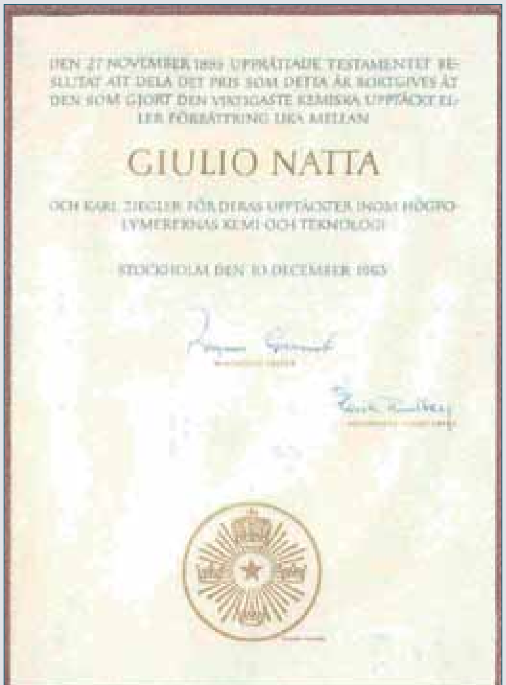

Il “diploma” del Nobel a Giulio Natta

Italo Pasquon

MEMORIES OF THE WORK AND PERSONALITY OF GIULIO NATTA

The stereospecific polymerization has been a revolution in the field of macromolecular chemistry. Besides the discoverer, Natta was its undisputed ruler. With his brilliant insights and tireless work, he was able to guide and coordinate the interdisciplinary work of his collaborators to the discovery and the study of more than a hundred of new polymers, over a period of fifteen years. The synthesis of isotactic polypropylene was the last great discovery - in terms of economic importance - still possible in the traditional field of industrial chemistry.

After 50 years since the attribution of the Nobel Prize for Chemistry to Giulio Natta, it is interesting to recall the importance of the scientific and industrial discoveries that he achieved working at the Institute of Industrial Chemistry of Politecnico di Milano, along with some personal episodes that bring out the personality of this great scientist.

On May 11 1954, in Natta’s laboratories, isotactic polypropylene was synthesized for the first time. This polymer has a sterically ordered structure, similar to those found in some polymers in nature. This meaningful aspect was also emphasized by Prof. Fredga of the Swedish Academy in his speech at the customary ceremony of the Nobel Prize on December 10, 1963, when he stated: ‘Natta has broken the monopoly of Nature’. In 1955, Paul J. Flory, one of the most eminent scientists in the macromolecular chemistry field and future Nobel Laureate in Chemistry (1974), wrote to Natta: “The results disclosed in your extraordinary manuscript are of interest, perhaps one should call them revolutionary in significance”.

The revolution brought about by Natta in the field of macromolecular chemistry involved the entire scientific and industrial world specialized in that area. Soon after 1954-1955, a lot of university and industrial research laboratories around the world started to work, to a more or less relevant extent, on activities concerning the novel stereospecific polymerization. For several years, starting from 1954, the most significant results obtained in the field of stereospecific polymerization continued to come from Natta’s laboratories. Since then, the stereospecific polymerization continues even nowadays to be subject of study.

The importance of these researches in the scientific field is not only limited to the discovery of stereospecific polymerization. Crucial have been the work on the identification of various catalyst systems and their behavior in polymerization processes of various monomers and those on the determination of the structure of new polymeric substances, on the relationship between properties and structure and on asymmetric synthesis.

It is impossible to describe in a few lines words the full extent of this research. I will only report a list of the main research topics and the new polymers synthesized by Natta and his School at Politecnico di Milano (Tab. 1).

The results of these studies are reported in about a thousand of scientific publications appeared between 1955 and 1971 (concentrated between the years 1955 and 1967) and in 280 “families” of patents which led to approximately 4,000 patents granted in several countries.

On the application side, this research led to the discovery of new types of polymers of considerable industrial interest, such as:

- isotactic polypropylene (and isotactic polybutene);

Tab. 1 - Research topics addressed by Natta and his School in the field of stereospecific polymerization
Synthesis, structure characterization at the crystalline state and determination of chemical, physical and mechanical properties of more than 130 new types of polymers
Preparation and characterization of catalytic systems based on transition metal and a metal organic compound (Ziegler-Natta catalysts), or only a metal organic compound
Studies on the mechanisms and kinetics of different polymerization processes
Synthesis of polytactic polymers
Asymmetric synthesis
Polyolefinic copolymer synthesis with random distribution and their application for the preparation of elastomers
Synthesis of alternating crystalline copolymers
Preparation and characterization of saturated and unsaturated elastomers and fibers
Graft polymers
Stereoregular polymers obtained by inclusion compounds
Use of polymers in the pharmaceutical field

- 1,4-cis polybutadiene;
- elastomers based on copolymers of ethylene and propylene.

The importance of polypropylene from the commercial point of view is evident from the fact that the world production of various types of polypropylenes now stands at about 60 million tons/year.

It is estimated that the related global economic value approaches the second place over all synthesis products, after the polyethylenes, together with ammonia and before other products such as urea, polymers of styrene and vinyl chloride, of nylon, etc.

For their part, the 1,4-cis polybutadiene and copolymers based on ethylene and propylene occupy today, respectively, the second and third place in terms of worldwide production and market value among synthetic elastomers, after the styrene-butadiene rubbers (SBR).

The editorial in the November 1963 issue of "Chemistry and Industry", dedicated to Natta after the Nobel Prize, says: "...the field of industrial chemistry has been 'plowed' so thoroughly that it will be difficult to relive the surprise of discoveries of such importance and significance'. A systematic analysis leads to the conclusion that the synthesis of isotactic polypropylene has been the last great discovery still possible - in terms of economic importance - in the field of traditional industrial chemistry. Almost 60 years after the synthesis of isotactic polypropylene these claims have not yet been denied (Tab. 2).

We can now ask how such significant results could be achieved in such a short time. An essential contribution came from Montecatini, which provided financial resources and made available, over a period of fifteen years, dozens of very young valid researchers (chemists and engineers). They worked together with Natta's assistants (few units and also mostly very young) constituting the so called "School of Natta."

Nevertheless the essential component was a "mind" with an appropriate scientific background, which can provide ideas and coordinate an interdisciplinary work covering various fields of organic chemistry, inorganic chemistry, metallurgical and macromolecular physical chemistry, thermodynamics, catalysis, kinetics, structural chemistry, experimental analysis (RX, Raman, NMR, IR, UV, ESR, radiochemistry) of physics and engineering, up to the study of the physical and mechanical properties of plastics, elastomers and fibers and of the mechanics for the construction of stainless steel autoclaves. Natta had all these features.

Unlike most of the other Nobel Prizes for chemistry, he was not an "expert" in a specific field. Before addressing the issue of stereospecific polymerization, Natta had carried out research in the fields of molecular structures (applied to the study of various inorganic and organic polymeric substances), catalysis and kinetics, in particular concerning the chemistry of carbon monoxide (synthesis of methanol, higher alcohols and formaldehyde), the synthesis of butadiene, synthetic rubbers and the fractionation of mixtures of C_4 hydrocarbons, the oxo-synthesis and organometallic and also (in times of self-sufficiency) of coal gasification and preparation of chemical derivatives from vegetable raw materials.

Another peculiarity of Natta was his openness to industrial applications, as evidenced by the granting of numerous patents, as early as 1927, and the construction of industrial plants, in Italy and abroad, based on his research results.

His insights can best be illustrated by a few episodes.

Shortly after the discovery of the stereospecific polymerization, discussing with his collaborators he observed that the rotation around the carbon-carbon bonds of polyethylene was facilitated by the absence of steric hindrance and this property was typical of bonds present in polymeric chains of elastomers. It would have been possible to get an ethylene-based elastomer, avoiding the crystallization of the linear polyethylene through the introduction into its chain of some irregularities, obtainable by copolymerizing ethylene with propylene. A few days later the first ethylene-propylene random copolymer was obtained and its elastomeric properties were characterized. Three years later, in 1957, a first industrial plant was started in Ferrara. On another occasion, he asked us to "find" the syndiotactic polypropylene, whose existence was only a hypothesis. We examined the X-rays spectra of numerous samples of polypropylene already prepared. We observed that the spectra of the polymers obtained with a given type of catalytic system included a small peak that Corradini immediately attributed to a new polymer. A few days later the structure of the syndiotactic polypropylene was identified. This new polymer, however, was present only in a small percentage in the raw polymers. With the tips that Natta provided to us, Pegoraro separated the polymer with a high degree of purity. Shortly afterwards, we prepared with Zambelli a stereospecific catalyst for the synthesis of the new polymer. We cannot say whether these and many other important results would have been achieved without Natta's suggestions and insight. Tactfully and politely, but very firmly, Natta coordinated the activities of the various research groups, each with their own skills, accepting the personality of each collaborator.

Tab. 2 - New polymers synthesized by Natta and his collaborators at the Politecnico	
Isotactic and syndiotactic polymers of 1-alkenes. Optically active polymers	- Isotactic polypropylene and other isotactic polymers of linear and branched aliphatic or alicyclic 1-alkenes. - Optically active isotactic poly 1-alkenes. - Isotactic polymers of 1-alkenes containing cycloalkane or aromatic end groups. - Isotactic polymers of 1-alkenes with end groups containing heteroatoms. - Syndiotactic polypropylene.
Isotactic vinylaromatic polymers	- Isotactic polystyrene and others isotactic vinylaromatic polymers containing alkyl-aril- or halogen groups.
Stereoregular polymers of conjugated dialkenes. Optically active polymers	- trans-1,4-and cis-1,4-polybutadiene. - Isotactic and syndiotactic 1,2-polybutadiene. - trans-1,4-and cis-1,4-polyisoprene. - trans-1,4-and cis-1,4 optically active isotactic polypentadiene. - cis-1,4 syndiotactic polypentadiene. - 1,2 syndiotactic polypentadiene. - trans-1,4- and cis-1,4-poly 2-alchil or phenyl 1,3-butadiene. - cis-1,4-poly 2,3 -dimethylbutadiene. - trans-1,4- and cis-1,4-poly 2-methyl-1,3-pentadiene. - 1,2 isotactic poly 4-methyl-1,3-pentadiene. - trans-1,4 threo-diisotactic poly (E,E) -2,4-hexadiene. - trans-1,4 isotactic poly 5-methyl-1,3-pentadiene.
Cycloalkene polymers	- Erythro-diisotactic and erythro-disyndiotactic polycyclobutenamer. - Stereoregular polynorbornene. - Stereoregular polycyclopentene and other polyalckenamers.
Polymers of acetylenic monomers	- Linear crystalline polyacetylene. - Linear crystalline poly-1-hexyne
Other hydrocarbon polymers	- Poly(trans,1,2-divinylcyclobutane). - Polyallene. - Polytetraindan and polytetraindene. - Polycyclodialkenes.
Copolymers of unsaturated hydrocarbons monomers	- Ethylene-propylene and other ethylene-1-alkenes amorphous random copolymers. - Heteroblock 1-alkene copolymers. - Crystalline copolymers of vinylaromatic monomers. - Erythro-diisotactic ethylene-cis-2-butene and ethylene-cycloalkenes with an odd-membered ring, crystalline alternating copolymers. - Ethylene-trans-2-butene and etylene-cycloalkenes with an even-membered ring, amorphous alternating copolymers. - Ethylene-trans-1,4-butadiene crystalline alternating copolymers.
Polymers of halogenated 1-alkenes	- Isotactic poly(hexafluoropropylene). - Syndiotactic poly(vinylchloride). - Syndiotactic poly(vinylfluoride).
Polymers of vinyl- and alkenyl ethers- Optically active polymers	- Isotactic and syndiotactic polyvinylethers and polyalkenyl ethers. - Diisotactic and optically active poly-β-substituted vinyl ethers.
Polymers of acrylic esters	- Isotactic poly (i-propylacrylate). - Isotactic poly (t-butylacrylate). - Isotactic poly (methylmethacrylate). - Crystalline poly [β-(N-carbazyl) ether]. - Isotactic poly (allylacrylate).
Polymers of carboalkoxybutadienes and of 1-cyanobutadiene. Optically active polymers	- trans-1,4-erythro- and threo-diisotactic poly(methyl sorbate). - Crystalline poly (cis-1-cyano-1,3-butadiene). - Optically active crystalline polymers from esters of sorbic acid and β-styrylacrylic acid.
Other polymers from monomers containing heteroatoms	- Poly(o-and p-methoxystyrene). - Stereoregular poly (N-vinylcarbazole) - Crystalline poly (N-vinyldiphenylamine). - Isotactic poly (methacrylonitrile) and other poly (α-alkylacrilonitrile)s. - Stereoregular poly (crotonitrile). - Isotactic poly (2-vinylpyridine). - Amorphous poly (3- and 4-vinylpyridine). - Crystalline poly (α,β-unsaturated lactone)s. - Amorphous poly (α,β-unsaturated cyclicketone)s. - Crystalline poly (n-butylisocyanate). - Isotactic poly (2-etyl-N-morfolil). - Crystalline alternating copolymers of 2-vinylpyridine with α-stilbazole.
Polymers from unsaturated monomers containing heteroatoms in the main chain	- Isotactic polyacetaldeide and other isotactic polymers of higher aldehydes. - Crystalline polymers of ketene. - Crystalline polydimethylketenes with various type of structures. - Crystalline copolymers of dimethylketene with acetone, benzaldehyde or furfural. - Alternating copolymers dimethylketene-formadehyde.
Polymers prepared by matrix control. Optically active polymers	- Crystalline polybutadiene and polypentadiene from monomers included in perhydrophenylene. - Optically active, crystalline, isotactic trans-1,4-polypentadiene from monomer included in optically active perhydrophenylene.
Grafted polymers	- Poly 1-alkene grafted with polystyrene, polyacrylates or polyacrylic acid. - Ethylene-propylene copolymers grafted with polystyrene, polyvinylchloride, polyacrylic acid or polyvinyl acetate.

Natta was a tireless worker. After a full day spent at the Institute - where, until his health allowed, he continued to teach his lectures and personally examine every student - Natta almost every evening after dinner received, in turn, his collaborators at home in Via Mario Pagano 54, to discuss about research. The same he usually did in the weekend. On Sundays we had lunch with him and then we discussed research results until 5 p.m., when Mrs. Rosita brought all of us to church. During vacations and some weekends some of us were guests (sometimes with their families) in their holiday homes: we spent the morning walking in the woods, or looking for mushrooms, and in the afternoon we worked. Natta was a connoisseur of mushrooms, botanical and minerals.

When he had no one to talk to, we wrote. I keep some of his letter (one written on December 31st).

At the same time, Natta coordinated also research carried out by the various branches of Montecatini, other universities and CNR (National Research Council) and maintained close relations with the outside world, documented with a substantial correspondence that essentially covers the 1950-1970 time period, preserved at Politecnico di Milano and reproduced on the website 'Giulio Natta archive'. The material on file concerns Natta's relations with:

- more than 500 people, Italian and foreign (USA, D, GB, F, B, USSR, CH, NL, J, S, CDN, etc.), including several Nobel Prize winners, universities and other scientific institutions (not only epistolar relations, but also visits and family invitations);
- more than 300 large companies in the world (of which about half in the USA) to discuss research and also licensing;
- almost all the divisions of Montecatini, Montecatini-Edison (Hydrocarbons, Department of resins, Donegani Institute, Acna, Sector Projects and Studies, Division of Chemical Industry), wherein studies and researches directed by him and by his collaborators were also carried out;

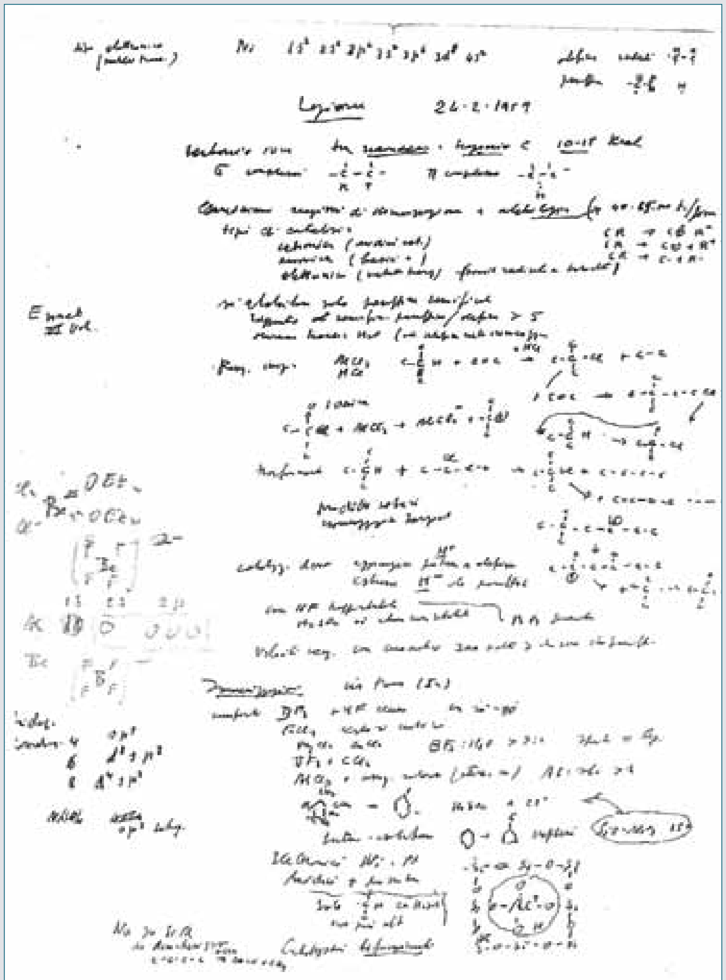

Fig. 1 - Una pagina di appunti di Giulio Natta

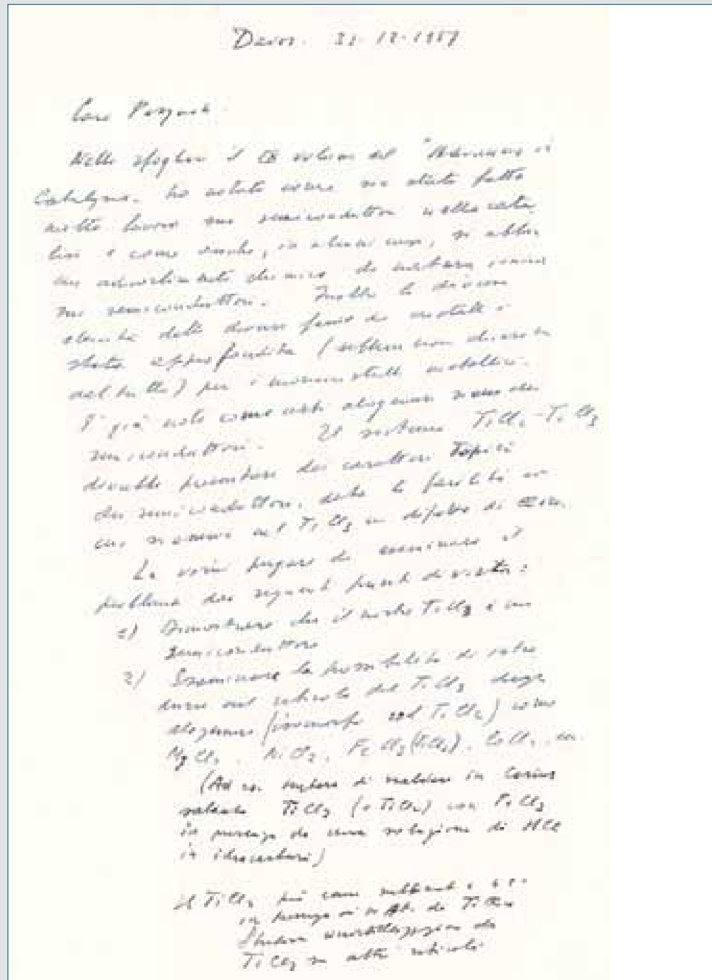

Fig. 2 - Lettera di Giulio Natta a Italo Pasquon

- the Montecatini Managing Director ing. Piero Giustiniani of Montecatini, concerning a wide range of topics;
- companies representing Montecatini abroad;
- the Montecatini Patent Office, with which he followed the very laborious and complex procedure for filing patents in Italy and their extension and grant abroad. It is worth of note that the correspondence relating to the grant of the isotactic polypropylene patent in the USA (filed in the U.S. in 1954 and granted only in 1963) occupies three huge binders!;
- the CNR, where the National Center for Macromolecular Chemistry - with several locations in Italy - and the National Institute of Macromolecular Chemistry (ICM) were created (Natta was named president of them);
- the National Academy of Lincei and other Italian and foreign academies and scientific-cultural Associations, of which he was a member;
- the Rectorate of the Politecnico di Milano and the Dean of the Faculty of Engineering;
- various Italian and foreign journals and publishers.

Natta was a reserved man. With everybody he could establish truly human relations, even if masked by an apparent detachment, of course due to shyness. He commanded respect without ever raising his voice. For all he was the "Professor".

He passed the last years of his life next to his daughter Franca in Bergamo, where he died May 2, 1979, after many years of suffering, borne with great fortitude.

He was born in Imperia on February 26, 1903.

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Riassunto

Ricordi sul lavoro e la personalità di Giulio Natta

La polimerizzazione stereospecifica è stata una rivoluzione apportata nel campo della chimica macromolecolare. Oltre che lo scopritore, Natta ne è stato il dominatore incontrastato. Con le sue geniali intuizioni e con un'instancabile attività, egli ha saputo guidare e coordinare il lavoro interdisciplinare dei suoi collaboratori, fino alla scoperta e allo studio, nell'arco di una quindicina d'anni, di oltre un centinaio di nuovi polimeri. La sintesi del polipropilene isotattico è stata l'ultima grande scoperta - in termini di importanza economica - ancora possibile nel campo della chimica industriale tradizionale.