

346

G. NATTA

1960

N. 1 del *Supplemento* al Vol. 15, Serie X,
del *Nuovo Cimento* - pag. 3-8

~~350~~

G. NATTA

**Crystalline Synthetic High Polymers
with a Sterically Regular Structure**

BOLOGNA

TIPOGRAFIA COMPOSITORI

1960

Crystalline Synthetic High Polymers with a Sterically Regular Structure.

Introduction.

G. NATTA

Istituto di Chimica Industriale del Politecnico - Milano

(ricevuto il 7 Agosto 1959)

The discovery of stereospecific polymerization processes leading to new linear high polymers of vinylic and diolefinic hydrocarbons having a regular structure, also with regard to the steric configuration of the monomeric units, probably represents the most important event in the pure and applied macromolecular chemistry, during these last 20 years.

Even if it is a fairly recent discovery (the first patents on the subject were filed in June 1954 [1] and the first scientific communication was presented in December 1954 [2] before the Accademia dei Lincei) nevertheless its influence was considerable and roused a wide international movement of researches, to which thousands of chemists devoted themselves in university and industrial research laboratories. These researches brought to the discovery of a great number of new stereo-ordered polymers.

The new processes are important because with the old processes a great number of simple monomers, able to give asymmetric monomeric units by polymerization, could only be polymerized to products having an irregular structure due to the random distribution along the chain of isomeric monomeric units with different steric configurations. As a result of chemical and steric structure irregularities, the macromolecules presented in the solid state lack of crystallinity and of suitable mechanical properties and therefore there were only a few possibilities of valuable applications [3].

Even before the discovery of the stereospecific polymerization processes, different types of synthetic and natural macromolecules with sterically regular structures were known. Some of these macromolecules are thoroughly related to many phenomena of the organic life.

In the field of linear macromolecules, some crystalline natural products (*i.e.* cellulose, silk, etc.) show sterically regular structures, because they contain asymmetric carbon atoms, but only one of the two possible enantiomorphous forms is present. Thus the steric structure regularity of those polymers is due to a regularity already existing in the monomers which contain asymmetric carbon atoms. The monomers of those natural products exhibit an optical activity; in fact they rotate the plane of the polarized light; therefore the steric regularity of the corresponding polymers is not determined by the polymerization process which does not modify the steric structure of the monomeric units.

The new stereospecific polymerization processes recently discovered give the possibility of obtaining sterically regular polymers (which contain asymmetric carbon atoms) also starting from monomers which, actually, do not have asymmetric carbon atoms, owing to the fact that the asymmetric carbon atoms are formed only during the polymerization reaction. They give the possibility of realizing a synthesis which can be defined as asymmetric in respect to the monomeric units of a single macromolecule with a sterically regular structure [3]. The crystallizability of the macromolecules of this kind is due to the presence, at least for long sections of the main chain, of asymmetric carbon atoms having the same steric configuration.

Other examples of natural polymers with steric regularity (which imply the so-called geometrical asymmetries and not the optical ones) are given by natural rubber and guttapercha, both being isoprene polymers with 1-4 enchainment: the former being almost completely ($\sim 97\%$) formed of *cis* units, the latter of *trans* ones. The poor elastic properties of all synthetic rubbers known before 1954 in comparison with natural rubber, depended on the reason that the chemists were then unable to produce diolefin polymers having a high steric purity due to *cis* 1-4 enchainment.

The new processes of stereospecific synthesis allowed the U.S. chemists to produce a sterically regular *cis* 1-4 isoprene polymer very similar to natural rubber [4] and the Italian ones to synthesize for the first time the *trans* 1-4 polyisoprene [5] and all the stereoisomer polymers [6] (*isotactic* 1-2, *syndiotactic* 1-2, *trans* 1-4, *cis* 1-4) of butadiene (a diolefin less expensive than isoprene). The synthetic rubbers produced with these processes, having *cis* 1-4 enchainment and a very high steric purity, have, as natural rubber, high elasticity, low hysteresis and high tensile strength also in vulcanizates without reinforcing fillers [7].

Physico-chemical methods (in particular the interpretation of the X-ray and electron diffraction and of the I.R. spectra) mostly contributed to the discovery of the new stereoregular polymers and to their characterization; they also helped to determine the inward structure of the polymeric chains and of their crystalline aggregates, to distinguish polymers with different types of

enchainment and of steric order, and to determine the degree of steric purity.

On the specific results in the field of cristallinity obtained by these methods we have published only preliminary works till now, which were sufficient to recognize and distinguish the new types of macromolecules. We did not publish the whole set of works because we were to devote most of our time to the study of catalysts, of the polymerization processes and of the other properties of the new polymers. Just recently we had the possibility of reorganizing the various experimental works we collected during these years of researches.

I therefore accepted the kind proposal of Prof. POLVANI who, last year, invited me to publish some significant parts of our researches in the macromolecular field in this Journal, limiting them to the above-mentioned field of the polymeric structures in the crystalline state.

Considering the character of this review, I do not describe the nature and mechanism of the chemical processes of stereospecific polymerization developed to synthesize linear head-to-tail polymers, where monomeric units with a certain type of steric structure are orderly disposed. At the end of this issue we report the bibliographies of a great number of papers concerning the chemical processes of polymerization carried out at the Polytechnic of Milan. This introduction is followed by ten notes: in the first note are described our original observations, on the principles determining the chain conformation of the linear high polymers in crystals. We proved the remarkable usefulness of these principles to interpret the structures of the new isotactic polymers and, recently, also to determine the structure of syndiotactic alpha-olefin polymers and of the di-isotactic ones we synthesized. The crystalline structure of some stereo-ordered polymers is described in the following 7 notes. The two last notes on I.R. spectroscopy complete the study of cristallinity with methods which are more suitable and sensitive than X-ray methods for the determination of limited degrees of order.

To make the reader realize the importance, in the macromolecular field, of cristallinity which depends on the regularity of the chemical and steric structure of the polymers I shortly summarize the difference in the mechanical properties which can be observed among the stereo-ordered polymers in comparison with those having a complete or partial steric disorder.

In the field of alpha-olefins, which are remarkably important because of the low cost of monomers (some of them are by-products of the petroleum industry), two types of steric orders are possible: the « *isotactic* » and the « *syndiotactic* » ones.

The isotactic structure of polymers is characterized by the fact that monomeric units (which may exist in two enantiomorphous forms, which cannot be superposed, one being the mirror image of the other) follow each other in

the chain, at least for long chain sections, with the same steric configuration [8]. In the syndiotactic structure of polymers, on the contrary, a different type of order can be observed, owing to the fact that enantiomorphous monomeric

units follow each other alternately [9].

Fig. 1 shows the chains of the isotactic [10] and of the syndiotactic polypropylene recently obtained in its crystalline state [11].

For the atactic polymers there is no order in the succession of the enantiomorphous monomeric units, and this is the reason for the lack of crystallinity.

Properties, which are very different from those of the stereoreordered macromolecules (isotactic or syndiotactic) and from those of the sterically disordered atactic macromolecules, are shown by products with a degree of an intermediate order, which allows just a very little part of the polymeric chains to crystallize.

We called «stereoblock», the polymers formed of chain sections of different steric composition, which present a low degree of crystallinity [12].

As examples, we report some properties of high molecular weight

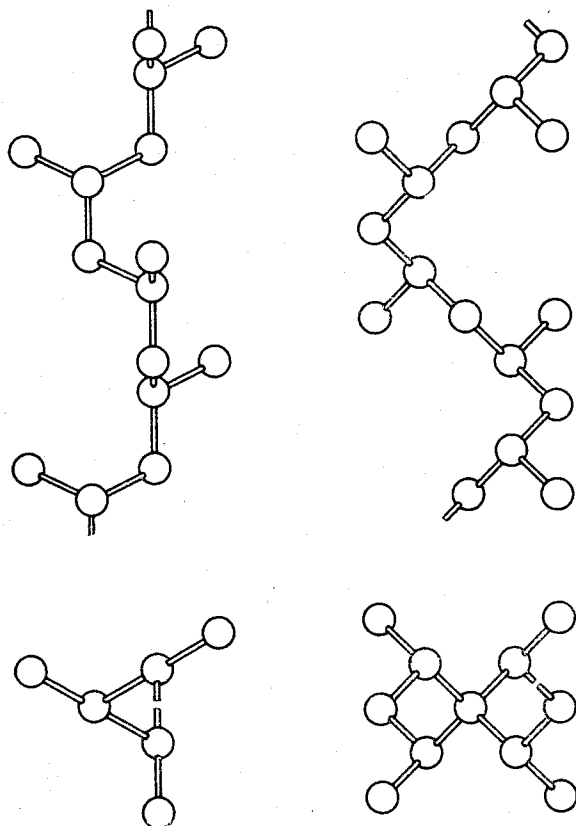


Fig. 1. - Conformations found in the crystals for the chains of isotactic (left) and syndiotactic (right) polypropylenes.

(> 50 000) linear polypropylenes of different steric composition. The isotactic sterically pure polymers have a melting point of about 175 °C; in the non-oriented state they can be interesting as thermoplastic materials with elastic moduli (150 ÷ 200) kg/mm², maximum tensile strength by traction of about 4 kg/mm² and ultimate elongation of (400 ÷ 700)%. In the oriented state they furnish transparent films with a resistance to tensile stress in two orthogonal directions of about 20 kg/mm².

Oriented fibres exhibit elastic moduli of (300 ÷ 360) kg/mm² and resistance to tensile stress of (60 ÷ 70) kg/mm². Their lightness (density of 0.91 instead of 1.50 of cotton and of 1.14 of nylon), excellent mechanical characteristics, low cost, and high insulating properties, are strong arguments to consider these products as some of the most interesting in the field of synthetic textile fibres [13].

Atactic polypropylenes, on the contrary, are amorphous; if they are subjected

to protracted stresses, they show high viscous creeps; in the vulcanized state they behave as elastomers. The inconvenience of the high elastic hysteresis of atactic polypropylenes can be reduced, introducing, as we did, by copolymerization, more flexible ethylene monomeric units in the polypropylene chain; as a result, the amorphous ethylene-propylene copolymers represent interesting synthetic rubbers, which are cheaper and more ageing-resisting than natural rubber [14].

The influence which crystallinity exerts on the properties of diolefin polymers is very important. As regards butadiene stereo-ordered polymers, isotactic and syndiotactic polymers with 1-2 enchainment, are crystalline and have high melting temperatures (respectively 125 °C, 155 °C). They are hard materials with a high elastic modulus and they are thermoplastic if cross-linking is absent.

The corresponding atactic polymer is a rubber which shows high elastic elongations, low moduli and relatively high elastic hysteresis because the presence of vinyl side groups introduces a certain hindrance to the free rotation of the C—C bonds of the main chains.

The polymers with 1-4 enchainment have been prepared in two sterically ordered forms: cis [5] and trans [6] respectively. The trans form of polybutadiene has a high melting temperature (148 °C) and only if crystallinity is hindered either by an increase of temperature or by different systems of plasticization or by vulcanization, it behaves as an elastomer: it gives hard rubber-like products having a fairly high elastic modulus.

The cis 1-4 polybutadienes with a high steric purity crystallize at room temperature under stretching (as natural rubber and cis 1-4 synthetic polyisoprene), while the previously known synthetic rubbers did not crystallize. The initial elastic modulus is low, but crystallinity, produced by the orientation of macromolecules because of stretching, causes an increase of the elastic modulus, with the increase of the elastic deformation, and furthermore gives a very high value of the ultimate tensile stress [15].

Contrary to natural rubber, sterically pure cis 1-4 polybutadiene shows low hysteresis even at very low temperatures, and high resistance to abrasion.

The technological information we give in this short introduction, has been reported with the purpose of pointing out the importance of the steric order on crystallinity and on the mechanical properties, and in particular on the elastic properties of the new polymers. Fuller details are reported in the original works. They can make anybody realize the enormous interest which was introduced by the discovery of stereospecific polymerization processes in the field of plastics, of synthetic fibres and of elastic rubbers.

REFERENCES

- [1] G. NATTA, P. PINO and G. MAZZANTI: Italian Patent No. 535 712 (8-6-1954).
- [2] G. NATTA: *Atti Accad. Naz. Lincei, Memorie*, **4** (8), 61 (1955); *Journ. Polym. Sci.*, **16**, 143 (1955).
- [3] G. NATTA: *Chimie Ind.*, **77**, 1009 (1957); *Materie Plastiche*, **7**, 541 (1957).
- [4] GOODRICH-GULF CHEMICALS Co.: Belgian Patent 543 292 (2-12-1954); F. W. STOWELY and Co-workers: *Ind. Eng. Chem.*, **48**, 778 (1956); H. HSICH and A. V. TOBOLSKY: *Journ. Polym. Sci.*, **25**, 245 (1957).
- [5] G. NATTA, L. PORRI and G. MAZZANTI: Italian Patent No. 536 631 (12-3-1955); G. NATTA, L. PORRI, P. CORRADINI and D. MORERO: *La Chim. e l'Ind.*, **40**, 362 (1958).
- [6] G. NATTA and L. PORRI: Italian Patent No. 538 453 (15-7-1955); G. NATTA, L. PORRI and A. PALVARINI: Italian Patent No. 563 507 (14-4-1956); G. NATTA, L. PORRI and P. CORRADINI: Italian Patent No. 566-940 (31-7-1956); see also [5].
- [7] G. NATTA: *Rubber and Plastics Age*, **38**, 6 (1957); *La Chim. e l'Ind.*, **39**, 653 (1957); G. NATTA, L. PORRI, A. MAZZEI and D. MORERO: *La Chim. e l'Ind.*, **41**, 398 (1959).
- [8] G. NATTA: *Angew. Chem.*, **68**, 393 (1956); *La Chim. e l'Ind.*, **38**, 751 (1956); G. NATTA and F. DANUSSO: *Journ. Polym. Sci.*, **34**, 3 (1959); G. NATTA: *Conference presented at the International Symposium of Macromolecular Chemistry, Wiesbaden (October 1959); Makrom. Chem.*, in press.
- [9] G. NATTA and P. CORRADINI: *Journ. Polym. Sci.*, **20**, 251 (1956).
- [10] G. NATTA, P. CORRADINI and M. CESARI: *Rend. Accad. Naz. Lincei*, **21** (8), 365 (1956); G. NATTA and P. CORRADINI: *Suppl. Nuovo Cimento*, **15**, 40 (1960).
- [11] G. NATTA and P. CORRADINI: see also [8]; *Makrom. Chem.*, in press.
- [12] G. NATTA, G. MAZZANTI, G. CRESPI and G. MORAGLIO: *La Chim. e l'Ind.*, **39**, 275 (1957).
- [13] G. NATTA: *La Chim. e l'Ind.*, **41**, 647 (1959).
- [14] G. NATTA and G. CRESPI: *La Chim. e l'Ind.*, **41**, 123 (1959); G. CRESPI and M. BRUZZONE: *La Chim. e l'Ind.*, **41**, 741 (1959).
- [15] G. NATTA: Paper presented at the *XVth Annual Technical Conference of the Society of Plastics Engineers*, New York, January 27-30 (1959). *S. P. E. Journ.*, **15**, 373 (1959).

G. NATTA

1960

N. 1 del *Supplemento* al Vol. 15, Serie X,
del *Nuovo Cimento* - pag. 3-8