



The gold medal given by prof. Natta to his collaborators after the Nobel Prize

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## GIULIO NATTA: AN ITALIAN NOBEL PRIZE FOR CHEMISTRY, AFTER 50 YEARS\*

*The paper is divided in 2 parts. The first part is meant to illustrate some statistical aspects relating to long-chain polymers (among which the stereoregular polymers discovered by Giulio Natta), specifically correlated a) to the initial formation of the polymer crystals and b) to the energy dissipation resulting from the chain motion and the overcoming of intra-molecular energy barriers. The second part is meant to describe some aspects of the family life of Giulio Natta, after receiving the biggest honour in his life.*

### Part 1 Some statistical properties of polymers

I had the privilege to make acquaintance with Professor Giulio Natta as a student at the 4<sup>th</sup> year course of Chemical Engineering, at the Polytechnic University (our "Politecnico") in Milan. Unfortunately, in the following years his teaching would be reduced very much by his progressive Parkinson disease. He looked gentle and shy and was very kind to us students; at that time his physical movements appeared to be only slightly impaired by the disease, yet. It became soon apparent that his shyness would disappear whenever he described chemical processes and plants, whether to produce ammonia, sulphuric acid, or to synthesize polymers. He also appeared fascinated when describing the power of X-ray diffraction to determine the atomic structure of crystalline substances, which he had done as a pioneer in earlier days under the guidance of prof. Bruni in Milan, then of prof. Staudinger and of dr. Seemann in Freiburg. Stimulated by Natta and encouraged by Italo Pasquon, then our Professor of Industrial Chemistry, I started to visit regularly the Laboratory of X-ray diffraction, becoming a friend-pupil of Paolo Corradini's and learning in his lab the basic elements of crystal structure and X-ray diffraction. This gave me the opportunity to visit "il Professore" (Natta) rather frequently. Although the first signs of

Natta's illness became soon evident as motion difficulties, nonetheless he would lecture rather frequently and would always pay attention to any chemistry-related question from the students. I was especially impressed by the intensity of his recalling any detail connected with polymer synthesis and structure. And he always was very kind, no matter how naïve my questions would be.

I graduated as a Chemical Engineer under the assistance of Italo Pasquon with an experimental work on the crystallization kinetics of a newly synthesized polyamide (experimentally, a systematic series of density measurements, after careful thermal treatments). Later on I was partly assigned to Italo's, partly to Paolo's Labs and a great adventure started for me, since the beginning of '59. In 1970, I was appointed a Professor of Chemistry at the University of Trieste. Still later (1973) I was appointed again a Professor of General Chemistry at the same original University, i.e., the Polytechnic of Milan.

### Intense research work in Natta's Institute

As soon as I got my Chemical Engineering Degree (in '59), following my curiosity for the three-dimensional structure of molecules, at the invitation by Paolo Corradini - then a young and brilliant coworker of Natta's - I chose the X-ray lab. Also, in addition to maintaining ev-

\*In this context it has been avoided as much as possible to give attribution of individual merits in the scientific work done within our Department.

eryday contacts with Italo Pasquon, I also started to interact with other Natta's coworkers - Porri, Bassi, Paiaro, Peraldo, Ganis, Cesari, Perego - all of them either synthetic or structural chemists, or both. Meanwhile, Paolo Corradini was appointed a Full Professor in Cagliari, only to be invited by the prestigious University "Federico II" in Naples after a few months. Nonetheless he kept making frequent visits to the Politecnico di Milano, thus maintaining the whole research network previously established; sometimes I would act as his substitute by visiting him in Naples, instead. In this atmosphere of intense scientific interactions, usually involving a few co-workers, from time to time I was invited by Natta to discuss with him aspects of the crystal structure of a polymer or of a catalyst; it goes without saying that these personal invitations made me feel proud and gratified.

### TiCl<sub>3</sub> vs CrCl<sub>3</sub>, two polymerization catalysts

One of such discussions, particularly interesting for me, dealt with the surface structure of single crystals of CrCl<sub>3</sub>, also a catalyst for the stereospecific polymerization of propylene, as it is the case of TiCl<sub>3</sub>. CrCl<sub>3</sub> had already been recognized as structurally similar to  $\alpha$ -TiCl<sub>3</sub>, a usual component of the catalytic system for the industrial synthesis of isotactic polypropylene. CrCl<sub>3</sub> is less easily oxidized or hydrolyzed than TiCl<sub>3</sub>, usually displays larger crystals but is less effective catalytically. As shown in Fig. 1, both CrCl<sub>3</sub> and two polymorphs of TiCl<sub>3</sub> (i.e.,  $\alpha$ -TiCl<sub>3</sub> and  $\gamma$ -TiCl<sub>3</sub>) consist of hexagonal tri-layers wherein a layer of metal atoms is enclosed between two similar layers of Cl atoms. By induction, we hoped that the structure of CrCl<sub>3</sub> crystals would be more regular than that of  $\alpha$ -TiCl<sub>3</sub> (because of the larger crystal size), thus possibly leading to more regular, better crystallisable polymers (the other layered form of TiCl<sub>3</sub>, i.e.,  $\gamma$ -TiCl<sub>3</sub>, consists of the same (Cl/Ti/Cl) layers as  $\alpha$ -TiCl<sub>3</sub>, see Fig. 1, but with a disordered sequence of the layer-to layer vectors).

Using the modern electron-microscopy equipment then available at the Milan Polytechnic (prof. Gino Bozza, at the time Head of the Polytechnic, or *Rettore*, was in charge of the equipment), it was apparent that even the most regular CrCl<sub>3</sub> crystals showed evidence of the same sliding irregularities between the layers, as we observed with  $\alpha$ -TiCl<sub>3</sub>. As expected, from X-ray spectra the structural and morphological aspects of the two salts appeared very much alike, although the crystals of CrCl<sub>3</sub> were much larger and more air-stable. In spite of the similar stereoregular specificity of the two salts - only the polymerization rate was different, being larger for  $\alpha$ -TiCl<sub>3</sub> - that piece of research had aroused a keen interest both in Giulio Natta and in myself. As a result, eventually I felt gratified, in spite of having missed the finding of a new catalyst, as we hoped. We still believed that other ways of preparing the crystals could

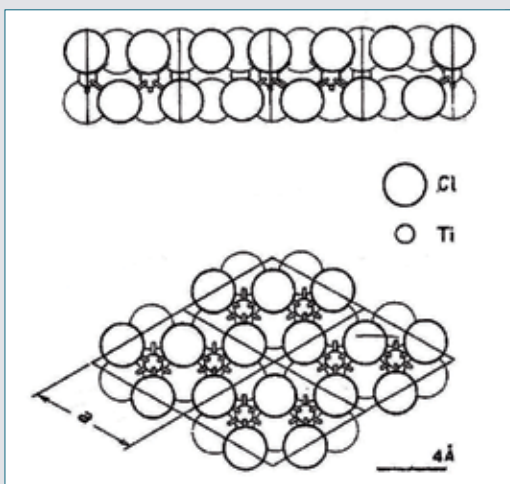


Fig. 1 - Stereochemical model of the structural layer that characterizes layer modifications of TiCl<sub>3</sub>

lead to success, although momentarily we put the issue aside. My own X-ray structural work, mostly in collaboration with the other members of the lab (Bassi, Cesari, Perego, Ganis; Corradini was a Chemistry Professor in Naples, at the time), was mainly centred i) on the molecular structure of single crystals of organo-metallic complexes comprising the same metal atoms as present in the active catalysts for the synthesis of stereoregular polymers (like titanium cyclopentadienyl trichloride), and ii) on the statistical, disordered structure of finely ground components of the catalytic systems for polymerization, like  $\alpha$ - and, especially,  $\gamma$ -TiCl<sub>3</sub>. An important general conclusion was established, namely the layered forms, like  $\alpha$ - and  $\gamma$ -TiCl<sub>3</sub> or CrCl<sub>3</sub>, are catalytically active and produce a stereoregular polymer, unlike the non-layered  $\beta$ -form (see Fig. 2); this conclusion appeared to hold no matter how much statistical disorder was induced by grinding into the layered forms.

Meanwhile, our interest (especially that of Natta, Corradini, Ganis and mine) for the statistical investigation of disorder both in crystals and in polymer chains was growing. Concerning the polypropylene chains, at the beginning of our investigation we were inclined to believe that the same spirals chain conformation as resulting from the chemical synthesis would be retained in the crystalline state. In other words, the threefold helices would form directly as such from the chemical synthesis. Only gradually the concept of a higher softness within most polymer chains (including isotactic polypropylene) was accepted, so that the initial helical portions were recognized on average to be no longer than a few chain bonds ( $\square$  10-15 at most) both in the melt and in solution. Otherwise said, the force-field chosen by us, dictating the strength of the energy interactions was *much too strong* in comparison with reality. The "chain softness" concept, together with the recognition of inter-segment attractive forces, helped us to understand the spontaneous formation of very small crystal-like objects, termed *lamellae*, clearly observable under the electron microscope (see in Fig. 3 a model for a large lamella, most lamellae

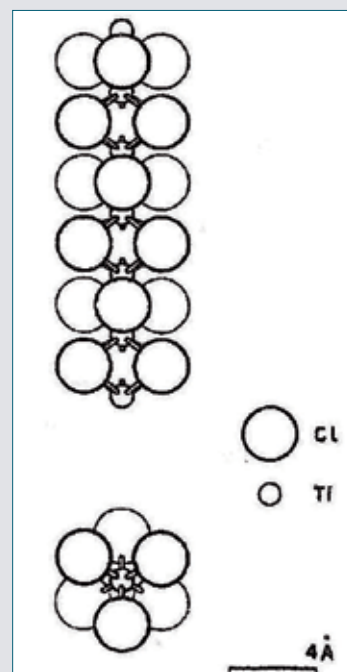


Fig. 2 - Stereochemical model of the linear macromolecule TiCl<sub>3</sub> that characterizes TiCl<sub>3</sub>

are constituted by fewer *stems*, or straight chain segments). Only the concerted action of many attractive forces would lead to formation of lamellae (Fig. 4), and aggregation of the crystallites would in turn lead to *spherulites* (Fig. 5), the largest crystalline entities statistically uniform, consisting of several lamellar fibrils (i.e., elongated lamellae), and having a roughly spherical shape overall. We may roughly describe the transformation process from *fibrils* to spherulites as follows: Under the strong mechanical forces acting on the polymer during spinning, the lamellar fibrils will partially unfold to produce a relatively compact, approximately spherical assembly of lamellae, that we define “spherulite”(see Fig. 5).

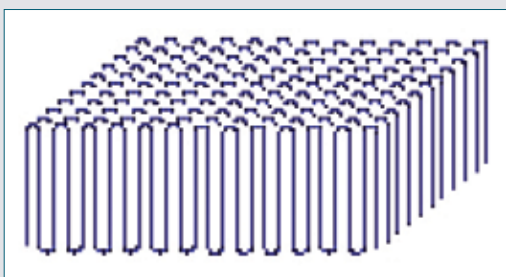


Fig. 3 - Idealized model of a polymer lamellae

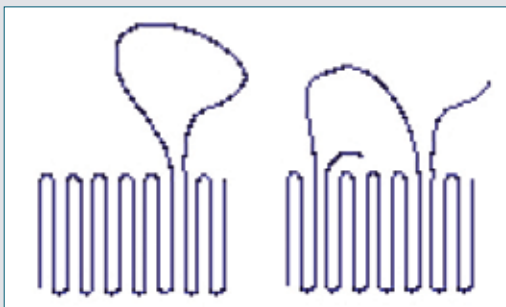


Fig. 4 - Polymer lamellae showing chains “switchboard-like”

## Statistical averages

From these initial investigations on polymer crystal formation, interest on *statistical studies* concerning polymers became more and more attractive both to me and to Paolo, and it spread over several subjects, among which:

- 1) the structure and behaviour of polymeric rubber;
- 2) the chain's internal viscosity, i.e., the viscosity effect arising from inside the chains depending on their rate of extension or contraction;
- 3) the statistical analysis of the crystalline portions at the very beginning of polymer crystallisation in solution and the bundle model.

## Expectations and reality

With the set of force constants used at the beginning of the statistical study with Paolo Corradini, the average length of the straight polymer segments appearing in Figs. 3-5, usually denoted as *stems*, should have been much longer than resulting from viscosity measurements (actually, each stem encompasses a relatively long, average length along the chain contour, and may be conceived as spherically jointed with its neighbours). With the initial force field the calculated length of the right-handed and the left-handed stems in isotactic polypropylene would oscillate wildly. After adopting a more realistic “force field” with weaker average forces we could easily reach smaller lengths obtaining essential agreement with observation. Also, microscopic observations were showing that the classical spherulite model shown schematically in Fig. 5 for crystallization of linear polymers in the bulk was also observable in isotactic polypropylene, as expected.

At about the same time, viscosity measurements from several laboratories were showing that the characteristic ratio  $C_{\infty}$  of isotactic polypropylene, measuring the average length of the chain segments in solution (straight portions, on average), was consistent with the mechanical measurements of the polymer yarns' tenacity, as expected. A similar convergence of the calculation data towards observation results was

achieved with syndiotactic polypropylene.

A very special case of a polymer essentially unable to attain conformational equilibrium in the liquid state is *isotactic* polystyrene. The inversion from a left-handed to a right-handed helix is virtually impossible because the phenyl rings sticking out of the chain axis tend to hinder their relative motion. Conversely, *syndiotactic* polystyrene may easily change its local chain shape by exploiting conformational transitions to zig-zag planar arrangements whereby the chain may disentangle itself and reach any conformation. It should be stressed that these same difficulties to change the conformation in the liquid state are at the base of the very difficult crystallization of isotactic polystyrene.

## The internal chain viscosity

Any significant motion of a long chain (say with more than 500 skeletal bonds) implies performing a broad set of skeletal rotations. In turn, each rotation implies surmounting some potential energy maximum. Already H.A. Kramers in 1940 showed that this sort of process should entail some energy loss, similar to a friction process. This author developed a statistical theory which connects the energy loss in any dynamical change of the chain (1989). D. Richter and co-workers performed very accurate light-scattering measurements to (successfully) check the theory.

Internal viscosity in a polymer chain is a force acting against any conformational change (i.e., skeletal rotations). Richter and collaborators were able to measure this sort of energy dissipation by performing dynamic experiments in solution both on poly(dimethyl siloxane) (PDMS) and on poly(isobutylene) (PIB). Assuming reasonably that PDMS should be essentially free from internal chain viscosity effects, unlike PIB, Richter and coll. obtained for PIB the following result for the characteristic time (in seconds)

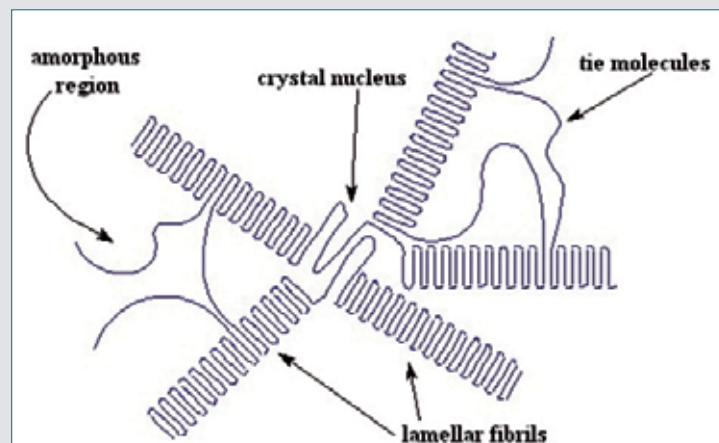


Fig. 5 - A spherulite model of a crystalline polymer and its parts

$$\tau_0 = 1,27 \times 10^{-12} \exp(3.1/RT)$$

in very good agreement with expectation from current spectroscopic data. Notice the energy 3.1 kcal/mol, within the exponential, equal to the energy barrier around chain bonds, and the factor preceding the exponential, very close to the natural oscillation frequency around the bonds.

### Pre-crystallization phenomena: the bundle model

A wide set of experimental data on polyethylene crystallization under different conditions of concentration, temperature and (average) chain length obtained by Keller, Sadler, Spels, Wignall, Stamm and Fischer were subjected to statistical analysis to see whether they could be interpreted according to the statistical theory proposed by Allegra, Meille and Famulari (AMF) (Fig. 6).

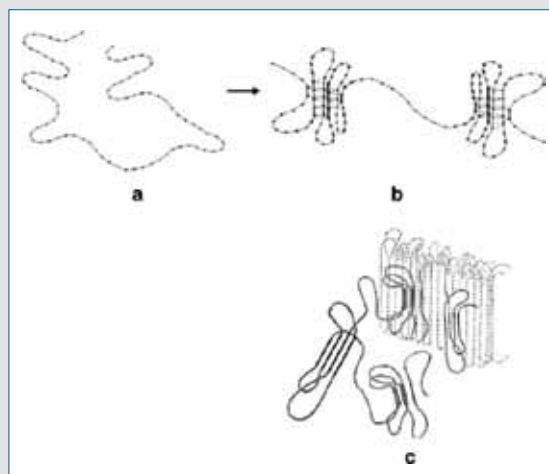


Fig. 6 - Bundles adjoin side surface of a lamellar crystal

## Part 2 Giulio Natta: his wife, his family, his illness

Giulio Natta's family, his wife Rosita, his sons Franca and Giuseppe, spent their summer vacations in their beautiful, mountain-style villa in Champoluc, and I also used to spend my family vacations in Antagnod, six kilometres away, in the same Vallée d'Ayas, Val d'Aosta Province. In 1967, when Giulio Natta's illness was so serious that all his motions were impaired, I made it clear to Mrs. Rosita Natta that I would be very happy, if needed, to drive Il Professore from Milan to Champoluc and vice-versa. Although these trips were not frequent, I was extremely happy to be of some help to Prof. Natta and to his nice, loveable wife. It was during these trips - about 2 hours each - that I realized how Prof. Natta's interests were still centred on polymers and their industrial production; in particular "to relieve the poor African and Asian people from cotton-picking and all the related enslaving". Perhaps the major problems of mankind in the future will not derive from cotton growth, but I think Natta's worries were very well directed, in essence. In Natta's Villa, at that time, apparently life was going on as usual; and my three children (age from three to six years) were very curious and amused in watching all the beautiful paintings and the furniture inside, and the several guests outside, some of them playing bowls in the al-

ley (and the Professore was among them, enjoying himself with some help). In following years the Villa was given as a grant to the local municipality and used for shows and meetings.

In that same summer 1967, I was invited by Mrs. Rosita to pick mushrooms in the wide Val d'Ayas, centred on Champoluc. Of course, I was eager to accept (I liked mushrooms if prepared as a food, and to some extent I liked to search for them in the woods, but my division line between edible and dangerous mushrooms was much too restrictive on the edible ones; in conclusion, I used to throw away the large

majority of them). Mrs. Rosita taught me some very simple rules, and just obeying them I could at least double my everyday collection. This rather solid knowledge, I learnt very soon, derived from the quasi-scientific knowledge of her husband!

Then there was the chapter of snails! In Natta's villa snails would be frequently served as an appetizer! That is why, going back to Milan from the Valley, of Champoluc, after stopping at a rather modest restaurant my son Andrea (5 years old) once said to the waiter, with a rather authoritative accent: "Escargots à la Bourguignonne, please!"

In the autumn of that same year, 1968, all of us were sadly hit by the news that Mrs. Rosita had a breast cancer; only three months later she died. This was really a tremendous hit for Giulio and for all the relatives and friends of the Natta's family! Just at the end of November I, my wife Carla and my three children Chiara (7), Andrea (6) and Giulia (4) were reaching New York (by boat - the Michelangelo - after a very rough transatlantic crossing). Just in the late summer of that year 1969, when we were suffering a very hot and suffocating summer and the first men walked on the Moon, Prof. Natta with his first daughter Franca, came to New York, to experiment the L-dopa treatment against the Parkinson disease. As soon as we were informed of their arrival, with my wife Carla, I jumped to the Medical Section of the Columbia University (N.Y.). Prof. Natta and Mrs. Franca were happy to see us, of course, but the emotional top was reached when Giulio Natta wanted to cross the big room in diagonal, slowly but firmly, and a great enthusiasm caught all of us. Unfortunately, of course, the illness was there to take on again, but for a small minute we had the illusion that perhaps a miracle was there to happen...

## Riassunto

### Giulio Natta: un Nobel italiano per la chimica, cinquant'anni dopo

L'articolo è diviso in due parti. Nella prima parte vengono illustrati alcuni aspetti statistici riguardanti i polimeri a lunga catena (tra i quali i polimeri stereo regolari scoperti da Natta), nello specifico correlati a) alla formazione iniziale di cristalli di polimeri e b) alla dissipazione di energia risultante dal movimento della catena e dalle barriere energetiche intramolecolari. Nella seconda parte vengono descritti alcuni aspetti della vita familiare di Giulio Natta, dopo aver ricevuto la più grande onorificenza della sua vita.