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Constrained Powder-Profile Refinement Based on Generalized Coordinates. Application to X-ray Data of Isotactic Polypropylene

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Abstract

A computer program combining Rietveld's procedure of powder-profile refinement with the use of constrained variables has been set up with the purpose of studying polymeric materials in the presence of amorphous fractions with their own diffraction patterns. The program, suitable for both X-ray and neutron radiation applications, lends itself to treating any kind of constraint. A flexible profile function, *viz* Pearson's VII, which generalizes the Gauss, Lorentz and Cauchy distribution functions, is considered. An X-ray application, namely the structure of isotactic polypropylene (α form) in the unoriented state, is illustrated. The three models already proposed, *Cc*, *C*2/*c* [Natta & Corradini (1960). *Nuovo Cimento Suppl.* **15**, 40–51] and $P2_1/c$ [Mencick (1972). *J. Macromol. Sci. Phys.* **6**, 101–115] are analysed. The third is found to be the most reliable, but with a helix disordering mode rather different from that suggested by Mencick.

Introduction

The use of powder-profile-refinement techniques in crystal structure analysis by diffraction methods (Rietveld, 1967, 1969) has received growing attention in recent years. So far, however, application of the method has been confined to problems with a moderate

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number of positional unknowns, mainly from inorganic chemistry and using mainly neutron data. Only recently (Malmros & Thomas, 1977; Young, Mackie & Von Dreele, 1977) has the method received attention in the X-ray diffraction field.

Although of general validity, the powder-profile method suffers from the exceedingly large number of positional unknowns if applied to complex structures such as large organic molecules, crystalline polymers, disordered structures *etc.* This is especially the case when X-rays are involved because of both the unfavourable behaviour of the atomic scattering factors and the occurrence of several aberrations in X-ray profiles.

In most of the above cases, however, quite a lot of structural information is *a priori* available, often with a higher accuracy than that expected from the refinement: *e.g.* known bond lengths or angles, known structures of rigid groups of atoms, higher than crystallographic molecular symmetry, structural equivalence of chemically equivalent groups, *etc.* Such information may usefully be introduced in the refinement process in order to reduce the number of variables and to improve the convergence and the significance of the shifts.

The merits of constrainted refinement (with special reference to single-crystal problems) were pointed out by Pawley (1971). According to this author the number of parameters to be refined can be considerably reduced by using, instead of the usual crystal coordinates, a 'constrained parameter set' so defined that the parameters are *mutually independent* (or fixed) within the assumed constrained model. In the case of molecular crystals, appropriate parameters are the bond lengths, bond and torsion angles (defining the molecular structure) besides overall translations and Euler angles (defining the crystal structure). In some cases, however, such as non-rigid cyclic molecules or polymeric structures, the choice of parameters which fulfil the requirement of being mutually independent becomes troublesome and it is necessary to have recourse to unusual quantities such as ratios of lengths or differences *etc.* In a recent work (Immirzi, 1978) we have termed these non-conventional parameters 'generalized coordinates' (g.c.).

A number of structure refinements from neutron diffraction profile data have been carried out by Pawley and co-workers using constraints (see *e.g.* Pawley, Mackenzie & Dietrich, 1977; Bacon, Lisher & Pawley, 1979). Pawley's program *EDINP* (the detailed features of which are not known to us) seems suited for neutron diffraction analysis of ordinary crystalline substances. In the case of polymeric materials, however, and especially if X-rays are used, a few improvements in the program seem to be opportune, *viz* (i) the use of a more appropriate profile function; (ii) the use of a refinable background line; (iii) the use of double wavelength for the α_1-α_2 splitting occurring in the X-ray case (see Young, Mackie & Von Dreele, 1977).

We have thus prepared a new computer program which combines the Rietveld method with the idea of constrained refinement particularly suited for studying polymeric materials of limited crystallinity. This program, presumably similar to Pawley's *EDINP* as far as the treatment of the structural variables is concerned, is applicable, of course, to any kind of constraints using both neutron and X-ray profiles.

The profile function

Neutron diffraction powder-profile refinements are currently based on Gaussian profile functions (Rietveld, 1969) with the width parameter H_k only dependent on the 2θ angle. In the case of X-rays, other distribution functions have been used such as the modified Lorentz (Malmros & Thomas, 1977) or Cauchy (Khattak & Cox, 1977).

In the case of polymeric materials in which particle size can become very small such distributions are not fully satisfactory, the tails being too narrow in the Gauss case and too broad in the Cauchy and Lorentz cases. A more flexible profile function based on Pearson's VII distribution has been recommended recently by Hall, Veeraraghavan, Rubin & Winchell (1977):

$$I_{2\theta} = \frac{2\Gamma(m)(2^{1/m}-1)^{1/2}}{\sqrt{\pi}\,\Gamma(m-\frac{1}{2})}\,\frac{I_k}{H_k} \times \left[1+4\left(\frac{2\theta-2\theta_k}{H_k}\right)^2(2^{1/m}-1)\right]^{-m}.$$

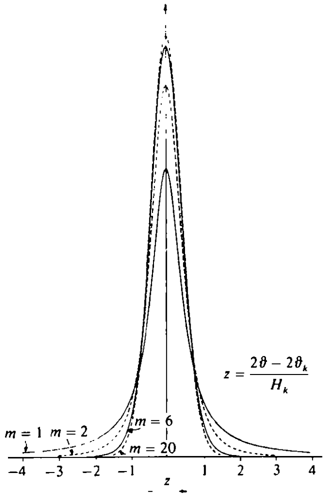

Fig. 1. Normalized Pearson's VII function for m = 1, 2, 6 and 20. Note that m controls the shape but not the width of the peaks; the full-width at half-height is in all cases H_k.

The advantage of this distribution (see Fig. 1) is that as m varies, the distribution changes continuously going through the Cauchy ($m = 1$), modified Lorentz ($m = 2$) and Gauss ($m = \infty$). We have also considered the possibility of adjusting the m parameter itself. While this feature seems of limited interest in the presence of poor diffraction patterns (as in the specific case treated in this work), it has proved to be feasible in more favourable conditions. This is, for instance, the case in the X-ray Rietveld analysis of the polymeric phosphate $Na_3H(PO_3)_4$ (Immirzi, 1980) where m, refined together with 14 other non-structural parameters, converged to $m = 1{\cdot}52$ with a standard error $\sigma = 0{\cdot}09$.

The background

In dealing with materials of limited crystallinity, *e.g.* stereospecific synthetic polymers, the definition of the background intensity may become troublesome owing to the amorphous material which has its own diffraction pattern with one or more bumps, possibly collapsed in part (Natta, Corradini & Cesari, 1957). To perform the least-squares refinement we use a calculated rather than a fixed background, so introducing a few additional parameters to be adjusted. The background line is assumed (see Fig. 2*a*) to be made up of straight segments with a number of bell-shaped curves superimposed. The latter are calculated by using again the Pearson formula with its own (and possibly adjustable) m' parameter. The heights of the intersection nodes and the $3 \times n$ parameters defining the n bumps are also adjustable.

Although this approach to the background problem is empirical, it seems very satisfactory. Fig. 2(*b*) illustrates the case of the amorphous acrylic resin Technovit 4030-b [used as the diluting material in the cited work on $Na_3H(PO_3)_4$ to eliminate preferred-orientation effects]. It appears that a very accurate fit of the observed and calculated diffraction patterns is fulfilled by using a seven-parameter curve with two Gauss-shaped bumps.

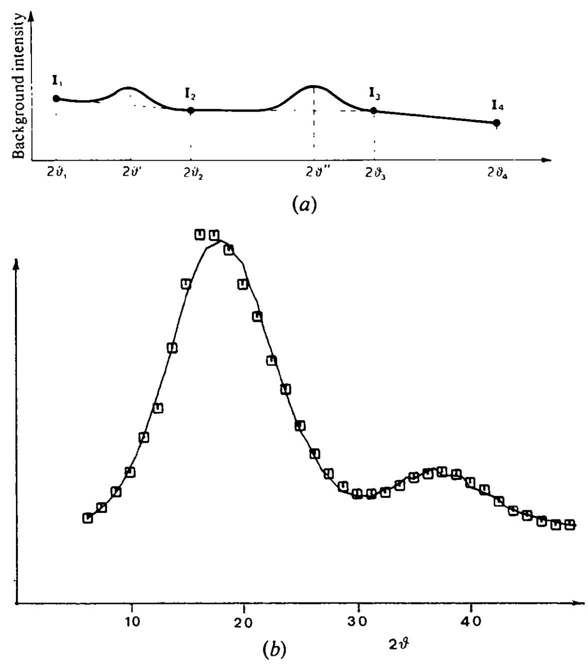

Fig. 2. (*a*) Functional form for the background considered in the program. The line is defined by N_1 points plus N_2 bell-shaped curves obeying to a Pearson function with its own m' parameter. The adjustable quantities are the N_1 intensities I_i, the m' parameter and the $3 \times N_2$ parameters defining the bell-shaped curves., *i.e.* the intensity, width and 2θ position for each curve. (*b*) Observed X-ray diffraction pattern (Cu $K\alpha$, Ni-filtered) of the amorphous resin Technovit 4030-b (small squares) and corresponding calculated pattern (full line) using two Gauss-shaped bumps of equal half-height width and adjustable area and position. The base line is defined by two points only. The R_2 index for this fitting is 2·9%.

Helix structures: isotactic polypropylene

The use of constraints in helix structure analysis is of considerable utility as in most cases helix symmetry is not compatible with crystal symmetry and the crystallographic asymmetric units often contain many chemically equivalent units. On the assumption that all monomeric units are structurally equivalent and that the characteristic ratio m/t (number of monomeric units per helix turn) is known, the following treatment is applicable, which refers to any helix with only two kinds of atoms in the chain (*e.g.* vinyl polymers, polyacetals *etc.*). Fig. 3 illustrates the g.c. system by considering an 11_3 helix as a worked example. The two quantities τ and φ (see Fig. 3) can be selected as g.c. Actually, from the couple τ, φ and from the repeat per monomeric unit p (note that p is *not* an independent

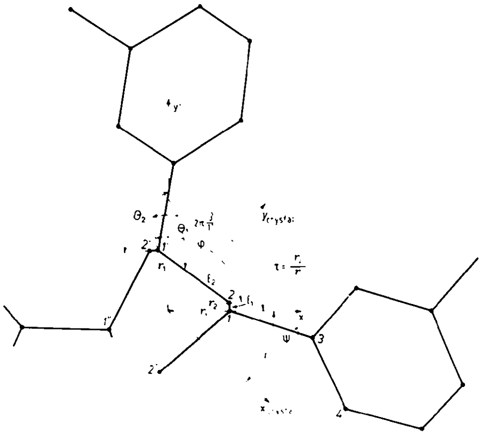

Fig. 3. Example of helix structure described by using generalized coordinates. The figure shows two adjacent units in the chain of poly(*m*-methylstyrene) in the 11_3 helix conformation (Corradini & Ganis, 1960).

quantity since it is a known fraction, t/m of a lattice constant), the Cartesian coordinates of the chain atoms referred to an internal frame $x'y'z'$ [see Fig. 3, z' origin is on C(2″)] are calculated as follows:

$$\mu = \cos\varphi - \cos\left(2\pi\frac{t}{m} - \varphi\right), \quad \nu = 1 + \frac{l_1^2 - l_2^2}{p^2},$$

$$q_1 = \left(l_1^2 - \frac{1}{4}p^2\nu^2\right)\frac{p^2}{\tau^2\mu^2},$$

$$q_2 = (1 + \tau^2 - 2\tau\cos\varphi + \tau\mu\nu)\frac{p^2}{2\tau^2\mu^2},$$

$$r_1 = \sqrt{(q_1 + q_2^2)^{1/2} - q_2}, \quad r_2 = \tau r_1,$$

$$x'_1 = r_1, \quad y'_1 = 0, \quad z'_1 = \frac{r_1 r_2 \mu}{p} + \tfrac{1}{2}\nu p,$$

$$x'_{2''} = r_2\cos\varphi, \quad y'_{2''} = -r_2\sin\varphi, \quad z'_2 = 0.$$

The repeated application of the 11_3 screw operator to atoms C(2″) and C(1) affords the completion of the main chain. A number of additional g.c. such as the θ_1, θ_2 and Ψ angles (see Fig. 3) complete the molecular structure. Finally three overall translations x_0, y_0, z_0 (or less depending on the space group) and an overall rotation Φ complete the crystal structure description.

The illustrated formalism has been used in the analysis of the structure of isotactic polypropylene. This polymer has been studied by X-ray diffraction of the stretched fibre by Natta & Corradini (1960) and subsequently by Mencick (1972). Both assigned to the polymer a 3_1 helix chain structure and a monoclinic unit cell, but they reached different conclusions on the crystal symmetry. According to the former authors the space group is *Cc* or *C*2/*c*, with a preference for *C*2/*c*, while according to the latter author it is *P*2$_1$/*c* with a fraction (~25%) of disordered helices (see Fig. 4).

Furthermore, in the bulk (unoriented) state other crystalline polymorphs, the β and γ forms, do exist, having presumably the same chain structure but different crystal packing (Turner Jones, Aizlewood & Beckett, 1964). Such forms *cannot* be studied by means of stretched fibres as they transform to the more stable α form under the mechanical action.

The structure analysis of isotactic polypropylene in the bulk state thus appears interesting both in order to decide among the *Cc*, *C*2/*c* and *P*2$_1$/*c* models in the case of the α form, and to establish the structures of the β and γ forms. We intend to study both the neutron and the X-ray profiles of this polymer. As the X-ray analysis has been completed while the neutron analysis is only at a very preliminary level we shall present in this paper only the X-ray part of the work as an example of the application of the g.c. approach.

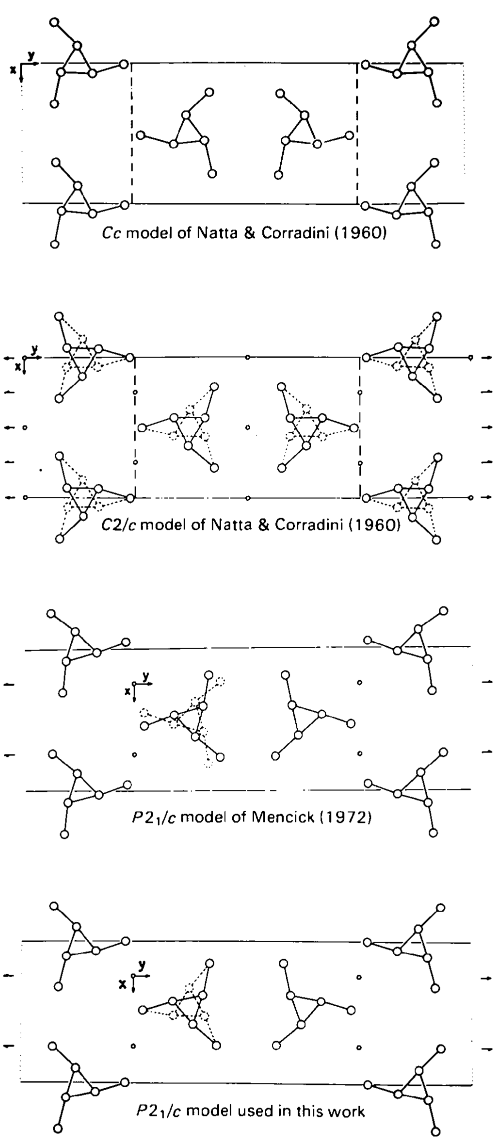

Fig. 4. Comparison of four crystal-packing models for isotactic polypropylene. The same schematic molecular geometry is represented for clarity in all cases [H atoms neglected; C(1) and C(2) are overlapped]. The broken chains indicate alternative positions related to the parent ones by a twofold axis perpendicular to the chain axis. In the *C*2/*c* the distribution is 50–50 imposed by symmetry; in the *P*2$_1$/*c* cases it is 79–21 (Mencick, 1972) or 78–22 (our model). In the *P*2$_1$/*c* cases only one broken chain is represented in order to show that disorder is not imposed by symmetry.

Description of polypropylene structure by means of generalized coordinates

The 3_1 helix of isotactic polypropylene can be described using the above illustrated formalism for helices with the fraction $\frac{1}{3}$ replacing t/m. In view of the desirable neutron diffraction study we consider also the H atoms. Besides the g.c. τ and φ for the backbone atoms C(1) and C(2) (see Fig. 5), the four g.c. θ_1 θ_2 θ_3 and θ_4 are used for defining the C(3) and H(1) positions. For H(2) and H(2′) we assume local C_{2v} symmetry introducing the H—C—H θ_5 angle as g.c., and for H(3), H(3′), H(3″) we assume local C_{3v} symmetry and locate the H atoms through the valence angle θ_6 and the torsion angle Ψ. In the present X-ray analysis the angles concerning hydrogens, *i.e.* θ_3, θ_4, θ_5, θ_6 and Ψ, are kept fixed at their canonical values.

The overall g.c. x_0, y_0, z_0 and Φ are treated differently in the three cases considered. In the *Cc* model x_0 and z_0 are arbitrary (origin definition) and y_0, Φ are unknown quantities to be adjusted. In the *C*2/*c* case, according to Natta's model, the C(3) atom lies on a diad parallel to the *y* axis and the helix axis also crosses this diad; this imposes fixed x_0, z_0 and Φ. Lastly, in the $P2_1/c$ case, all four values are unknown and also the additional parameter *f* expressing the fraction of disordered helices must be adjusted. Note in Fig. 5 that the Φ angle is measured from the x'' axis [crossing C(3)] instead of the x' axis [crossing C(1)] in order to have $\Phi = 0°$ in the *C*2/*c* case.

Mencick (1972) imposed on the chain axis the condition $x = \frac{1}{4}$ and adjusted z_0 and the Φ angle. Also, he generated the 'disordered' helices by means of a twofold axis parallel to the *y* axis at $z = \frac{1}{4}$. This was justified by packing considerations. In our opinion, however, it is not the chain axis but one of the methyl side groups that ought to be 'forced' to $x = \frac{1}{4}$ because of the necessity to balance the packing distances. Moreover, a more realistic crystal-packing arrangement is obtained by waiving the condition $x = \frac{1}{4}$ and generating the disordered chains through a twofold axis perpendicular to the chain axis and crossing a methyl C atom (these diads are perpendicular to *z* but not parallel to *y*). We have considered both Mencick's and our $P2_1/c$ models in separate refinements.

Table 1. *Experimental details for X-ray diffraction profile measurement of isotactic polypropylene*

Instrument	Philips PW 1050 powder goniometer equipped with diffracted-beam graphite monochromator, step-scan attachment, proportional counter and Soller slits.
Radiation	Cu $K\alpha$
Divergenge slit	0·5°
Receiving slit	0·1°
Angular range	7–50° (2θ)
Step width	0·05° (2θ)
Count time	60 s per step to $2\theta = 23{\cdot}5°$; 120 s per step beyond 23·5°

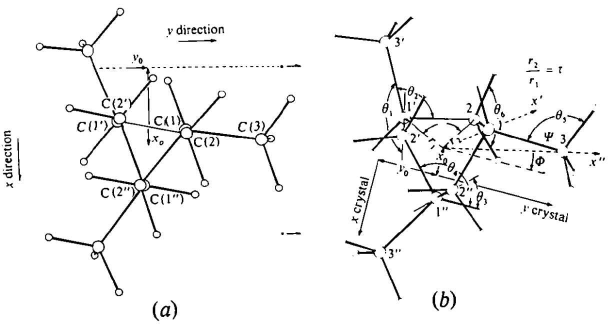

Fig. 5. (*a*) Molecular model for isotactic polypropylene resulting from $P2_1/c$ refinement, case *G*. The inversion centres $(0,\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},0)$ and the overall translation x_0, y_0 are also indicated. (*b*) The same polymer in a different arbitrary conformation and crystal position illustrating the system of generalized coordinates used.

X-ray diffraction measurements and structure refinement

A slab of width 0·91 mm was obtained by hot pressing (~463K) a sample of commercial isotactic polypropylene manufactured by Shell Co. (No. 5520). The sample was annealed at ~433 K for 12 h to favour crystallization and elimination of the β and γ forms. The diffraction profile was measured as indicated in Table 1. The intensities I_n were corrected for the low absorption effect (Klug & Alexander, 1970) dividing each I_n by $1 - \exp(-2\mu s/\sin\theta_n)$ (s = slab width, μ = linear absorption coefficient, θ_n = diffraction angle). Then the I_n values were twice smoothed according to the averaging function $I_n = (2I_n + I_{n-1} + I_{n+1})/4$.

Owing to the limited resolution of the diffraction pattern, the use of the Pearson profile function with *m* adjustable was not attempted and *m* was adjusted by trials to *m* = 1 (Cauchy profile) considering the sole profile below $2\theta = 20°$.

The least-squares refinement is based on the minimization of $\sum w_n(I_{n,\text{obs}} - I_{n,\text{calc}})^2$ with w_n (weight factors) set to $(\text{count-intensity})^{-1}$ and on the following refinable quantities: (i) lattice parameters; (ii) *U*, *V*, *W* peak-width controlling parameters [see Table 2, note (*b*)]; (iii) scale factor and overall thermal factor; (iv) background line without bumps, defined by three points in the early stages and six points subsequently; (v) generalized coordinates for defining the crystal structure as illustrated above.

The lattice constants and *U*, *V*, *W* parameters were refined first with fixed g.c. and then the latter were released. The overall thermal factor can be refined only very roughly and has been allowed to vary only in the final stages. For some parameters (especially τ and φ) the convergence is slow as a shift oscillation occurs with alternating positive and negative values; to increase the convergence rate, the program was temporarily modified introducing, for each variable, a shift cutting-off of 50% whenever the calculated shift is larger than the standard deviation and nearly the opposite of the previous one. The complete history of the refinement is indeed less straightforward due to lack of experience, errors, modification of the refinement strategy, *etc.* In any case, in the final stages, all parameters were simultaneously refined for several

Table 2. *Structural parameters for isotactic polypropylene at the end of the seven refinements performed*

Standard errors are in parentheses. Some relevant geometrical quantities, related to the refined parameters, are also given.[a]

	A *Cc* (Natta & Corradini, 1960)	*B* *C*2/*c* (Natta & Corradini, 1960)	*C* $P2_1/c$ (Mencick, 1972)	*D* $P2_1/c$ (this work)	*E* $P2_1/c$ (this work) with $V \neq 0$	*F* $P2_1/c$ (Mencick, 1972) with $2\theta > 23{\cdot}5°$	*G* $P2_1/c$ (this work) with $2\theta > 23{\cdot}5°$
100 a^{*2} (Å^2)	0·57947 (37)	0·57970 (36)	0·57967 (35)	0·58075 (31)	0·58098 (31)	0·58538 (54)	0·58678 (53)
100 b^{*2} (Å^2)	0·05686 (4)	0·05685 (4)	0·05686 (4)	0·05682 (3)	0·05682 (3)	0·05722 (5)	0·05700 (4)
100 c^{*2} (Å^2)	0·60087 (67)	0·60084 (60)	0·60162 (60)	0·060187 (57)	0·060144 (58)	0·59908 (47)	0·60015(45)
50 $a^*c^* \cos \beta^*$ (Å^2)	0·17689 (89)	0·17645 (86)	0·17613 (80)	0·17498 (68)	0·17502 (72)	0·17544 (161)	0·18153 (177)
Peak-width controlling parameters[b]							
V	–	–	–	–	0·69 (19)	1·05 (25)	1·05 (25)
W	0·2219 (83)	0·2199 (81)	0·2224 (71)	0·2154 (70)	0·103 (29)	0·104 (18)	0·095 (16)
Scale factor (from absolute intensities to count intensities)	0·0152 (5)	0·0140	0·0159 (2)[d]	0·0168 (7)	0·0170 (6)	0·0254 (7)	0·0175 (2)
Overall isotropic thermal parameter B (Å^2)	5·81 (75)	1·85 (99)	2·94 (30)[d]	2·94 (70)	2·02 (73)	2·94[e]	2·02[e]
Fraction f of disordered helices	–	–	0·213 (23)	0·223 (18)	0·229 (18)	0·213[e]	0·223[e]
$\tau = r_2/r_1$	0·675 (44)	0·677 (50)	0·991 (68)	1·224 (67)	1·211 (68)	1·306 (51)	1·009 (32)
φ (°)	129·3 (13)	129·8 (17)	121·2 (19)	118·8 (27)	116·4 (26)	132·4 (26)	125·0 (17)
θ_1 (°)	100·7 (12)[c]	100·0 (15)[c]	98·8 (39)	93·4 (32)	95·9 (32)	88·4 (11)	99·1 (13)
θ_2 (°)	100·7 (12)[c]	100·0 (15)[c]	106·1 (19)	114·0 (17)	113·6 (18)	99·7 (8)	113·9 (9)
x_0 (Å)	0	0	0	–0·250 (10)	–0·260 (10)	0	–0·103 (12)
y_0 (Å)	2·683 (14)	2·672 (12)	7·953 (11)	7·971 (7)	7·976 (6)	7·870 (8)	7·863 (9)
z_0 (Å)	0	0	–0·150 (60)	–0·162 (27)	–0·146 (26)	–0·150 (20)	–0·393 (16)
Φ (°)	–0·3 (9)	0	–8·8 (8)	–6·1 (5)	–8·1 (5)	–12·2 (5)	2·7 (4)
Number of refined variables	18	17	2 + 19	22	23	13 + 7	13 + 8
Last shift/σ ratio	0·20	0·20	0·85	0·88	0·13	0·4	0·2
$R_2 = \sum \lvert I_o - I_c \rvert / \sum I_o$	0·118	0·115	0·107	0·093	0·094	0·069	0·057
$R_3 = [\sum w(I_o - I_c)^2 / \sum w I_o^2]^{1/2}$	0·143	0·139	0·132	0·118	0·117	0·080	0·071
$R'_2 = \sum \lvert I_o - I_c \rvert / \sum I_{\text{net}}$[f]	0·211	0·207	0·196	0·167	0·154	0·172	0·142
Lattice constants							
a (Å)	6·643	6·642	6·641	6·634	6·633	6·608	6·605
b (Å)	20·968	20·970	20·969	20·974	20·976	20·902	20·942
c (Å)	6·523	6·524	6·519	6·517	6·519	6·532	6·531
β (°)	98·6	98·6	98·5	98·5	98·5	98·5	98·8
Chain bond angles (°) C(2″)–C(1)–C(2) and C(1)–C(2)–C(1′)	104·3–120·9	103·7–121·4	113·7–114·2	120·0–109·4	120·5–110·2	117·4–105·6	113·4–113·0
Chain torsion angles (°) C(1)–C(2)–C(1′)–C(2′) and C(2′)–C(1)–C(2)–C(1′)	168·4–65·6	168·1–65·7	178·3–60·5	178·8–60·2	177·0–59·1	165·8–66·0	175·0–61·9
Shortest packing distances (Å)	4·22, 4·36, 4·53	4·22, 4·36, 4·55	4·20, 4·25, 4·38	4·12, 4·21, 4·30	4·11, 4·20, 4·28	4·16, 4·39, 4·50	3·55, 4·16, 4·3

Notes: (*a*) The geometrical quantities kept fixed are: all C–C bonds – 1·54 Å; all C–H bonds = 1·08 Å; θ_3 and θ_4 = 109°; θ_5 and θ_6 = 110°; Φ – 180°. (*b*) According to the relationship (Caglioti, Paoletti & Ricci, 1958) $H_k^2 = U\tan^2\theta_k + V\tan\theta + W$, and assuming $U = 0$ everywhere and $V = 0$ in cases *E*, *F*, *G* only. (*c*) Assuming $\theta_1 = \theta_2$. (*d*) Overall *B* and scale factors refined in separate runs. (*e*) Overall *B* and *f* assumed to be as in *C*, *D*; *V*, *W*, scale factor and lattice constants refined in separate runs. (*f*) $I_{\text{net}} - I_{\text{obs}} - I_{\text{background}}$.

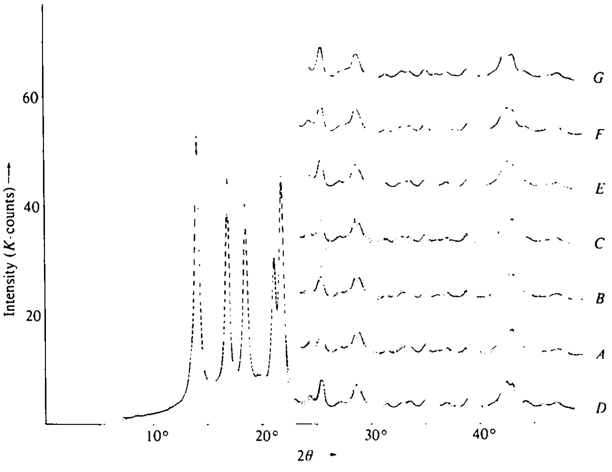

Fig. 6. Observed (full line) and calculated (dashed line) profiles for isotactic polypropylene at the end of the seven refinements performed. In cases *A*, *B*, *C* and *E* the profile below $2\theta = 23{\cdot}5°$ has been omitted in the drawing as it is almost identical to case *D*. In cases *F* and *G* the profile below 23·5° has also been ignored in the refinement.

cycles and shifts all below the standard errors were eventually obtained.

The results obtained in seven different refinements are summarized in Table 2, while the corresponding observed and calculated profiles are shown in Fig. 6.

Cases A and B

The results of the *Cc* and *C*2/*c* refinements agree very closely except for the overall *B* value. In both cases the refinement was carried out by imposing $\theta_1 = \theta_2$ since in the absence of this condition θ_1 assumed unacceptable values. The final *R* indices are also very similar. The resulting chain bond angles appear in both cases to be unreliable.

Case C

The $P2_1/c$ model of Mencick (1972) was refined by imposing $x = \frac{1}{4}$ for the chain axis and considering for each crystallographic position a statistical distribution of $(1-f)$ regular helices plus f helices related to the previous ones through the operator $-x, y, \frac{1}{2}-z$. In this case the simultaneous refinement of all variables failed because of the exceedingly large and meaningless shifts of the overall B value. The refinement has been carried out considering first an arbitrary value of $B = 3{\cdot}0$ Å^2 and refining all other parameters until convergence, then varying B and the scale factor only (rapid convergence in a single cycle), and lastly refining all other parameters with B and the scale factor being kept fixed. The resulting chain bond angles are almost equal with acceptable values also for θ_2, while θ_1 is rather unreliable, but with a high error. The fraction of disordered helices is close to the value given by Mencick (25%).

Case D

The $P2_1/c$ model has been tried again under different conditions from those considered by Mencick as described in the preceding paragraph. The various R indices are the lowest ones, but of the two chain bond angles θ_2 is reliable while θ_1 is rather low, but again with a high standard error. Examination of the observed and calculated profiles (Fig. 6) seems to indicate a better fit in this case, although discrepancies are present, mainly in the 2θ positions.

Case E

Case D has been subjected to further refinement by trying a variable peak width, considering the Rietveld dependence $H_k^2 = U \tan^2 \theta + V \tan \theta + W$ with $U = 0$ and V, W adjustable. Although a V value notably different from 0 was obtained, R indices and geometrical quantities seemed to be scarcely affected.

Cases F and G

Owing to the low absorption of the material, appreciable aberrations might be present in the X-ray profile at low angles (Klug & Alexander, 1970, ch. 5); see also the marked dissymmetry of the first strong peak. For these reasons both Mencick's and our $P2_1/c$ models were subjected to further refinements using only the weak part of the profile above 23·5°. These trials were performed, however, varying only the g.c. and lattice parameters in the early stages and the g.c. only in the last stages. In both cases an appreciable reduction of the R indices takes place: R_2', evaluated within the angular range considered, drops from 0·244 (Mencick) and 0·204 (our model) to 0·172 and 0·142 respectively. The resulting θ_1, θ_2 and chain bond angles are decidedly better in case G and also the fit of the observed and calculated profiles (Fig. 6) appears excellent. Although not all values are fully satisfactory (see θ_1 angle and some packing distances) we believe that our $P2_1/c$ model is the most reliable. The F and G refinements point out that the structural information contained in the weak part of the spectrum is anything but trivial and, considering the significant differences in the lattice constants, it supports the conjecture that low-angle aberration plays a critical role.

Recently, Petraccone, Pirozzi, Vidal & Corradini (1979) have studied the dependence of the diffracted intensity of stretched fibres on the annealing temperature. They have proposed a structural model for the transition from a disordered $C2/c$ structure to an ordered $P2_1/c$ structure. The verification of this model by the Rietveld method requires the use of peak-width parameters variable with h, k, l which is beyond the actual features of our least-squares program. In the future work with neutron radiation, however, we intend to improve the program in order to check this model too.

Conclusions

The present powder-profile X-ray diffraction analysis, conceived as a preliminary to a neutron diffraction study, does not pretend to be exhaustive or to give a definitive answer to the structural problem of isotactic polypropylene, including the precise nature of the chain disorder. While the analysis of more sosphisticated models such as that proposed by Petraccone *et al.* (1979) remains very desirable, the present study already demonstrates that structure analyses and refinements are feasible even in the case of X-rays with the consequent scarcity of intensity and resolution at the higher diffraction angles. Indeed, the accuracy of the results might even exceed expectations if the systematic angular errors were accounted for.

More generally, this work demonstrates the applicability of Rietveld's method under unfavourable conditions of complexity of structure and poor profile resolution. The use of constrained refinement is certainly of primary importance in these cases and we believe that the general program described in this work would be useful in solving other complicated structural problems using both X-ray and neutron diffraction.

The author wishes to acknowledge that Dr A. Albinati (Polytechnic of Milan) is also performing a Rietveld analysis of isotactic polypropylene using liquid-He-temperature neutron data from a deuterated product. He informed me of his preliminary results obtained with an unconstrained analysis.

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