The Scientific Activity of Giulio Natta from 1949 to 1973

by Piero Pino

This most significant period of the scientific activity of Prof. Natta started with his first contacts with the U.S.A. chemical industry, where a very rapid development of petrochemistry was producing substantial and unexpected changes. The profound emotions that Professor Natta felt during his first trip to the U.S.A. are well described in a paper published in *La Chimica e l'Industria* [1].

Since Natta had received his education in chemistry and chemical engineering in the twenties, *i.e.* when industrial organic chemistry was mainly based on coal and fermentation products, he was fascinated by the new possibilities offered to the chemical industry by the practically unlimited availability of unsaturated hydrocarbons like ethylene, propylene, butenes and butadiene easily obtainable from petroleum and he immediately recognized the industrial potential of the chemistry of aliphatic compounds.

P. Giustiniani - at that time General Manager of Terni SpA, and later Managing Director of Montecatini SpA - with whom Natta visited the U.S.A. for the first time, shared his enthusiasm. Thus, by the end of the forties, the Industrial Chemistry Institute of the Politecnico of Milan and Montecatini Company (later Montedison) established that fruitful collaboration which was to produce extremely important industrial achievements, among which the commercial production of isotactic polypropylene. On his trip to the U.S.A., Professor Natta was impressed by the number of scientists who worked at the research laboratories and by the way in which research was organized.

In 1948 he wrote: "It often happens that the number of chemists working in those huge laboratories is 400 to 600. A few years ago it amazed us that the number of chemists working at the I.G. laboratory of Reppe was about 100, and that the research on nylon was carried out by 30 scientists. Now, compared with the present number of U.S.A. researchers, these figures seem insignificant" [1]. In the same article he also writes: "In my life as a modest researcher there were ten at the most chemists under my direction, and to follow them all seemed to be a very hard work to me. I wonder how a single man can direct 500 to 600 researchers". Being highly interested in research organization, he often urged me to describe how research was carried out at the Organic Chemistry Laboratory of the Polytechnic Institute of Zurich, where I had gone in 1950 to specialize in organic chemistry under the direction of Professor Ruzicka, a scientist whom Natta admired for his achievements in the field of organic syntheses.

Thinking that the academic world - scarcely ready for substantial innovations - could hardly have provided young graduates with the up-to-date preparation required for the large-scale introduction of petrochemistry in Italy, and, at the same time, wishing to avail himself of a research team capable of competing with the U.S.A. teams, Natta proposed, and Mr. Giustiniani agreed, that 10-20 graduates in chemistry and industrial chemistry should be engaged every year to be trained in industrial aliphatic organic chemistry at the Industrial Chemistry Institute of the Politecnico, before they would start to work in the Montecatini laboratories. After the didactic experience made in the more developed countries in Europe and in the U.S., the trainee would have to carry out a research project independently and attend courses on industrial organic chemistry, as well as on advanced topics of organic chemistry, physical chemistry, and instrumental analysis. It is to Mr. Giustiniani's credit that he acceded to Natta's request without faltering. Actually, Natta's plans would never have been realized without the support of the industry.

Thanks to the careful selection of the trainees and to the high quality of the teachers (in addition to Prof. Natta himself, I wish to mention Prof. A. Quilico, Prof. G.B. Bonino, the late Prof. R. Piontelli, as well as notable industrial managers, such as G. Greco and the late F. Tredici), and to the climate in which the trainees were able to develop their sci-

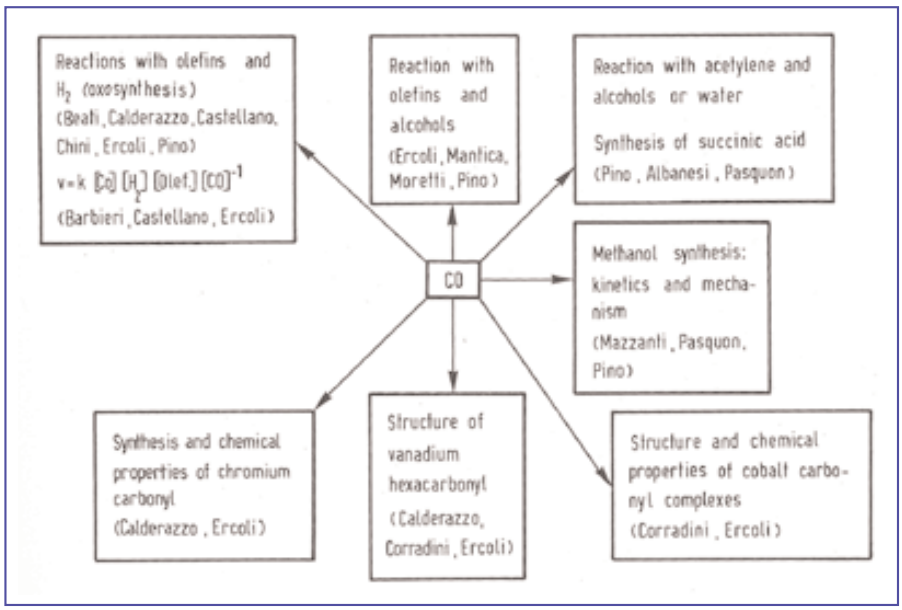

Figure 1 - Summary of Natta's research in the field of carbon monoxide chemistry

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entific work, the chemists educated at the Milan Politecnico in the early fifties still constitute the supporting structure of the major laboratories of the Italian chemical industry. Some of their names and present positions are mentioned in parentheses in Figures 1 and 6, after the description of the research works they collaborated on.

I have dwelt on this project because, in my opinion, it largely contributed to the extraordinary results that Natta achieved in the period from 1953 to 1963. These very results were obtained also because the Institute was provided not only with modern equipments for x-ray and electron diffraction studies (the traditional field of Natta's research activity), but also with adequate equipment for Ir and Uv spectrography, which at the time were considered pioneering techniques. Various research teams and services were established within the Institute, even if informally. An important step in the life of the Institute was the creation of the Plastics Testing Laboratory, set up by Natta with the collaboration of Prof. D. Pagani, and with the financial support of Milanese firms [2]. The space available for the Institute was considerably increased with the construction of a new building and the acquisition of the building formerly housing the "Stazione Sperimentale per i Combustibili". The scientific activity developed by Natta from 1948 onwards followed two main trends of high theoretical and practical interest, which are still valid even if 30 years have elapsed, *i.e.* the chemistry of carbon monoxide and the synthesis and properties of macromolecular compounds. Natta's early research on the chemistry of carbon monoxide dates back to the twenties. In the early forties he became acquainted with the "oxo-synthesis", a reaction discovered by Dr. Rohlen of Ruhrchemie.

Realizing its commercial importance, Natta investigated this reaction after 1943 (with E. Beati [3]) with the twofold purpose of extending the scope of this reaction - originally applied to ethylene only - to various organic substrates, and of studying the mechanism of the same as well as of analogous carbonylation reactions investigated by Reppe during World War II. Being convinced that the catalytic activity of the cobalt-based catalysts discovered by Rohlen was higher than that of the nickel catalysts discovered by Reppe, Natta reinvestigated the carbonylation of acetylene.

The research he carried out in this field from 1947 to 1954 resulted finally in a new one step synthesis of succinic acid from acetylene [4]. A pilot plant based on this research was later implemented with the collaboration of I. Pasquon and G. AIbanesi. As early as 1944 Natta realized that the olefins hydroformylation rate was independent of the total pressure of the 1:1 carbon monoxide and hydrogen gaseous mixture. However, it was only after ten years that Natta succeeded in demonstrating that the said independence was connected with a reaction of first order with respect to hydrogen and of order (-1) with respect to carbon monoxide (with the late R. Ercoli, full Professor of Industrial Chemistry, Palermo University, and S. Castellano, Carnegie Mellon Institute, Pittsburgh, Pa. U.S.A. [5]). Natta's interest in the chemistry of carbon monoxide remained alive even in subsequent years. As a matter of fact, he investigated the preparation and reactivity of chromium hexacarbonyl and its arenic derivatives, and synthesized vanadium hexacarbonyl, thus obtaining the first carbonyl of a metal of the 5th group of the periodic table and the first paramagnetic metal carbonyl (with R. Ercoli and F. Calderazzo, now full Professor of General Chemistry, Pisa University [6, 7]). The above very important results obtained by Natta in the field of carbon monoxide chemistry correspond only to a minor part of his scientific activity. Indeed Natta obtained his most important achievements in the field of high polymers. His first research in this field started in 1932 during his stay in Freiburg im Breisgau where he met Professor H. Staudinger [18]. Later, he contributed to the first production of synthetic rubber in Italy. After World War II, polymers remained to be one of his main research interests, even though after the end of the initial activity in the field of synthetic rubber no experimental research was in progress in his Institute till the end of the forties.

In the early fifties Natta started to investigate some physical properties of the polymers, e.g. the rate of ultra-sonic waves in melted polymers (with M. Baccaredda [8]) and the structure of crystalline polyethylene (with P. Corradini [9]). However, he never ceased to be interested in the synthesis of macromolecular compounds. His talk often turned to the high-molecular-weight linear paraffins of which, during a trip to Germany, he had received a sample produced by the Fischer-Tropsch reaction in the presence of ruthenium catalysts.

Natta resumed his experimental activity in the field of macromolecular syntheses after he had attended the lecture that Professor K. Ziegler delivered in Frankfurt (1952) about the ethylene polymerization in the presence of alkyl aluminum compounds (Ziegler's "Aufbaureaktion" [10]). At the end of the above lecture, which I also attended, Natta asked for my opinion about Ziegler's research: I was most favorably impressed by Ziegler's research on such a difficult subject, but I felt doubtful about the commercial prospects for Ziegler's results.

On this last point Natta's opinion was opposite to mine: being well acquainted, thanks to his previous work on synthetic rubber, with radical polymerization, he at once realised - probably even before Ziegler himself - that the German scientist had found a completely new principle as far as the synthesis of polymer chains was concerned. In fact the polymerization of ethylene carried out by Ziegler did not occur by monomer addition to a free radical or to a free carbonium ion (Figure 2), located at the end of a growing chain, but by monomer insertion between a

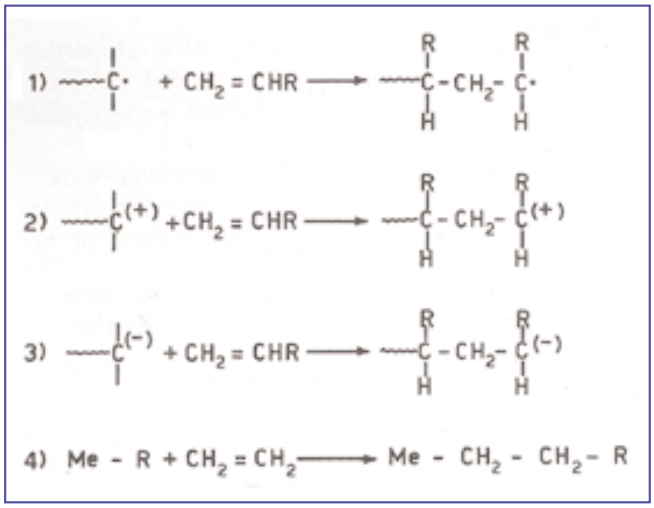

Figure 2 - Chain growth by monomer addition to an activated chain end (1, 2, 3) or by monomer insertion into a metal-to-carbon bond [4]

metal atom and the growing chain bound to it. In Natta's opinion this offered greater possibilities for controlling the polymer chain structure during the synthesis. Excited by this idea, Natta suggested to the Montecatini Company to enter into a collaboration agreement with K. Ziegler, and charged me to establish at his Institute a research team entrusted with the task of repeating Ziegler's experiments, of separating ethylene polymers with as high as possible a molecular weight, and of investigating the kinetics of polymerization. It was also envisaged to send a few members of the new team to Ziegler's Institute. Thanks to the collaboration of a number of chemists of exceptional capacity (it is enough to mention the late Prof. P. Chini, M. Farina, now full Professor at the Milan University, R. Magri, L. Luciani, E. Giachetti), Ziegler's tests were repeated, ethylene polymers were fractionated by solvent extraction, and the study of the "Aufbaureaktion" kinetics was started.

Under the agreement between Montecatini and K. Ziegler, at the beginning of 1954 Prof. Natta was given the text of Ziegler's patent on the preparation of ethylene high polymers in the presence of catalysts obtained by causing $TiCl_4$ and alkyl aluminum compounds to react. Thanks to the extensive knowledge of the aluminum alkyl chemistry already existing at the Institute, the research in the new area could immediately be started.

At this point, Natta was able to give full proof of his extremely great creative talent. After learning of Ziegler's results, and using his great experience in the field of heterogeneous catalysis and radical polymerization, he assumed as a working hypothesis that the formation of ethylene high polymers was due to a higher rate of growth of the polymer chains, caused by the presence of a heterogeneous catalyst activating the ethylene molecule before it is inserted in the aluminum-carbon bond (Figure 3).

Thinking that Ziegler could rapidly progress in his research on polyethylene Natta decided to prepare small quantities of the new polyethylene for the purpose of studying its structure, but at the same time, he decided to start the investigation of the polymerization of propylene. As a matter of fact, as he knew that by reacting propylene in the presence of aluminum alkyls, dimers or at most trimers of propylene could be obtained, he hoped that the new heterogeneous catalysts found by Ziegler might give, as in the case of ethylene, propylene high polymers, which would be suitable for application in the field of synthetic rubber with which he was so well acquainted.

Somewhat reluctantly - we were all engaged in research in other fields - we started to prepare and purify propylene to be used in the polymerization experiments. At the beginning of March 1954, P. Chini obtained a small quantity of a yellow-brown gummy product which clearly was nonhomogeneous. The polymerization of propylene immediately became the most important subject of our research; in particular, G. Mazzanti, who at the time was at the head of Montecatini's trainees, dealt with the problem with P. Longi and E. Giachetti.

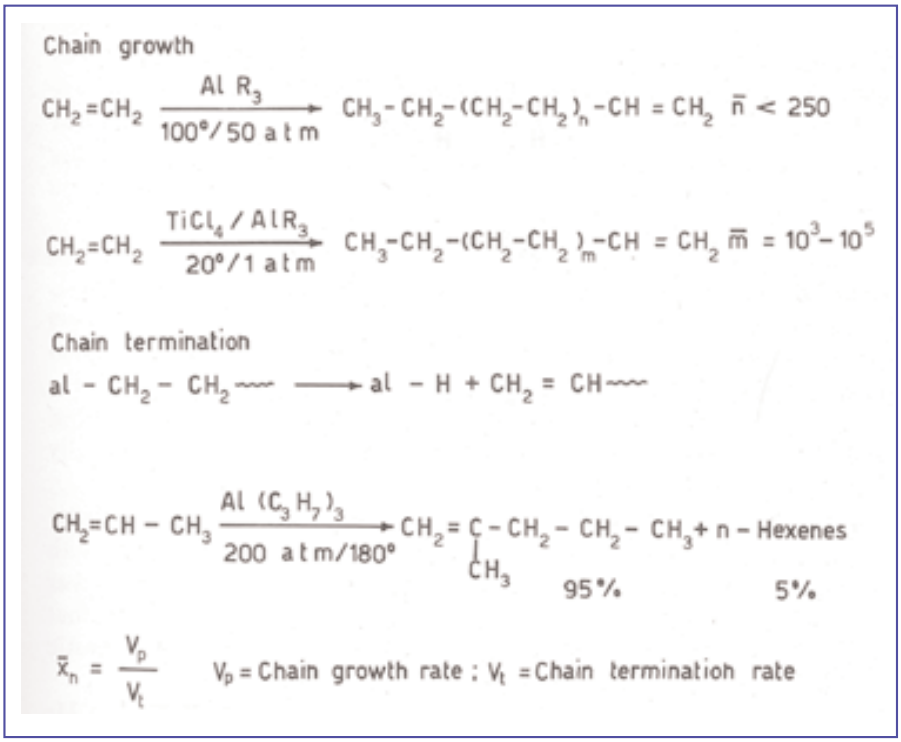

Figure 3 - Chain growth and chain termination in ethylene polymerization and propylene dimerization with organometallic catalysts

All resources Natta had at his Institute were employed for the characterization of the new polymers. P. Corradini performed x-ray investigations, and a high crystallinity was found in the less soluble polymer fractions.

Furthermore, after determining the polymer chain identity period, he observed that there existed no planar zig-zag conformation of the type found in linear paraffin, at least in the crystal state. E. Mantica with M. Peraldo and L. Bicelli carried out the Ir analyses and found that the methyl to methylene ratio in the polymer was about 1. Furthermore, the spectra of the amorphous and crystalline polymers were found to be similar, except for some bands, present in the latter which disappeared upon melting. F. Danusso and G. Moraglio investigated the behavior of the various polypropylene fractions in solution and found that they had substantially different molecular weights. Natta's early idea was to use propylene for the production of synthetic rubber: in March 1954 he insisted on copolymerizing propylene with butadiene with the idea of obtaining a vulcanizable product. However as soon as the crystaline polypropylene was isolated, he realized that the new polymer, being a high melting one, could be used as a plastic material in many fields, different from those for polyethylene. By availing himself of very simple apparatus, and with the help of Mr C. Origgi, a technician of exceptional skill who directed the workshop of the Institute, in May 1954 Natta succeeded in making the first fibre from polypropylene.

The mechanical characteristics of the fiber were studied at the Plastics Testing Laboratory with G. Lutzu. At the same time, Natta and his collaborators started to discuss the structure of polypropylene and the reasons for the crystallinity of the heptane-insoluble fractions. At first, the difference between the crystalline

and noncrystalline fractions was assumed to depend on the different molecular weights. However, Natta was not fully satisfied with this explanation: as a matter of fact, the molecular weights did not undergo a regular variation with the decreasing of the fractions solubility in the organic solvents, but were considerably different in the crystalline and the non-crystalline fractions. Natta liked repeating the saying *"Natura non facit saltus"* and urged us to look for other reasons on which the said differences might be based. From a thorough bibliographic investigation we were able to ascertain that some crystallinity had been previously observed in a vinyl polymer, the poly(isobutylvinylether), obtained by C.E. Schildknecht in 1948 by cationic polymerization in heterogeneous phase. This polymer exhibited a very low crystallinity, lower than that of non-fractionated polypropylene [11].

On the basis of the x-ray diffraction spectra, whose interpretation was difficult just because of the low crystallinity of the samples, Schildknecht and collaborators had set forth the hypothesis that the polymer chains in the crystals had a planar zig-zag conformation, which was inconsistent with what P. Corradini had found for polypropylene. Schildknecht's work focused the attention of Natta and his group on the relevance of the steric regularity in the polymer main chain to the physical properties of the vinyl polymers. After countless discussions the hypothesis was formulated that the crystalline and noncrystalline polypropylene fractions were different because of the existence in the crystalline polymer of steric regularity in the main chains of the macromolecules. In his first paper on the topic [17], Natta stated that in the crystalline fractions the asymmetric carbon atoms may have the same steric configuration at least for long chain portions, and proposed to call the said carbon atoms, and consequently the polymers containing them, "isotactic" (Figures 4 and 5). The determination of the molecular structure of polypropylene paved the way for the discovery that some catalysts based on titanium halides and aluminium alkyls - found by Ziegler - had a very important and quite unexpected property: the stereospecificity, which we now know to be exceptionally high, *i.e.* equal to or even higher than that of enzymes. To fully appreciate the level of Natta's creative skill, it is enough to point out that only three months elapsed from the first synthesis of crude polypropylene to the first patent application conveying all data about isotactic polypropylene.

To give a few examples, Ziegler obtained his first crude nonfractionated polypropylene eight-nine months after his first patent on polyethylene. Some U.S.A. industrial laboratories (e.g. Standard Oil of Indiana and Phillips Petroleum), succeeded in obtaining from propylene, by methods other than Natta's, mixtures of polypropylenes with different stereoregularities but they did not fully understand the structure even after years of research.

Finally, the DuPont Company that in August 1954 - approximately two months after the first patent of Natta - had filed a patent on the preparation of a polypropylene mixture with catalysts similar to Ziegler's, only obtained isotactic polypropylene from the said mixture in 1955, *i.e.* after becoming acquainted with Natta's papers. After submitting his first patent application on polypropylene [12], Natta decided to develop research on the polymerization of other alpha olefins. These studies resulted in the patenting of many new isotactic polymers.

He then focused his attention on the factors determining the stereospecificity of Ziegler's catalytic systems. On the basis of the hypothesis that it is a transition metal solid compound that activates the olefin before the occurrence of the insertion in the metal-alkyl bond, Natta assumed that stereospecificity was caused by the surface regularity of the solid. With the aim of obtaining more regular catalytic surfaces, Natta decided to prepare the catalysts using crystalline $TiCl_3$, insoluble in the reaction medium, instead of $TiCl_4$.

Once again Natta's intuition proved true: the isotactic polymer content in the crude polymer was increased from 40% to 85%. The way was paved for the commercial production of the isotactic polymer. I have dwelt on the discovery of isotactic polypropylene as being Natta's masterpiece. In this research - more than in any other - Natta's imagination,

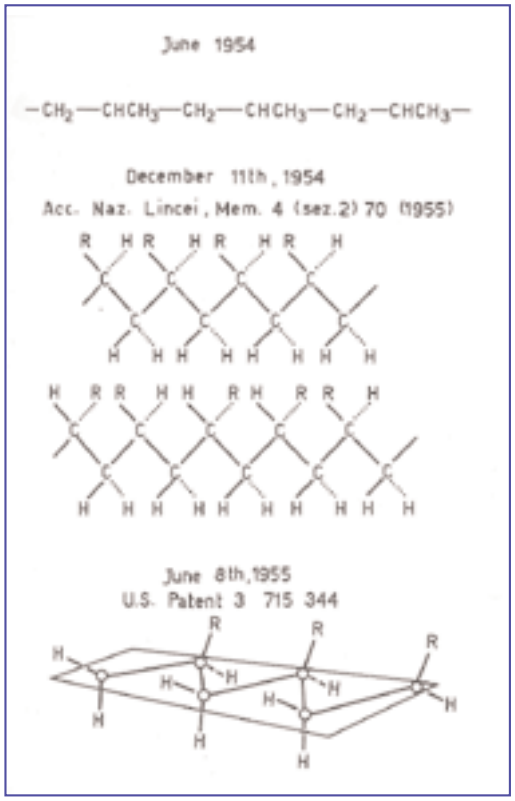

Figure 4 - First representation of an isotactic polymer chain

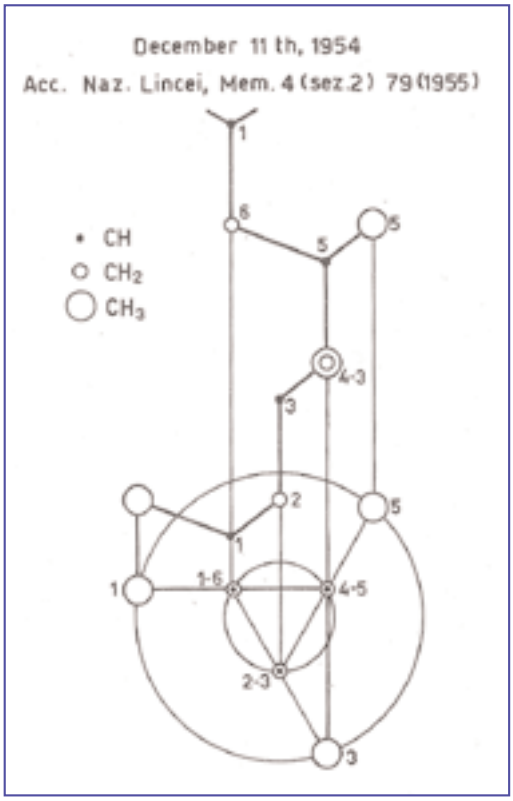

Figure 5 - First representation of 3/1 helix of isotactic polypropylene

deep and wide scientific knowledge, decisiveness perseverance, and incredible skill blended harmonically. After this discovery, Natta developed a series of research projects of outstanding importance in the new field. Indeed, Sir Robert Robinson wrote that Natta "developed the theme of polymerization as a grandiose fugue" [13]. The results that Natta and his collaborators obtained concerning the stereospecific polymerization and related fields can hardly be listed. However, the development of this research may be inferred from Figure 6, drawn from a summarizing paper that Natta published in 1963 [14]. The research that Natta developed in the sixties followed the main trends described above. He continued to direct the research at his Institute till 1973, when having reached retirement age, Natta left the Institute he had directed for more than 35 years.

G. NATTA: **Evolution des recherches sur les hauts polymères à l'Ecole Polytechnique de Milan**, *Chim. Ind. (Paris)* 89, 545 (1963).

1) First stereospecific syntheses of isotactic poly(alphaolefins) (CORRADINI, DANUSSO, LONGI, MAZZANTI, PINO).
2) Conjugated polyolefins (PORRI; CRESPI).
3) Kinetic study of olefins polymerization (GIACHETTI, PASQUON; DANUSSO, SIANESI).
4) Investigations on the catalysts (GIANNINI, MAZZANTI, PINO; PASQUON, ZAMBELLI; PORRI, CORRADINI).
5) Syndiotactic polypropylene (PEGORARO; PASQUON, ZAMBELLI).
6) Non-hydrocarbon polymers (MAZZANTI, LONGI, DALL'ASTA, BERNARDINI, FARINA).
7) Synthesis and characterization of di-isotactic polymers (FARINA, PERALDO).
8) Asymmetric syntheses (FARINA; PORRI).
9) Crystalline copolymers: a) Alternate copolymers (DALL'ASTA, MAZZANTI, PASQUON, PREGAGLIA); b) Copolymers with a statistical distribution (DANUSSO, SIANESI; PORRI).
10) Saturated elastomers (CRESPI, MAZZANTI, SARTORI, VALVASSORI).
11) Grafted polymers (BEATI, SEVERINI).
12) Chemical-physical methods of analysis and separation (ALLEGRA, BASSI, CORRADINI; DANUSSO, MORAGLIO; PEGORARO; GIUFFRÈ; CIAMPELLI, MANTICA, PERALDO, ZERBI; LOMBARDI).

Figure 6 - Development of the research of Natta and co-workers on stereospecific polymerization

The importance of Natta's discoveries for the progress of polymer science was immediately understood on an international scale. As early as in January 1955, Professor P.J. Flory made the following comments on Natta's first paper on isotactic polymers submitted to JACS [17a]: "The results described in your manuscript are of extraordinary interest; perhaps one should call them revolutionary in significance" [15].

This was also the opinion of Prof. Tobolsky of Princeton University when he published his paper "Revolution in Polymer Chemistry" in 1957 [19]. In addition to a large number of international awards, in U.S.A., Soviet Union and Europe, in 1963 Natta was awarded the Nobel Prize, shared with K. Ziegler. However he considered the best acknowledgments for his research to be the data he often received about the commercial production of the new polymers, and the news about the progress of the scientific and industrial research in the area he had started. In twenty years the rise in the commercial production of isotactic polypropylene has been impressive: the present production amounts to more than 3 million tons per year (Figure 7). Concerning the rapid development of stereospecific polymerization, he was very proud of the number of patents that researchers all over the world had applied for, in the field, in the period from 1954 to 1960 [13]: 4 in 1954 (when the discovery took place), 25 in 1955, approx. 150 in 1956, about 200 in 1957, 1958, 1959, 1960, for a total of about 1.000 patents in six years! Now, I wish to briefly hint at the activity of Prof. Natta as an educator and at the impetus he gave to the progress of macromolecular chemistry in Italy.

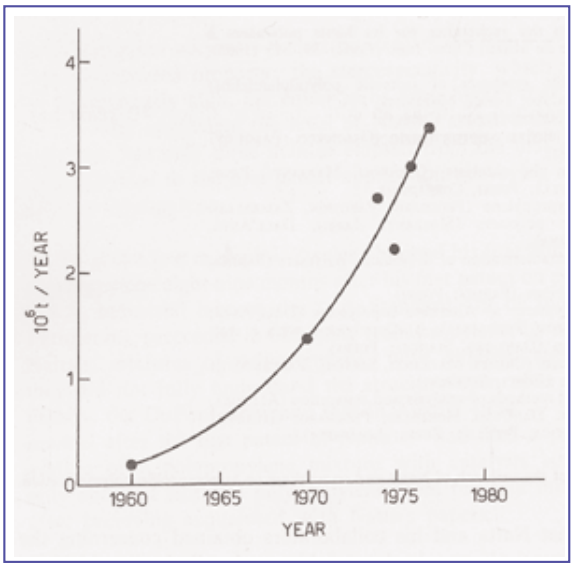

Figure 7 - World production of isotactic polypropylene

In 1960 he succeeded in persuading CNR (Italian National Council for Research) to establish a National Center of Macromolecular Chemistry, consisting of eight sections located in Milan, Padua, Turin, Genoa, Pisa (two sections), Rome and Naples.

In the sixties, thanks to this Centre, macromolecular chemistry in Italy reached a high level on an international scale. The former Sections were later replaced by an Institute, some laboratories, and some Research Centres. The activity of Giulio Natta as an educator over almost 40 years has been so successful that it seems unnecessary to recall it here.

While he was convinced that the formal lectures were of little use for the education of the young students, Natta deeply believed in the formative value of discussions on specific research topics, and in particular in the formative value of the experimental research work and of the mastering of the theory necessarily connected to it. He had an admirable faith in research: "Scientific research is truly fascinating, and those who do it are interested in every new application", he wrote [16] to conclude his last paper dated 1972. "As far as I am concerned, should I begin anew, I would devote my life to research". He followed his scholars with the greatest interest, and although he was somewhat critical of their work, particularly from the point of view of the practical importance of their research, he was very proud and happy for their success. It was his opinion that success in research may be achieved by those who make a careful choice of the research subjects and who never neglect the possible application for the results obtained. The research subjects chosen should be dealt with through hard work, utmost scientific exactitude, and criticism. "In this way only", he used to say smiling, "if fortune smiles on us, any success is possible". The importance of Natta's school for the Italian uni-

versity and industry may be inferred from the following. Of his scholars, about twenty have been appointed as full university Professors in Italy and abroad.
The number of those who attained outstanding positions in the industry is certainly higher; I only recall the few with whom I was more closely acquainted: G. Mazzanti, the former President of Eni; M. Bruzzone and W. Marconi, heading Assoreni's laboratories; G. Crespi, coordinator of Montedison's research; G. Pregaglia, head research and technology of Montedison Petrolchimica, and former President of the Italian Chemical Society; A. Valvassori, Managing Director of Donegani Institute SpA; A. Palvarini, head of Farmoplant's research; B. Calcagno, of the Pirelli Company; G. Dall'Asta, former head of Snia Viscosa's research Center of Colleferro; P. Longi, M. Ragazzini, E. Giachetti, G. Paleari, G. Negri, I. Ronzoni, U. Soldano, and many others. Their professional and human qualities hold in honour the School in which they were formed.
By his example and work, Giulio Natta left a message that everybody should ponder and convey to the young researcher who did not have the luck to meet him a message of faith in research and in the benefits deriving to mankind from science and technology.
Natta's optimism about the beneficial effects of science and technology for the future of mankind was the result of the events he had witnessed and of the successes he had attained: the synthesis of ammonia - on which industry of fertilizers is based - through which the ever increasing world population may be provided with food; the progress achieved is certainly higher; I only recall the few with whom I was more closely in the knowledge of biochemical mechanisms on which life in our world is based; of the discovery of new materials, often useful and sometimes necessary for the sort of life mankind wants to lead at the present time. Natta's message should especially be considered by all those who seek any opportunity to attack research and the chemical industry under the guise of philosophical and ecological motivations that they do not care to analyse in a critical and conscious way.

Acknowledgement

I wish to thank Mrs R. Lamma Fontani, who for many years was Prof. Natta's faithful secretary, for her help in finding the documentation necessary for this commemorative paper.

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