly(dienes), to be seen in Fig. 5. For the first time, a polymer with an alternate placement of the lateral substituent was obtained: it was called syndiotactic. After few months, isotactic polybutadiene was obtained and finally, a polybutadiene with the same configuration as natural rubber. For the first time, the same monomer led to different stereoisomers **[5]**.
If there were so many members of the polybutadiene family, was isotactic polypropylene an only child? By carefully examining the X-ray patterns of many isotactic samples, Corradini and Natta attributed some “strange” peaks to syndiotactic polypropylene, which was successfully isolated by fractionation and subsequently prepared directly through synthesis **[5]**.
Many other monomers were polymerized to isotactic polymers, as can be seen in Tab. 1.
And many other stereoregular polymers were prepared. Crystalline copolymers, such as random copolymers with isomorphic monomeric units (butadiene/1,3-pentadiene (1,4-*trans*), styrene/monofluorostyrene) and polyesters from dimethylke-

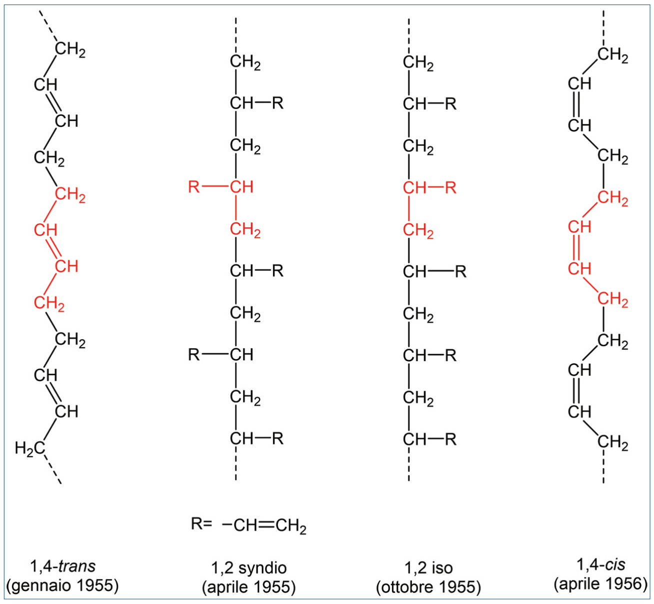

Fig. 5 - Stereoisomers of poly(1,3-butadiene)

Monomer	Catalyst
vinyl alkyl ethers, trans-alkenylalkyl ethers, *cis*-β-chlorovinylalkyl ethers, *trans*-β-chlorovinylalkyl ethers 4-methoxystyrene; *N*-vinylcarbazole; *N*-vinyldiphenylamine, benzofuran	Cationic
vinylpyridine; sorbates; acrylates; aliphatic aldehydes	Anionic

Tab. 1 - Monomers other than olefins polymerized to isotactic polymers tene and aldehydes. Stereoregular alternate copolymers, ethylene/1,3-butadiene, ethylene/dimethylbutene, ethylene/cyclopentene.

Catalyst

All these results demonstrated the key role of the catalyst: indeed, both different transition metals and different ligands led to different stereoregular polymers. In the early 1970s, the titanium halide was supported on $MgCl_2$, identified by Corradini and Ivano Bassi. Giannini conceived the use of Lewis bases (donors), to enhance the stereospecificity of the catalyst: they coordinate on the (110) face of $MgCl_2$ and $TiCl_4$ forms dimeric species only on the (100) face, leading to highly isospecific sites **[8]**. As shown in Tab. 2, several generations of donors have been developed. The achieved isotacticity index is as high as 99% **[9]**.

In the following decades, the interpretation of stereospecific induction was developed and experimentally demonstrated by Natta's collaborators: Giuseppe Allegra, Corradini, Pino, and pupils such as Gaetano Guerra, and was based on the non-bonded interactions between the approaching olefin and the catalytic site **[10, 11]**. The participation of the growing chain in the enantioface discrimination was revealed: the chiral orientation of the growing chain induces the selection of the enantioface. The absence or presence of the growing chain is responsible for the opposite topicity of the 1-olefin insertion **[12]**.

"I don't' know exactly how many stereoregular polymers Natta and his collaborators have synthesized, but I think more than 90. The crystal structures of these polymers were determined. Their chemical, physical, and, for some of them, mechanical properties were investigated. The relationship between physical properties and stereoregularity was studied. Suitable catalysts for the production were identified. The mechanism of stereoregulation was studied. And finally, the foundations of polymer stereochemistry were laid **[13]**".

Elastomers

Immediately after the synthesis of polypropylene, Natta set the goal of preparing an elastomer, with properties similar to those of natural rubber but without double bonds in the chain, hence more resistant to degradation. He decided to move from the polyethylene chain: "The free polymethylene molecule should theoretically behave as a good, if not a very good, rubber. We all know that polymethylene is not a rubber… excessively easy crystallization. The problem has been solved with the ethene-propene copolymers" **[14]**. Propylene was thus given the task to prevent crystallization. Decades after, it was demonstrated that 2,1-propylene mis-insertions, obtained with the vanadium catalysts, play a key role in preventing crystallization **[15]**.

In 1955 the ethylene/propylene copolymers were born and in 1958 they were on a commercial scale.

Patents

Patent applications began to be filed in the very first months of the research. The protection of a discovery is a driver of innovation. The Republic of Venice, in 1469, granted the first patent to a German printer for printing with movable types. This decision then allowed everyone to use printing and gave rise to publishing, even on an international scale.

On 6 June 1954, the first patent was filed in the name of Giulio Natta, claiming new high-crystallinity propylene polymers, still thinking about the decisive role of chain length. The second patent, filed on 27 July in the name of Natta, Pino and Mazzanti, claimed solid propylene polymers and the preparation of the catalyst in the presence of the monomer. This patent referred to the orderly arrangement of carbon atoms in space and began to discuss applications, from films to fibers. At the Politecnico, polypropylene was immediately extruded and spun,

Generation (year)	Catalyst composition	Productivity (kg_{PP}/g_{cat})	Xylene insoluble (%)
1st (1954)	δ-$TiCl_3$·0.33$AlCl_3$ + $AlEt_2Cl$	2-4	90-94
2nd (1970)	δ-$TiCl_3$·+ $AlEt_2Cl$	10-15	94-97
3rd (1971)	$MgCl_2$/$TiCl_4$/Benzoate + AlR_3/Benzoate	15-30	95-97
4th (1980)	$MgCl_2$/$TiCl_4$/Phtalate + AlR_3/Silane	40-70	95-99
5th (1988)	$MgCl_2$/$TiCl_4$/Diether + AlR_3	100-130	95-98
	$MgCl_2$/$TiCl_4$/Succinate + AlR_3/Silane	70-100	98-99
"next" (1999)	$MgCl_2$/$TiCl_4$/Diether + AlR_3/Silane	40-70	95-99

Tab. 2 - Heterogeneous Ziegler-Natta catalysts for isotactic polypropylene. Data taken from **[9]**

mainly by Giovanni Crespi. The first two patents were then extended to many countries. On 3 and 16 December 1954, patents were filed claiming the ideal catalysts for obtaining amorphous or stereoregular and crystalline polymers. For the first time, the term isotactic was written in a patent.
Natta's work has always been characterized by the goal of developing new discoveries and solving problems on an industrial scale. One could say that basic research benefits greatly from clear objectives. Natta has demonstrated that science and application are not an oxymoron but a synergy. His output includes 610 scientific articles and educational texts and 333 patent families. Research and development within the company - first at Montecatini and then at all the companies that followed - has always been characterized by a profound scientific content. This led to the development of robust technologies and intellectual property. Decades after the birth of the stereoregular polymers, more than 60% of the plants in the world operated under license from Montedison.

Seminal works

The works by Natta and coworkers were indeed seminal.
As demonstrated by the synthesis of polyacetylene, achieved in 1958 **[16]**, the Nobel Prize awarded in 2000 to Alan Heeger, Alan MacDiarmid and Hideki Shirakawa for the discovery and development of conductive polymers owes much to the work of Natta's group. Shirakawa talked about the science of serendipity: "The initial purpose of this study was to determine the polymerization mechanism of polyacetylene using the Ziegler-Natta catalysts. The accidental use of a hypercatalytic amount of a Ziegler-Natta catalyst (a thousand times more) gave polyacetylene films… an unforeseeable experimental failure" **[17]**.
Polyalkenamers were obtained in the early 1960s from ring opening metathesis polymerization with the aid of anionic coordination Ziegler catalysts **[18]**. In 2005, the Nobel Prize in Chemistry was awarded to Chauvin, Grubbs and Schrock was for the development of the metathesis method in organic synthesis.

A Revolution in Polymer Chemistry

A revolution occurred in polymer chemistry. And this was acknowledged by the scientific community.
Paul Flory (Nobel Prize for chemistry in 1974) wrote in a letter to Natta: "Your discoveries can be considered revolutionary in their significance" **[19]**. In a paper entitled "Revolution in polymer chemistry", the following was noted: "It is Natta who first recognized the chemical revolution that was taking place" **[20]**. When the first synthetic rubber award was given to Giulio Natta, "unusual originality, drive and power of sustained work" was reported **[21]**. Natta was aware of what was going on as well. When he asked Giorgio Mazzanti to work during summer, he added, "Don't worry. If things continue like this, we could win the Nobel Prize". And he said that what they were doing would continue to be researched in the coming century. Before March 1954, a stereoregular polymer had never been prepared, isolated and recognised. In the introduction to the Nobel Prize ceremony, Prof. Fredga said that Giulio Natta had broken nature's monopoly: 'The scientific and technical consequences of your discovery are immense and cannot even be fully estimated'.

Polypropylene today

In 2024, global polypropylene production was more than 80 million metric tons and the global market was valued more than 150 billion USDollars, that is about 0.2% of the gross domestic product of the entire planet. It is the most produced polymer and finds application in many different fields. More than 65% of propylene coming from petrochemical processes is used for polypropylene.
Around 60% of the over 400 million tonnes of plastic produced worldwide each year ends up as waste in landfill sites or dispersed in the environment. Primo Levi wrote: "It's the big problem with packaging that every experienced chemist knows about... polyethylene... flexible, lightweight and wonderfully waterproof, but also a little too incorruptible" **[22]**. However, most applications favour plastics for a lower impact on climate change. Plastic products emit 10-90% less CO_2-eq over their full life cycle than the nearest alternative **[23]**.

Legacy for today and the future

Intuition, ability, open-mindedness, passion, perseverance, awareness, a huge amount of work were definitely at the origin of such great results. But here, the interdisciplinarity, stemming from brilliant scientists with different backgrounds, should also be highlighted . Corradini used to say: "To achieve great things, one must be close in space and far in competence". An indispensable pillar, as mentioned above, was the constant funding. All these conditions were due to the cooperation with a large company.

Synthetic rubber **[2]** and stereoregular polymers. Driving force and organisation, with Giulio Natta protagonist, led to revolutionary discoveries and industrial production within just a few years of the initial phase. The organisation was based on the cooperation between a University and a large company, with a model that today could be called open innovation. Materials for the second world war and for the post-war recovery were the driving forces in the last century.

Today, sustainable development should be the motivation. A new generation of sustainable materials, from bio-sources and wastes should be prepared. In the age of artificial intelligence, it is perhaps useful to remember that "The foundation of any device, whether degradable or permanent, electrical or mechanical, is the stuff it's made of. Nothing would exist without the materials. That's really the distinguishing characteristic of the technology" **[24]**. Chemistry has a clear mission.

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Università e grande industria per un trasferimento tecnologico di successo.
Parte 2: polimeri stereoregolari

Nel 1954 iniziò una rivoluzione nel mondo dei polimeri: Giulio Natta e i suoi collaboratori al Politecnico di Milano prepararono, isolarono e identificarono i polimeri stereoregolari. Fu rotto il monopolio della natura. La collaborazione con Montecatini portò in pochi anni allo sviluppo industriale del polipropilene isotattico e degli elastomeri poliolefinici. Il modello di cooperazione tra un'università e una grande industria, che oggi verrebbe definito *open innovation*, si rivelò vincente per il trasferimento tecnologico.