polymer review

The impact of the discovery of the polymerization of the α-olefins on the development of the stereospecific polymerization of vinyl monomers[*]

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After a short survey of the first indications on the existence of stereoregularity in the main chains of the vinyl polymers, the first syntheses of stereoregular poly(vinylethers) and polystyrene are briefly summarized. The difficulties encountered in the early investigations of the propylene polymerization by the $CoO/MoO_3/Al_2O_3$ and $CrO_3/SiO_2/Al_2O_3$ catalysts are considered and the isolation and identification of a crystalline component in the mixture of diastereomeric macromolecules thus obtained, are discussed. The results obtained by different research groups, independently investigating the stereospecific polymerization of vinyl monomers, are compared and finally an attempt is made to explore the origin of the very rapid progress made in this field by Natta and coworkers in connection with their discovery of the stereospecific polymerization of α-olefins with the 'Ziegler–Natta catalysts'.

(Keywords: stereospecific polymerization; vinyl polymers; polypropylene, crystalline vinyl polymers; stereoregular vinyl polymers; isotactic polymers)

INTRODUCTION

In 1955 a communication to the editor of the Journal of American Chemical Society from Natta and coworkers dated 10 December 1954[1] stimulated much interest among polymer scientists. The paper describes different high molecular weight linear polymers of α-olefins in terms of intrinsic viscosity, density, identity period along the chain axis determined by X-ray diffraction, melting point, infra-red spectra and solubility in boiling solvents. The results are explained assuming that, in the synthesis, different linear polymers are formed from the same monomer which can be separated by boiling solvent extraction and that their main chains differ in stereochemistry, the stereoregular polymers of propylene being insoluble in boiling n-heptane and the stereoirregular polymers being soluble in diethylether. The stereoregular polymers consist of macromolecules in which all the tertiary carbon atoms have, at least for long sections of the main chain, the same absolute configuration and can crystallize and adopt in the crystals a 3/1 helical conformation.

The interest created by this paper is best exemplified by a letter from Prof. P. Flory to Prof. Natta dated 21 January 1955 in which the following opinion was expressed:

'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 polymerizations are of the utmost importance, I am sure.'

This opinion was later confirmed by Professor A. V. Tobolsky in a paper published in 1957 entitled 'Revolution in Polymer Chemistry'[2] in which he says:

'Natta and coworkers (Milan) using Ziegler-type catalysts, prepared isotactic polypropylene and polystyrene among others. It is Natta who first recognized the chemical revolution that was taking place.'

The importance of the research of Natta and coworkers was finally emphasized in 1963 by Professor Fredga[3] in the Motivation of the Nobel Award for Chemistry to Professors Ziegler and Natta, as follows:

'In der lebenden Natur gibt es viele Macromoleküle mit sterisch einheitlichem Bau, z.B. Cellulose und Katschuk. Das haben wir bisher als ein Monopol der Natur betrachtet; solche Macromoleküle werden mit Hilfe von Enzymen aufgebaut. Professor Natta hat dieses Monopol gebrochen.'

In this paper we shall try to summarize some possible reasons why this research created such a large interest and started a new era in the field of the polymerization of vinyl- and other unsaturated monomers and why other authors, who obtained similar results before Natta, polymerizing vinyl ethers[4], propylene[5,6] and other α-olefins[6], did not understand, or understood only in part, the relevance of the results they had obtained.

DIASTEREOISOMERISM IN VINYL POLYMERS AND INFLUENCE OF STEREOREGULARITY ON CONFORMATION OF POLYMER MAIN CHAINS

In 1932 Staudinger[7] recognized that in linear structurally regular polymers, such as polystyrene, a large number of diastereoisomers can form during the synthesis due to the

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presence of asymmetric carbon atoms in the main chain and that such stereoirregular macromolecules were not able to crystallize.

Taking into account the difficulties existing in the synthesis of single antipodes of low molecular weight compounds containing e.g. one asymmetric carbon atom, the achievement of a stereospecific synthesis of a macromolecule of a vinyl polymer containing 10^3–10^4 asymmetric carbon atoms had certainly appeared hopeless at least at that time. Nevertheless some years later Bunn[8] published a paper predicting that in a stereoregular vinyl polymer chain the steric interaction between the lateral chains could be easily released by rotation around the single $\geqslant$C–C$\leqslant$ bonds of the main chain. The resulting low energy conformation of the main chain would not be, in this case, the usual zig-zag planar conformation found for the linear paraffins, but a helical conformation. For a hypothetical vinyl polymer macromolecule having the steric structure later called 'isotactic' he predicted a 3/1 helical conformation of the main chain with an identity period of 6.2 Å. This important paper, which might have helped the pioneers in the field of the stereospecific polymerization of the vinyl monomers to interpret their results, was completely overlooked and it was Bunn who called[9] the attention of Natta, who had independently interpreted[10] the structure of the crystalline polypropylene in terms of a 3/1 helix, to his correct forecast made 12 years before Natta's research. The overlooking of the Bunn forecast is perhaps due to the fact that his publication belongs to a series of papers with the title 'Molecular structure and rubber-like elasticity' which was probably not considered in detail by researchers working in the field of vinyl polymers.

After the pioneering ideas of Staudinger[7] the main chain stereochemistry was proposed by Huggins[11] and by Schulz[12] to be the origin of some discrepancies in the solution properties of polystyrenes previously prepared[13] at different temperatures by Mark and coworkers. Furthermore Marvel and coworkers[14] attempted, unsuccessfully, to induce stereoregularity in radical polymers using optically active initiators.

The stereochemistry of the polymer main chains was discussed mainly in connection with the appearance of crystallinity in vinyl polymers[4,12,15], the existence of an alternation of the two possible absolute configurations of the tertiary carbon atoms of the vinyl polymer main chain being in general preferred to other types of stereoregularity which however should have been considered after the Bunn paper[8].

FIRST HINTS CONCERNING THE EXISTENCE OF CRYSTALLINITY AND STEREOREGULARITY IN VINYL POLYMERS

The first vinyl polymer for which crystallinity was clearly proved is poly(vinyl alcohol). Previously in 1935 a repeat distance of 2.52 Å was found[16], and a zig-zag planar conformation of the vinyl chain was proposed with all the –OH groups on one side of the main chain plane.

However, Bunn showed quite convincingly in 1948[17] that this was not the case and that crystallinity arose, because of the small size of the –OH groups, even if the –OH groups were randomly distributed on both sides of the main chain plane.

In 1936 Natta and coworkers[18] showed, using electron diffraction, that some crystallinity was present in poly(vinyl chloride), poly(vinyl bromide) and polystyrene produced via free radical polymerization, but they did not relate the crystallinity to the steric structure of the polymers.

These data were confirmed by Fuller[15] who obtained a fibre period of 5.0±0.05 Å for poly(vinyl chloride); he concludes that *'this value ... in view of the proof of the 1–3 structure of vinyl chloride[19] necessitates that every other chlorine atom be differently disposed along the chain'*.

Until 1954 the appearance of crystallinity in vinyl polymers was in general attributed to the presence, in the polymer main chains, of sections having a stereoregularity of the type described by Natta as syndiotactic[20] and not to the existence of mixtures of stereoregular and stereoirregular macromolecules.

In fact in 1954 Bunn[21] describes the situation in poly(vinyl chloride) as follows:

> *'Actually poly(vinyl chloride) does show some evidence of crystallinity but the indications are that such crystallinity, as it does possess, is due to the presence of a certain proportion of chain segments of regular structure containing chlorine atoms alternately in left and right hand positions.'*

In other words the crystallinity was attributed to the presence of stereo-block copolymers containing stereoregular sections of a syndiotactic type (*Figure 1a*) and nobody had conceived the possibility that a polymer synthesized in a single experiment could consist of a mixture of stereoregular and stereoirregular macromolecules (*Figure 1b*). As a consequence, because in stereoblock macromolecules the crystallizable and the non-crystallizable sections could obviously not be separated, nobody before Natta and coworkers had tried systematically to separate stereoregular and stereoirregular macromolecules and to investigate the polymer fractions thus obtained separately. In our opinion the attribution of crystallinity in polymers to the existence of stereoblock macromolecules has largely contributed to the delay in the development of the stereospecific polymerization of vinyl monomers.

FIRST SYNTHESES OF HIGHLY STEREOREGULAR VINYL POLYMERS

In 1947–1948 Schildknecht and coworkers[4,22,23] thoroughly investigated the already known synthesis of

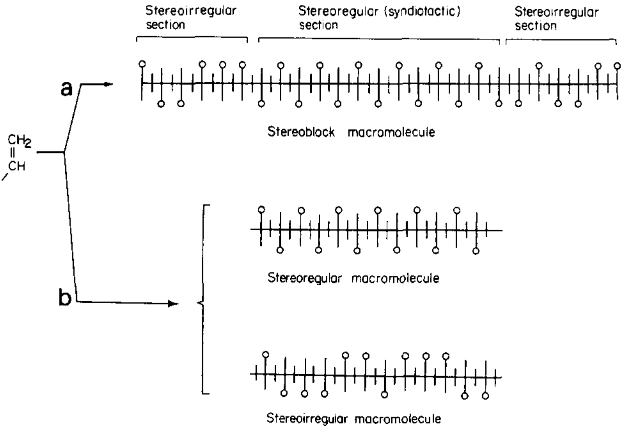

Figure 1 Some possible structures of the macromolecules of a partially crystalline vinyl polymer

poly(vinyl ethers) with cationic initiators. They discovered that carrying out the polymerization of isobutylvinylether in liquid propane at very low temperatures (−80°C−−60°C) and using complexes of borontrifluoride with ethers as initiators, a non-rubber-like polymer was obtained showing 'pronounced X-ray fibre patterns' in contrast to the well-known rubber-like polymer. A series of polymers was prepared varying the alkylgroup (R) of the monomer (methyl, isopropyl-n-butyl, isobutyl) and in all cases rubber-like and crystalline non-rubber-like polymers were obtained depending on the polymerization conditions. The crystalline poly(isobutyl vinyl ether) was fractionated by fractional precipitation, but, although about one half of the polymer precipitated in the first fraction, showing that solubility was not influenced only by molecular weight, the most insoluble fraction was not re-investigated by X-ray diffraction. This fact is in keeping with the attribution of the crystallinity to the steric order of 'local segments of macromolecules'[21], following the general views in this field mentioned in the previous section of this paper, and indicates the lack of the conception that a mixture of stereoregular and stereoirregular macromolecules could be produced in the same experiment. Indeed a classification of the vinyl- and related polymers is also proposed by the authors[4], in which the symmetry of the local chain segments is emphasized.

From X-ray diagrams of Schildknecht and coworkers correctly find an identity period of 6.2 Å for poly(isobutyl vinyl ether) fibres; according to this value they conclude that the main chain of the polymers is not fully extended and that the 'minimum number of vinyl groups per repeating unit will be three'.

Unfortunately they were apparently not aware of the paper of Bunn[8], mentioning the 3/1 helix with an identity period of 6.2 Å for an 'isotactic' vinyl polymer and probably Bunn did not pay attention to the work of Schildknecht. As a consequence, Schildknecht correctly attributed the crystallinity to 'a more orderly arrangement of the polar–OR groups along the molecules of the crystalline types of polyvinylisobutylether'. However, although different distributions of the alkoxy groups along the chains were considered ('all on one side, alternating or some other regular sequence[22]') the 'syndiotactic' arrangement was preferred on the basis of the analysis of Fischer–Herschelder models, and, as a further factor influencing the properties of the polymers, 'restricted rotation about the main carbon chain' was assumed, and generally accepted[24].

The structure of the crystalline poly(isobutyl vinyl ether) was established later by Natta and coworkers[25,26]. On the basis of their experiments on propylene polymerization they assumed that the 'crude' polymer as obtained from the polymerization might be a mixture of fully stereoregular and stereoirregular macromolecules, they fractionated the Schildknecht polymers by solvents extraction and obtained a highly crystalline polymer[27] giving very sharp X-ray and electron diffraction patterns[26]. After confirming the identity period found by Schildknecht, Natta assumed for the poly(vinyl ether) chains in the crystals the helical conformation he had previously found in the crystalline poly-α-olefins and found a very good agreement with the experimental data attributing to the crystalline poly(vinyl ethers) the isotactic structure. In this way it was shown for the first time that the isotactic structure was not a peculiarity of the polymers prepared with the Ziegler catalysts.

The second 'isotactic' vinyl polymer which was prepared, but not recognized, was the polystyrene synthesized using the 'alfin' catalysts[28]. Morton[28], investigating the butadiene polymerization to 1,4-*trans*-polybutadiene with the 'alfin' catalyst, clearly recognized the importance of the stepwise insertion of a monomer into a polarized metal–carbon bond, to control the structure of the polymer. In fact in the introduction of his conclusive paper in this field[28] he writes:

'Alfin catalysts are special combinations of sodium salts ... it is helpful to keep in mind two important principles which apply to all reactions and reagents in the field of organosodium compounds. ... One is the tendency of organometallic reactions to consist of multiple steps which tumble over each other as if in cascades until the end is reached. The other is the control which inorganic compounds of the reagents and other inorganic salts exert on the process.'

However, when he polymerized styrene with the same catalytic system he did not apply this concept to the synthesized polystyrene which, on the other side, had a very high molecular weight and did not crystallize during the polymerization.

After the synthesis and the characterization of the crystalline isotactic polystyrene by Natta and coworkers[20,25,29], Williams[30] reinvestigated the polystyrene prepared with the alfin catalyst and succeeded in obtaining, after refluxing the polymer suspension in a suitable high boiling solvent, crystalline polystyrene identical to the isotactic polystyrene prepared by Natta and coworkers.

The fact that Morton missed the stereospecificity of his catalyst in styrene polymerization shows again how far removed the possibility of synthesizing stereoregular and highly crystalline vinyl polymers was from the thinking of polymer chemists in the early fifties.

FIRST SYNTHESES OF 'ISOTACTIC POLYPROPYLENE'

According to the documents presented by the different parties during a long patent litigation in the United States[31–33], the first chemist who had in his hands a linear head-to-tail propylene polymer showing crystallinity of the isotactic type was D. R. Carmody, in the laboratory of Standard Oil Co. (Indiana). In an experiment, identified as EP-35, carried out in 1950 using a reduced $CoO/MoO_3/Al_2O_3$ polymerization catalyst, discovered by A. Zletz in the same laboratory, he obtained a solid polymer, precipitated from xylene solution with methylethylketone at room temperature, the i.r. spectrum of which (*Figure 2*) showed the absorption bands which were later found by Natta and coworkers[1] to be characteristic of isotactic polypropylene. However, this spectrum also showed a broad band of relatively low intensity in the 13.7–13.9 micron region, indicating the existence in the polymer of sequences of two or more (CH_2) groups.

Pure propylene being used as a monomer, the origin of the $(CH_2)_n$ $(n>1)$ sequences was not understood and remained unclear for some years. In fact in the sixties it was shown by Mazzanti[34] and by Banks and Bailey[35] that the reduced MoO_3/Al_2O_3 or $CoO/MoO_3/Al_2O_3$

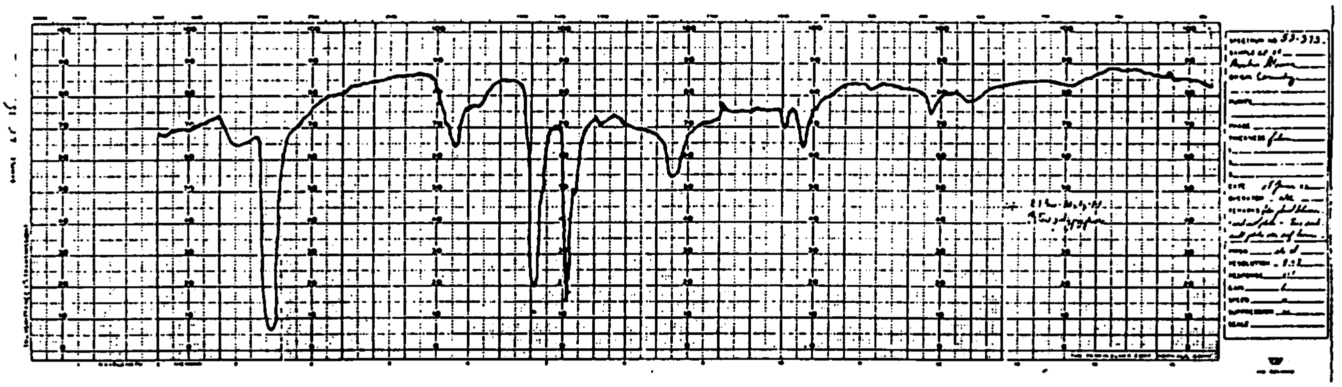

Figure 2 I.r. spectrum of the polymer obtained by D. R. Carmody in the experiment identified as EP. 35[58]

polymerization catalysts are also catalysts for olefins' methathesis, an unusual reaction unknown in the early fifties, which transforms e.g. propylene into an equimolecular mixture of butenes and ethylene (*Figure 3*). Therefore, it appeared that the $(CH_2)_n(n>1)$ sequences originated from the inclusion of monomeric units $(CH_2)_2$ arising from ethylene in the polypropylene chains. In principle the Carmody polymer might consist of ethylene–propylene block copolymers or of mixtures of isotactic polypropylene macromolecules and ethylene–propylene copolymers. Unfortunately the i.r. spectrum available does not allow a clear distinction between the two cases and further research would be necessary to decide between the two possibilities*.

The amount of copolymerized ethylene was different in the polymers obtained by Carmody and successively by Peters, but it was always significant in the polymers prepared in 1950. Sometimes, with reduced MoO_3/Al_2O_3 catalysts, the amount of ethylene was so high that crystallinity of the polyethylenic type was present. The presence of the $(CH_2)_n\,(n>1)$ sequences and the non-reproducibility of the results remarkably hindered a rapid development of the knowledge in this field.

In fact a good knowledge of the crystalline structure of the propylene polymers produced in the laboratories of Standard Oil Co. (Indiana) was achieved only in April 1954 (practically at the same time as the structure determination by Natta and Corradini[10]). A xylene insoluble polymer (identified as P-1-1) prepared in 1953 by Peters was investigated, in which the ethylene content was much lower than in the product of EP-35. Even then some doubts were still existing, as the X-ray expert W. Kimball wrote on 12 April 1954: '*It is believed that the hydrocarbon chain is helical in form with a linear carbon to carbon projection of 1.06 Å. Four chains of 3 propylene units each running throughout the unit cell fulfill this nicely but the expected intensities of several Miller indices of such system do not check too well.*'[36]

Furthermore the i.r. expert, R. R. Hopkins, on 23 February 1954, stated that such polymer had a CH_2/CH_3 ratio of 1 or 2, even if he recognized that on the basis of the absorption between 13.7 μ and 13.9 μ the product contained little if any methylene sequences[37].

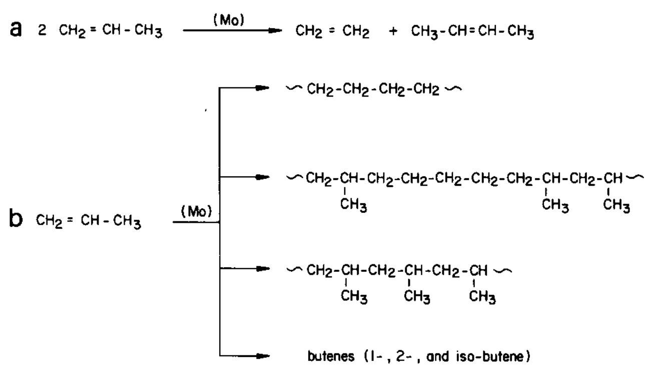

Figure 3 Reactions of propylene in the presence of Mo containing catalysts. (a) R. L. Banks and G. C. Bailey[35]; (b) D. R. Carmody[33] and G. Mazzanti[34]

In the same years the Hogan's group, at the Phillips Petroleum Company, was attempting to polymerize ethylene, propylene and other α-olefins using catalysts prepared supporting transition metal oxides on SiO_2/Al_2O_3 supports. The first polypropylene was prepared in this laboratory in 1951 by E. Francis[38] using a $CrO_3/Al_2O_3/SiO_2$ catalyst.

This polymer was fractionated by G. Nowling by fractional dissolution and, besides a fraction soluble in benzene and chloroform, a fraction insoluble in these solvents was obtained, which was indicated as a 'polypropylene gel'. The i.r. of both fractions were determined by V. Thornton. The comparison of these spectra with the table reporting the absorption bands of 'atactic' and 'isotactic' polypropylene, published by Natta and coworkers in 1955[1], shows that both fractions consist of substantially linear propylene polymers, the one indicated as 'polypropylene gel' having (*Figure 4*) a large content of crystallized isotactic polypropylene sequences. There is therefore no doubt, *today*, that Hogan and coworkers prepared in 1951 a mixture of linear head-to-tail polypropylenes, a small fraction of which, insoluble in chloroform and benzene, had an isotactic structure. It is surprising, in view of the recognized skilfulness of the Hogan group in the field of hydrocarbon polymers, that the Phillips team achieved full understanding of the nature of the 'polypropylene gel' (*Figure 4*) they had in their hands since 1951, only at the end of 1955, after Natta and coworkers had published that, in the polymers from propylene obtained with catalysts of the type used by Phillips, a small amount of crystalline polypropylene was present[39]. It is interesting,

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* The District Court of Delaware (ref. 32, pp. 707–8) ruled that such a polymer, owing to the presence of a significant amount of $(CH_2)_n$ sequences, was not a polypropylene 'consisting essentially of recurring propylene units' disregarding the possibility that the Carmody polymer might be a mixture of polypropylene and ethylene–propylene copolymers.

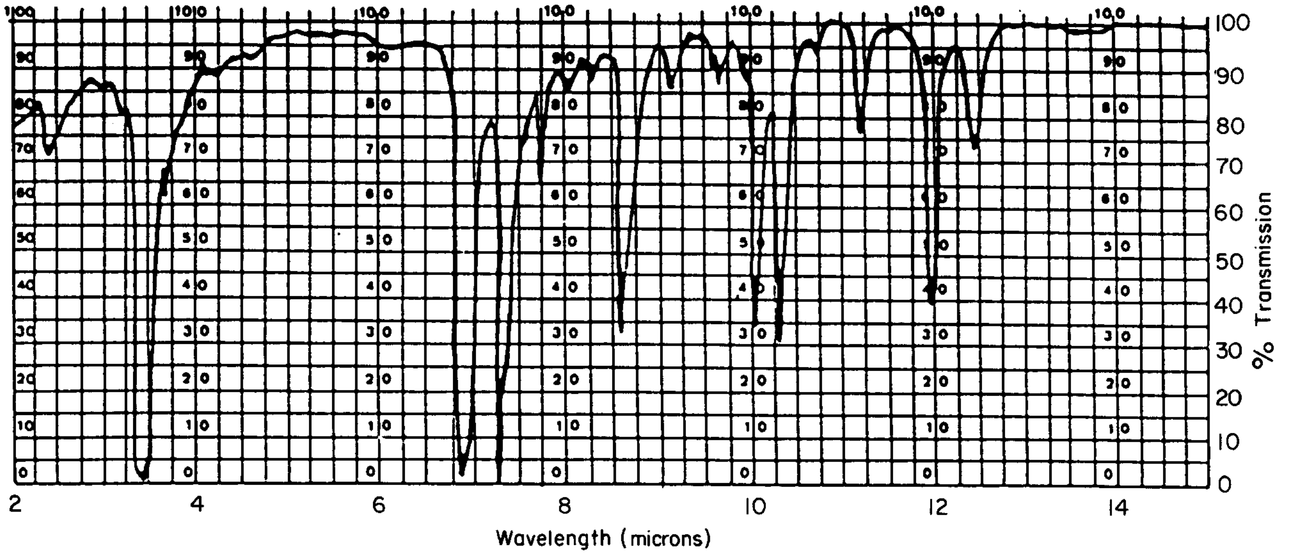


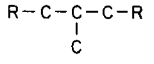
Figure 4 I.r. spectrum of the 'polypropylene gel' obtained by J. P. Hogan and coworkers at the Phillips Petroleum Co. as appearing in US Patent 4376851

in the history of the discovery of poly(α-olefins), to speculate about the reasons which caused this delay.

The only data on the 'polypropylene gel' available in the Phillips laboratories in 1951–1952 were the i.r. spectra. On three other 'insoluble' polypropylene fractions prepared at that time with the same catalysts, melting point, density, solubility in different solvents, intrinsic viscosity data were available in addition to the i.r. spectra. However not all data were concerned with the same sample[38].

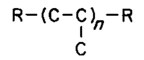
The i.r. spectra of the polypropylene fraction *soluble* in most of the organic solvents obtained in 1951, was correctly interpreted in 1952 by V. Thornton who proposed for the polypropylene chain a linear head-to-tail structure. Unfortunately, he was apparently confused by the remarkable differences between the i.r. spectra of the soluble polypropylenes and of the 'polypropylene gel'; in fact concerning this last fraction he stated in his 1952 report (ref. 32, pp. 719–720) the following:

'The absence of a band at 8.63 microns eliminates structures of the type



$\mathrm{R-C-\underset{\substack{|\\ C}}{C}-C-R}$

Since we have eliminated the possibility of the structure



$\mathrm{R-(C-\underset{\substack{|\\ C}}{C})_n-R}$

as the prominent one and a highly branched molecule is indicated (absence of bands at 12.7–13.9 microns) then the spectrum of the gel portion must indicate a pattern of branching.'

This unequivocal statement* can perhaps explain why the key experiments which are connected with the conception of the existence of crystallinity and which lead Natta and coworkers to the identification of the isotactic polypropylene[1] were never made at the Phillips laboratory before 1955. In fact an X-ray examination of the Francis 'polypropylene gel' was made only by the end of 1955 and the comparison of the i.r. spectra of the solid, the melted and the non-crystallizable polypropylenes, which would easily have solved the problems created in the interpretation of the i.r. spectrum of the 'polypropylene gel', on the basis of the available records was never carried out at the Phillips laboratories.

In conclusion the i.r. spectrum of the 'polypropylene gel' as well as that of any insoluble propylene polymer could not give, *per se*, any indication concerning crystallinity before 1955. In fact it was only in early 1955 that a correlation between polypropylene structure and its i.r. spectrum was published by the Natta group[1].

These scientists, knowing from the X-ray examinations that some polypropylene fractions were crystalline and some others were amorphous, proved for the first time that the bands at 10.03 μ and at 11.85 μ are characteristic of the crystalline structure of isotactic polypropylene, as they do not exist in the stereoirregular (atactic) polypropylene and disappear when the crystalline polymer is examined in the molten state.

Among the other properties of the solid polypropylenes determined by Hogan and coworkers, density, intrinsic viscosity and insolubility in some organic solvents none could give, in 1951–1952, any indication concerning the structure and particularly the existence of crystallinity of the samples examined. In fact before Natta, no pairs of amorphous and crystalline stereoisomeric hydrocarbon

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* It is interesting to note the position of the court on the above reported unequivocal statement by Thornton (ref. 32, p. 720): 'he was only required to appreciate enough about the available infra-red scans to justify the conclusion that Phillips's material was polypropylene, consisting essentially of polypropylene units. Thornton satisified this requirement by describing and appreciating that 4721-16 and -26 (the two first 'insoluble' polypropylenes prepared by Phillips in 1951) produced the infra-red recognition pattern of crystalline polypropylene'. Unfortunately there is, even today, no way to foresee, theoretically, the i.r. pattern connected with the crystallinity in a new polymer and in any event the first identification of the i.r. crystallinity pattern of a stereoregular polypropylene was published only three years later[1]. Therefore, before 1955 there were no 'infra-red recognition pattern characteristics of crystalline polypropylene' available and in 1952 the i.r. spectrum of 'polypropylene gel', *per se*, could not contribute to prove that crystallinity was present in this product. To a scientist there is not much doubt that, concerning 'the polypropylene gel', Thornton explicitly excluded the head-to-tail structure and had no possibility at all of hypothesizing, on the basis of his i.r. spectrum of the 'polypropylene gel', the existence of crystallinity in the product he examined. Therefore, at the time he wrote his report he unfortunately did not recognize that the 'polypropylene gel' was at least in large part a head-to-tail crystalline polypropylene.

polymers had been described in the literature and therefore very little was known about the possible differences between the physical properties of stereoisomeric hydrocarbon polymers.

The shape of the cooling curve of the non-tacky polymers obtained in the Phillips laboratory[33] could have indeed given a plausible indication of the existence of crystallinity in the samples examined. However, before 1955 apparently no attention was paid to these results, which might well be the first hints of the existence of crystallinity in poly(α-olefins). In fact the significance of these results* was stressed neither in the patent application filed by Phillips in 1953[6] nor in the pertinent laboratory books of the Phillips scientists which became available during the already mentioned patent litigation, nor in a second patent application filed later[40].

Even scientists undoubtedly skilled in the art as Natta and coworkers, who were avidly searching in the literature in order to find catalysts different from Ziegler's 'organometallische Mischkatalysatoren', and able to produce crystalline poly(α-olefins), did not find any indication of the presence of crystallinity in the non-tacky solid polypropylene described in the Phillips patent applications available in 1954 and 1955[41]. In fact in a paper published in 1955[39] they stated that in the Phillips patents '*non era mai stata segnalata la presenza di polimeri cristallini fra i prodotti di polymerizzazione delpropilene ottenuto con tale processo*'. Being interested in knowing if the Phillips catalysts would produce a crystalline polypropylene, they were compelled to polymerize propylene in their laboratory with $CrO_3/SiO_2/Al_2O_3$ catalysts, and were actually the first to prove[39], by X-ray analysis and by comparison with the properties of an authentic sample of isotactic polypropylene, that the solid polymer produced with the $CrO_3/Al_2O_3/SiO_2$ catalyst was crystalline and had an isotactic structure.

Some experts appointed by Phillips to discuss the case before the court of Delaware[32], having at their disposal all of today's knowledge in this field, including the proof that crystallinity actually existed in the Phillips polypropylenes achieved by comparing the i.r. spectra of the Francis 'polypropylene gel' with the data of the i.r. spectra published by Natta and coworkers[1], asserted in 1977, during the patent litigation, that the hints arising from the laboratory data of Phillips would actually have been sufficient to recognize the existence of crystallinity in the solid polypropylene prepared in the Phillips laboratories in 1951–1952.

In our opinion, without the benefit of the large amount of data accumulated after 1954 on the properties of poly(α-olefins), it would have been extremely difficult to connect the hints on the existence of crystallinity in the 'polypropylene gel' arising from the different measurements, and to reach the conclusion that the 'polypropylene gel' was actually a crystalline polymer, a conclusion conflicting with a great deal of data and with the concepts generally accepted at that time on the structure of the vinyl polymers[15,21].

The very able reconstruction of the facts made by the experts before the Delaware court[32] shows, at most, that sufficient hints were available in the Phillips laboratory by early 1953 to enable an 'idealized' scientist to conclude that the 'polypropylene gel' was actually a crystalline polypropylene. This 'idealized' scientist should have ignored all the data available in 1953 on the α-olefins polymerization and should not have shared the prejudices existing at that time against the possibility of synthesizing stereoregular macromolecules containing e.g. thousands of asymmetric carbon atoms with the same configuration. Indeed, having one of us been confronted with the same problem in 1954[1], the existence of such an idealized scientist seems very doubtful, and actually much more convincing experimental evidence on sterically pure samples (e.g. X-ray spectra) were necessary to overcome the prejudices on the possibility of synthesizing stereoregular α-olefins polymers existing at that time[1].

In any case the above mentioned reconstruction of the facts made '*a posteriori*' does not in any way prove that some of the Phillips scientists putting together all the experimental data available, actually established the existence of crystallinity in their polypropylene, before 1955. As we discussed above, the behaviour of the Phillips group, after the discovery of the 'polypropylene gel', can be actually explained in two ways: (i) either the Phillips scientists did not understand, before 1955, the structure of the 'polypropylene gel' and did not appreciate the existence of crystallinity in the solid polypropylene they had synthesized, or (ii) they did not understand the importance of their discovery. In our opinion, in view of the recognized skilfulness of the Phillips group, the first alternative is by far more satisfactory for a polymer scientist even if it was apparently discarded by the Delaware court (USA) before which the case was discussed[38]. Indeed, the words 'crystalline' and 'crystallinity', in connection with polypropylene, were found in none of the documents dated 1951–1954 produced by Phillips in the patent litigation. The first mention of crystalline polypropylene was found in a report, dated 25 March 1955, by W. B. Reynolds, Assistant Director of Research at Phillips, commenting on the Natta results, given to him by H. Mark.

Research on polypropylene started in 1954 at Dupont, and a crude polypropylene was obtained in May 1954 by W. N. Baxter using a $TiCl_4/C_6H_5MgBr$ catalytic system (ref. 32, p. 698). The existence of crystallinity in the non-fractionated product was proved in July 1954 by X-ray diffraction but the isolation of a prevailingly isotactic polypropylene was only carried out later, by D. Payne[42], after the first publication[1] of Natta and his coworkers. Finally Ziegler produced a 'crude' polypropylene which was a mixture of isotactic and stereoirregular macromolecules, in July 1954[43], and after this, other Companies such as Höchst and Hercules who had access to the Ziegler data started to prepare their own modified 'Ziegler catalysts' to produce the isotactic polypropylene on an industrial basis.

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* Concerning the absence in the Hogan and Bank patent application and notebooks of any mention, in connection with the shape of the cooling curve, of the presence of crystallinity in the non-tacky polypropylene, we totally agree with the statement of the Delaware court (ref. 32, p. 701) in rejecting the attempt by Dupont to prove the recognition of crystallinity in its product prepared in May 1954 on the basis of i.r. spectra only: '*it is illogical to believe that anyone who discovered a new product and realized that its distinguishing feature was its crystalline nature would fail to record that realization*'. Although the court inexplicably did not apply this statement in the case of the Phillips notebooks and patent application, the absence of the word 'crystallinity' in the description of the products for which the melting curve was determined is a strong indication that the presence of crystallinity in the non-tacky propylene polymers was actually never seriously considered in the Hogan group before 1955.

SYNTHESIS AND CHARACTERIZATION OF POLYPROPYLENE AND OTHER POLY(α-OLEFINS) BY NATTA AND COWORKERS

The first polymerization of propylene by Natta and coworkers which yielded a stereoregular polymer was carried out in March 1954; in the same month the crude polymer was fractionated and the isotactic fraction was isolated. Between March and May 1954 the linear regular structure of the crystalline and amorphous polymer was characterized by i.r. and the steric structure of the polymer was correctly understood on the basis of the X-ray analysis. The potential uses of the isotactic polymers in the field of films, fibres and molten articles was established in the same period. All the data were collected in a patent application filed in June 1954[44,55]. Successively, in the few months till November 1954, the isotactic polymers of styrene and 1-butene were prepared and characterized[45] and new catalysts for the selective production of isotactic poly(α-olefins) were prepared[46]. The difference in the research efficiency between Natta's groups and the other groups involved in the same field is astonishing as shown in the *Table 1* and it is worth attempting an analysis of the factors which determined this difference.

A first very important point is the precise perception by Natta of the substantial difference between the polymerization of vinyl monomers by polyinsertion and the well-known free radical or free ions polymerization[47]. In fact while in the latter two cases the structure of the polymers could be controlled only by the structure of the growing chain ends, in the former case, as already realized by Morton[28] for the 'alfin' catalysts, both the inorganic part of the catalytic sites and the structure of the growing chain end could determine the structure of the growing polymer chain.

At a lecture given in 1952 by Ziegler on the 'growth reaction'[48], Natta, as he mentioned in one of his publications[39b], 'was impressed by the fact that using organometallic catalysts it was possible to obtain from each α-olefin one dimer only'.

Therefore, as soon as Natta knew that Ziegler obtained high polymers of ethylene with $TiCl_4$–AlR_3 catalytic systems[49], he correctly interpreted the results assuming that the transition metal component increased the rate of chain growth more than the rate of the polymer chain termination reaction(s)[47]. Knowing that with aluminium alkyls essentially one dimer was produced from propylene he immediately decided to polymerize propylene with the new catalytic systems and, because of the double control of the chain growing process by the inorganic catalyst and by the growing chain, he hoped to obtain new types of propylene polymers, e.g. a linear rubber-like polymer of propylene hypothesized but not yet described at the time[50].

As soon as polymers were obtained from propylene he started a systematic investigation of the polymer properties using mainly X-ray and i.r. analysis. Fortunately his coworkers who synthesized the polymers decided to purify and fractionate the polymers by boiling solvent extraction, a fractionation method little used in Polymer Science at that time as it is not efficient in fractionating polymers having similar structure, according to their molecular weight. However, this method had been used previously to separate low boiling paraffins from solid paraffins obtained by the Fischer and Tropsch synthesis[51] and it was adopted in Natta's laboratory from 1953 to separate the low molecular weight products from the solid hydrocarbons in the mixtures obtained on polymerizing ethylene with aluminium alkyls.

In the case of the crude polypropylenes this method allowed separation of a fraction consisting of an amorphous polymer, a fraction consisting of a polymer with relatively low crystallinity and melting point and finally a highly crystalline high melting fraction. The three fractions were characterized separately; all of them consisting of linear head-to-tail polypropylenes according to elemental and i.r. analysis, the differences between the crystalline and the amorphous polymers disappearing in solution or when the crystalline polymer was investigated above its melting point.

Finally the X-ray diffraction spectra were satisfactorily interpreted assuming that all the asymmetric carbon atoms of the main chain had, at least for long chain sections, the same steric configuration.

Certainly the theoretical interest in the structure of the polymer has largely stimulated the interest of the scientists of the Natta group involved in the first research phase; however, Natta's interests were equally subdivided between theoretical aspects and practical applications. Besides directing the work of his research team, he personally investigated with some technicians the possibility of obtaining films and fibres from the new crystalline polypropylene he named 'isotactic'[1].

Besides the above very important factors, some fortuitous events have certainly helped to rapidly develop the research on polypropylene in Natta's group (*Table 2*). The first factor was the relatively high productivity of the catalyst used; in the first experiments about 150–200 g of

Table 1 Time elapsed between the first preparation of stereoregular vinyl polymers and the identification of their structure

Head of the research group	Type of polymer	First date available on preparation of a 'non-tacky' polymer	Recognition of the existence of crystallinity by X-ray diffraction	Full structure determination of the crystalline polymer
C. E. Schildknecht	Poly(isobutyl vinylether)	1947	1948	1954 (by Natta *et al.*[26])
A. A. Morton	Polystyrene	1950	–	1956 (by J. L. R. Williams *et al.*[30])
A. Zletz	Polypropylene	1950	1953	1954[36]
P. Hogan	Polypropylene	1951	1955 (December)	1955 (September) (by Natta *et al.*[39])
G. Natta	Polypropylene	1954 (March)	1954 (March)	1954 (May)[41]
W. N. Baxter	Polypropylene	1954 (May)	1954 (July)	–

Table 2 Results of the early investigations on the polymerization of vinyl monomers to crystalline polymers

Research group leader	Year	Productivity[a]	Selectivity[b]	Molecular weight of the non-tacky fraction	Fractionation	Characterization	
C. Schildknecht	1947–1949	high	high	high	Fractional[c] Precipitation	X-rays Density	on non fractionated samples
A. Zletz	1950–1953	low	low	n.r.[e]	Precipitation[d]	I.r. X-rays	on partially fractionated samples
P. Hogan	1951–1953	medium	low	low <20 000	Fractional Dissolution	I.r. Density cooling curves	on partially fractionated samples
G. Natta	March 1954–June 1954	high	moderate	high >100 000	Successive extraction with boiling solvents	X-rays I.r. Density	on fractionated samples
W. N. Baxter	May 1954–July 1954	low	moderate	n.d.[f]	No fractionation	X-rays I.r.	on non fractionated samples

[a] g of polymers/g of catalyst
[b] g of non-tacky 'solid' polymer/g of total polymer
[c] by addition of non solvents
[d] by cooling
[e] not reported
[f] no data

crude polymer with a high average molecular weight were easily obtained using a few grams of catalyst components. On the contrary in the few successful experiments with $CrO_3/SiO_2/Al_2O_3$ catalyst, carried out in the Natta laboratory in 1955, only very small amounts of low molecular weight solid crystalline polymer were obtained, whose structure could be immediately identified only because i.r. and X-ray data on isotactic polypropylene were already available within the Natta group.

A second factor was the sufficiently high stereospecificity of the catalyst used; in fact 30–40% of the polymer produced in the first experiments consisted of highly isotactic macromolecules with average viscosimetric molecular weight over 100 000.

Finally the solvents chosen for the fractionation of the polymers happened to be extremely selective, the boiling diethylether dissolving only substantially stereoirregular polymers and the n-heptane not being able to dissolve high macromolecular weight substantially isotactic macromolecules[55] as shown later by the ^{13}C n.m.r. spectra, of the different polypropylene fractions[52].

Concerning the stereospecific polymerization of vinyl monomers, we can say that the above research by Natta and coworkers on poly(α-olefins) proved that, in polyinsertion, not only the structure of the vinyl polymer main chains, but also the steric configuration of the tertiary carbon atoms of the main chain can be controlled, opening the way to today's hypothesis on the existence of enantiomeric catalytic sites[53] as the main controlling factor in stereospecific polymerization. Furthermore it was shown that a crude polymer showing some crystallinity on X-ray examination could be a mixture of stereoirregular non-crystallizable polymer fractions and of highly stereoregular fractions, a case which, as previously mentioned, was not considered before Natta's research.

Finally the above research has shown that the isotactic structure is rather common in crystalline vinyl polymers and can be easily synthesized not only when organometallic catalyst precursors, reduced $CoO/MoO_3/Al_2O_3$, or $CrO_3/SiO_2/Al_2O_3$ catalysts are used, but even when cationic or anionic initiators are employed depending on the type of monomers and on the polymerization conditions. In the latter two cases the polymerization occurs via non-solvated ion pairs and the type of structural- and stereocontrol corresponds in these cases to that found in polyinsertions.

COMPARISON OF THE FIRST RESULTS OBTAINED BY DIFFERENT RESEARCH GROUPS IN THE STEREOSPECIFIC POLYMERIZATION OF VINYL MONOMERS

We must still deal with the question concerning the possible reasons for the large impact in Polymer Science, of the research of Natta and coworkers in comparison with the impact of the research of other groups working in the field who had obtained isotactic polymers well before Natta. Some important factors affecting the significance of the research of the different groups are summarized in the *Table 2*.

The research on the vinyl ethers did not lead to clear conclusions concerning the molecular origin of the crystallinity; in fact the authors state at the end of their third paper[4] on this subject: '*all of these arguments are not so convincing as the authors would like them to be. Since this seems to be a new effect, there is little basis for comparison and the conclusions must be tentative*'. The main reason for this is the lack of X-ray investigations of the fractionated samples and the relatively poor quality of the X-ray fibre diagrams of the non-fractionated polymers which did not give sufficient experimental background to control the hypothesis on the conformation of the main chain in the solid state. The unfortunate overlooking of the Bunn paper[8] indicating the possibility of helical conformations for the isotactic vinyl polymers in the crystalline state certainly contributed to the lack of total success and left the authors uncertain about the impact of atropoisomerism and distribution of tertiary carbon atoms with the same absolute configuration along the main chain on the properties of the polymers. The fact that no important application could be found for the crystalline poly(vinyl ethers) certainly contributed to the interruption of this very significant research.

The lack of recognition of the isotactic structure in the polystyrene produced with an 'alfin' catalyst by Morton[28] is probably due to the fact that the interest of Morton was mainly focused on conjugated diene polymerization, coupled with the absence of crystallinity in the native polystyrene produced with 'alfin' catalysts. It is an interesting case in which the researcher had a clear intuition of the factors regulating the structure of the polymer chains, obtained results in perfect agreement with his hypothesis (the *trans*-1,4-polybutadiene and the isotactic polystyrene), but did not realize the generality of his hypothesis.

Concerning the Zletz group research[5] the interest was mainly directed toward synthesizing commercially useful polymers, and the low productivity and low selectivity in propylene polymerization of their catalytic system did certainly not contribute to encourage their research.

As already mentioned the $CoO/MoO_3/Al_2O_3$ catalytic systems catalyse not only the polymerization of the olefins but also the olefins metathesis (*Figure 1*).

In the early research in this field, catalysts active in polymerization but with low activity in metathesis were only occasionally prepared, producing polymers having a very small content of ethylene units. Furthermore the polymer used for the X-ray analysis, obtained by precipitation from xylene, was not sterically pure and the spectra also left some doubts in the minds of some X-ray experts[36] even in 1954. Being mainly interested in the polymerization of ethylene, which polymerized quite easily with their catalysts, the Zletz group limited the research in the field of α-olefins to polypropylene and the extension of their data to other vinyl polymers was not obvious. From the records it appears that no theory concerning the formation of isotactic polymers was formulated in the Standard Oil of Indiana laboratories and in any case the Zletz research had not been published until 1956, when foreign patents and patent applications appeared corresponding to US Patent application 462,480[5]. Therefore, these results could not have influenced the development of 'Polymer Science' before that date.

As already discussed a great deal of research on α-olefin polymerization was carried out by Hogan and his group in the Phillips laboratories[54]. The record shows that this team first considered the insoluble crystalline polypropylene as a 'gel', probably meaning a crosslinked irregular polymer, in contrast with the linear head-to-tail highly soluble stereoirregular polymer obtained in the same experiments. Apparently they did not pay any attention to the possibility that crystallinity existed in their α-olefin polymers as no X-ray investigation of these polymers appears in their reports before 1955 although the X-ray investigations were used in the same laboratory to characterize polyethylenes. Indeed crystallinity is never mentioned in their 1953 and 1954 patent applications[6,39,40] indicating that crystallinity had not yet been recognized. In fact the presence of crystallinity in poly-α-olefins was such a revolutionary advancement in the state of the art, that no scientist who had convincingly proved to have a crystalline polypropylene in the hands would have neglected to mention it in his notebook and in his first patent applications on this subject.

Differently from the case of Zletz, relatively large laboratory quantities of solid polypropylene were produced but finally, although Hogan considered the production of a solid polypropylene as a 'surprising result' (ref. 32, p. 719) and as a 'unique solid material', the Phillips scientists, differently from Natta, apparently did not realize the practical significance that a solid propylene polymer could have if a higher molecular weight could be achieved. In fact some three years after the discovery of the isotactic polypropylene by Natta and coworkers the first industrial plant started its production in Italy. On the contrary, three years after the first preparation of the solid polypropylene by Francis, the Phillips Company had not described in any detail the possible important industrial applications of solid polypropylene, which was still regarded only as a wax modifier (ref. 32, p. 721). Certainly the low molecular weight of the polymer synthesized and the low selectivity of the catalyst used in producing the solid polymer must have shaded the importance of the discovery and can explain the lack of emphasis in the Phillips laboratories on the research of the new product.

In any case the research of Hogan and coworkers remained undisclosed until 1955[40,41], and their early interesting patent applications, mainly disclosing rather sophisticated heterogeneous catalysts very active in ethylene polymerization, did not significantly contribute to the development of the polymerization of vinyl monomers. For instance it was necessary for the Natta group to synthesize in their laboratory the Phillips non-tacky polymer from propylene in order to understand its structure[39].

CONCLUSIONS

Although other research groups had in their hands stereoregular vinyl polymers earlier than the Natta group it was the research by Natta and coworkers which accelerated substantially the understanding of the stereospecific polymerization of vinyl monomers and caused an unprecedented increase in the level of research in this field.

The main reason for this was the intuition of Natta that the insertion polymerization discovered by Ziegler with his outstanding work on the use of aluminium alkyls could lead, during the synthesis of macromolecules, to a better control of the polymer structure than the free-radical or free-ion initiated polymerization processes, well known since the thirties. To this one should also add the simultaneous occurrence of a series of favourable circumstances, which have been discussed in an earlier section of this paper. If one considers the experiments carried out by other research groups in the field (*Table 2*) in no case can one observe such a co-existence of favourable circumstances.

Differently from the case of poly(vinyl ethers) the easy availability and low cost of the α-olefins, particularly of propylene, on the one hand, and the outstanding properties possessed by the polymers, by virtue of their crystalline structure, on the other, certainly played an important role in attracting the interest of so many scientists in their stereospecific polymerizations.

It is perhaps surprising that the very large commercial importance of polypropylene was immediately recognized by Natta who was a University Professor, rather than by scientists working in a number of well known industrial laboratories. One possible explanation is that the process as experimented (for instance in the Phillips and Standard Oil of Indiana laboratories) in the early stages of development yielded only very small amounts of low molecular weight crystalline polypropylene, while looking very promising in the polymerization of ethylene. Therefore, it is understandable that research was concentrated on linear polyethylene delaying intensive work with the higher olefins.

Finally, one should not disregard the impact of the human qualities and the scientific approach to industrial research of Natta, as a group leader, on the research work and the success of the Italian research team.

Our analysis of the facts leading to the present knowledge in the field of the polymerization of vinyl polymers is certainly open to improvements. From the discussion above, however, one cannot but confirm that the results obtained by the Natta group in the short period of three months brought about a 'revolution in polymer science'[2]. As a result of that work it became clear for the first time to the scientific community:

(1) That the synthesis, from vinyl monomers, of macromolecules containing 10^4–10^5 asymmetric carbon atoms with the same absolute configuration was indeed possible.

(2) That a single catalytic system could produce structurally similar but sterically different macromolecules.

(3) That in vinyl polymers the stereochemistry of the main chain plays a fundamental role in determining the physical and engineering properties of the polymers as previously recognized for other types of macromolecules (e.g. poly-1,4-isoprene).

The fact that, through the vicissitudes and procedures of patent examination and litigation, the priority on certain patent claims to crystalline polymers of propylene was, granted in the USA[56] and Canada[57] to inventors belonging to different groups, cannot to any extent detract from the importance that the contribution of Natta and coworkers has had in the development of polymer science.

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58 This spectrum is one of the exhibits mentioned in ref. 32. We thank Standard Oil of Indiana for sending us a photocopy of the exhibit