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Up-down disorder in the crystal structure of form III of isotactic poly(4-methyl-1-pentene)

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The crystal structure of form III of isotactic poly(4-methyl-1-pentene) is refined with the full-profile X-ray powder diffraction refinement procedure (Rietveld method). Chains with 4/1 helical conformation are packed in a tetragonal unit cell according to the space group $I4_1$. In the limit-ordered regions of the crystal every chain is surrounded by four enantiomorphous and isoclined chains. A small amount of disorder, characterized by statistical substitution of anticlined helices, could be present at boundary regions which separate pieces of ordered crystals, composed by all up helices and all down helices, coherently juxtaposed.

(Keywords: poly(4-methyl-1-pentene); crystal structure; up-down disorder)

INTRODUCTION

Isotactic poly(4-methyl-1-pentene) (P4MP) presents a complex polymorphic behaviour. Five different crystalline forms have been described[1–5]. The different modifications can be obtained from crystallization in semidilute solutions depending on the solvent and the thermal history of the solutions[4,5]. Form I is the ordinary crystalline form which occurs in melt-crystallized samples and in extruded fibres; it is characterized by chains in (7/2) helical conformation packed in a tetragonal unit cell with axes $a = 18.66$ Å, $c = 13.80$ Å[1–3,6]. Form III was obtained by isothermal crystallization from dilute solutions in xylene[7–9] and in decalin[10,11] and, more recently, by crystallization from solutions in linear (5–7 carbon atoms) and branched (6–7 carbon atoms) alkanes as well as in carbon tetrachloride and cycloalkanes containing 6–10 carbon atoms[4,5].

Charlet *et al.*[4] proposed, from electron diffraction of single crystals of form III, a tetragonal unit cell with axes $a = 19.38$ Å, $c = 6.98$ Å with chains in 4/1 helical conformation, according to the unit cell previously proposed by Kawasaki and Takayanagi[8,9]. Form III transforms into modification I after annealing at ≈100°C and under stretching[4].

In a recent paper[12] we have proposed a preliminary model for the crystal structure of form III, even though fibre samples are not available. For the limit-ordered regions, we suggested a body-centred tetragonal space group $I4_1$. Every right-handed 4_1 helix is surrounded by four left-handed helices and vice versa[12]. Four chains are included in the unit cell, the asymmetric unit being composed of two independent monomer units belonging to the two enantiomorphous chains[12].

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Space groups $I4_1/a$ or $I4_1cd$, found for other isotactic polymers with chains in 4_1 helical conformation, (polyvinylcyclohexane[13] and poly(*o*-methylstyrene)[14], respectively) were ruled out[12] by the observations, in the electron diffraction spectra, of the presence of the $hk0$ reflections with $h = 2n + 1$ and $k = 2n + 1$ (which are absent for the space group $I4_1/a$) and by the observation of the different intensities of the $hk0$ and $h\bar{k}0$ reflections (which are equivalent reflections in the space group $I4_1cd$). The proposed model[12] accounted for both experimental observations.

In this paper the proposed structural model for form III of P4MP has been refined through the Rietveld method using the same approach employed for the crystal structure refinement of other polymers[15–18]. In this analysis we will consider different models of packing in the space group $I4_1$ arising from the possibility that the two independent enantiomorphous chains in the unit cell could be isoclined or anticlined. Moreover, the possible presence of statistical disorder in the positioning of up and down helices in the structure will be analysed.

In our refinement procedure special attention has been paid to the evaluation of the background contribution to the diffraction spectrum of the semicrystalline polymer: the background intensity has been accurately evaluated, recording the X-ray powder diffraction profile of a suitably prepared amorphous sample.

EXPERIMENTAL

P4MP was prepared using Ziegler–Natta-type catalysts. The sample used was also employed in a previous study[12]. Modification III of P4MP was obtained from crystallization in n-heptane solutions, as described in ref. 12. The sample of amorphous P4MP was prepared with a Cp_2ZrCl_2 homogeneous catalyst.

X-ray powder diffraction spectra were recorded at room temperature with a Philips diffractometer, using Ni-filtered Cu Kα radiation and a step scan procedure. The range of 2θ diffraction angles examined was 3–55°, the count time for each step was equal to 60 s/step, and the step width was 0.05° (2θ).

We ensured that the preferred orientation of the crystallites in the sample was reduced to a minimum. Indeed, X-ray powder diffraction photographic spectra of our sample (obtained in transmission geometry, by rotating the sample) give diffraction rings in the same intensity ratio as the integrated intensities, deduced through automatic collection.

For the refinement procedure we used the program DEBVIN, first developed by Immirzi[15] and subsequently revised and implemented by Bruckner and colleagues[16–19].

Method of refinement

In a full-profile X-ray powder diffraction refinement procedure for the crystalline structure of polymers, it is possible to refine simultaneously the chain conformation, the packing parameters, the cell constants and non-structural parameters.

The minimized function is:

$$F = \sum W_i(Y_{ci} - Y_{oi})^2 + \Sigma u_j(G_{oj} - G_j)^2$$

with Y_{oi} and Y_{ci} the observed and the calculated values of the intensity profile at the diffraction angle $2\theta_i$ and W_i the weight factor, placed equal to $W_i = 1/Y_{oi}$ for $2\theta > 6.50°$ and equal to $W_i = 0.1/Y_{oi}$ for $2\theta \leqslant 6.50°$; G_{oj} and G_j are the values which a given geometrical variable (i.e. bond lengths, bond angles, dihedral angles, distances between non-bonded atoms, etc.) is desired to assume and the corresponding value assumed by that variable at the given point of the refinement procedure, respectively. To introduce these constraining conditions ($G_{oj} - G_j = 0$), Lagrange's undetermined multipliers u_j are employed[20].

In carrying out the structural refinement using the present approach, the agreement factor R_2' is defined as:

$$R_2' = \sum |Y_{oi} - Y_{ci}| \Big/ \sum Y_{ni}$$

with $Y_{ni} = Y_{oi} - Y_{bi}$ where Y_{bi} is the background intensity, including the amorphous contribution.

In *Figure 1* a portion of the chain of P4MP is shown with the definition of the torsion angles θ_1, θ_2, θ_3 and θ_4. The torsion angle θ_4 is defined with respect to the hydrogen atom of the $CH(CH_3)_2$ groups.

In this paper we have treated all the dihedral angles as dependent variables, being a function of the position and of the orientation of the asymmetric unit with respect to the axes of the unit cell. In brief, the coordinates of all atoms in the asymmetric units (two independent monomer units) were first generated with respect to a frame with origin located on the carbon atoms of the CH_2 group, the z axis lying along the CH_2–CH bond, the CH–R bond (R is the lateral CH_2–$CH(CH_3)_2$ group) lying in the yz plane and the x axis completing a right-handed orthogonal frame. Rotations Ω_x, Ω_y and Ω_z around the axes and translations X, Y and Z along the axes of the orthogonal frame were hence introduced as independent variables to be optimized in the refinement procedure. Geometrical restraints are then introduced[20]; bond lengths and valence angles joining atoms belonging to successive asymmetric units were kept constant at the values listed in *Table 1*. At the beginning of the process of structural refinement it was useful to introduce additional restraints, keeping the values of distances between atoms of adjacent chains within distances compatible with the sum of the corresponding van der Waals radii. At the final stages of the refinement procedure, when the mean-square convergence was reached, the restraints on the distances for non-bonded atoms were relaxed. Hydrogen atoms were not considered; the cell constants were of course refined.

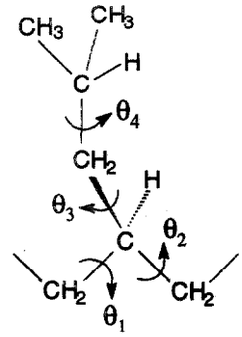

Figure 1 Definition of the dihedral angles in P4MP. The torsion angle θ_4 is defined with respect to the hydrogen atom of the $CH(CH_3)_2$ group

Table 1 Bond lengths and bond angles used to build the model chain of P4MP and kept constant in the refinement procedure

Bond lengths (Å)	
C–C	1.53
Bond angles[a] (deg)	
C″–C′–C″	111.0
C′–C″–C′	113.0

[a] C′ indicates a methine carbon atom; C″ indicates a methylene carbon atom

Some non-structural parameters were refined. In particular, it was necessary to refine the scaling factor for the amorphous X-ray powder diffraction profile, in order to put the latter profile on the same intensity scale of the spectrum of the semicrystalline polymer. An additional segmental line was considered that spanned the whole spectrum with nodes having abscissa $2\theta = 3°$ and 55° and the ordinate to be refined on the intensity scale.

The peak shape was assumed to be a Cauchy function with half-height width H equal to:

$$H = (U\tan^2[\theta] + V\tan[\theta] + W)^{1/2}$$

with θ the diffraction angle, U and V two variables to be optimized, and W depending on the (hkl) values through an adjustable estimation of crystallite dimensions L_a, L_b and L_c along the axes of the unit cell a, b and c, respectively[19,21,22]. A zero-point correction of the experimental 2θ scale was evaluated. The thermal parameters of all the atoms were always kept constant at a value of 8 Å^2.

RESULTS AND DISCUSSION

The X-ray powder diffraction profile of form III of P4MP is reported in *Figure 2*. The refinement was performed starting from different models of packing in

Table 2 Refined values of the structural parameters for the four independent chains[a] in the statistical model. The numbers in parentheses represent the standard deviations

Space group	$I4_1$			
a (Å)	19.46(1)			
b (Å)	19.46(1)			
c (Å)	7.022(3)			
α, β, γ	90°[b]			
R_2'	13%			
	Chain up_1	Chain $down_1$	Chain up_2	Chain $down_2$
θ_1 (deg)	82	82	−81	−81
θ_2 (deg)	−154	−154	153	153
θ_3 (deg)	73	73	−73	−73
θ_4 (deg)	−44	−44	44	44
Ω_z (deg)	−45.0(7)	24.9(8)	22.9(9)	−131.0(7)
Ω_x (deg)	−16.0(7)	9.1(7)	10.1(6)	−10.1(9)
Ω_y (deg)	12.6(7)	12.0(8)	12.8(7)	−15.8(8)
X (Å)	6.11(2)	3.96(2)	5.81(2)	4.34(3)
Y (Å)	4.27(3)	3.98(2)	15.50(2)	13.39(2)
Z (Å)	−2.20(4)	3.77(9)	1.18(4)	1.54(9)

[a] The chains up_1 and $down_1$ are isomorphous (left-handed) chains in the same site of the lattice with chain axes in the position 1/4, 1/4, z. The chains up_2 and $down_2$ are isomorphous (right-handed) chains in the same site of the lattice with chain axes in the position 1/4, 3/4, z.
[b] Not refined

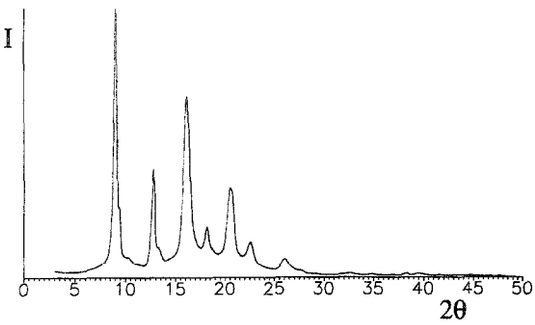

Figure 2 X-ray powder diffraction spectrum of form III of P4MP

the space group $I4_1$. In the first model the two independent enantiomorphous chains included in the unit cell are assumed to be isoclined, as in the preliminary model suggested in ref. 12; in the second one the two independent chains are assumed to be enantiomorphous and anticlined and, finally, in the third model the presence of statistical disorder, characterized by statistical substitution of isomorphous anticlined chains in each site of the lattice, is assumed.

In the last model pairs of upward and downward isomorphous helices can exist at those specific positions with probabilities that have to be refined. Moreover, the occupation factors of the atoms of the four independent monomer units in the disordered model (two up and two down) were kept constant during the optimization; the values of the occupation factors which give the best agreement factor were found performing different optimizations with occupation factors variable between 0 and 1.

The refinement of the model with all isoclined chains packed in the space group $I4_1$ (model suggested in ref. 12) gives an agreement factor $R_2' = 15\%$. The model with the enantiomorphous helices assumed anticlined gives an agreement factor $R_2' = 20\%$.

Although the enantiomorphous and anticlined helices have independent positioning in the unit cell, the latter refined model roughly corresponds to the space group $I4_1/a$, already ruled out in ref. 12 by the observation of the presence in the electron diffraction spectra of $hk0$ reflections with $h = 2n + 1$ and $k = 2n + 1$[4,23]. These results indicate that a model of packing with isoclined helices in the unit cell has to be preferred at least in the 'limit-ordered regions' of the crystals[24].

If the limit-ordered regions, constituted by isoclined helices, are small, neighbouring ordered crystals, characterized by all up helices and all down helices, could be easily juxtaposed, diffracting, at least in part, coherently. The presence of these neighbouring anticlined regions and the presence of the corresponding disorder arising at their boundaries, may be simulated by a model with up and down isomorphous helices which take up each site of the lattice with a probability depending on the occupation factor.

The latter model has been refined, performing different optimizations with occupation factors of the atoms of the isoclined chains variable between 0 and 1. The lowest value of the agreement factor, $R_2' = 13\%$, is obtained when the occupation factors of the atoms of the two independent isoclined chains are close to 0.8. This indicates that a model with some kind of disorder is the most probable for the crystal structure of form III of P4MP, at least for the sample studied. A small amount of disorder in the distribution of up and down helices is present, the major ordered regions being characterized by the packing of all isoclined helices.

The values of the refined structural parameters for the statistical model are reported in *Table 2*. It is apparent that the refined values of the torsion angles θ_1, θ_2, θ_3 and θ_4, which characterize the conformation of the chains, are very similar to those suggested in the previous paper[12].

The refined fractional coordinates of the atoms of the asymmetric unit are reported in *Table 3* with the

Table 3 Refined fractional coordinates and occupation factors of the asymmetric unit for the statistical disordered model of form III of P4MP of *Figure 4*. The asymmetric unit corresponds to four independent monomer units: atoms 1–6: atoms of the chain up_1; atoms 7–12: atoms of the chain $down_2$ (in the same site of up_2); atoms 13–18: atoms of the chain $down_1$ (in the same site of up_1); atoms 19–24: atoms of the chain up_2

	x/a	*y/b*	*z/c*	Occupation factor
1	0.314	0.219	−0.313	0.8
2	0.297	0.198	−0.107	0.8
3	0.342	0.137	−0.043	0.8
4	0.417	0.157	−0.006	0.8
5	0.464	0.093	−0.004	0.8
6	0.424	0.198	0.181	0.8
7	0.223	0.688	0.223	0.2
8	0.202	0.701	0.015	0.2
9	0.140	0.656	−0.041	0.2
10	0.160	0.580	−0.068	0.2
11	0.096	0.533	−0.062	0.2
12	0.200	0.569	−0.255	0.2
13	0.203	0.205	0.536	0.2
14	0.220	0.192	0.325	0.2
15	0.196	0.121	0.260	0.2
16	0.117	0.116	0.240	0.2
17	0.092	0.154	0.062	0.2
18	0.093	0.040	0.238	0.2
19	0.298	0.796	0.169	0.8
20	0.281	0.810	0.379	0.8
21	0.302	0.883	0.438	0.8
22	0.381	0.892	0.458	0.8
23	0.401	0.968	0.454	0.8
24	0.407	0.856	0.640	0.8

Table 4 Refined non-structural parameters. The numbers in parentheses represent the standard deviations

Zero shift (deg)	0.067(2)
Profile function parameters (deg^2)	
U	7.9(8)
V	−0.33(9)
Dimensions of the crystallites (Å)	
$L_a = L_b$	99(1)
L_c	71(2)

corresponding occupation factors, and the refined non-structural parameters are reported in *Table 4*.

A comparison between the observed (curve a) and calculated (curve b) X-ray powder diffraction profiles is reported in *Figure 3*. The X-ray profile of the amorphous sample suitably scaled (curve c) and the difference between observed and calculated profiles (curve d) are also shown.

The statistical model of packing of the chains in form III of P4MP, as refined in the present analysis, is reported in *Figure 4*. The values of the most relevant distances between non-bonded atoms are all within the limits allowed by the sum of the van der Waals radii. The lowest distance is 3.8 Å; it is present only in the disordered regions, being a contact between methyl groups belonging to anticlined chains.

As described above, the small amount of disorder in the distribution of up and down helices could be present at boundary regions which separate pieces of ordered crystals characterized by all up helices and all down helices coherently juxtaposed. One of these boundaries is shown, as an example, in *Figure 5*.

It is worth noting that a similar kind of disorder in the up and down positioning of helices has been suggested

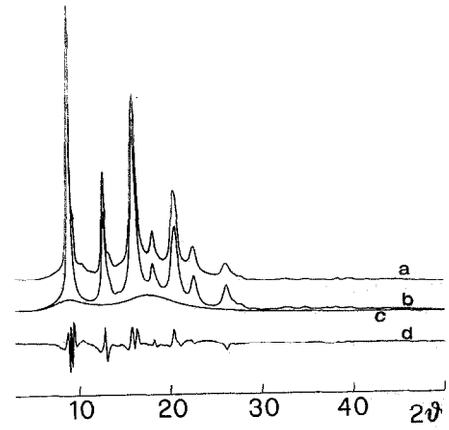

Figure 3 Comparison of observed (curve a) and calculated (curve b) X-ray powder diffraction profiles of form III of P4MP. Curve c is the X-ray diffraction spectrum of the amorphous sample; curve d is the difference profile

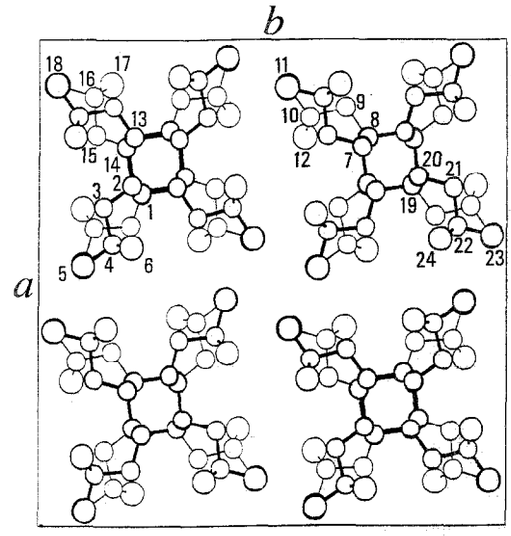

Figure 4 Refined packing model of form III of P4MP for the space group $I4_1$. With thin lines are sketched the chains $down_1$ and $down_2$ (see *Tables 2* and *3*) which have probabilities of 0.2 to substitute the chains up_1 and up_2, respectively

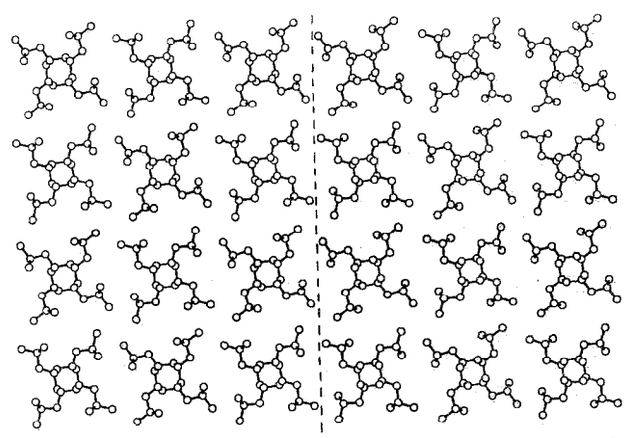

Figure 5 Possible model of packing of form III of P4MP showing a boundary (dashed line) that separates two pieces of ordered crystals characterized by all up helices (on the left of the dashed line) and all down helices (on the right of the dashed line)

for isotactic polypropylene[25], the degree of disorder being a function of the thermal and mechanical histories of the sample[26,27]. In the case of form III of P4MP this dependence cannot be investigated because thermal treatments or stretching of the sample produce transition in the ordinary form I of P4MP.

CONCLUSIONS

The crystal structure refinement, based on the X-ray powder diffraction profile, of form III of P4MP clearly indicates that form III is characterized by chains in 4/1 helical conformations packed in a tetragonal unit cell according to the space group $I4_1$, the limit-ordered regions of the crystal being characterized by the feature that every right-handed chain is surrounded by four left-handed and isoclined helices and vice versa[12]. In the sample studied a small amount of disorder, characterized by statistical substitution of anticlined helices in each site of the lattice, is present, however. This disorder could be present at boundary regions which separate pieces of ordered crystals characterized by all up helices and all down helices coherently juxtaposed. The refined positions of the isoclined chains are very similar to those in the preliminary model proposed in ref. 12.

A fairly good agreement between calculated and experimental profiles was obtained.

ACKNOWLEDGEMENT

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