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Crystal Structure of Form II of Isotactic Poly(4-methyl-1-pentene)

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ABSTRACT: The crystal structure of form II of isotactic poly(4-methyl-1-pentene) is presented. Samples of isotactic poly(4-methyl-1-pentene) in the pure form II have been obtained by crystallization from tetramethyltin solutions. The crystal structure has been determined by using X-ray powder diffraction data and packing energy calculations. Chains in 4_1 helical conformation are packed in a monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$, according to the space group $P2_1/b$. Four chains are included in the unit cell with a calculated density of 0.862 g/cm^3, according to the experimental density of 0.850 g/cm^3. Statistical disorder in the position of up and down chains in each site of the lattice is present in the structure. This structure provides an example of *symmetry breaking* in polymer crystals since the local 4_1 helical symmetry of the chains is not maintained in the lattice as crystallographic symmetry. As a consequence, the chains do not pack in a tetragonal lattice, as generally occurs for chains in 4_1 helical conformation but are packed in a monoclinic lattice having lower symmetry.

Introduction

Isotactic poly(4-methyl-1-pentene) (i-P4MP) presents a complex polymorphic bahavior.[1−6] Five different crystalline forms have been found. They can be obtained from crystallization in semidilute solutions depending on the solvent and the thermal history of the solutions.[5,6]

Form I is the most stable crystalline form which occurs in melt crystallized samples and in extruded fibers;[1−4] it can be also obtained from crystallization in solutions of high-boiling point solvents, like normal alkanes with number of carbon atoms greater than 9, branched dodecane and branched decane.[6] Form I 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,[1−4] according to the space group $P\bar{4}$.[2,3] Slight deviations from the uniform 7_2 helical conformation and space group $P\bar{4}b2$ have been suggested for form I in a successive refinement of the structure.[4]

Form II was prepared for the first time by isothermal crystallization at 20 °C from dilute xylene solutions[7−9] and, more recently, by crystallization from tetramethyltin solution,[6] or as a minor component in a mixed structure crystallized in carbon disulfide solutions.[6] A tetragonal unit cell with axes $a = 19.16$ Å, $c = 7.12$ Å and chains in 4_1 helical conformation has been proposed for form II by Takayanagi et al.,[9] from X-ray diffraction patterns on single-crystal mats.

Form III was obtained from dilute solutions in xylene (by isothermal crystallization at 65 °C)[7−9] and in Decalin.[10,11] It is also obtained in linear (5−7 carbon atoms) and branched (6−9 carbon atoms) alkanes, as well as in carbon tetrachloride and cycloalkanes containing 6−10 carbon atoms.[5,6] The crystal structure of form III has been recently determined and refined;[12,13] chains in 4_1 helical conformation are packed in a tetragonal unit cell with axes $a = 19.46$ Å, $c = 7.02$ Å, according to the space group $I4_1$.[12,13] The proposed low symmetry packing model of form III has been recently confirmed by a solid state ^{13}C NMR analysis.[14] This structure has been considered as an example of the phenomenum of "*symmetry breaking*",[15] for which a mode of packing with low symmetry may occur even in the case of polymers which crystallize in highly symmetric single crystals.[12] Form III of i-P4MP gives, indeed, regular square single crystals,[5,16] indicating a tetragonal packing, but the asymmetry of the corresponding electron diffraction pattern[5,16] indicates low symmetry of the space group.[12] The low symmetry originates from the presence of two independent chains, not related by any element of symmetry, in the tetragonal unit cell.[12,13] Form III transforms into form I after annealing at ≈100 °C and under stretching.[5]

Form IV was obtained, in both unoriented and uniaxially oriented state, by annealing form I above 200 °C under pressure (4500 atm).[17] The same crystalline modification has been obtained also from cyclopentane solutions.[18] Stretching of an unoriented sample in form IV leads to a fiber in form I;[18] however a partially oriented sample in form IV,[18] and more recently, well oriented fibers of pure form IV,[19] have been obtained by swelling fibers of form I in saturated cyclopentane vapor at 50 °C.[18,19] From the X-ray fiber diffraction pattern[19] and the solid state ^{13}C NMR spectrum,[14] a 3_1 helical conformation of the chains has been proposed for the form IV.[19,14] Moreover, a hexagonal unit cell with axes $a = 22.17$ Å, $c = 6.5$ Å has been also suggested.[18,19] Form IV transforms into form I by annealing a 130 °C.[18]

Form V has been obtained from concentrated cyclohexane gels[20] and by crystallization from cyclohexane and carbon tetrachloride solutions.[6] Form V transforms into form I by annealing at ≈90 °C.

It is worth noting that only for form I and form III has a complete crystal structure been reported.[2−4,12,13] Only not feasible unit cell parameters have been proposed for form II.[9]

In the case of form II, neither fiber samples nor single crystals can be obtained. Samples of i-P4MP in form II transform, indeed, into the most stable form, form I, by stretching, whereas only single crystals of forms I and III have been obtained by solution or epitaxial crystallization.[5,6,16,21] Therefore, only a few diffraction data from powder samples are available for form II. For this reason, the crystal structure of form II has not been solved yet, even though tentative values of the unit cell

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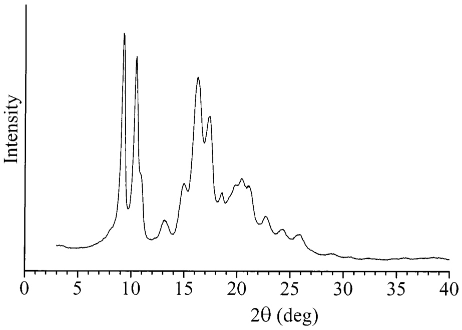

Figure 1. X-ray powder diffraction profile of form II of i-P4MP.

parameters have been proposed long ago.[9] In this paper, the crystal structure of form II is solved despite the few available diffraction data, by using only the X-ray powder diffraction profile.

Experimental Part and Method of Calculation

i-P4MP was purchased from Aldrich (high molecular weight grade).

Samples of i-P4MP in form II were prepared by crystallization from tetramethyltin solution following the method described in ref 6. The solutions (polymer volume fraction $\phi = 0.05$) were prepared in sealed glass tubes in air atmosphere. Dissolution was achieved by heating the sealed tube at the temperature of 165 °C for 20 h, to obtain homogeneous solution. The solution was then rapidly cooled to room temperature and the polymer was recovered by evaporation of the solvent at room temperature. Different solvents or different crystallization procedures produce mixtures of crystals of forms I and II or forms I and III.

X-ray powder diffraction patterns were obtained with nickel-filtered Cu Kα radiation with an automatic Philips diffractometer. The crystallinity of powder samples in form II was evaluated from the X-ray powder diffraction profiles, whereas the density of the same samples was obtained by flotation in water−ethyl alcohol solutions at 25 °C. Crystallinity of 65% and density of 0.850 g/cm^3 were obtained.

The packing energy was evaluated as half the sum of the interaction energies between the atoms of one monomeric unit and all the surrounding atoms of neighboring macromolecules. The calculations were performed with the same function as used for the calculations of the conformational energy of i-P4MP,[12,19] i.e., with the constants reported by Flory et al.[22] and with the methyl groups taken 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 having radii twice the sum of the van der Waals radii for each pair of atoms.

Calculated structure factors were obtained as $F_c = (\Sigma|F_i|^2M_i)^{1/2}$, where F_i is the structure factor and M_i the multiplicity factor of the reflection *i*, and the summation is taken over all reflections included in the 2θ range of the corresponding diffraction peak observed in the X-ray powder diffraction profile. A thermal factor $B = 8$ Å^2 and atomic scattering factors as in ref 24 were assumed. The observed structure factors, F_o, were evaluated from the intensities of the reflections observed in the X-ray powder diffraction profile, $F_o = (I_o/\mathrm{LP})^{1/2}$, where LP is the Lorentz−polarization factor for X-ray powder diffraction: $\mathrm{LP} = (1 + \cos^2 2\theta)/(\sin^2\theta\cos\theta)$. The experimental intesities I_o were evaluated by measuring the area of the peaks in the X-ray powder diffraction profile, after subtraction of the amorphous halo. The disagreement factor has been calculated as $R' = (\Sigma|F_o - F_c|)/\Sigma F_o$.

Results and Discussion

The X-ray powder diffraction profile of form II of i-P4MP is reported in Figure 1. The Bragg angles, the Bragg distances, and the intensities of the reflections observed in the powder profile are listed in Table 1. As discussed in the Introduction, a tetragonal unit cell with axes $a = 19.16$ Å, $c = 7.12$ Å with chains in 4_1 helical conformation have been proposed for form II by Takayanagi et al.,[9] from X-ray diffraction patterns of single-crystal mats. However, since we have obtained samples in the pure form II and with high crystallinity, the diffraction profile of Figure 1 presents much more reflections than those reported in ref 9. The indices *hkl* and the Bragg distances of the reflections calculated for the proposed tetragonal unit cell are also reporetd in Table 1.

Table 1. Diffraction Angles $2\theta_{obs}$, Bragg Distances d_{obs} and Intensities I_{obs} of the Reflections Observed in the X-ray Powder Diffraction Profile of Form II of i-P4MP of Figure 1[a]

$2\theta_{obs}$ (deg)	d_{obs} (Å)	I_{obs}[b]	$(hkl)_{tetra}$[c]	d_{tetra} (Å)[c]	$(hkl)_{mon}$[d]	d_{mon} (Å)[d]
9.2	9.61	vs	020	9.58	100	9.61
10.3	8.59	vs	210	8.57	020	8.65
10.8	8.19	m	?		$1\bar{2}0$	8.29
13.2	6.71	mw	011, 101	6.67	011	6.59
15.0	5.91	m	021	5.71	$1\bar{1}1$	5.87
16.2	5.47	vs	211	5.48	021, $1\bar{2}1$	5.50
17.3	5.13	s	?		$2\bar{2}0$, 111	5.17
18.4	4.82	m	040	4.79	200	4.80
19.8	4.48	m	330	4.52	031	4.48
20.5	4.33	m	420	4.28	040, 121	4.32
21.2	4.19	m	321	4.26	$2\bar{2}1$	4.19
22.8	3.90	mw	411	3.89	$2\bar{3}1$, $1\bar{4}1$	3.93
24.2	3.68	w	421	3.67	041	3.70
25.7	3.47	w	112	3.44	140, $1\bar{1}2$	3.46
28.8	3.09	vw	032	3.11	141	3.10
30.4	2.94	vvw	322	2.96	$2\bar{1}2$	2.94
32.4	2.76	vvw	541	2.76	042	2.75

[a] The indices *hkl* and the Bragg distances of the reflections calculated for the tetragonal unit cell, $(hkl)_{tetra}$, with axes $a = b = 19.16$ Å and $c = 7.12$ Å, proposed in the literature,[9] and for the monoclinic unit cell $(hkl)_{mon}$ with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$, proposed in this paper, are reported. [b] Key: vs = very strong, s = strong, m = medium, mw = medium weak, w = weak, vw = very weak, and vvw = very very weak. [c] $a = b = 19.16$ Å; $c = 7.12$ Å. [d] $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, $\gamma = 113.7°$.

The hypothesis of the tetragonal unit cell seems in agreement with the simple principle of packing of polymer chains in helical conformations $\mathbf{s}(M/N)$.[25] Chains in 4_1 helical conformation are, indeed, generally packed in tetragonal lattices with high-symmetry space groups $I4_1cd$, for instance, isotactic poly(*o*-methylstyrene)[26] and poly(α-vinylnaphthalene),[27] and $I4_1/a$, for instance, isotactic poly(vinylcyclohexane)[28,29] and almost all polyaldehydes.[30] However, the tetragonal unit cell proposed by Takayanagi et al.[9] does not account for the presence in the powder profile of Figure 1 of the reflections at $2\theta = 10.8$ and 17.3° and, most important, cannot explain the very strong intensities of the two first reflections at $2\theta = 9.2$ and 10.3° (Figure 1 and Table 1). The latter data indicate that, very likely, the values of the *a* and *b* axes of the unit cell are different, and therefore, the symmetry of the lattice is lower than tetragonal.

Other experimental data which suggest a lower symmetry of the crystal lattice of form II come from the solid state ^{13}C NMR spectrum of powder samples in the pure form II reported in ref 14 and shown in Figure 2. In this spectrum, the resonances of the methyl carbon atoms C_5 and C_6 are split into two signals separated by nearly 1 ppm. This splitting can be traced back to packing effects and indicates that methyl carbons of different chains in the unit cell are not equivalent; that

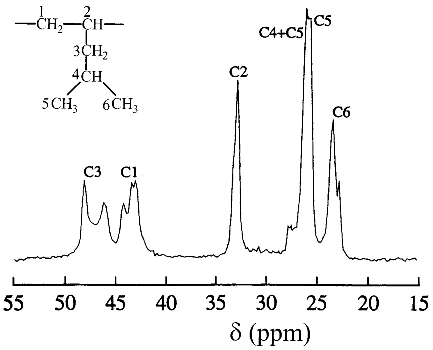

Figure 2. Solid state ^{13}C NMR CPMAS spectrum of form II of i-P4MP. Reprinted from ref 14. Copyright 1997 American Chemical Society. The assignment of the observed resonances to carbon atoms of the monomeric unit is shown.[14]

is, they have different crystallographic environments. This suggests a low symmetry of the lattice.

The solid-state NMR spectrum of Figure 2 also gives strong evidences of the 4_1 helical conformation of the chains in form II.[14] The analysis of the solid-state spectra of four crystalline forms of i-P4MP has, indeed, shown that the resonances of similar nuclei in the different polymorphic forms are different depending on the chain conformation, i.e., on the values of the backbone torsion angles.[14] The resonances observed in the spectra of forms II and III are markedly deshielded compared to forms I and IV. Moreover, the resonances in the spectrum of form I are deshielded compared to those of form IV. This deshielding has been consistently interpreted with the hypothesis that in chains having helical conformation $\mathbf{s}(M/N)$, characterized by succession of nearly gauche and nearly trans torsion angles, $(\mathrm{T'G'})_n$, the amount of the γ-gauche shielding effect depends on the exact value of the gauche and trans torsion angles of the main chain.[14] The resonances of nuclei in form IV are shifted to higher field, indicating a complete γ-gauche shielding effect and, hence, chains in 3_1 helical conformation.[14] Nearly similar values of the resonances of nuclei in forms II and III, shifted at lower field, are instead observed.[14] This indicates that the conformation of the chains in form II is basically the same as in form III,[12,13] that is a 4_1 helical conformation. The γ-gauche shielding effect is reduced due to the deviation of nearly 20° of the values of the backbone torsion angles ($\theta_1 = 83°$ and $\theta_2 = 205°$ in 4_1 helical chains)[12,13] from the exact trans and gauche values, typical of the 3_1 helical conformation.[14]

On the basis of this consideration, a value of the chain axis $c \approx 7$ Å, similar to that found for the chains of form III,[12,13] has been assumed for the 4_1 helical chains of form II. The 4_1 helical conformation assumed for the chains of i-P4MP in form II is shown in Figure 3.

Possible unit cells having symmetry lower than tetragonal have been analyzed. The reflections observed in the X-ray powder diffraction profile of Figure 1 and Table 1 are all accounted for by a monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$. The calculated density for this unit cell containing four chains of i-P4MP in 4_1 helical conformation, is 0.862 g/cm^3, in agreement with the experimental density of 0.850 g/cm^3, measured at 25 °C by flotation for a sample with X-ray crystallinity close to 65% (the density of the amorphous is 0.830 g/cm^3). The indices *hkl* and the Bragg distances of the reflections calculated for this monoclinic unit cell are reported in Table 1. The indexing of the observed reflections indicate the systematic absence of *hk*0 reflections with *k* odd. This suggests that a possible space group, compatible with the presence of four chains in the unit cell, could be $P2_1/b$.

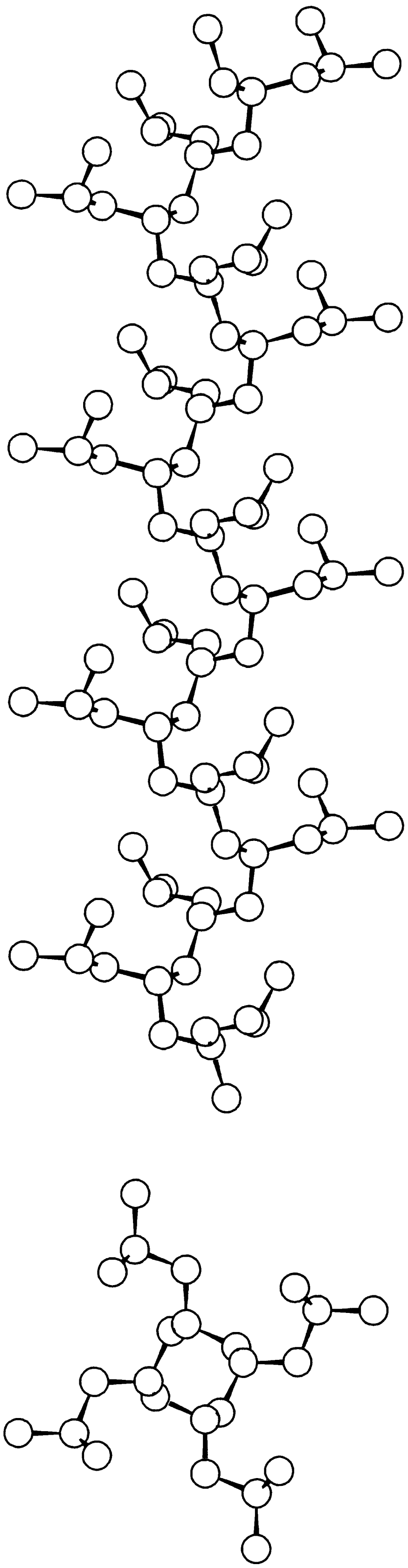

Figure 3. Side view and projection along the chain axis of the 4_1 helical conformation of the chains in form II of i-P4MP.

As a consequence of the choice of this monoclinic space group, the 4_1 helical symmetry of the chains is not

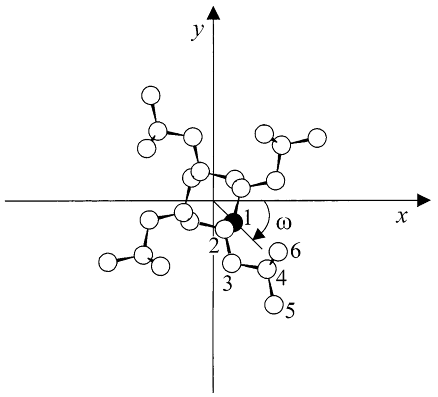

Figure 4. Definitions of the variables ω and z used in the packing energy map. The value of ω is positive for a clockwise rotation, and z is the height of the carbon atom indicated as a filled circle.

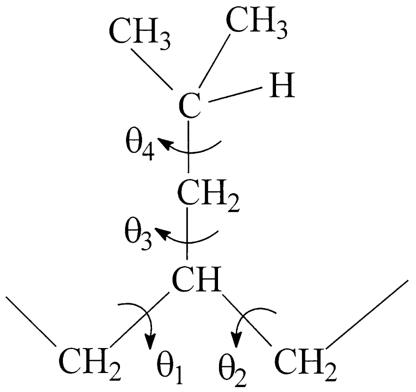

Figure 5. Definition of the torsion angles θ_1 and θ_2 in the main chain of i-P4MP, and torsion angles θ_3 and θ_4, in the lateral group. The torsion angle θ_4 is defined with respect to the hydrogen atom of the methine group in the $CH(CH_3)_2$ lateral group, $\theta_4 = H-C-CH_2-CH$.

maintained in the lattice as crystallographic symmetry. The chains can be positioned in the unit cell with their chain axes coincident with the crystallographic 2_1 axes of the space group $P2_1/b$.

Possible models of packing have been found performing calculations of the packing energy for the space group $P2_1/b$. Since the position of the chain axis inside the unit cell has been fixed at the fractional coordinates $x/a = 0$, $y/b = 0.25$, the lattice energy has been calculated varying only the orientation of the chain around its axis (defined by the angle ω, shown in Figure 4), and the z coordinate, which defines the relative heights of the chains in the unit cell. The axes of the unit cell have been maintained constant at the experimental values $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$.

The 4_1 helical conformation of the chains, shown in Figure 3, is also constant in these calculations and assumed the same as found in the resolution of the crystal structure of form III.[12,13] According to the definition of the torsion angles shown in Figure 5, the values of the torsion angles of the main chain are $\theta_1 = 83°$ and $\theta_2 = -154°$, whereas the torsion angles which define the conformation of the lateral groups are $\theta_3 = 77°$ and $\theta_4 = -50°$ (the latter is defined with respect to the hydrogen atom of the methine group in the side group $CH(CH_3)_2$, see Figure 5). The torsion angles relative to the two methyl carbon atoms C_5 and C_6 are $\theta_4(C_5) = -168°$ and $\theta_4(C_6) = 68°$. Bond angles $C-CH_2-C = 113°$ and $C-CH-C = 111°$ are assumed, either in the backbone or in the lateral groups.

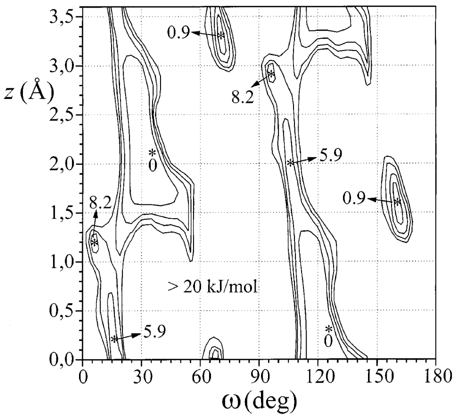

Figure 6. Map of the packing energy as a function of ω and z for the monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$, and space group $P2_1/b$. The chains in constant 4_1 helical conformation have their chain axes coincident with the crystallographic 2_1 helical axes of the unit cell in the space group $P2_1/b$. The curves are drawn at intervals of 5 kJ/(mol of monomeric unit) with respect to the absolute minimum of the map assumed as zero. The energy of the relative minima are also shown.

A map of the lattice energy as a function of ω and z for the space group $P2_1/b$ is reported in Figure 6. The map is periodic over $\omega = 180°$ and $z = c/2 = 3.56$ Å; therefore, only the regions with $\omega = 0-180°$ and $z = 0-3.56$ Å are shown. The map presents four energy minima, which are periodically repeated after a rotation of $\omega = t = 90°$, where t is the unit twist of the 4_1 helix, $t = 2\pi/4$, and a translation of $z = h = c/4 = 1.78$ Å, where h is the unit height of the helix. The absolute minimum is at $\omega = 32°$ and $z = 2.3$ Å.

Calculations of structure factors have been performed for models of packing corresponding to the energy minima in the map of Figure 6. Moreover, since the region of the absolute minimum is rather broad and flat, structure factors calculations have been performed also for different models obtained varying ω and z around the absolute minimum, in the range $\omega = 20-50°$ and $z = 1.5-3.5$ Å.

A good agreement between calculated structure factors and experimental intensities observed in the X-ray powder profile of Figure 1, has been obtained for the model of packing corresponding to $\omega = 24°$ and $z = 2.25$ Å, reported in Figure 7. A comparison between calculated (F_c) and observed structure factors (F_o) is reported in Table 2. Even though the intensities of most of the observed reflections are well accounted for by the model of Figure 7, the agreement is not acceptable mainly because the intensities of the 031 and $\bar{2}21$ reflections at $2\theta = 19.8$ and 21.2°, respectively, are calculated much higher than the experimental ones. This disagreement is always present for any model corresponding to values of ω and z in the region of the energy minimum.

We have analyzed the possibility that this discrepancy might be related to the presence of structural disorder in crystals, which produce a reduction of the intensities of the first layer lines reflections and, in particular, of the 031 and $\bar{2}21$ reflections. A possible kind of disorder could be the statistical substitution of isomorphous anticlined (up and down) chains in each site of the lattice. This type of structural disorder is typical of isotactic chains in helical conformation, and has been found in the crystal structures of many isotactic poly-

Table 2. Comparison between Observed Structure Factors $F_o = (I/LP)^{1/2}$, Evaluated from the Intensities I Observed in the X-ray Powder Diffraction Profile of Form II of Figure 1, and Calculated Structure Factors, $F_c = (\Sigma|F_i|^2M_i)^{1/2}$, for the Ordered and Disordered Models of Packing of Figures 7 and 8, Respectively, for the Space Group $P2_1/b$[a]

hkl	$2\theta_{obs}$ (deg)	$2\theta_c$ (deg)	$F_o = (I/LP)^{1/2}$	$F_c = (\Sigma\|F_i\|^2M_i)^{1/2}$ (Figure 7)		$F_c = (\Sigma\|F_i\|^2M_i)^{1/2}$ up/down (Figure 8)	
100	9.2	9.21	76		80		75
020	10.3	10.23	103	109	114	99	110
$1\bar{2}0$		10.66		34		48	
011	13.2	13.43	52		50		55
$1\bar{1}1$	15.0	15.09	70	79	97	66	68
101		15.48		56		19	
021	16.2	16.11	163	97	158	84	159
120		16.32		15		21	
$1\bar{2}1$		16.39		124		134	
$2\bar{2}0$	17.3	17.14	149	104	153	96	157
111		17.44		112		124	
200	18.4	18.47	74	29	47	51	73
$1\bar{4}0$		18.82		37		52	
$1\bar{3}1$	19.8	19.05	105	70	180	17	103
031		19.80		166		102	
040	20.5	20.54	119	81	87	50	118
121		20.55		33		107	
$2\bar{1}1$	21.2	21.15	110	73	144	43	78
$2\bar{2}1$		21.22		116		64	
$2\bar{4}0$		21.42		44		12	
201	22.8	22.32	100	127	133	33	97
$2\bar{3}1$		22.51		19		88	
$1\bar{4}1$		22.61		36		25	
041	24.2	24.07	90	60	63	26	50
131		24.39		11		25	
211		24.55		–		12	
220		24.55		15		9	
$2\bar{4}1$		24.83		6		31	
$3\bar{2}0$	25.7	25.49	130	24	168	10	149
012		25.51		55		57	
140		25.77		34		44	
$1\bar{1}2$		26.44		105		108	
102		26.67		41		39	
$1\bar{5}1$		26.73		42		21	
022		27.05		15		14	
$3\bar{4}0$		27.19		26		33	
$1\bar{2}2$		27.23		38		38	
221		27.60		82		28	
300	28.8	27.86	70	16	161	1	79
112		27.89		52		27	
$2\bar{5}1$		27.96		79		32	
$3\bar{2}1$		28.44		83		28	
$1\bar{6}0$		28.52		28		7	
051		28.68		83		31	
141		28.79		2		36	
$3\bar{3}1$		28.76		12		5	
$1\bar{3}2$		28.94		27		4	
$2\bar{6}0$		29.02		3		6	
$3\bar{1}1$		29.08		30		5	
032		29.46		24		36	
122	30.4	29.98	58	43	74	31	74
$3\bar{4}1$		29.99		5		13	
$2\bar{1}2$		30.41		31		12	
$2\bar{2}2$		30.45		20		2	
301		30.61		18		34	
060		31.02		4		3	
$1\bar{6}1$		31.21		14		6	
202		31.25		33		33	
231		31.26		26		9	
$3\bar{5}1$	32.4	32.05	45	53	74	5	39
$3\bar{6}0$		32.38		36		1	
042		32.55		5		21	
132		32.80		5		1	
212		32.92		5		20	
311		32.92		18		18	
240		32.98		21		3	
$2\bar{4}2$		33.13		27		17	

[a] The Bragg angles (Cu Kα) calculated for to the monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$ ($2\theta_c$) and observed ($2\theta_{obs}$) in the X-ray powder diffraction profile of form II of Figure 1 are also shown.

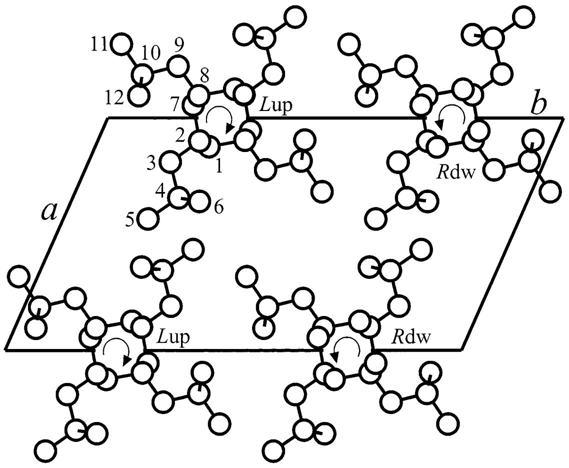

Figure 7. Limit ordered model of packing of form II of i-P4MP in the monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$, for the space group $P2_1/b$. *L*up = left-handed up helix; *R*dw = right-handed down helix.

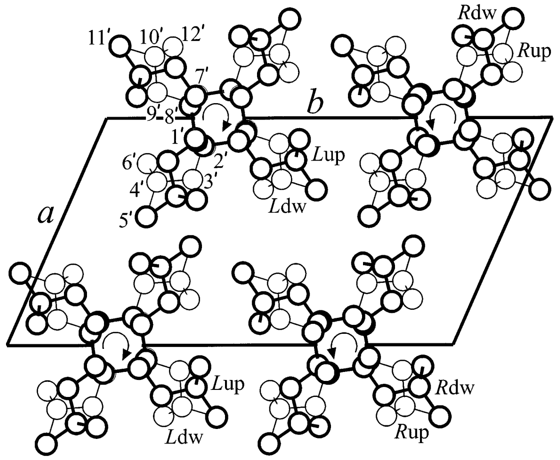

Figure 8. Limit disordered model of packing of form II of i-P4MP in the monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$, for the space group $P2_1/b$, containing statistical disorder in the positioning of up and down chains. In each site of the lattice up and down isomorphous chains are present with the same probability. *L*up = left-handed up helix (thick lines); *L*dw = left-handed down helix (thin lines); *R*up = right-handed up helix (thin lines); *R*dw = right-handed down helix (thick lines).

mers, such as polypropylene,[31,32] polybutene,[33] polystyrene,[34] and even forms I and III of i-P4MP.[3,4,13] The model of packing of form II of Figure 7, containing statistical up−down disorder is reported in Figure 8; in each site of the lattice up and down 4_1 helical chains, having the same chirality, are present with the same probability.

The calculated structure factors for the disordered model of Figure 8 are reported in Table 2. A comparison between the experimental X-ray diffraction profile of Figure 1, after the subtraction of the amorphous halo, and the calculated profiles for the models of Figures 7 and 8, is reported in Figure 9. It is apparent that the presence of up−down disorder reduce the intensities of the 031 and $2\bar{2}1$ reflections, and a fairly good agreement is obtained for the model of Figure 8 (Table 1 and Figure 9C). A disagreement factor $R' = 10\%$ for all the observed reflections has been obtained. The fractional coordinates of the carbon atoms of the asymmetric units (two monomeric units) for the models of Figures 7 and 8 are reported in Table 3. In the models of Figures 7 and 8,

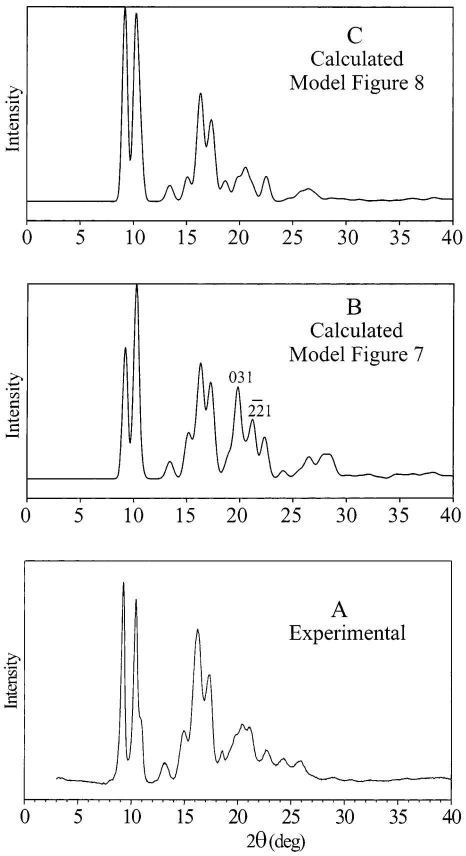

Figure 9. Comparison between experimental X-ray powder diffraction profile of Figure 1, after the subtraction of the amorphous halo (A), and calculated diffraction profiles for the ordered model of packing of Figure 7 (B) and the statistical disordered model of packing of Figure 8 (C).

Table 3. Fractional Coordinates of the Carbon Atoms of the Asymmetric Unit (Two Monomeric Units) for the Models of Figures 7 and 8 of the Structure of Form II of i-P4MP in the Space Group $P2_1/b$[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	occupancy factor
C_1	0.124	0.250	0.316	0.5
C_2	0.100	0.223	0.522	0.5
C_3	0.190	0.179	0.576	0.5
C_4	0.343	0.232	0.612	0.5
C_5	0.434	0.186	0.624	0.5
C_6	0.359	0.281	0.789	0.5
C_7	−0.055	0.175	0.560	0.5
C_8	−0.096	0.178	0.767	0.5
C_9	−0.223	0.104	0.821	0.5
C_{10}	−0.185	0.034	0.856	0.5
C_{11}	−0.317	−0.041	0.869	0.5
C_{12}	−0.095	0.046	0.034	0.5
C_1'	0.090	0.219	0.932	0.5
C_2'	0.122	0.244	0.726	0.5
C_3'	0.270	0.253	0.672	0.5
C_4'	0.281	0.175	0.636	0.5
C_5'	0.434	0.186	0.624	0.5
C_6'	0.200	0.135	0.458	0.5
C_7'	−0.101	0.181	0.177	0.5
C_8'	−0.066	0.173	0.971	0.5
C_9'	−0.113	0.088	0.916	0.5
C_{10}'	−0.271	0.047	0.881	0.5
C_{11}'	−0.317	−0.041	0.869	0.5
C_{12}'	−0.313	0.078	0.703	0.5

[a] Atoms C_1−C_{12}: chain up (Figure 7). Atoms C_1'−C_{12}': chain down (Figure 8).

the values of the most relevant distances between nonbonded atoms are all within the limits allowed by the sum of the van der Waals radii.

The presence of disorder in the positioning of up and down chains is reasonable because, as already shown for form III of i-P4MP,[13] up and down 4_1 isomorphous helical chains may substitute each other in the lattice sites without affecting the steric interactions with neighboring chains. One of the two lateral methyl groups in up and down chains are, indeed, basically in the same position (Figure 8). It has been clearly demonstrated that for other isotactic polymers, as for instance in polypropylene, the amount of up−down disorder present in the structure depends on the thermal and mechanical histories of the sample.[35−37] In the case of form II of i-P4MP this dependence cannot be investigated because thermal treatments and stretching induce transition into the more stable form I. However, also for form II of i-P4MP the proposed models for the crystal structure of Figures 7 and 8, in the space group $P2_1/b$, should be considered as limit ordered (Figure 7) and limit disordered (Figure 8) models, characterized by ideal order and statistical disorder, respectively.[15] The real crystalline modifications are probably intermediate between the ideal models, characterized by variable degrees of up−down disorder depending on the crystallization conditions.

The concept of disordered modifications intermediate between limit ordered and limit disordered models has been used to describe not only the up−down disorder but also other types of structural disorder,[15] as for instance disorder in the orientation of chains around the chain axis in poly(vinilidene fluoride),[38] or disorder in the positioning of right- and left-handed helical chains in syndiotactic polypropylene.[39]

The proposed model for the crystal structure of form II of i-P4MP accounts for the solid state ^{13}C NMR CPMAS spectrum of form II reported in Figure 2. The assignment of the observed resonances to carbon atoms of the monomeric unit (Figure 2) has been shown in ref 14. The presence of two distinct resonances of the methyl carbons C_5 and C_6 indicates that the two methyl carbon atoms belonging to the monomeric unit, are not equivalent. As shown in ref 14 this can be explained on the basis of the proposed conformation of the polymer chains. From Figures 3 and 4, it can be easily realized that the methyl carbons C_5 and C_6 have the same methine carbon C_2 in the γ-position, but C_2 is in nearly gauche arrangement with respect to the methyl C_6 (the value of the torsion angles $\theta_4(C_6)$ is 68°) and in nearly trans arrangement to the methyl C_5 (the value of the torsion angles $\theta_4(C_5)$ is −168°). The methyl carbon C_6 is therefore shielded by one γ-gauche effect and its resonance occurs at 4−5 ppm upfield from that of C_5 (Figure 2).[14]

Moreover, both resonances of the methyl carbon atoms C_5 and C_6 show narrow splittings (1−2 ppm), which should be traced back to packing effects. Doublets at $\delta = 26.24$ and 25.71 ppm for the resonance of C_5, and at $\delta = 23.44$ and 22.73 ppm for the resonance of C_6, are indeed observed in the spectrum of Figure 2.[14] As already shown for forms I and III of i-P4MP,[14] this splitting provides a chance of testing the packing model of low symmetry proposed for form II. We observe that since the 4_1 helical symmetry of the chains is lost in the lattice, two successive monomeric units, which constitute the asymmetric unit in the space group $P2_1/b$, are not crystallographically equivalent. It is apparent from the packing model of Figure 7 that, because of the monoclinic symmetry of the lattice, the methyl carbons

C_5 and C_6 of different monomeric units, and/or of different chains in the unit cell, present different chemical environments since the contact distances with the neighboring atoms are different. At least two nonequivalent kinds of methyl carbons C_5, and two nonequivalent kinds of methyl carbons C_6 are included in the unit cell, according to the splitting of the resonances of the methyl carbon atoms observed in the spectrum of Figure 2.

It is apparent from the solid-state NMR spectrum of Figure 2 that the resonances of the methylene carbon atoms C_1 and C_3 also show narrow splittings, which could be due to slight distortions from the regular 4_1 helical conformation of the chains. Since the 4_1 symmetry is lost in the lattice and, as discussed above, two successive monomeric units are not crystallographically equivalent, it is probably true, in principle, that successive monomeric units along the helical chains are not related by the exact uniform 4_1 symmetry. Distortions from uniform M/N symmetries have been observed in various structures of polymers; we recall, for instance, that, in the case of form I of i-P4MP[4] and in poly(ethylene oxide),[40] chain conformations distorted from the uniform 7_2 helical symmetry have been found.

It is worth noting that, as discussed above, the proposed model for the crystal structure of form II of i-P4MP (Figures 7 and 8) has a symmetry lower than that expected for the structure of polymer chains in 4_1 helical conformation.[25] In fact polymer crystals are generally built up according to the energy principle of close-packing[25,41] and the entropic principle, which states that *a molecule in a crystal tends to maintain its symmetry elements, provided that this does not cause a serious loss of density*.[41] In a more symmetric position, a molecule has a greater feedom of vibration, that is, the structure corresponds to a wider energy minimum.[41] On the basis of these principles the mode of packing of polymers basically depends on the outside envelope of the chains.[25] Depending on the conformation, the form of a polymer chain may be approximated by a cylinder of radius r, corresponding to the outside envelope of the atoms of the main chain, bearing a periodic helical relief of radius R, corresponding to the atoms of the lateral groups.[25] When the ratio r/R is different from 1 the form of the chain may be approximated by a cylinder in which hollows and bulges are periodically repeated, that is, the chains have an outside envelope similar to a screw.[25] Values of the ratio r/R in the range $0.3-0.8$ are obtained in the cases of many vinyl polymers with chains in 4/1 helical conformation or in complex helical conformation $\mathbf{s}(M/N)$ with a fractional ratio M/N. A good mode of packing for these kinds of helices is generally obtained in a teragonal packing of enantiomorphous chains, with coordination number equal to 4.[25] Each right-handed chain is surrouded by four left-handed chains and vice versa, and a tight fitting of threads into grooves is achieved.[25] In the case of chains in 4/1 helical conformation, the local 4/1 symmetry of the chains is generally maintained in the lattice, as crystallographic symmetry. Various isotactic polymers, having chains in 4-fold helical conformation or in complex helical $\mathbf{s}(M/N)$ conformation, with M and N not corresponding to very small integers, or with fractional ratio M/N, crystallizes in tetragonal lattices. Typical examples are given by forms I and III of i-P4MP (7_2 helices and space groups $P\bar{4}$ or $P\bar{4}b2$ for the form I,[1-4] 4_1 helices and space group $I4_1$ for the form III),[12,13] form II of isotactic poly(1-butene)[42,43] and isotactic poly(m-methylstyrene)[44] (11_3 helices and space group $P\bar{4}$),[42-44] isotactic poly[(R),(S)-4-methyl-1-hexene) (7_2 helices and space group $P\bar{4}$),[3] form I of isotactic poly(vinylcyclohexane)[28,29] and polyaldehydes[30] (4_1 helices and space group $I4_1/a$),[28-30] isotactic poly(o-methylstyrene),[26] and poly(α-vinylnaphthalene)[27] (4_1 helices and space group $I4_1cd$).[26,27] Among syndiotactic polymers, only one example has been found so far, that is syndiotactic poly(4-methyl-1-pentene), characterized by $\mathbf{s}(12/7)2$ helical chains packed in a tetragonal lattice with space group $P\bar{4}$.[45]

Exceptions to this simple rule and examples of "*symmetry breaking*",[15] have been found for form III of isotactic poly(1-butene), characterized by 4_1 helical chains packed in an orthorhombic lattice with space group $P2_12_12_1$,[46] for isotactic poly(3-methyl-1-butene), characterized by 4_1 helical chains packed in a monoclinic lattice with space group $P2_1/b$,[47] and form II of syndiotactic poly(1-butene) with $\mathbf{s}(5/3)2$ helical chains packed in a monoclinic lattice with space group $P2_1/a$.[48] According to the analysis reported in this paper, the crystal structure of form II of i-P4MP provides another example of *symmetry breaking*.[15] Chains in 4_1 helical conformation are not packed in a tetragonal lattice, and the local symmetry of the chains is lost in the lattice. The chains are packed in a monoclinic symmetry and the structure is very similar to that of isotactic poly(3-methyl-1-butene).[47]

Conclusions

Samples of i-P4MP in the pure form II have been obtained by crystallization from tetramethyltin solutions. Oriented fibers cannot be obtained because form II transforms into the more stable form I by stretching. Despite the few diffraction data available, the crystal structure of form II has been determined by using the X-ray powder diffraction profile and packing energy calculations.

Chains in 4_1 helical conformation are packed in a monoclinic unit cell with axes $a = 10.49$ Å, $b = 18.89$ Å, $c = 7.13$ Å, and $\gamma = 113.7°$, according to the space group $P2_1/b$.

This structure provides another example of "*symmetry breaking*", recently described for various isotactic and syndiotactic polymers.[15] Although chains in 4_1 helical conformation are generally packed in tetragonal lattices, in the structure of form II of i-P4MP the local 4_1 helical symmetry of the chains is not maintained in the lattice as crystallographic symmetry. The 4_1 symmetry is lost and the tetragonal symmetry is broken. The chains are, indeed, packed in a monoclinic lattice having lower symmetry. Structural disorder is present in the structure, characterized by the statistical substitution of up and down chains in each site of the lattice.

The proposed model of packing of form II with low monoclinic symmetry, accounts for the narrow splittings of the resonances of the methyl carbons observed in the solid state ^{13}C NMR CPMAS spectrum of form II. Because of the low symmetry of the lattice, the methyl carbon atoms of two successive monomeric units, related by the local 4/1 helical symmetry of the chains, are not crystallographically equivalent. They present different chemical environments inside the unit cell since the contact distances with the neighboring atoms are different, producing two distinct resonances in the NMR spectrum.

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