

Giulio Natta and the Origins of Stereoregular Polymers

S Sivaram

The name of Natta is entwined inextricably with that of Ziegler, in the famous catalyst systems known by their names and used to make polyethylene and polypropylene. Unlike ethylene, which is achiral, propylene is a prochiral molecule and upon polymerization can lead to interesting stereochemical and regiochemical enchainment sequences. Natta's prescience in recognizing this unique feature of propylene led to the discovery of crystalline isotactic polypropylene and the beginning of a new industry. The story of how Natta discovered polypropylene is an engrossing one – one of stiff competition amongst contemporaries, Natta's intimate relationship with the Italian industries, and his unique scientific background. Natta's identification of isotactic polypropylene as a right-handed three fold 'single helix' in March 1954, in quick succession to the discovery of DNA 'double helix' by Watson, Crick, and Rosalind Franklin (March 1953), and the coiled-coil motif of 'triple helix' of collagen by G N Ramachandran (August 1954), makes this period the 'golden age of macromolecular crystallography'.



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Giulio Natta: The Early Years

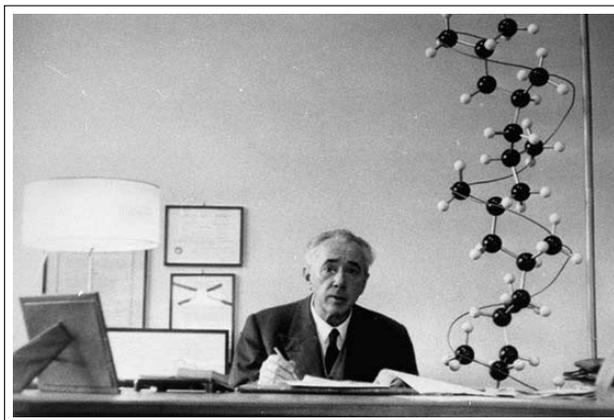
Natta was born in Imperia, Italy on 26 February 1903 (*Figure 1*). He was a child prodigy and by the time he was eight, had made up his mind to study chemistry, rather than law, which his father advocated. Natta studied mathematics at the University of Genoa. He then moved to Milan Polytechnic Institute and enrolled in the industrial chemistry course. He began his research training under Professor Giuseppe Bruni who was a student of Jacobus van't Hoff – the first Nobel Prize winner in Chemistry for the discovery

Keywords

Isotactic polypropylene, crystalline polypropylene, stereoregular polymers, Ziegler's catalysts, ethylene-propylene rubbers.



Figure 1. G Natta and the helical polypropylene.



The only difference between theoretical (fundamental) and industrial (applied) problems is that the latter is more difficult to resolve because you have to take into account lot of factors that you can neglect in the former.

– G Bruni

of the tetrahedral geometry of molecular carbon which laid the foundation of stereochemistry. It was perhaps this lineage that eventually led Natta to the discovery of stereoregularity in polymers! Professor Bruni saw deep connections between scientific problems and industrial applications and often stated that, “the only difference between theoretical (fundamental) and industrial (applied) problems is that the latter is more difficult to resolve because you have to take into account lot of factors that you can neglect in the former.” Natta imbibed this philosophy and often said that, “the essence of knowledge, once you have got it, is to apply it,” a quote attributed to Confucius.

Natta began his research career studying organic sulfur compounds. During the wartime, in military service, he studied mustard gas and its effects. Later, he worked on catalysts for methanol synthesis and made important observations on the physical and surface properties of these catalysts. He established a new process for the separation of butadiene which contributed to the production of synthetic rubber in Italy. He extensively worked in the area of industrial applications of carbon monoxide. Clearly, Natta’s early work was very much ‘applied’, aimed at fulfilling the needs of his country engaged in war.

In 1935, during a visit to Vienna with his newly married wife, Rosita Beati, he visited the laboratories of Professor Herman Mark, who was a pioneer in the application of X-ray and elec-



tron diffraction to study large synthetic molecules such as cellulose. Incidentally, Linus Pauling built the first electron diffraction facility to probe molecular structures at Caltech with the assistance of Professor Mark and went on to create history. Thus began Natta's interest in chemical structures. Later, he had an encounter with Professor Hermann Staudinger at Freiburg, Germany. Staudinger had proposed the concept of macromolecules in 1920, an idea that organic chemists of the day refused to accept. Natta brought back some samples of macromolecular substances synthesized by Staudinger and began examining their structures using the then newly emerging tools of X-ray and electron diffraction.

Natta established a new process for the separation of butadiene which contributed to the production of synthetic rubber in Italy.

Natta quickly rose through the academic ranks and became a Professor and Chair of industrial chemistry at Milan Polytechnic Institute in 1939. The following two decades were the golden years of Natta's research which eventually led to the seminal discovery of stereochemistry of polymers. When fascist Italy under Mussolini was reeling under the sanctions imposed by the League of Nations in 1938 to protest Italy's invasion of Ethiopia, Natta turned his attention to the area of synthetic rubber, a strategic wartime need. During this period, he developed the catalysts and chemistry for the preparation of high *cis*-polybutadiene.

Natta was able to quickly see the connection between science and its applications from the very early part of his training. He believed that industrial research is a necessity for economic development. Natta trained a large number of students and placed them in industries. He was an active industrial consultant and received generous support from the industries to run his laboratories and equip them with many sophisticated facilities.

Ziegler and Natta, whose hyphenated names are inextricably linked to one of the most successful catalysts for the manufacture of polyolefins, were in fact, like cheese and chalk, in terms of their personalities and research philosophies. While Ziegler was a purist when it came to research pursuits and abhorred problems that had practical applications, Natta was challenged by and enjoyed looking at problems which had industrial applications. His intimate



industrial connections influenced the projects he chose to pursue. In fact, it was this quality that led Natta to see the commercial possibilities of Ziegler's work with organoaluminum compounds when he first heard Ziegler's lecture at Frankfurt in 1952. He was quickly convinced and brought in the vast resources of an Italian industry to examine the opportunities, and eventually beat Ziegler in the race to make polypropylene using Ziegler's own catalyst! Along the way, he assured himself a place in the history of chemistry which otherwise would have belonged to Ziegler alone!

Natta passed away on 02 May 1979, at the residence of his daughter at Bergamo, Italy, after fighting a long battle with Parkinson's. His bout with the disease began in 1956, and he needed his children's assistance in 1963, to deliver the Nobel address. In spite of his physical debilitation, he continued to be active in research till his death. A model of a helical polypropylene molecule decorates his burial place, reminding us of the rich scientific legacy that he left behind for the succeeding generations.

Natta's Tryst with Ziegler and its Consequences

Natta recognized the significance of Ziegler's findings, maybe even beyond Ziegler's comprehension at that time.

Natta and a few of his co-workers attended a lecture by Ziegler in 1952, at a meeting of the German Chemical Society at Frankfurt. To a majority of the audience, there was nothing very spectacular about the lecture. However, Natta recognized the significance of Ziegler's findings, maybe even beyond Ziegler's comprehension at that time. Ziegler described his work on Aufbau reaction and the growth of a polymer chain by repetitive addition of an olefin across a carbon-aluminum bond. Natta returned to Italy and convinced a company called Montecatini located near Milan to invite Ziegler to Italy. This visit resulted in an agreement between Montecatini and Ziegler in January 1953. The agreement granted exclusive license to Montecatini in Italy for certain rights concerning *the conversion of olefins with the use of organometallic compounds, any ancillary processes as well as other future processes which would be developed in the field of olefin conversion with the use of organometallic compounds as catalysts*. At



the time this agreement was negotiated, polymerization of ethylene to polyethylene was yet to be discovered. Montecatini made a down payment of 600,000 Deutch Mark, certainly a princely sum to an academic professor. Was Ziegler swayed by the money offered to him and therefore, agree to such a broad-scoped and open-ended agreement? This decision was to haunt Ziegler for many years as many more discoveries began emanating from his laboratory and legal questions arose regarding all such subsequent developments falling within the scope of the 1953 agreement.

As a part of the agreement, Montecatini in February 1953, placed two scientists and an engineer in Ziegler's laboratory to gain first-hand experience of preparing organoaluminum compounds – an expertise which only Ziegler's students had the mastery of. The three scientists from Montecatini, being located at Ziegler's laboratory, were inadvertently and informally being exposed to the excitement in the laboratory on experiments being conducted to polymerize ethylene to polyethylene. The historic experiment, which resulted in solid polyethylene, was conducted and recorded by H Briel on 26 October 1953. On 16 November 1953, Briel extended the reaction to propylene and recorded that, "no solid, but only liquid products, dimerisate." It was on account of this observation that when Ziegler drafted the patent, his claim was only to a method for preparing high molecular weight polyethylene useful as a plastic.

During their stay at Mülheim, the three scientists from Montecatini maintained written communication with their supervisors and also Professor Natta. The discovery of a catalyst for polyethylene at Mülheim had been communicated to Montecatini as early as November 1953, even while the patent to this discovery was under drafting! Montecatini, formally requested Ziegler that the production of high molecular weight polyethylene be covered under the scope of the January 1953 agreement. For the first time, Ziegler realized that he had possibly given away more than he had bargained for!

Ziegler's work became an intense topic of discussion and analysis in Natta's laboratory in January 1954. In March 1954, Ziegler



met Natta at Milan Polytechnic, and they mutually agreed that while Ziegler's group would continue to work on the chemistry and catalyst systems for the polymerization of olefins, Natta was free to examine the kinetics of polyethylene formation and X-ray analysis of the structure of polyethylene. Clearly, this was an attempt by Ziegler to restrain Natta from exploring catalyst systems for the polymerization of propylene!

Natta, however, had other plans! Natta had an intimate knowledge of the catalysts used by Ziegler, through both formal and informal channels of communication. He instructed one of his students, Paolo Chini (who was one of those seconded to the laboratories of Ziegler at Mülheim) to polymerize propylene using Ziegler's catalysts. Chini recorded on 11 March 1954 that, "using triethylaluminum and titanium tetrachloride (Al/Ti: 4) in pentane, a propylene pressure of 12 atm at 75 °C for 1.25 hours resulted in 3.5 g of a solid polymer". Another of Natta's students, Paolo Corradini pressed the polymer into a film, stretched it to 500% of its original length, and recorded its X-ray diffraction. Natta noted down in his diary on the same day "made polypropylene!" On 12 March 1954, Corradini examined the polymer with the aid of X-ray crystallography. The polymer showed the features of a crystalline material (*Figure 2*). Natta immediately recognized that polypropylene consisted of several diastereoisomers with very different physical properties. Between March and May 1954, several experiments were conducted and a method of fractionating the polymers into two fractions was established. Fractionation from diethyl ether and heptane resulted in an 'amorphous' soluble fraction and an insoluble 'crystalline' fraction (with a $T_m \sim 160^\circ\text{C}$). All these results were freely shared with Montecatini, which applied for an Italian Patent on 08 June 1954 (Number 535712; Dated 17 November 1955; Inventor: G Natta; US Patent 3,112, 200; 08 June 1954, Inventors: G Natta, P Pino, and G Mazzanti), just seven months after Ziegler submitted his patent application on polyethylene. The first public announcement of the discovery occurred at the National Lyncean Academy in 1955.

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Ironically, in July and August 1954, Heinz Martin in Ziegler's



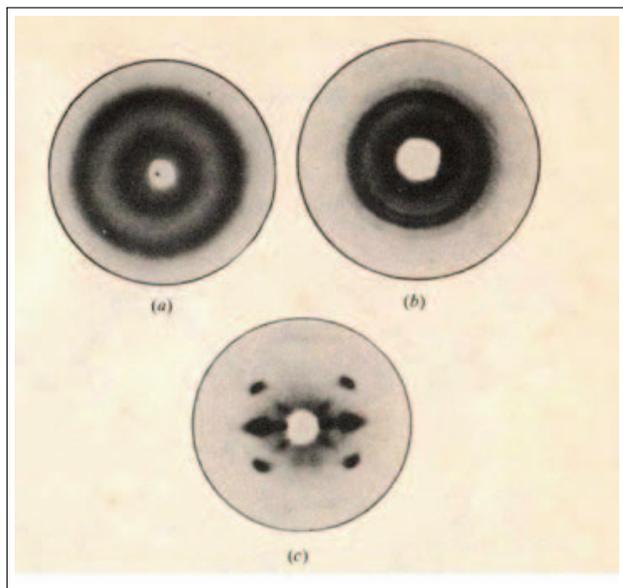


Figure 2. X-ray of polypropylene (a) Atactic (b) Unoriented isotactic, and (c) Drawn and oriented isotactic (Source: C C Price, *Geometry of Molecules*, McGraw Hill, 1971).

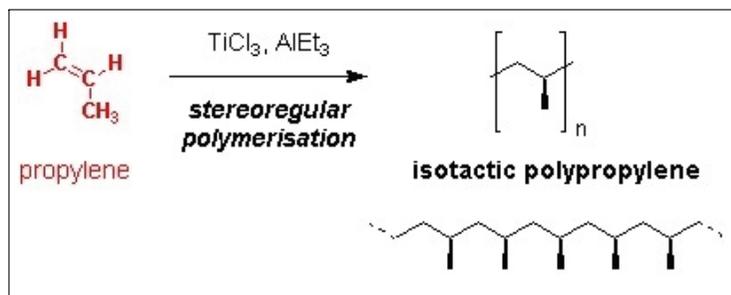
laboratory, redirected his attention to the polymerization of propylene using diethylaluminum chloride and titanium tetrachloride and was successful in making solid polypropylene. A patent was issued to Ziegler and his co-workers – German patent number 1, 257, 430 with a priority date of 03 August 1954. However, Natta had beaten Ziegler to the finish line by less than two months.

Why did Ziegler not pursue his initial experiment with propylene, albeit an unsuccessful one, to its logical conclusion?

Was this a deliberate breach of agreement by Natta? Why did Natta not share his results with Ziegler as was demanded by the 1953 agreement between Ziegler and Montecatini? Why did Ziegler not pursue his initial experiment with propylene, albeit an unsuccessful one, to its logical conclusion? Why did he miss adding propylene (or α -olefins) to the exemplary claim of his October 1953 patent? Was he too preoccupied with his work on polyethylene and the licensing activities that began soon after? Did Ziegler really believe that propylene could not be polymerized to high molecular weight polypropylene and therefore, did not pursue this line of thought? Even if he had made crystalline polypropylene, would Ziegler have been able to deduce its structure since he was not familiar with the tools of structural chemistry? These questions shall forever remain unanswered.



Figure 3. Catalytic polymerization of propylene.



Montecatini commenced the production of isotactic polypropylene at Ferrara, Italy in 1957, using a catalyst consisting of an α form of TiCl_3 (violet in color) and diethylaluminum chloride in heptane as the diluent.

Montecatini commenced the production of isotactic polypropylene at Ferrara, Italy in 1957, using a catalyst consisting of an α form of TiCl_3 (violet in color) and diethylaluminum chloride in heptane as the diluent (*Figure 3*). Today, the global capacity for polypropylene is more than 60 million tons per annum at an estimated market value of over 75 billion USD. The commercial importance of isotactic polypropylene elastomers based on ethylene, propylene, and 1,4-*cis*-polybutadiene is evident from the fact that polypropylene is ranked third in terms of commercial value, while 1,4-*cis*-polybutadiene and copolymers based on ethylene and propylene occupy second and third positions respectively in the ranking of synthetic rubbers.

Crystalline Polypropylene: The Origins of Polymer Stereochemistry

Notwithstanding the controversies above, it was Natta who recognized the crystalline property of polypropylene as soon as the first few samples were synthesized in the laboratory. Natta was trained in X-ray crystallography, and this enabled him to quickly determine the structure of polypropylene. Natta's creative skills are evident in the way he used both concepts and experiments to deduce the structure of polypropylene. Thus was born one of the most fascinating fields of polymer science – the stereochemistry of polymers.

Natta submitted a short communication to the *Journal of American Chemical Society* on 10 December 1954, which was initially



rejected by a referee because Natta did not disclose the nature of the catalyst used. Fortunately, the editor of the journal at that time was Paul J Flory¹, who immediately grasped the significance of Natta's results. Flory overruled the referee and wrote to Natta, and I quote, "The results described 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 utmost importance, I am sure", (Letter from P J Flory addressed to G Natta, June 7, 1955).

Natta's creative skills are evident in the way he used both concepts and experiments to deduce the structure of polypropylene.

The communication titled 'Crystalline High Polymers of α - Olefins,' appeared in the 25 March 1955 issue of the journal (*Figure 4*). Natta pointed out in this paper that, "the large number and the cleanness of the X-ray reflections obtained from drawn fibers of the new polyhydrocarbons demonstrate the unusual regularity of their chain structure. By comparing X-ray and density data are seen that each stretch of the principal chain, included in the elementary cell, corresponds to three monomeric units (-CH₂-CHR-) and therefore contains an odd number of asymmetric carbon atoms. We attribute to the new crystalline polymers a structure in which at least for long portions of the principal chain, all the asymmetric carbon atoms have the same configuration. In this case, if the principal chain of a crystalline polymer of a α -olefin (-CH₂-CHR-), is represented arbitrarily as a planar fully extended chain, all the R groups must be placed on the same side of the plane of the principal chain. Such planar structure is impossible because of the steric impediments among the R groups and in order to reach the crystalline state a spiralization of the principal chains must take place". Natta also introduced the terminology to define such structures. He proposed that such chains be designated as 'isotactic chains', from the Greek words 'and' and 'to set up' – the polymer chains having an exceptionally regular structure, containing series of asymmetric carbon atoms with the same steric configuration ('isotactic' asymmetric carbon atoms) (*Figure 5*).

¹See *Resonance*, Vol.22, No.4, 2017.

Stereoisomerism in polymers arises from different spatial arrangements or configurations of the atoms or substituents which can be interconverted, only by the breakage and reformation of the chemical bond.

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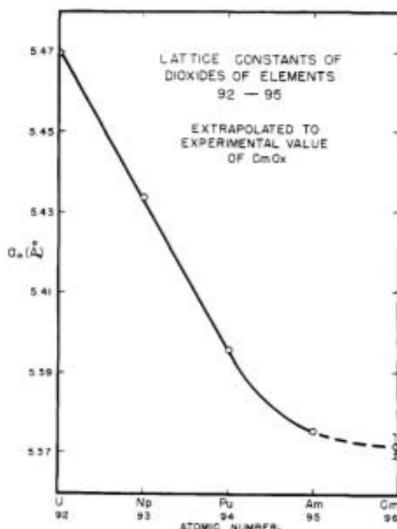


Fig. 1.

lattice constants. A reasonable extrapolation of the smooth curve would give ~ 5.37 for the expected value of CmO_2 . Our value of 5.372 would indicate that the ratio of O/Cm must be close to 2, showing the existence of an "average valence" of Cm approaching 4.

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CRYSTALLINE HIGH POLYMERS OF α -OLEFINS

Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained¹ by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

Using various heterogeneous solid catalysts which will be described elsewhere,² we have synthesized linear crystalline polymers of α -olefins and we are now reporting some properties of

(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 56.

(2) Details on the polymerization processes will be published in the *Journal of Polymer Science and Atti dell'Accademia Nazionale dei Lincei*.

crystalline polypropylene, poly- α -butylene, and polystyrene. Depending on the structure of the catalyst, different amounts (ranging from 0 to 100%) of the polymerization products are crystallizable and can be separated easily from the much more soluble non-crystalline polymers by solvent extraction. In the case of polypropylene and polystyrene the X-ray diagrams of drawn fibers show reflections from about fifty different planes. Both equatorial and higher order X-ray reflections of polystyrene may be indexed on the basis of a hexagonal cell with $a = 21.9 \text{ \AA}$, and $c = 6.65 \text{ \AA}$. (space-group R 3c or R 3c). One of the two different crystal forms we observed for the poly- α -butylene seems to have a similar cell with $a = 17.3 \text{ \AA}$ and $c = 6.7 \text{ \AA}$. We have not yet collected sufficient data to establish the correct unit cell of polypropylene: the identity period along the fiber axis c is, in this case, 6.50 \AA ; the equatorial X-ray reflections may be indexed on the basis of an oblique cell with $a = 6.56 \text{ \AA}$, $b = 5.46 \text{ \AA}$ and $\gamma = 106^\circ 30'$.

In Table I the physical properties of the crystalline polypropylene and poly- α -butylene have been compared with those of the corresponding solid non-crystallizable substantially linear polymers obtained as by-products by the same polymerization processes.

The new crystalline polyhydrocarbons show higher melting point, higher density and lower solubility in organic solvents, than the corresponding "amorphous" polyhydrocarbons having intrinsic viscosity of the same order of magnitude.

The infrared spectra³ of crystalline polypropylene, of melted samples of the same polymer and of the "amorphous" polypropylene show between 2 and 7.5 μ the high adsorption regions characteristic of hydrocarbons. The wave lengths of the absorption bands between 7.5 and 15 μ in normal and polarized light have been reported in the Table II. Most of the differences between the infrared spectrum of the crystalline and of the non-crystalline polypropylene⁴ disappear on melting the crystalline product and reappear after cooling the melted sample.

The large number and the cleanness of the X-ray reflections obtained from drawn fibers of the new polyhydrocarbons demonstrate the unusual regularity of their chain structure. By comparing X-ray and density data are seen that each stretch of principal chain, included in the elementary cell, corresponds to three monomeric units ($-\text{CH}_2-\text{CHR}-$ and therefore contains an odd number of asymmetric carbon atoms.

For these reasons we have excluded the presence of sequences of asymmetric carbon atoms having alternatively d and l configuration in the principal chain of the polymer, as was proposed for the crystalline poly-alkylvinyl ethers.⁵

(3) A Beckmann IR 2, a Perkin-Elmer model 112, and a Perkin-Elmer model 21 spectrometer with NaCl prisms have been used.

(4) The infrared spectra of the crystalline and of the linear not crystallizable polypropylenes are very different from infrared spectra of branched polypropylenes produced using AlEt₃ as catalyst.

(5) C. E. Schildknecht, et al., *Ind. Eng. Chem.*, **40**, 2164 (1948); C. E. Schildknecht, S. T. Gross and A. O. Zoss, *ibid.*, **41**, 1998 (1949); C. E. Schildknecht, A. O. Zoss and F. Grosser, *ibid.*, **41**, 2091 (1949).

Figure 4. The historic communication to the editor that appeared in *J. Am. Chem. Soc.*, in 1955, announcing the discovery of isotactic polypropylene.

be interconverted, only by the breakage and reformation of the chemical bond. Polymers derived from α -olefins may consist of structural units containing a tertiary carbon, so that in a polymer with a defined length, this carbon atom may be considered

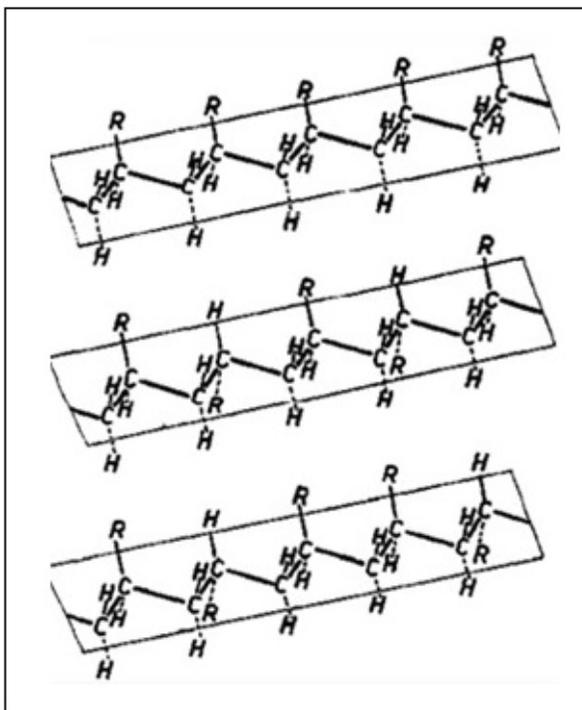


Figure 5. Natta's original representation of isotactic, syndiotactic, and atactic polypropylene.

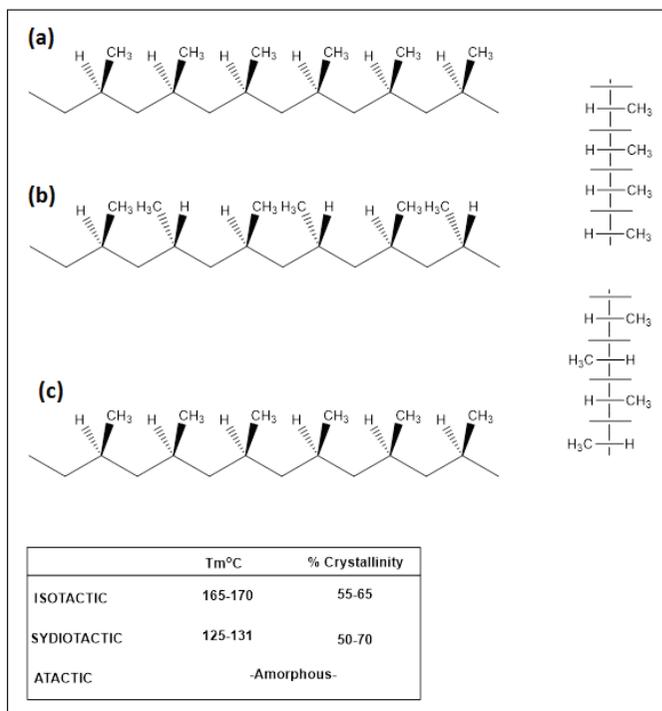
asymmetric. Regularity in the configuration of successive chiral, asymmetric or pseudo-chiral carbon (C^*) determines the tacticity² of the polymer chain. Isotactic and syndiotactic polymers have ordered arrangements of groups. Hence, the chains can pack closely together and develop high crystallinity. The stereoregular polypropylene defined by Natta as isotactic is a crystalline powder with a density lower than that of water and a melting point of 170°C , whereas, non-stereoregular polypropylene (atactic) is amorphous and rubbery in nature (Figure 6).

The placement of each methyl group in a given segment could be on the front or the rear side of the plane represented by the carbon atoms of the polymer chain backbone in its *trans* conformation. Each methyl group can have the same configuration, *i.e.*, all methyl groups can be on the same side. This arrangement of chiral groups in the same configuration is termed as isotactic (Figure 7(a)). The methyl group could have alternating config-

²Tacticity is the relative stereochemistry of adjacent chiral centers within a macromolecule. A tactic macromolecule is one in which essentially all the configurational units are identical. In a linear asymmetric polymer chain, the pendant groups can be arranged into orderly configurations or they can be completely random. The steric order is called tacticity. Tacticity is particularly significant in polymers of the type $-\text{H}_2\text{C}-\text{CH}(\text{R})-$.



Figure 6. Stereoregular polypropylenes (a) Isotactic (b) Syndiotactic, and (c) Atactic, and Fisher projections of (a) and (b).



Isotactic sequence is one where the probability of each adjacent group having the same configuration is unity, syndiotactic is where this probability is zero, and atactic where the probability is 0.5.

urations, *i.e.*, one in front and each adjacent one in back. This regular alternating configuration is called ‘syndiotactic’ (*Figure 7(b)*). There is also a random arrangement configuration, which is called ‘atactic’. Isotactic sequence is one where the probability of each adjacent group having the same configuration is unity, syndiotactic is where this probability is zero, and atactic where the probability is 0.5. One can then envision any degree of tacticity – from 100% isotactic to 100% syndiotactic. Note that the configuration is built into the polymer and is not changed by altering the conformation. X-ray diffraction shows that isotactic polypropylene does not crystallize in an all-*trans* conformation of the backbone but in a regular helical conformation. The reasons for the helical conformation is best understood by examining the possible conformations skew 1, *trans*, and skew 2 as shown in the Newman projection (*Figure 8*). Skew 1 will be unfavorable, whereas, skew 2 and *trans* have equal energy. Thus, if all the methyl groups have the same configuration, the chain will tend

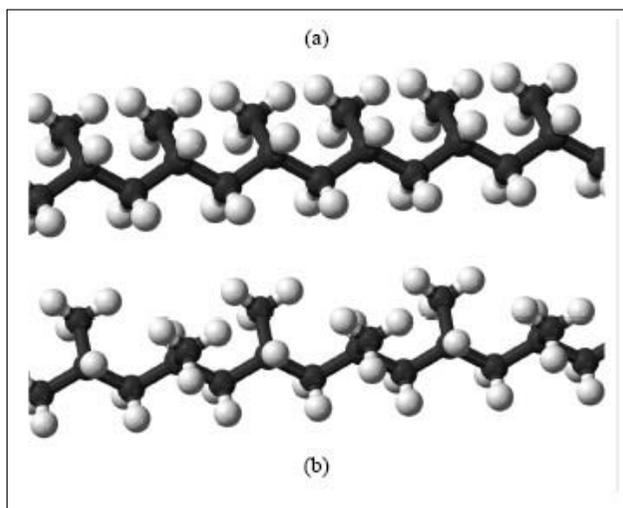


Figure 7. Chain structure of (a) Isotactic polypropylene (b) Syndiotactic polypropylene.

to skew in just one sense, as is necessary to form a regular helix. The other important hindrance factor, which helps in shaping the preferred conformation of isotactic polypropylene is the overlap, which would occur for the adjacent methyl groups in the all-*trans* conformation. Two consecutive *trans* conformations isotactic polypropylene are thus disfavored by van der Waals repulsion between the adjacent methyls, which is entirely relieved by alternate *trans*, skew 2, *trans*, skew 2 conformations. This conformation does provide a regular helical arrangement of the chains in the crystal, in agreement with the repeat distance of 6.7 Å observed by Natta. Each skew 2 bond introduces a twist of 120° so that three are required for producing a monomer unit in the same orientation as the first. Isotactic polypropylene is a right-handed helix (containing three monomer units in the repeat period); symmetry derived purely from the need of the chain to minimize steric interactions. Syndiotactic polypropylene is a right-handed helix containing 4 monomeric units in the repeat period. (Figures 9(a) and (b)).

Natta soon realized that randomly introducing propylene sequences in the polymers could disrupt the crystallinity of ethylene in polyethylene. Soon, he demonstrated the synthesis of a completely amorphous ethylene-propylene copolymer, which is an excellent elas-



merization, using enantiomorphic catalytically active site, had a far-reaching impact on the progress of polymer science and technology. The June 1961 issue of the *Journal of Polymer Science*, dedicated to Natta as *the father of stereoregular polymers* states, “Seldom has a scientific contribution aroused such a profound fundamental interest and been followed by such a rapid technical development as the series of publications by Professor Giulio Natta and his co-workers on the stereospecific polymerization of olefins, which started to appear in the Italian journals several years ago and have continued ever since. Many prominent scientists in many 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 in this field of polymer chemistry and continues to surprise his colleagues by new and unexpected discoveries along the general principles of stereoregulation.”

Between 1954 and 1964, Natta and his associates synthesized as many as 130 new types of stereoregular polymers, determined their crystal structures, investigated their physical, chemical, and mechanical properties, and explored the mechanism of stereocontrol of the catalysts. The output from his laboratory was prolific – close to 600 papers and over 333 patents! *The Giulio Natta Archive* is a treasure house of over 50,000 pages of his correspondences, unpublished manuscripts, and other related documents that chronicle the life and work of this great scientist!

Natta shared the Nobel Prize in 1963 with Ziegler. His contribution was acknowledged by the following remarks made at the time of the award of the Prize and I quote, “However, Professor Natta has found that certain type of Ziegler catalysts leads to stereoregular macromolecules, *i.e.*, macromolecules with spatially uniform structures. If all the side groups point to the right or left, these chains are called isotactic. Nature synthesizes many stereoregular polymers, for example, cellulose and natural rubber. This ability has so far been thought to be the monopoly of Nature. Professor Natta has broken this monopoly.”

Steering clear of the controversies surrounding who should be

The Giulio Natta Archive is a treasure house of over 50,000 pages of his correspondences, unpublished manuscripts, and other related documents that chronicle the life and work of this great scientist!



given the priority for the discovery of polypropylene, the Nobel Prize committee credited Ziegler with the discovery of the catalysts for the polymerization of olefins and Natta with the discovery of the chain configuration of polypropylene.

Lessons From Natta's Life

A close examination of the life and work of Natta offers us many insights concerning the secret behind his success.

1. Natta created an ambience in his laboratory where scientists with experience in diverse fields worked together as a team. Natta's group comprised organometallic chemists, catalyst chemists, polymer chemists, structural chemists, and organic chemists. He did not define the field of his interest narrowly.
2. Natta created an environment in a university laboratory, where fundamental questions were asked while not losing sight of applications.
3. Natta maintained close ties with the industry, which constantly challenged him with many scientific problems and provided much stimulus for his basic research.
4. He trained students for the industry and had a seamless relationship with the industries that provided him money as well as people to pursue his research. Transcending mere transactional relationship, his industrial associations were sustained and long-term, built on mutual trust and faith, not merely restricted to contracts and agreements.

Natta's discovery of stereochemistry of polymers did not come from a lifelong obsession with this problem; there is little evidence in his published work before 1954 that he was preoccupied with this objective. His journey was driven by both curiosity as well as the potential of making useful polymers from monomers other than ethylene; a thought provoked by his close interaction with Ziegler (academia) and Montecatini (industry). Along the way, he discovered crystalline polypropylene, one of the most versatile polymers that we know today. His deep insight into the



structure of the molecule opened up the world of stereochemistry of polymers with limitless potential. The journey of Natta and Ziegler teach us that useful and impactful discoveries can be made starting from either end of the spectrum (or continuum) of basic and applied research, provided one pursues a problem with an open mind, diligence, persistence, imagination, intuition, and creativity.

Suggested Reading

- [1] G Natta, A New Class of Polymers of α -olefin Having Exceptional Regularity of Structure, *Atti Acc. Naz. Lincei Mem.*, Vol.4, No.8, p.61, 1955.
- [2] Giulio Natta, Piero Pino, Paolo Corradini, Ferdinando Danusso, Enrico Mantica, Giorgio Mazzanti, Giovanni Moraglio, Crystalline High Polymers of α -Olefins, *Journal of American Chemical Society*, Vol.77, No.6, p.1708, 1955.
- [3] I Hargittai, A Comotti and M Hargittai, *Chem. & Eng. News*, Vol.81, p.26, 2003.
- [4] H Martin, *Polymers, Patents and Profits*, Wiley-VCH, Weinheim, Germany, p.9, 2007.
- [5] Giulio Natta Archive, www.guilionatta.it/ENG/archivo.html.
- [6] Paolo Corradini, The Discovery of Isotactic Polypropylene and its Impact on Pure and Applied Science, *J. Polymer Science: Part A: Polymer Chemistry*, Vol.42, p.391, 2004.

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