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Crystal structure of syndiotactic poly(4-methyl-1-pentene)

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A model for the crystal structure of syndiotactic poly(4-methyl-1-pentene) is presented. According to the present analysis, chains having helical conformations with unit twist $t = 210°$ (1.714 conformational repeat units, each composed of two monomeric units per helix turn) and unit height $h = 3.91$ Å, corresponding essentially to $s(12/7)2$ symmetry, are packed in a tetragonal unit cell with $a = 18.03$ Å. The density is $0.878\ \mathrm{g\,cm^{-3}}$ with four chains in the unit cell, space group $P\bar{4}$.

(Keywords: poly(4-methyl-1-pentene); crystal structure; X-ray diffraction)

INTRODUCTION

The recent discovery of homogeneous catalysts[1–6] based on the group 4A metallocene/methylaluminoxane system for the polymerization of 1-alkenes has allowed the obtainment of new stereoregular hydrocarbon polymers and has induced new structural studies on polyalkenes. Studies conducted in our laboratories on the polymorphism and crystalline structures of some of the so-obtained new syndiotactic polymers (polystyrene[7–15], poly(*p*-methylstyrene)[16], poly(1-butene)[17,18] have been recently reported.

The syndiospecific catalytic system described by Ewen *et al.*[5] for the polymerization of propene is able to produce highly syndiotactic polymers of other 1-alkenes[6], such as crystalline poly(4-methyl-1-pentene). Also, it has been recently found that the homogeneous catalyst which promotes the syndiotactic polymerization of styrene[3,4] is able to polymerize several 1,3-alkadienes[19]. In particular, from the polymerization of 4-methyl-1,3-pentadiene, syndiotactic poly[1,2-(4-methyl-1,3-pentadiene)] is obtained[19]. Catalytic hydrogenation of this polymer constitutes an alternative route for the obtainment of crystalline syndiotactic poly(4-methyl-1-pentene)[19].

In a recent paper[20] we presented a preliminary structural characterization of highly syndiotactic poly(4-methyl-1-pentene) (s-P4MP) using samples obtained from two different synthetic routes. A helical conformation of the chains with a sequence of dihedral angles of the kind $(\mathrm{TTGG})_n$ having 1.714 ± 0.002 structural units (two monomeric units) per helix turn, corresponding essentially to $s(12/7)2$ symmetry, and an identity period $c = 46.9$ Å was suggested on the basis of the X-ray diffraction data and conformational energy calculations[20].

In this paper a model for the crystal structure of s-P4MP is reported on the basis of a quantitative comparison between X-ray diffraction intensities and calculated structure factors.

EXPERIMENTAL AND METHOD FOR CALCULATIONS

Two different samples of s-P4MP were used. The first one, supplied by the Department of Physics of the University of Salerno, was obtained by hydrogenation of syndiotactic poly[1,2-(4-methyl-1,3-pentadiene)] as described elsewhere[19]. The second one, supplied by Himont Italia, was obtained by polymerization of 4-methyl-1-pentene in the presence of homogeneous catalysts based on a group 4A metallocene/methylaluminoxane system[6]. The inherent viscosities were $0.62\ \mathrm{dl\,g^{-1}}$ and $0.29\ \mathrm{dl\,g^{-1}}$, respectively.

Oriented specimens were obtained only for the sample of higher molecular weight by drawing at room temperature, at a draw ratio of nearly 2, the compression-moulded amorphous samples (obtained by quenching in liquid N_2 of the melt). The crystallinity of each sample was then increased by annealing at 100°C.

Wide angle X-ray fibre diffraction spectra were obtained with nickel-filtered CuKα radiation and a cylindrical camera.

Calculated structure factors (F_c^2) were obtained from $F_c^2 = |F_i|^2 M_i$, where M_i is the multiplicity factor. The experimental intensities were observed for values of ξ up to $0.35\ \text{Å}^{-1}$ for the layer lines with $\zeta = 0$–$0.213\ \text{Å}^{-1}$ and up to $0.45\ \text{Å}^{-1}$ for the layer lines with $\zeta = 0.256\ \text{Å}^{-1}$ and $\zeta = 0.298\ \text{Å}^{-1}$. The calculations of the structure factors are reported for these ranges of ξ. The calculated intensities for larger ξ values (not reported) were all below the observable limit. A thermal factor $B = 8\ \text{Å}^2$ and the atomic scattering factors given elsewhere[21] were assumed.

The packing energy was evaluated as half the sum of

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the interaction energies between the atoms of one monomeric unit and all the surrounding atoms of the neighbouring macromolecules. The calculations were performed with the same function as used for the calculations of the conformational energy given elsewhere[20], i.e. with the constants reported by Flory *et al.*[22] and taking the methyl groups as a single rigid unit[23]. The conformation of the chain (and hence the c axis) was kept constant and the interactions were calculated within spheres of twice the sum of the van der Waals radii for each pair of atoms.

RESULTS AND DISCUSSION

The X-ray spectrum of s-P4MP fibre is reported in *Figure 1*. All the reflections observed in the fibre spectrum are listed in *Table 1*. Some of these data have already been presented elsewhere[20]; in this paper more reflections are observed in the X-ray fibre spectrum of *Figure 1*, which in fact was obtained in a vacuum cylindrical camera with double the radius used earlier[20]. As shown earlier[20], these data are consistent with a helical conformation of the chains of the kind $(\mathrm{TGGT})_n$ having 1.714 structural units per helix turn, each structural unit containing two monomeric units with the conformation TGGT. Each monomeric unit is related to the two neighbouring units by two-fold axes perpendicular to the chain axis.

This conformation corresponds essentially to $s(12/7)2$ symmetry, in which the chain repetition occurs after 12 conformational units repeating helically (24 monomeric units) after seven turns around the chain axis.

It is worth noting that for helical symmetry $s(M/N)$, it is well known that when the ratio M/N is irrational the repeat distance is formally absent[24–26]. In practice, the ratio M/N may be approximated by some rational fraction M'/N' which determines all the features of the X-ray pattern. The X-ray intensity will concentrate near layer lines defined by M'/N' which will be broadened and split[24–26] along ζ. The departure from the exact rational ratio does not introduce any discontinuity in the intensity pattern but prevents the definition of an exact identity period c. On the other hand, a repeat distance c is meaningful only when its value is small compared with the dimension of the crystal in the c direction. However, in this case an approximate value of nearly 46.9 Å can be given if we assume that the chain repetition occurs exactly after 12 structural units.

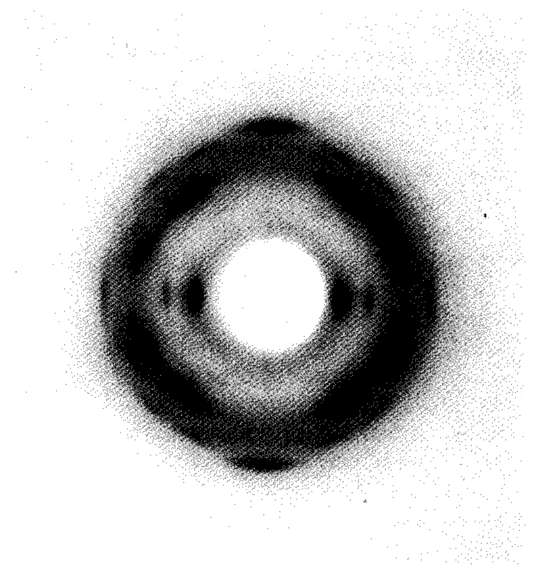

Figure 1 X-ray diffraction spectrum of an oriented sample of s-P4MP fibre

According to the previous[20] analyses, the values of the dihedral angles along the main chain of s-P4MP are $\theta_1 = 70^\circ$ and $\theta_2 = -164^\circ$ if the valence angles τ_1 and τ_2 are assumed to be 111° and 113°, respectively (C–C bond length = 1.54 Å), while the values of the dihedral angles which characterize the conformations of the lateral groups are $\theta_3 = 202^\circ$ and $\theta_4 = -50^\circ$. The definitions of the dihedral and bond angles are shown in *Figure 2*.

It is worth noting that the formation of $s(M/N)$ complex helical symmetry with M and N not corresponding to very small integers is a consequence of the bulkiness of the lateral groups[27] and corresponds to the isodistortion of the dihedral angles of the main chain from the staggered values[27] 180° and 60°, as already found for many isotactic polymers[27,28]. For syndiotactic polymers the isodistortion of the dihedral angles and the

Table 1 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l in the X-ray diffraction spectrum of s-P4MP fibre

$2\theta(^\circ)$	d(Å)	ξ(Å^{-1})	ζ(Å^{-1})	l^a	$I_{\mathrm{obs}}{}^b$
9.80	9.02	0.111	0	0	vs
13.8	6.41	0.156	0	0	m
20.1	4.42	0.226	0	0	vw
22.1	4.01	0.249	0	0	s
20.6	4.31	0.228	0.045	2	vw
22.6	3.94	0.250	0.045	2	vw
25.8	3.45	0.286	0.045	2	vw
29.5	3.03	0.327	0.045	2	w
18.8	4.72	0.202	0.062	3	s
21.0	4.24	0.227	0.062	3	vw
17.4	5.10	0.177	0.084	4	ms
14.6	6.05	0.126	0.106	5	vvw
20.2	4.38	0.202	0.106	5	m
22.5	3.96	0.229	0.106	5	m
25.1	3.55	0.251	0.128	6	w
17.2	5.17	0.124	0.149	7	vs
28.5	3.13	0.283	0.149	7	vw
33.0	2.71	0.337	0.149	7	vw
21.7	4.09	0.176	0.169	8	s
24.5	3.63	0.217	0.169	8	w
24.5	3.63	0.195	0.194	9	vw
31.8	2.81	0.297	0.194	9	vw
35.1	2.55	0.340	0.194	9	vw
36.9	2.44	0.361	0.194	9	vw
20.1	4.41	0.075	0.214	10	vw
21.4	4.16	0.110	0.214	10	m
24.5	3.63	0.174	0.214	10	vw
22.7	3.91	0	0.251	12	s
24.5	3.63	0.115	0.251	12	vw
31.9	2.81	0.253	0.251	12	w
43.4	2.09	0.409	0.251	12	vw
46.7	1.94	0.449	0.251	12	vw
28.2	3.16	0.119	0.293	14	vw
30.7	2.91	0.179	0.293	14	w
44.6	2.03	0.395	0.293	14	w
47.7	1.91	0.435	0.293	14	vw
50.1	1.82	0.464	0.293	14	vw
33.9	2.65	0.207	0.316	15	w
35.1	2.55	0.231	0.316	15	w

[a] $c = 46.9$ Å

[b] vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, vvw = very very weak

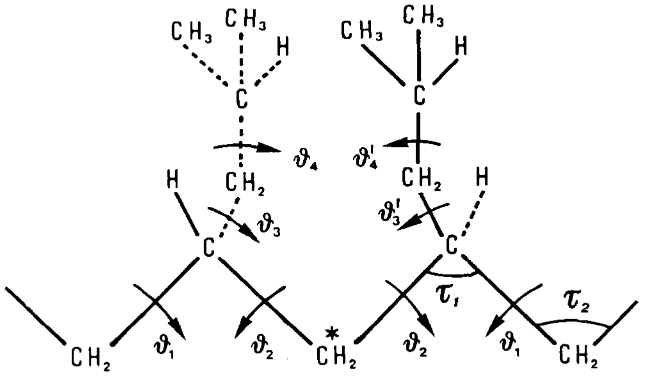

Figure 2 Definitions of the torsion angles θ_1, θ_2, θ_3 and θ_4 and the bond angles τ_1 and τ_2. The torsion angles which characterize the conformations of the lateral groups in the conformational repeat units (θ_3, θ_3') are defined with respect to the same CH$_2$ group (indicated by an asterisk)[20]. Both torsion angles θ_4 and θ_4' are defined with respect to the hydrogen atoms of the CH(CH$_3$)$_2$ groups. The binary axes crossing the CH$_2$ groups of the main chain for the $s(M/N)2$ symmetry impose $\theta_3 = \theta_3'$ and $\theta_4 = \theta_4'$

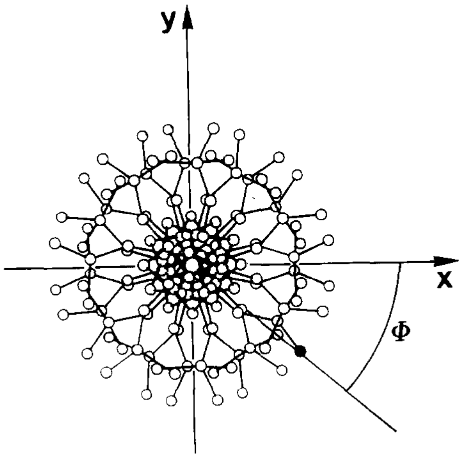

Figure 3 Definitions of the coordinates Φ and z used in the lattice energy map. The value of Φ is positive for a clockwise rotation, and z is the height of the methyl group (indicated as a filled circle)

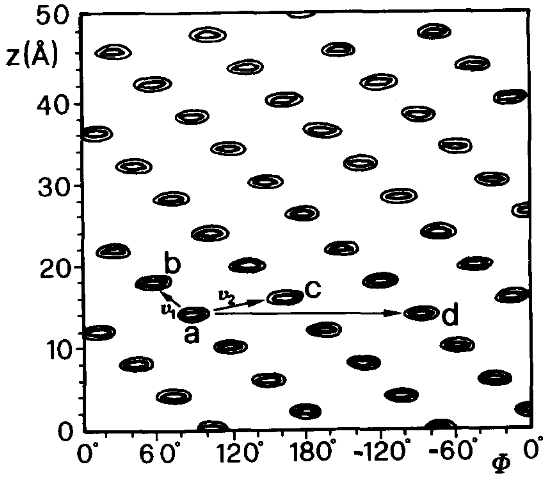

Figure 4 Map of the lattice energy as a function of z and Φ for the space group $P\bar{4}$. The curves are drawn at intervals of 20 kJ mol^{-1} of monomeric unit with respect to the absolute minimum of the map assumed as zero

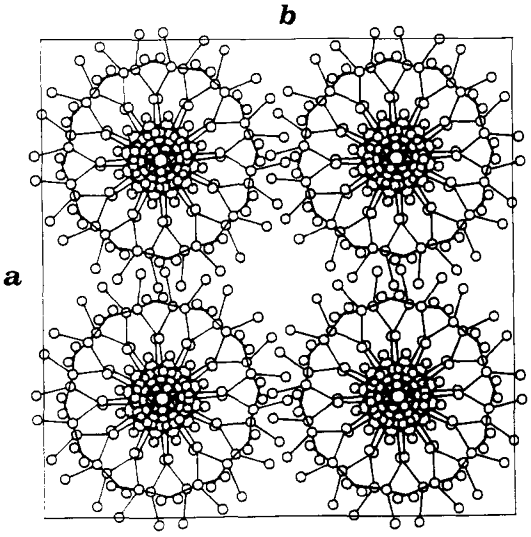

Figure 5 Possible packing model for s-P4MP with space group $P\bar{4}$

Table 2 Fractional coordinates of the carbon atoms of the structural unit (two monomeric units) for the chain model with the chain axis at the origin of the unit cell. (The fractional coordinates of the asymmetric unit for the model of *Figure 5* (space group $P\bar{4}$) can be obtained as described in the text)

	x/a	y/b	z/c
1	−0.018	−0.091	0.335
2	0.026	−0.052	0.358
3	0.067	−0.109	0.377
4	0.138	−0.139	0.363
5	0.168	−0.207	0.380
6	0.198	−0.078	0.361
7	−0.024	−0.002	0.376
8	0.020	0.055	0.394
9	0.053	0.116	0.375
10	0.120	0.155	0.389
11	0.141	0.226	0.373
12	0.187	0.102	0.391

formation of complex helical symmetries have been observed for form II of poly(1-butene)[17,29].

The reflections observed in the fibre spectrum are all accounted for by a tetragonal unit cell[20] with $a = 18.03$ Å. The calculated density for four chains in the cell (96 monomeric units) is 0.878 g cm^{-3}, in accordance with the experimental value ($d_{sp} = 0.852$ g cm^{-3} measured at 25°C by flotation for a sample with an X-ray crystallinity of $\sim 45\%$).

The cylindrical outside envelope of the chains[20] allows us to hypothesize a close packing of the helices in the tetragonal unit cell with a coordination number equal to 4, each chain being surrounded by four helices of the opposite chirality[30]. The space group compatible with this type of packing is then $P\bar{4}$ if conventional space group nomenclature is used for this incommensurable helical symmetry.

In order to find the best position of the chains inside the unit cell, calculations of the packing energy were performed for the space group $P\bar{4}$. The position of the chain axis inside the unit cell was fixed at the fractional coordinates $x/a = y/b = 0.25$, so that the lattice energy was calculated whilst maintaining the axes of the unit cell constant and varying only two parameters: the orientation of the chain around its axis (represented by the angles Φ defined in *Figure 3*) and the z coordinate that defines the relative heights of the chains in the unit cell.

Table 3 Comparison between experimental intensities I_{obs} observed in the X-ray fibre spectrum of s-P4MP and calculated structure factors F_c^2 for the model of *Figure 5* (space group $P\bar{4}$)

$h\ k\ l$	d_{calc} (Å)	d_{obs}(Å)	10^{-3} F_c^2	I_{obs}
2 0 0	9.016	9.02	1500	vs
2 2 0	6.374	6.41	110	m
4 0 0	4.507	4.42	180	vw
4 2 0	4.032	4.01	460	s
4 4 0	3.187		46	
6 0 0	3.005		22	
2 1 1	7.947		2	
3 2 1	4.973		8	
4 1 1	4.354		25	
4 3 1	3.595		66	
5 2 1	3.339		13	
6 1 1	2.958		4	
2 0 2	8.415		1	
3 1 2	5.540		15	
{ 4 0 2	4.426	4.31	100 } 220	vw
{ 3 3 2	4.182		120	
4 2 2	3.973	3.94	109	vw
5 1 2	3.497	3.45	37	vw
{ 5 3 2	3.066	3.03	230 } 360	w
{ 6 0 2	2.981		130	
2 1 3	7.166		37	
3 0 3	5.610		18	
3 2 3	4.763	4.72	440	s
4 1 3	4.211	4.24	144	vw
4 3 3	3.514		9	
5 2 3	3.274		6	
6 1 3	2.912		9	
2 0 4	7.147		18	
2 2 4	5.600		81	
3 1 4	5.128	5.10	197	ms
4 0 4	4.207		78	
4 2 4	3.813		10	
5 1 4	3.386		9	
4 4 4	3.076		1	
1 0 5	8.322		4	
2 1 5	6.116	6.05	54	vvw
3 0 5	5.061		1	
3 2 5	4.413	4.39	123	m
4 1 5	3.964	3.96	340	m
4 3 5	3.366		77	
5 2 5	3.153		4	
4 0 6	3.906		41	
4 2 6	3.383	3.55	74	w
5 3 6	2.875		1	
6 0 6	2.805		1	
2 1 7	5.154	5.17	1630	vs
3 2 7	4.008		6	
4 3 7	3.175	3.13	20	vw
5 2 7	2.995		18	
6 1 7	2.711	2.68	114	vw
2 0 8	4.916		27	
2 2 8	4.316		150	
3 1 8	4.088	4.09	360	ms
4 0 8	3.574	3.63	170	w
3 3 8	3.441		18	
4 2 8	3.322		41	
5 1 8	3.028		22	
2 1 9	4.377		2	
3 2 9	3.609	3.63	39	vw
4 1 9	3.350		27	
4 3 9	2.965		16	
5 2 9	2.817	2.81	125	vw
6 1 9	2.577	2.55	170	vw
5 4 9	2.478	2.44	177	vw
1 1 10	4.403	4.41	66	vw
2 0 10	4.162	4.16	140	m
2 2 10	3.778		6	
3 1 10	3.622	3.63	72	vw
4 0 10	3.250		13	
3 3 10	3.194		2	
5 1 10	2.824		5	
4 4 10	2.636		1	
5 3 10	2.582		2	
6 0 10	2.530		3	
3 2 11	3.245		3	
4 1 11	3.053		7	
4 3 11	2.754		13	
5 0 11	2.754		5	
5 2 11	2.633		8	
6 1 11	2.434		5	
0 0 12	3.909	3.91	610	s
1 1 12	3.738		5	
2 0 12	3.586	3.63	37	vw
2 2 12	3.332		4	
4 0 12	2.953		24	
4 2 12	2.807	2.81	88	w
4 4 12	2.470		17	
6 0 12	2.382		17	
6 2 12	2.303		21	
6 4 12	2.106	2.09	57	vw
7 3 12	2.025		1	
8 0 12	1.953	1.94	35	vw
3 2 13	2.926		4	
4 1 13	2.783		7	
4 3 13	2.551		5	
5 2 13	2.454		5	
6 1 13	2.290		3	
2 0 14	3.141	3.16	49	vw
3 1 14	2.889	2.91	51	w
4 0 14	2.689		11	
3 3 14	2.631		3	
5 1 14	2.432		1	
5 3 14	2.272		4	
6 0 14	2.237		1	
6 2 14	2.171		26	
{ 5 5 14	2.029	2.03	80 } 107	w
{ 7 1 14	2.029		27	
6 4 14	2.004		7	
{ 7 3 14	1.934	1.91	59 } 120	vw
{ 8 0 14	1.870		61	
8 2 14	1.831	1.82	83	vw
2 1 15	2.916		40	
3 0 15	2.774		24	
3 2 15	2.652	2.65	330	w
4 1 15	2.544	2.55	124	w
4 3 15	2.363		8	
5 0 15	2.363		3	
5 2 15	2.285		3	
6 1 15	2.151		2	

A map of the lattice energy as a function of z and Φ for the space group $P\bar{4}$ is reported in *Figure 4*. The map presents several equivalent minima; in fact, it is periodic over 180° (minimum 'a' repeats identically into minimum 'd'). Moreover, each minimum repeats identically along the directions v_1 and v_2. For instance, minimum 'a' repeats into minimum 'b' after a translation of v_1, which corresponds to a rotation of $\Phi = 180° - t = -30°$, where t is the unit twist ($t = 210°$), and a translation of $\Delta z = h$, where h is the unit height ($h = 3.91$ Å).

Minimum 'a' also repeats into minimum 'c' after a translation of v_2, which corresponds to a rotation of $\Phi = 180° - t/2 = 75°$, and a translation of $\Delta z = h/2$. The presence of these equivalent minima corresponds to the fact that the only important parameter that characterizes the structure is the shift along z between neighbouring chains.

Calculations of the structure factors were performed for different positions of the chain in the unit cell corresponding to the energy minima present in the map of *Figure 4*; all these models of packing gave the same calculated structure factors, indicating the equivalence of the minima present in the map of *Figure 4*. For this reason, only the results corresponding to the minimum at $\Phi = 50.9°$ and $z = 17.8$ Å (as an example) are reported. The model of packing corresponding to this energy minimum is shown in *Figure 5*.

The fractional coordinates of the carbon atoms of the structural unit (two monomeric units) for the chain model with the chain axis at the origin of the unit cell are reported in *Table 2*. The fractional coordinates of the carbon atoms of the asymmetric unit for the model of *Figure 5* (space group $P\bar{4}$) can be obtained starting from the coordinates of the structural unit of *Table 2* through the helical symmetry operation 12/7 (rotation of 210° plus translation along z of $c/12 = 3.91$ Å) and a translation of 0.25 along the axes a and b. If x_i, y_i and z_i are the 12 coordinates of the structural unit of *Table 2*, the fractional coordinates of the asymmetric unit are

$$x_i^n = (x_i^2 + y_i^2)^{1/2} \cos[\tan^{-1}(y_i/x_i) + nt] + 0.25$$

$$y_i^n = (x_i^2 + y_i^2)^{1/2} \sin[\tan^{-1}(y_i/x_i) + nt] + 0.25$$

$$z_i^n = z_i + n/c$$

where if $x_i < 0$, $\tan^{-1}(y_i/x_i)$ has to be $\tan^{-1}(y_i/x_i) + 180°$, t is the unit twist ($2\pi \times 7/12$) and n can assume all the integral values between 0 and 11.

A comparison between the calculated structure factors (F_c^2) for the model of *Figure 5* (space group $P\bar{4}$) and the experimental intensities observed in the fibre spectrum is given in *Table 3*. Fairly good agreement between observed and calculated intensities is apparent, although some discrepancies are still present. Indeed, a refinement of the crystal structure model that we suggest presents difficulties because of the poor X-ray diffraction data.

The discrepancies probably occur because our model is composed of uniform 12/7 helices; slight deviations from the uniform 12/7 helix are possible, as discussed before.

Similar deviations from the uniform 7/2 helix have been suggested in the refinement of the crystal structure of form I of isotactic poly(4-methyl-1-pentene)[31]. This refined model of the crystal structure of isotactic poly(4-methyl-1-pentene), with a slightly distorted conformation, is very similar to the model proposed elsewhere[32,33], but the discrepancies between the calculated and observed intensities were removed[31].

It is worth noting that the proposed model of packing for s-P4MP is similar to that for form I of isotactic poly(4-methyl-1-pentene)[31–33] in spite of the different configurations and conformations of the chains. This is also pointed out by the similarity of their X-ray powder diffraction spectra[20]. In fact, both the chains in isotactic (having $s(7/2)1$ helical symmetry) and syndiotactic (having $s(12/7)2$ helical symmetry) poly(4-methyl-1-pentene) have an outside envelope similar to that of a cylinder in which hollows and bulges are periodically repeated as occurs in a screw[30]. Such kinds of helices[30] are generally packed in tetragonal lattices with a coordination number equal to 4, giving rise to quite similar modes of packing.

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