Giulio Natta – His Life and Scientific Achievements

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EUPOC 2003 has been organized by the European Polymer Federation to honor Giulio Natta, on the occasion of the centenary of his birth. Karl Ziegler and Giulio Natta, as is well known, shared the 1963 Nobel Prize in Chemistry for their discoveries in the field of chemistry and technology of high polymers. In this introduction I would like to briefly highlight the life and scientific achievements of Giulio Natta.

Giulio Natta was born in Imperia, a small city near the Italian-French border, on February 26, 1903. He attended the middle schools in Genoa, then he moved to Milan as student in Chemical Engineering at the Polytechnic of Milan. After graduating in Chemical Engineering in 1924, he remained at the Polytechnic as post-doc and then as assistant Professor. He was a brilliant student. His great passion for Chemistry is demonstrated by the fact that he set up a small chemical lab in his apartment, to do chemical experiments at home.

His academic career was rapid: He was professor at the University of Pavia (1933-35), at the University of Rome (1935-37) and at the Polytechnic of Turin (1937-38). In 1938 he was called at the chair of Industrial Chemistry of the Polytechnic of Milan, where he would remain for 35 years, until his retirement in 1973.

At the beginning of his career, his main scientific interest was the study of chemical structures by x-ray and electron diffraction techniques. Later he became interested in reactions and processes of industrial importance, such as the synthesis of MeOH with new catalysts, and the hydroformylation reaction.

At the end of the '40s, he established a collaboration with Montecatini, the biggest chemical company in Italy at the time. As a result of this collaboration about 25 young chemists were working in Natta's Institute at the beginning of the '50s. As we'll see later this collaboration was of great benefit to both Natta and Montecatini.

The turning point in Natta's scientific career began in 1952. In May of that year Natta attended

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a conference given in Frankfurt by Karl Ziegler, Director of the Max-Plank Institut für Kohlenforschung in Mülheim. Ziegler reported on the oligomerization of ethylene catalyzed by $AlEt_3$ (the so-called *Aufbaureaktion*). Natta was impressed by Ziegler's results and convinced Montecatini to purchase the rights of the *Aufbaureaktion*. Three young chemists of Natta's group went to Mühlheim to become familiar with the experimentation using aluminum alkyls. Natta began to work on the *Aufbau* reaction in Milan.

In the 2nd half of 1953, Ziegler's group discovered that the combination $AlEt_3$-$TiCl_4$ was capable of polymerizing ethylene under very mild conditions. At the end of 1953 Montecatini and Natta were informed by Ziegler of the new discovery.

Natta started to investigate the polymerization of propylene with the catalyst of Ziegler and obtained a polymer in March 1954. The polymerization product appeared heterogeneous, consisting of a mixture of rubbery material and a white product. It was fractionated by extraction with successive boiling solvents. Boiling acetone removed all the oligomers, that is oily products. Boiling diethylether dissolved all the amorphous polypropylene.

The residue was crystalline polypropylene, which in turn could be separated into fractions having different degrees of crystallinity by extraction with heptane, toluene, xylenes.

The crystalline structure of polypropylene was determined, and it was found that the crystallinity was due to the fact that in each chain all the tertiary C atoms had the same configuration, at least for long sections of the polymer chain. Natta called these polymers isotactic. A Patent was filed in June '54. Butene-1 and styrene were also polymerized to isotactic polymers a few weeks later.

In November 1954, the group in Milan made a significant change to Ziegler's catalyst. $TiCl_4$ was replaced by $TiCl_3$, which increased the stereospecificity from 40 to ca. 80%. This paved the way for the commercial production of polypropylene, which started in Ferrara in 1957.

At the end of 1954 a letter was submitted to the editor of the *Journal of American Chemical Society*, which caused some surprise in the chemical world.

Paul Flory, a member of the Editorial Board of *J. Am. Chem. Soc.*, who was to get the Nobel Prize in Chemistry in 1974, wrote a letter to Natta (in January '55), in which he said inter alia: " The results disclosed in your manuscript are of extraordinary interest; perhaps one should call them revolutionary in significance. The possibilities opened up by such asymmetric polymerization are of the utmost importance, I am sure."

Other groups succeeded in polymerizing propylene during 1954, but, in their patents, polypropylene characterization was made only by I.R. methods. No fractionation or x-ray examinations were reported, so that they did not recognize the importance of what they had obtained.

However, the synthesis of isotactic polypropylene, polybutene and polystyrene was only the beginning of a long story. Natta understood that the new catalysts were causing a revolution in polymer chemistry and therefore decided to extend the investigation to other classes of monomers: diolefins, cycloolefins, acetylenes.

At the beginning of 1955, butadiene was polymerized to a crystalline polymer having a 1,2 structure in which the chiral configuration of the tertiary C atoms along each chain were alternated. Natta coined the term syndiotactic to indicate polymers of this structure (*syndio* meaning "two by two" was taken from Greek).

A few months later, in October 1955, butadiene was polymerized to a polymer having a 1,2 isotactic structure, which showed for the first time that a monomer can be polymerized to iso- or syndiotactic polymer depending on the catalyst used. It now appears obvious that a monomer can give, at least in principle, iso- or syndiotactic polymers, but at that time, 1955, it was not.

Other two stereoregular polymers were obtained from butadiene (with a cis-1,4 and a trans-1,4 structure), so that all the four foreseeable stereoregular polybutadienes were obtained in a few months.

Stereoregular polymers were also obtained from other 1,3-dienes (such as isoprene, 1,3-pentadiene, several other substituted butadienes), small ring cycloalkenes (such as cyclobutene and norbornene), and from acetylenes.

Syndiotactic polypropylene was also isolated and characterized in 1958, and more or less at the same time crystalline alternating copolymers of ethylene/cyclopentene, ethylene/2-butene, ethylene/butadiene were obtained.

Various propylene homologs were polymerized to isotactic polymers, e.g. 3-Me-1-butene, 4-Me-1-pentene, 4-Me-1-hexene, 5-Me-1-hexene, 5-Me-1-heptene and vinylcyclohexane. Work on these monomers allowed one to formulate general rules determining the structure of linear macromolecules. In particular, the data on these isotactic polymers indicated that fourfold or higher order helices exist besides the threefold one observed in isotactic polypropylene.

Stereoregular polymers were also obtained from non-hydrocarbons monomers, such as vinylalkylethers, alkenylethers, O-methoxystyrene, N-vinylcarbazole, benzofuran, using either cationic initiators, Mg-alkyls or even $AlEt_3$.

I don't know exactly how many stereregular 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.

In 1961 the *Journal of Polymer Science* devoted an issue (vol. 51, issue 156) to Giulio Natta, "to express appreciation to the man who first established with vigorous scientific methods the existence of stereoregular polymers". Natta was called the father of stereoregular polymers. The editor wrote in the introduction to this issue.

> *"Seldom has a scientific contribution aroused such profound fundamental interest and has been followed by such a rapid technical development as the series of publications by Professor Giulio Natta and coworkers on the stereospecific polymerization of olefins, which started to appear in Italian journals several years ago and have continued ever since. Many prominent scientists in very large research laboratories have become interested in the new technique and have focused their interests and efforts on its promotion. Yet Professor Natta has succeeded in maintaining undisputed leadership and continues to surprise his colleagues by new and unexpected discoveries along the general principles of stereregulation."*

In my opinion there are two reasons for this success:

1. The intuition of Natta, who was the first to realize that Ziegler catalysts were causing a revolution in polymer science. He gave a name to the stereoregular polymers, isotactic and syndiotactic, and one gives a name when he realizes that something new and important has been created.
2. The organization that Natta gave to his Institute, where chemists, physicists, spectroscopists, crystallographers were working together on the same project, which allowed an interdisciplinary approach to the problems. Most of the people working in

Natta's Institute were Montecatini employees and without their work and the financial support of Montecatini it would have been impossible to maintain for several years the leadership in polymer science.

At the end of this introduction I wish to cite what Sir Robert Robinson said when he introduced Natta who was awarded in London in 1961 the First International Synthetic Rubber Award (Rubber and Plastics Age, 1961, p.1195):

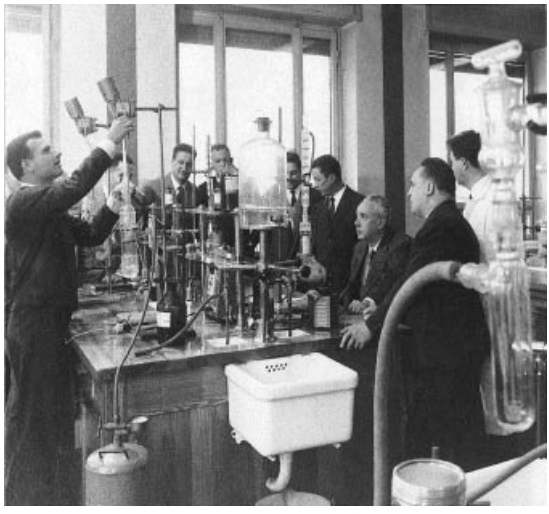
"Natta has developed the theme of polymerization as a grandiose fugue. The successful initiation, prosecution, and completion of so much and so varied research is the result of his most unusual originality, drive and power of sustained work."

A few words about Natta as a man.

He was a very simple person, who dedicated all his life to science. He was the opposite of what we call an ambitious person. When he received the Nobel Prize, he attributed all his scientific success to luck: "We have been lucky", he said.

No doubt that luck often plays an important role in scientific discoveries. However, in science, luck is not blind. It only helps intelligent people, those who are intuitive, inquisitive, hard working, and able to quickly seize the importance of an event.

Giulio Natta was a man of this type.



Professor Natta with some collaborators (1963).
From the left: Lido Porri, Piero Pino, Raffaele Ercoli, Enrico Mantica, Ferdinando Danusso, Giulio Natta, Gino Dall' Asta, Mario Farina.