

Data... **7 aprile 1959****PROMEMORIA****G/ra**

per il Signor

**BREV  
SEPS  
SEID**→ **Prof. NATTA**

e, p.c.

**VERE**ISTITUTO DI  
INDUSTRIALE DEL POLI. LOM

\* 9 APR. 1959 \*

**R** 2420*Cartella  
I. C. I*

La **I.C.I.** ha praticamente firmato il contratto per la cessione della licenza del polipropilene.

La I.C.I. desidera avere, subito dopo la firma del contratto, i seguenti quantitativi di Moplen, secondo specifica che allego alla presente per il SEID :

- a) subito dopo la firma 150 tonn. di materiale Melt Index 6
- b) 50 tonn/mese per il resto del 1959 della stessa qualità
- c) 100/150 tonn./mese nel 1960

SEID esaminerà insieme con VERE e senza ritardi la possibilità di far fronte, anche parzialmente a queste esigenze tenendo conto delle necessità del mercato interno e di quelle prevedibili per gli altri licenziatari.

Per Vostra norma l' I.C.I. afferma essere possibile acquistare polipropilene anche all' estero e da tale fonte essa si approvigionerebbe qualora non fossimo in grado di fornire le quantità prodotte.

Cordiali saluti.

per SEID : un allegato



# Imperial Chemical Industries Limited

PLASTICS DIVISION

Bessemer Road, Welwyn Garden City, Herts

Telephone: WELWYN GARDEN 23400 Telex: 22613 ICIPLAST, WELWYN

*Carbelle*

Professor G. Natta,  
Istituto di Chimica Industriale  
del Politecnico,  
Piazza Leonardo da Vinci, 32,  
Milano.

Your ref:

Our ref: ATJ/JAB/RES.

RECEIVED  
11 NOV 1963  
R 972

4th November 1963

*to  
do*

Dear Professor Natta,

Since I wrote to you on the 23rd October about our paper on the  $\beta$  and  $\gamma$ -forms of polypropylene for publication in "Die Makromolekulare Chemie", we have carried out some preliminary calculations to see whether small movements of the helices from their positions in Figure 10 c will be sufficient to give approximately the right relative intensities for the principal equatorial reflections but have not been entirely successful so far. An exhaustive examination has not been made and unfortunately owing to the pressure of other work I cannot now undertake further calculations on this topic. I still feel the packing of Figure 10c might be basically correct, but it will be best to delete this suggested packing from the paper since it is open to the criticism you have made.

We have accordingly made the appropriate alterations and have sent them direct to the Editor of "Die Makromolekulare Chemie" and are enclosing herewith copies of the altered text and diagram which I hope now meet the point you raised, and also a copy of my letter to Professor Kern.

Yours sincerely,

*A. Turner-Jones*

A. Turner-Jones  
Research Department

Prof. Dr. V. Kern,  
Mainz,  
Organ. Chem. Institut der Universität,  
Johann-Joachim-Becher-Weg 18-20  
Germany.

ATS/JAB/RES.

4th November 1963

Dear Sir,

I was glad to receive your acknowledgement dated 22nd October 1963 of our paper "Crystalline Forms of Isotactic Polypropylene" forwarded to you by Professor Natta.

I understand that Professor Natta informed you that we would be making some small corrections to the galley proofs. In fact, to meet the point he raised we have made rather more extensive alterations to Page 19 and to Figure 10 than can conveniently be corrected at the galley proof stage. As we have rearranged the text somewhat to fit these alterations, it has seemed simplest to retype pages 17, 18, 19 and 22 and we are accordingly enclosing replacements for these pages and for Figure 10. We would also ask if you would kindly delete Reference 18 and the item marked 10c at the bottom of the page entitled "Captions to Figures".

I hope we have been able to make these alterations sufficiently quickly, so that you are not put to too much inconvenience.

I have sent a copy of this letter to Professor Natta and have explained to him the alterations we have made.

Yours faithfully,

*At*

A. Turner-Jones  
Research Department

We tentatively put forward the suggestion that an association of triplets of helices of the same hand might occur in the melt over a limited length of chain, and thus predispose the polymer to crystallise in the hexagonal form. Provided then the temperature of the polymer melt can be quickly reduced to below 100-130°C while no appreciable nucleation into the  $\alpha$ -form takes place, nucleation and further growth in the hexagonal form is likely to occur predominantly. It has already been shown that for this particular polymer B the nucleation and growth rates of the  $\alpha$ -form appear to be retarded for reasons which are not yet known. Alternatively, some extraneous substance may be present in the polymer which increases the nucleation rate into the hexagonal form.

As already mentioned Padden and Keith showed that the rate of growth of  $\beta$ -form spherulites was greater than that of  $\alpha$ -form spherulites when both were growing simultaneously. Since the addition of segments of polymer chain to the existing side-by-side packed chains of the existing crystallite would then occur by accretion of triplets, an inherently faster growth rate of  $\beta$ -crystallites compared with  $\alpha$ -crystallites is not unreasonable. However, it is appreciated that such ideas, based on such slight structural evidence, must be purely speculative.

#### 6. UNIT CELL AND CHAIN PACKING - $\gamma$ -FORM

The strong reflections at  $d = 6.37 \text{ \AA}$  and  $5.29 \text{ \AA}$  are certainly  $hk0$  reflections from planes parallel to the  $c$ -axis, but in considering possible unit cells it was borne in mind that reflections at  $4.415$ ,  $4.19$  and  $4.05 \text{ \AA}$  might each be either a  $hk0$  or a  $hk1$  reflection. An equatorial cell network with  $a_0 = 6.47 \text{ \AA}$ ,  $b_0 = 10.71 \text{ \AA}$ ,  $\gamma_0 = 99.07^\circ$  was readily found which accurately fitted the  $d$ -spacings of the first five reflections (see Table 1) which then have indices  $100$ ,  $1\bar{1}0$ ,  $020$ ,  $110$ ,  $1\bar{2}0$ . This cell is closely related to the  $\alpha$ -form equatorial network by halving the  $b$ -axis and slightly deforming the halved cell from the orthogonal (see Fig. 10a, b). Indications that the

reflection at  $4.415 \text{ \AA}$  was likely to be an  $hk0$  reflection have been obtained in photographs of  $\alpha$ -form fibres containing a small amount of the  $\gamma$ -form. Moreover, the positions of the first three strong reflections on X-ray photographs of pressed films in the  $\gamma$ -form showing preferred orientation were consistent with this equatorial cell network. If the chain repeat is assumed to be  $6.49 \text{ \AA}$ , as already found in the  $\alpha$  and  $\beta$  forms, both of which also have ternary helices, the density of any unit cell containing two chains per cell based on this equatorial network is  $0.94 \text{ g/cc}$ . The observed densities and per cent crystallinities given in Table 2 for samples B and D enable the approximate crystal density of the  $\gamma$ -form to be calculated (see Table 2); these values lie higher than that of the  $\alpha$ -form. A crystalline density higher than that of the  $\alpha$ -form, the preferred form in highly isotactic specimens is inherently unlikely, and probably arises because the crystallinity figures are not absolute and likely to be low.

Fig. 10.

Nevertheless, it appears that the  $\gamma$ -form crystal density must lie close to that of the  $\alpha$ -form, which is consistent with the value based on the above equatorial network and assumed  $g$  dimension. It was considered justified to assume a fibre repeat of  $6.49 - 6.60 \text{ \AA}$  and a crystal density not less than  $0.93 \text{ g./cc}$ . In considering possible equatorial networks, the value of  $\gamma_0$  is then limited by the values of  $a^* = 0.242$   $b^* = 0.1458$  and this minimum density;  $\gamma_0$  must lie between  $90^\circ$  and  $103^\circ$  to give a density greater than  $0.93 \text{ g./cc}$ .

The observed spacings did not fit a monoclinic cell based on the above equatorial cell network and range of  $g$  dimensions. Other equatorial cell networks based on the first 7 reflections were also considered but no orthorhombic or monoclinic cell could be found to fit the observed spacings and density. The cell is therefore triclinic.

The derivation of a triclinic cell from X-ray photographs of unoriented polymer specimens is not a very practical proposition. More than one cell was found based on the above equatorial network which fitted the observed spacings.  $\alpha$  generally lay close to  $90^\circ$  and  $\beta$  between  $90^\circ$  and  $100^\circ$ . Good packing could be achieved, with no methyl-methyl contacts less than  $4 \text{ \AA}$ , with left and right handed helices packed side by side in approximately the positions shown in Fig. 10b allowing small lateral movement of the helical axes and twists around these axes. With the helices in these positions in c-projection, preliminary structure factor calculations showed that approximately the right intensity distribution is obtained for the principal equatorial reflections.

It is, quite possible that the unit cell may be doubled in the a or b directions. Nevertheless, the axes of the helices must occupy positions close to those of Fig. 10b if the calculated intensities of the three strong equatorial reflections, with spacings of 6.37, 5.29 and  $4.415 \text{ \AA}$  (and these equatorial reflections only) are to remain sufficiently strong.

of the A and B blocks. It is likely that in any blocked chain the length of the blocks may vary widely. Nevertheless the fractionation will presumably have separated the chains into groups of a somewhat similar block structure and the length of the folds could be related to the shorter block lengths. The preference for the Y-structure over the  $\alpha$  is still unresolved but this picture of the Y-structure is consistent with the observation that on drawing fibres, only oriented  $\alpha$ -type crystallinity is formed, since, on drawing, the molecules are pulled out of their folded structure with regularly arranged discontinuities; these discontinuities would now be irregularly placed in the extended chains with consequent disruption of crystallinity. Here again cooling from the melt would be necessary to enable the blocks to take up the same helical configuration along the length of the chain if the folds occur in the  $gg$  plane (Fig. 10b), or right and left helices alternately if folding occurs parallel to the  $bg$  or  $1\bar{2}0$  planes.

The authors wish to thank Dr. C.W. Dunn for many useful discussions.



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*Carbells*  
*ICT*

Professor G. Natta,  
Istituto di Chimica Industriale  
del Politecnico,  
Piazza Leonardo da Vinci, 32,  
Milano.

899/1v &  
Your ref: 918/1v

Our ref: ATJ/JAB/RES.

23rd October 1963

936  
28 OCT 1963

Dear Professor Natta,

Thank you for your letter of October 10th, from which I was glad to learn that you are recommending the publication of our paper on the  $\beta$  and  $\gamma$ -forms of polypropylene in "Die Makromolekulare Chemie", and for your further letter of October 18th advising me that you have forwarded the paper for publication without waiting for any alterations arising from your comments on the alternative packing for the  $\gamma$ -form given in Fig. 10c.

This is certainly a valid criticism. I added in this second packing at the last minute after the paper was otherwise complete because the packing is in itself a good one and it was clear that the three reflections 200, 020 and  $2\bar{2}0$  at spacings of 6.37 Å, 5.29 Å and 4.42 Å respectively, ( $100$ ,  $020$  and  $1\bar{2}0$  on the smaller cell with a halved) would have large calculated intensities as required. I have not paid sufficient attention to the intensities of the weaker reflections  $2\bar{1}0$  and  $210$  ( $1\bar{1}0$  and  $110$  on the smaller cell). As shown in Fig. 10c this packing is effectively face centred on the C-face and therefore  $2\bar{1}0$  and  $210$  will be absent, or of very small intensity, depending on the precise arrangement of the helices (Right-up Right-down etc.).

The suggested arrangements of the helices in Figs. 10b and 10c were diagrammatic only and not meant to be their final positions. Small lateral movement of the helices and rotation around their axes are not precluded provided the interatomic distances remain reasonable. The main factor we considered was that the axes of the helices must have co-ordinates close to

$$\begin{array}{ll} a = 0 & a = 0 \\ b = \frac{1}{4} & b = \frac{3}{4} \end{array} \text{ in Fig. 10b}$$

or

$$\begin{array}{llll} a = 0 & a = 0 & a = \frac{1}{2} & a = \frac{1}{2} \\ b = \frac{1}{4} & b = \frac{3}{4} & b = \frac{1}{4} & b = \frac{3}{4} \end{array} \text{ in Fig. 10 c.}$$

if the three observed strong reflections, and no other equatorial reflections, are to have a sufficiently high calculated intensity.





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2.

L.

Your ref:

Our ref:

We are considering whether small movements of the helices are possible which will be sufficient to destroy the effective face-centering and give approximately the right relative intensities for the principal equatorial reflections. It is not worth considering reflections of spacings less than  $\approx 4 \text{ \AA}$  because it is not known with sufficient certainty whether they are equatorial reflections or not.

If we are successful we will redraw the diagram of Fig. 10 and make any necessary alterations to the text. If not, then it will be best to cut out the diagram of Fig. 10 c and all reference to this packing. We would hope to be able to do this before the galley proof stage.

With kind regards.

Yours sincerely,

*Annette Turner-Jones*

A. Turner-Jones  
Research Department

Oct.18, 1963

*Carbelle*

Miss A. Turner-Jones,  
I.G.I. Ltd.,  
Plastics Division,  
Bessemer Road,  
Welwyn Garden City, Herts

our ref.918/lv

Dear Miss Turner-Jones,

Further to my letter of Oct.10, 1963, reporting my remarks on your paper: "Crystalline Forms of Isotactic Polypropylene", I wish to inform you that to-day I have forwarded your text to Makromolekulare Chemie, otherwise its publication would be postponed too much.

I have also informed the editorial office of this journal that the author will make small corrections to it when checking the galley proofs.

With my best regards,

Giulio Natta

Carbetta  
I C I

Oct. 10, 1963

Miss A. Turner-Jones,  
I.C.I. Ltd.  
Plastics Division,  
Bessemer Road,  
Welwyn Garden City, Herts

our ref. 899/lv

Dear Miss Turner-Jones,

I have received the manuscript of the paper "Crystalline Forms of Isotactic Polypropylene" you sent to me for publication in "Die Makromolekulare Chemie".

I consider this paper very interesting and accurate; therefore I shall be glad to recommend its publication.

The results you obtained, concerning the obtainment of the  $\gamma$  modification, agree with our results, which have not been published yet.

However, a topic should be clarified: it should be pointed out in more detail on page 19 that the packings described in Figs. 10b and 10c are not equal, not even from an equatorial point of view; therefore, it cannot be stated "a priori" that the good agreement obtained on the equatorial reflections calculated on the basis of Fig. 10b might anyway support the structure of Fig. 10c. Therefore I would advise you to calculate the equatorial reflections again, also for this last structure, which you consider at least equally plausible. Only in this way, the last sentence on page 19 should be justified.

Before sending your manuscript for publication to Makromolekulare Chemie, I would like to learn your specifications on this respect.

With my kindest regards,

G. Natta



# Imperial Chemical Industries Limited

PLASTICS DIVISION

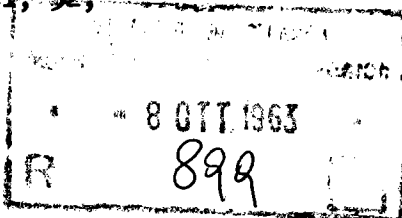
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Piazza Leonardo da Vinci, 32,  
Milano,  
Italy.

Your ref:

Our ref: ATJ/JW



1st October, 1963.

*Allegre Baron*

Dear Professor Natta,

Last May Dr. C. W. Bunn sent you a paper of mine entitled "Crystallinity in Isotactic Polyolefine with Unbranched Side-chains", which you were kind enough to forward to "Die Makromolekulare Chemie" for publication.

I am sending with this letter a paper on "Crystalline Forms of Isotactic Polypropylene" which I and two of my colleagues would like to publish in "Die Makromolekulare Chemie".

Polypropylene is a subject on which you and your colleagues have already published a great deal, more particularly on the principal  $\alpha$ -form and it seems appropriate to publish this paper in the journal where many of your own papers on stereoregular polymers have appeared.

This paper is concerned with the production and structures of the  $\beta$  (pseudohexagonal) and  $\alpha$  (tridinic) forms of polypropylene. We did not succeed in obtaining oriented fibres in these crystal forms and the deductions as to the structure of these two forms are necessarily tentative, since they are based on the rather limited data obtainable from X-ray photographs of unoriented polymers.

Dr. Bunn, as you perhaps know, has now left us and has just started work in Sir Lawrence Bragg's group at the Royal Institution.

I was very pleased to have the opportunity of meeting Professor Bassi and others of your colleagues at the recent Crystallography Conference in Rome and to hear of something of the work on which you are now engaged.

Yours sincerely,

*A. Turner-Jones*

A. Turner-Jones (Miss)