Crystal Structure of Form III and the Polymorphism of Isotactic Poly(4-methylpentene-1)

Claudio De Rosa,* Anna Borriello, Vincenzo Venditto, and Paolo Corradini

Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Napoli, Italy

Received December 15, 1993; Revised Manuscript Received March 16, 1994®

ABSTRACT: A preliminary model for the crystal structure of form III of isotactic poly(4-methylpentene-1) is suggested on the basis of structure factor calculations. Chains in 4_1 helical conformations are packed in a tetragonal unit cell with axes a = 19.38 Å and c = 6.98 Å; the space group is $I4_1$. The polymorphic behavior of poly(4-methylpentene-1) is discussed on the basis of conformational energy calculations on the isolated chain. The presence of different modifications is in accordance with energy minima present in the conformational energy map.

Introduction

The polymorphic behavior of isotactic poly(4-methylpentene-1) (P4MP) has been well-known for many years. Five different crystalline forms have been described. Form I is the ordinary crystalline form which occurs in melt crystallized samples and in extruded fibers; it is characterized by chains in the 7/2 helical conformation packed in a tetragonal unit cell with axes a = 18.66 Å and c = 13.80 Å.[1-4]

The different modifications can be obtained from crystallization in semidilute solutions depending on the solvent and the thermal history of the solutions.[5,6]

In high-boiling solvents, like normal alkanes with the number of carbon atoms greater than 9, a branched dodecane and branched decane, P4MP crystallizes into the ordinary form I, as found by Charlet and Delmas.[6]

Crystals of modification II were prepared for the first time by isothermal crystallization at 20 °C from dilute xylene solutions[7-9] and, recently, as a minor component in a mixed structure crystallized in carbon disulfide solutions.[6]

For the modification II, Takayanagi et al.[9] proposed, from X-ray diffraction spectra on single crystal mats, a tetragonal unit cell with axes a = 19.16 Å and c = 7.12 Å with chains in the 4/1 helical conformation.

In lower 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, modification III is recovered.[5,6] This form was already obtained from dilute solutions in xylene (by isothermal crystallization at 65 °C)[7-9] and in decalin.[10,11] Charlet et al.[5] have proposed, from electron diffraction of single crystals of form III, a tetragonal unit cell with axes a = 19.38 Å and c = 6.98 Å with chains in the 4/1 helical conformation, according to the unit cell previously proposed by Takayanagi et al.[8,9] Modification III transforms into modification I after annealing at ≈100 °C and under stretching.[5]

Modification IV was obtained, in both the unoriented and uniaxially oriented state, by annealing modification I above 200 °C under pressure (4500 atm).[12]

The same crystalline modification has been obtained also from cyclopentane solutions.[13] Stretching of an unoriented sample in form IV leads to a fiber in form I;[13] however, a partially oriented sample in form IV was obtained by swelling a fiber of form I in saturated cyclopentane vapor at 50 °C.[13] Charlet and Delmas[13] have proposed for form IV a hexagonal unit cell with axes a = 22.17 Å and c = 6.69 Å. Form IV transforms into form I by annealing at 130 °C.

Modification V has been obtained from concentrated cyclohexane gels[14] 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 has a complete crystal structure been reported.[2-4] Only unit cell parameters have been proposed for the tetragonal forms II and III[5,8,9] and for the hexagonal form IV.[13]

In this paper the polymorphic behavior of P4MP is discussed on the basis of conformational energy calculations on an isolated chain. Moreover a preliminary model for the crystal structure of form III of P4MP is suggested on the basis of structure factor calculations.

Experimental Part

P4MP was prepared with Ziegler-Natta type catalysts.

The most stereoregular fraction of the polymer (≈85% extracted in boiling n-heptane) presents an inherent viscosity, measured in decalin at 135 °C, of 1.35 dL/g, corresponding to a molecular weight of 5×10^4.

Modification III of P4MP was prepared from crystallization in n-heptane solutions following the method described in ref 6. The solutions (polymer volume fraction $\phi = 0.05$) were prepared in sealed glass tubes. Dissolution was achieved by heating the sealed tube at 135 °C for 20 h. The solution was then cooled rapidly to room temperature, and the polymer was recovered by evaporation of the solvent.

X-ray powder diffraction spectra were obtained with nickel filtered Cu Kα radiation with an automatic Philips diffractometer.

Observed structure factors (F_0) have been obtained as the square root of the experimental intensities corrected by $Lp = (1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$, $F_0 = (I/Lp)^{1/2}$. The experimental intesities have been evaluated by measuring the area of the peaks in the X-ray powder diffraction pattern, after subtraction of the amorphous halo.

Calculated structure factors (F_c) have been obtained as $F_c = (\sum |F_i|^2 M_i)^{1/2}$ where M_i is the multiplicity factor and the summation is taken over all the reflections included in the 2θ range of the corresponding reflection peak observed in the Geiger spectrum. Only the values greater than the observable limit are reported. A thermal factor B = 8 Å^2 and the atomic scattering factors as in ref 15 were assumed. For comparison with electron diffraction intensities, the calculations of structure factors have been performed with the atomic scattering factors for electrons calculated according to formula 16c of ref 16.

The conformational energy maps have been calculated with the method already described for other isotactic polymers.[17,18] The energy has been calculated as the sum of the terms

$$E = E_t + E_b + E_{nb}$$

where E_t is the sum of energy contributions associated with torsion

* Abstract published in *Advance ACS Abstracts*, May 15, 1994.

0024-9297/94/2227-3864$04.50/0

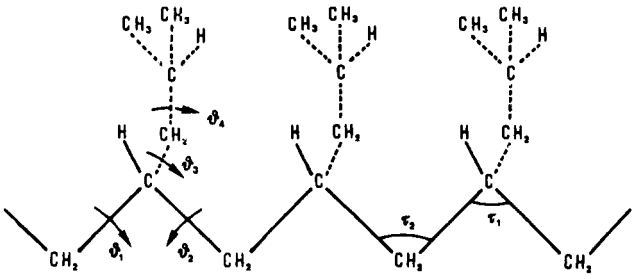

Figure 1. Portion of the chain of P4MP used in the conformational energy calculations. The definition of the torsion angles θ_1, θ_2, θ_3, and θ_4 and the bond angles τ_1 and τ_2 is also shown.

Table 1. Bond Lengths and Bond Angles Used in the Conformational Energy Maps of P4MP

	Bond Lengths (Å)		
C–C	1.53	C–H	1.10
	Bond Angles[a] (deg)		
C″–C′–C″	111.0	C′–C″–H	108.9
C′–C″–C′	113.0	H–C″–H	108.0
C″–C′–H	107.9		

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

angles around single bonds (θ), which are assumed to be of the kind

$$E'_t = (K_t/2)(1 + \cos 3\theta)$$

E_b is the sum of energy contributions due to bond angle deformations (τ), which are assumed to be of the kind

$$E'_b = (K_b/2)(\tau - \tau_0)^2$$

E_{nb} is the sum of energy contributions due to the nonbonded interactions between atoms separated by more than two bonds, which are assumed to be of the kind

$$E'_{nb} = Ar^{-12} - Br^{-6}$$

The calculations of the conformational energy have been performed on the portion of the isolated chain of P4MP shown in Figure 1. The nonbonded energy has been calculated by taking into account the interactions between the atoms of the first monomeric unit and the interactions between these atoms and the remaining atoms within spheres having radii twice the van der Waals distances for each pair of atoms. The potential energy constants are those reported by Flory,[19] treating the methyl groups as spherical domains.[20]

Results and Discussion

Conformational Energy Calculations. Conformational energy calculations have been performed by application of the equivalence principle[21] to successive constitutional units by assuming a line repetition group s(M/N) for the polymer chain. As a consequence the sequence of the torstion angles in the main chain is of the kind ...$\theta_1\theta_2\theta_1\theta_2$... (Figure 1). Torsion angles θ_4 are defined with respect to the hydrogen atoms of the CH(CH_3) groups.

The geometrical parameters assumed in the present calculations are reported in Table 1.

A conformational energy map for P4MP, as a function of θ_1 and θ_2, scanned every 10° in θ_3 and θ_4 (minimum energy values reported), is shown in Figure 2a. A detail of this map (with θ_3 and θ_4 scanned every 2.5°) is reported in Figure 2b. Two minima are present in the region $\theta_1 \approx G^+$, $\theta_2 \approx T$.

In the map of Figure 2b are also reported the loci of points corresponding to the s(7/2), s(4/1), and s(3/1) helical symmetries, with values of the unit twist $t = 2\pi N/M$ of

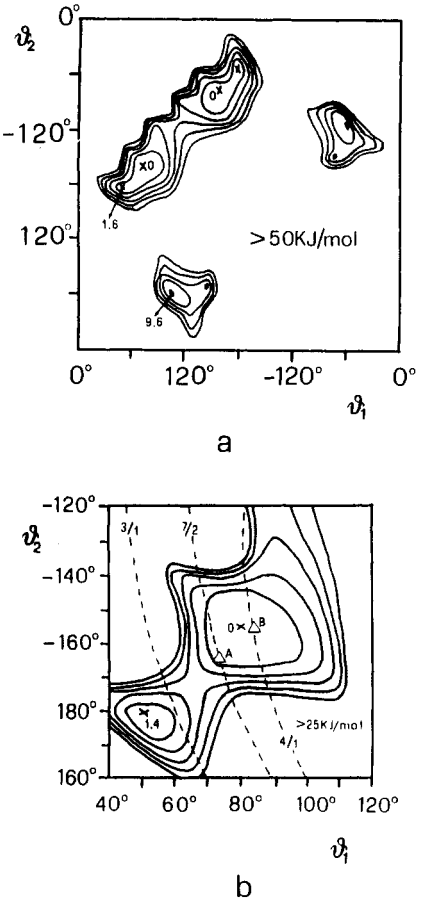

Figure 2. (a) Map of the conformation of energy as a function of θ_1 and θ_2 with θ_3 and θ_4 scanned every 10° in the s(M/N) line repetition group for $\tau_1 = 111°$ and $\tau_2 = 113°$. The curves are reported at intervals of 10 kJ/mol of monomeric units with respect to the absolute minimum of the map assumed as zero. The values of the energies corresponding to the minima (x) are also reported. (b) Detail of the energy map (a) with θ_3 and θ_4 scanned every 2.5°. The curves are reported at intervals of 5 kJ/mol of monomeric units. The dashed curves correspond to the loci of points for which the helical symmetries are s(7/2), s(4/1), and s(3/1). The triangles indicate the experimental conformations 7_2(A) and 4_1-(B), observed in forms I and III of P4MP, respectively.

102.8, 90, and 120°, respectively, and the pairs of torsion angles corresponding to the experimental conformations observed in form I (point A, observed unit height $h = c/7 = 1.97$ Å) and in forms II and III of P4MP (point B, observed unit height $h = c/4 = 1.74$ Å).

It is apparent that the conformations with symmetries 7/2 and 4/1 are very close to the absolute minimum of the map. They correspond to isodistortions for θ_1 and θ_2 from the precise *gauche* and *trans* values, due to the bulkiness of the lateral groups, already observed in various isotactic polymers.[22] A greater distortion of the torsion angles of the main chain is present in the helix 4/1, as revealed by the lower values of the unit height (1.97 Å for the 7/2 helix, 1.74 Å for the 4/1 helix).

It is worth noting that the relative minimum present in the map of Figure 2b is close to the dashed line corresponding to conformations with s(3/1) symmetry. This symmetry could characterize the conformation of the chains of the hexagonal modification IV.[13] Moreover, we observe that for chain conformations near the 3_1 helical symmetry, the bond angles which minimize the conformational energy are probably greater than $\tau_1 = 111°$, and $\tau_2 = 113°$, used in the calculation of the map of Figure 2b: e.g. for isotactic polypropylene we have $\tau_1 = 112°$ and 116°.[23]

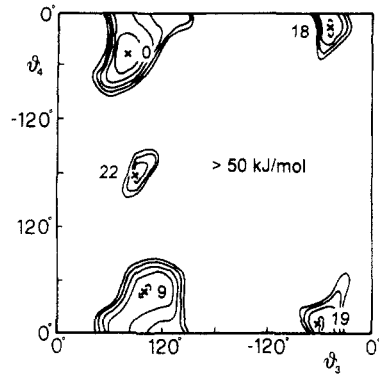

Figure 3. Map of the conformational energy of P4MP as a function of θ_3 and θ_4 for the fixed values $\theta_1 = 83°$ and $\theta_2 = 206°$. The curves are reported at intervals of 10 kJ/mol of monomeric unit with respect to the absolute minimum of the map assumed as zero. The value of the energies corresponding to the minima (x) are also reported.

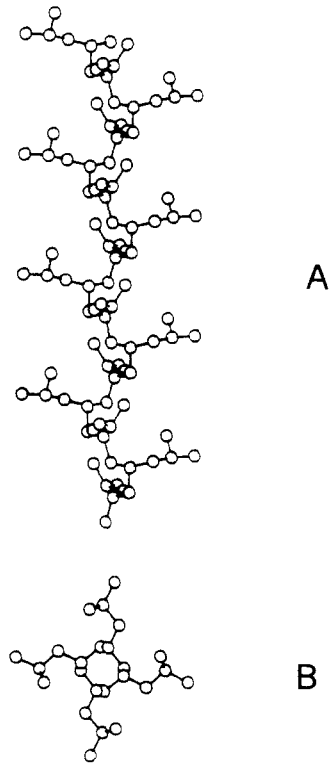

Figure 4. Side view (A) and a projection along the chain axis (B) of the model suggested for the chain conformation (4/1 helix) of form III of P4MP.

According to this geometrical and energy analysis, a model of the chain of form III of P4MP is built with the values of the dihedral angles along the main chain $\theta_1 = 83°$ and $\theta_2 = 206°$ (point B of Figure 2b). The conformational energy map of P4MP as a function of θ_3 and θ_4 for these fixed values of θ_1 and θ_2 is reported in Figure 3. It is apparent that only the conformation of the lateral groups near $\theta_3 \approx 77°$ and $\theta_4 = -50°$ corresponds to a deep energy minimum.

The projection along the chain axis and a side view of the present model for the chain conformation of form III of P4MP are reported in Figure 4.

Crystal Structure of Form III. The X-ray powder diffraction spectrum of form III of P4MP is reported in Figure 5. The reflections observed in the Geiger spectrum are listed in Table 2. All the reflections are accounted for by the tetragonal unit cell with axes a = 19.38 Å and c = 6.98 Å proposed by Charlet et al.[5]

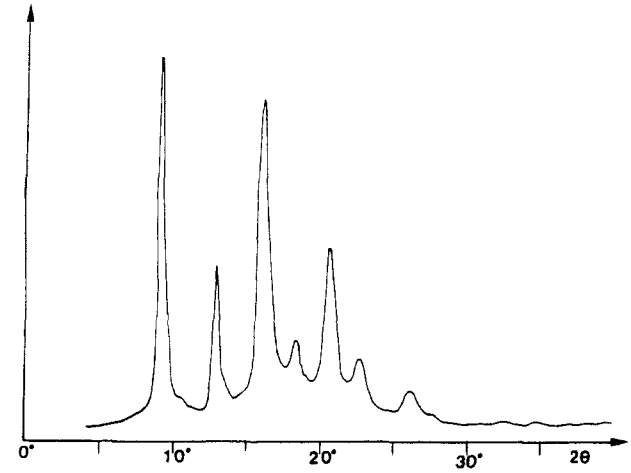

Figure 5. X-ray powder diffraction spectrum of form III of P4MP.

Table 2. Diffraction Angles 2θ and Bragg Distances d of the Reflections Observed in the X-ray Powder Diffraction Spectra of Form III of P4MP[a]

hkl	2θ (deg)	d (Å)	d_{calc} (Å)
200	9.2	9.61	9.69
220	12.9	6.86	6.85
211	16.3	5.43	5.44
400	18.3	4.85	4.84
420	20.6	4.31	4.33
321			4.26
411	22.7	3.92	3.90
431	26.2	3.40	3.39
501			3.39
600	27.6	3.23	3.23
521			3.20
541	32.6	2.74	2.78
710			2.74
422			2.72
512	34.9	2.57	2.57
701			2.57

[a] The indices hkl are given for the tetragonal unit cell with axes a = 19.38 Å and c = 6.98 Å.

From the data of Table 2 we observe the absence of the reflections hkl with $h + k + l = 2n + 1$. This suggests a body centered tetragonal (I) space group.

General considerations about the close packing of helices lead to the same conclusion. In fact from Figure 4 it is apparent that the chain of form III has an outside envelope similar to that of a cylinder in which hollows and bulges are periodically repeated as it occurs in a screw. A good mode of packing for these kinds of helices is obtained in a tetragonal lattice, with a coordination number equal to 4^{21} and every right handed helix surrounded by four left handed helices and vice versa.

If the conformation of the chains has a s(4/1) symmetry (as in form III of P4MP), the axis 4_1 may be the crystallographic element of symmetry; so, the space group of higher symmetry is $I4_1/a$ if the enantiomorphous chains are anticlined; it is $I4_1cd$ if the enantiomorphous chains are isoclined.

Examples of isotactic polymers, characterized by chains with the 4_1 helical conformation, packed in these space groups are poly(vinylcyclohexane)[24] (space group $I4_1/a$) and poly(*o*-methylstyrene)[25] (space group $I4_1cd$).

Other information about the possible space group for form III of P4MP can be taken from data of electron diffraction on single crystals of form III reported in the literature by Charlet et al.[5] and by Pradere et al.[26] With these data Charlet et al.[5] proposed the tetragonal unit cell with axes a = 19.38 Å and c = 6.98 Å. Moreover we observe,

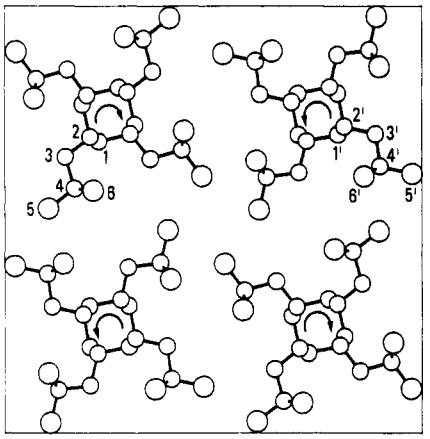

Figure 6. Possible model of packing for form III of P4MP for the space group $I4_1$.

besides the systematic absence of the hkl reflections with $h + k + l = 2n + 1$, the presence of $hk0$ reflections with $h = 2n + 1$ and $k = 2n + 1$ (like the 710 and 730 reflections).[5,26] This allows us to discard the space group $I4_1/a$. Moreover Pradere et al.[26] observed in their electron diffraction spectra (Figure 2a,b of ref 26) different intensities of reflections which are symmetric with respect to the a^* axis. In particular they have observed that the 420 reflection has a very strong intensity and the $4\bar{2}0$ reflection is absent or has a very weak intensity.[26] Similar observations were made with other reflections such as 710, $7\bar{3}0$, $8\bar{2}0$, and $10,\bar{2},0$, which are strong or medium, and their symmetric counterparts with respect to the a^* axis, i.e. $7\bar{1}0$, 730, 820, and 10,2,0, which are absent or have very weak intensities (Figure 2a of ref 26). The reverse occurs in another electron diffraction spectrum obtained when different areas are selected by the diffraction aperture all across a given single crystal (Figure 2b of ref 26); i.e. 420, 710, $7\bar{3}0$, $8\bar{2}0$, and $10,\bar{2},0$ are absent or have very weak intensities and $4\bar{2}0$, $7\bar{1}0$, 730, 820, and 10,2,0 have strong intensities.

In a tetragonal lattice the $hk0$ and $h\bar{k}0$ reflections are equivalent reflections (i.e. they have equal intensity) for space groups corresponding to the Laue group $4/mmm$; they are not equivalent for space groups corresponding the Laue group $4/m$. These observations allow us to discard space groups with Laue symmetry $4/mmm$ like the space group $I4_1cd$. The possible space group compatible with these observations for the limit ordered regions[27] giving $I(hkl) \neq I(h\bar{k}l)$ could be $I4_1$ with two independent chains in the unit cell, with chain axes in the positions $^1/_4$, $^1/_4$, z and $^1/_4$, $^3/_4$, z.

A preliminary model of packing of form III of P4MP for the space group $I4_1$ is reported in Figure 6. The two independent chains have different a–b projections of the lateral groups; they are enantiomorphous and assumed to be isoclined so that a good interlocking of the lateral groups is obtained.

The approximate positioning of the chains in the unit cell has been obtained by calculation of structure factors and by simple considerations of close packing. The fractional coordinates of the asymmetric unit of the model of Figure 6 are reported in Table 3. The principal intermolecular contact distances in the model of Figure 6 correspond to normal van der Waals distances.

It is worth noting that the position of the outward methyl groups of the two independent chains is almost at the same rotation angle around the 4-fold axes, within each ordered crystal; thus, it is probable that neighboring ordered regions with anticlined chains can be easily coherently juxtaposed.

Table 3. Fractional Coordinates of the Carbon Atoms of the Asymmetric Unit in the Model of Figure 6, Space Group $I4_1$[a]

	x/a	y/b	z/c
1	0.313	0.226	−0.315
2	0.302	0.205	−0.104
3	0.350	0.145	−0.049
4	0.425	0.167	−0.013
5	0.473	0.104	0.000
6	0.430	0.212	0.169
1′	0.297	0.798	0.185
2′	0.278	0.813	0.396
3′	0.296	0.888	0.451
4′	0.373	0.899	0.487
5′	0.391	0.976	0.500
6′	0.397	0.860	0.669

[a] The asymmetric unit corresponds to two independent monomeric units labeled in Figure 6.

Table 4. Comparison between Observed Structure Factors, F_o, from the X-ray Powder Spectrum of Form III (Figure 5) and Those Calculated, $F_c = (\sum|F_i|^2M_i)^{1/2}$, for the Model of Figure 6, for the Space Group $I4_1$

hkl	d_{obs} (Å)	d_{calc} (Å)	F_o	F_c	
200	9.61	9.69	269	237	
220	6.86	6.85	231	182	191
101		6.57		59	
211	5.43	5.44	510	470	
400	4.85	4.84	155	126	230
301		4.74		192	
420	4.31	4.33	488	246	426
321		4.26		348	
411	3.92	3.90	230	359	
440	3.40	3.43	300	46	351
431		3.39		261	
501		3.39		89	
112		3.38		212	
202	3.23	3.28	178	118	207
600		3.23		13	
521		3.20		170	
222		3.11	n.o. (95)[a]	74	
312		3.03	n.o. (98)[a]	122	
611		2.90	n.o. (102)[a]	134	
402		2.83	n.o. (105)[a]	114	
541	2.74	2.78	217	85	213
332		2.77		63	
550		2.74		31	
710		2.74		109	
422		2.72		85	
640		2.69		61	
631		2.67		89	
701	2.57	2.57	146	66	150
512		2.57		135	

[a] Reflections not observed (n.o.) in the Geiger spectrum. The numbers in parentheses represent the values of F_o corresponding to the threshold intensity, taken as equal to half of the minimum observed.

A comparison between observed structure factors, $F_0 = (I/Lp)^{1/2}$, from the X-ray powder diffraction spectrum of Figure 5, and those calculated, $F_c = (\sum|F_i|^2M_i)^{1/2}$, for the space group $I4_1$ for the model of Figure 6 is reported in Table 4. An analogous comparison between the experimental intensities observed in the electron diffraction spectra from Figure 2b of ref 26 and calculated structure factors, $F_c^2 = |F_i|^2M_i$, is reported in Table 5.

A fairly good agreement is apparent. In particular from Table 5 it is apparent that the different intensities of the $hk0$ and $h\bar{k}0$ reflections are reproduced for almost all the equatorial reflections.

Conclusions

Conformational energy calculations on an isolated chain of P4MP are able to interpret the polymorphic behavior

Table 5. Comparison between Experimental Intensities, Observed in the Electron Diffraction Spectrum Reported in the Literature (Figure 2b of Ref 26) and Calculated Structure Factors $F_c^2 = |F_j|^2 M_j$, for the Model of Figure 6, for the Space Group $I4_1$[a]

hkl	F_c^2	I_{obs}
200	840	vs
220	490	s
310	14	w
3$\bar{1}$0	61	w
400	250	ms
330	96	vw
420	88	w
4$\bar{2}$0	820	s
510	-	
5$\bar{1}$0	59	w
440	32	m
530	4	
5$\bar{3}$0	-	
600	2	
620	2	
6$\bar{2}$0	-	
550	14	w
710	39	
7$\bar{1}$0	140	s
640	1	w
6$\bar{4}$0	55	w
730	150	s
7$\bar{3}$0	4	w
800	17	m
820	490	m
8$\bar{2}$0	5	w
660	89	m
750	10	vw
7$\bar{5}$0		vvw
840	31	mw
8$\bar{4}$0	105	m
910	-	
9$\bar{1}$0	-	
930	9	m
9$\bar{3}$0	6	m
770	5	
860	2	w
8$\bar{6}$0	7	w
10,0,0	150	m
10,2,0	58	m
10,$\bar{2}$,0	1	vw
950	70	m
9$\bar{5}$0	-	
10,4,0	120	m
10,$\bar{4}$,0	3	vvw
11,1,0	55	w
11,$\bar{1}$,0	57	w
880	21	w
11,3,0	7	m
11,$\bar{3}$,0	-	vw
12,0,0	38	w
12,2,0	14	w
12,$\bar{2}$,0	-	vvw
12,4,0	8	w
12,$\bar{4}$,0	10	
12,8,0	4	
12,$\bar{8}$,0	16	w

[a] Key: vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak.

of P4MP. In particular, it has been shown that the absolute conformational energy minimum is very close to experimental conformations with symmetries 7_2 and 4_1 observed in form I and form III of P4MP, respectively. A relative minimum present in the conformational energy map is close to conformations with 3_1 symmetry that could characterize the conformation of the hexagonal form IV of P4MP.

A model for the crystal structure of form III is suggested even though fiber samples are not available. Chains with 4_1 helical conformations are packed in the tetragonal unit cell, with axes a = 19.38 Å and c = 6.98 Å, proposed by Charlet et al.[5] from electron diffraction of single crystals of form III. Comparisons between calculated structure factors and the experimental intensities, observed in our X-ray powder diffraction spectrum and in electron diffraction spectra reported in the literature, allow us to suggest for the limit ordered regions a body centered tetragonal space group $I4_1$. Every right handed 4_1 helix is surrounded by four left handed and isoclined helices. The two independent chains in the unit cell have different a–b projections of the lateral groups.

The proposed model accounts for the different intensities of the $hk0$ and $h\bar{k}0$ reflections observed in the electron diffraction spectra.

References and Notes

(1) Natta, G.; Corradini, P.; Bassi, I. W. *Rend. Fis. Acc. Lincei* **1955**, *19*, 404.
(2) Frank, F. C.; Keller, A.; O'Connor, A. *Philos. Mag.* **1959**, *8*, 200.
(3) Bassi, W.; Bonsignori, O.; Lorenzi, G. P.; Pino, P.; Corradini, P.; Temussi, P. A. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 193.
(4) Kusanagi, H.; Takase, M.; Chatani, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 131.
(5) Charlet, G.; Delmas, G.; Revol, F. J.; Manley, R. St. J. *Polymer* **1984**, *25*, 1613.
(6) Charlet, G.; Delmas, G. *Polymer* **1984**, *25*, 1619.
(7) Tanda, Y.; Kawasaki, N.; Imida, K.; Takayanagi, M. *Rep. Prog. Polym. Phys. Jpn.* **1966**, *165*, 9.
(8) Kawasaki, N.; Takayanagi, M. *Rep. Prog. Polym. Phys. Jpn.* **1967**, *10*, 337.
(9) Takayanagi, M.; Kawasaki, N. *J. Macromol. Sci.—Phys.* **1967**, *B1*, 741.
(10) Nakajima, A.; Hayashi, S.; Taka, T.; Utsumi, N. *Kolloid Z. Z. Polym.* **1969**, *234*, 1097.
(11) Nakajima, A.; Hayashi, S.; Taka, T. *Kolloid Z. Z. Polym.* **1969**, *233*, 869.
(12) Hasegawa, R.; Tanabe, Y.; Kobayashi, M.; Tadokoro, H.; Sawaoka, A.; Kawai, N. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 1073.
(13) Charlet, G.; Delmas, G. *Polym. Bull.* **1982**, *6*, 367.
(14) Aharoni, S. M.; Charlet, G.; Delmas, G. *Macromolecules* **1981**, *14*, 1390.
(15) Cromer, D. T.; Maan, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(16) Vainshtein, B. K. *Structure Analysis by Electron Diffraction*; Pergamon Press: London, **1964**; p 125.
(17) Corradini, P.; Napolitano, R.; Petraccone, V.; Pirozzi, B.; Tuzi, A. *Eur. Polym. J.* **1981**, *17*, 1217.
(18) Corradini, P.; De Rosa, C.; Gong Zhi; Napolitano, R.; Pirozzi, B. *Eur. Polym. J.* **1985**, *21*, 635.
(19) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(20) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.
(21) Corradini, P. In *The stereochemistry of macromolecules*; Ketley, A. C., Ed.; Marcel Dekker Inc.: New York, 1968; Vol. 3.
(22) Corradini, P.; Pasquon, I. *Rend. Fis. Acc. Lincei* **1955**, *19*, 453.
(23) Corradini, P.; Petraccone, V.; Pirozzi, B. *Eur. Polym. J.* **1976**, *12*, 831.
(24) Natta, G.; Corradini, P.; Bassi, I. W. *Makromol. Chem.* **1959**, *33*, 247.
(25) Corradini, P.; Ganis, P. *Nuovo Cimento, Suppl.* **1960**, *15*, 96.
(26) Pradere, P.; Revol, J. F.; Manley, R. St. J. *Macromolecules* **1988**, *21*, 2747.
(27) Corradini, P.; Guerra, G. *Adv. Polym. Sci.* **1992**, *100*, 183.