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Notes

Chain Conformation of Form IV of Isotactic Poly(4-methyl-1-pentene)

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Introduction

Five different crystalline forms of isotactic poly(4-methyl-1-pentene) (i-P4MP) have been found. They can be obtained from crystallization in semidilute solutions depending on the solvent and the thermal history of the solutions.[1,2]

Form I is the most stable crystalline form which occurs in melt crystallized samples and in extruded fibers;[3−6] it is characterized by chains in 7/2 helical conformation,[3−5] packed in a tetragonal unit cell with axes $a = 18.66$ Å and $c = 13.80$ Å according to the space group $P\bar{4}$.[4,5] 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.[6]

Form II was prepared for the first time by isothermal crystallization at 20 °C from dilute xylene solutions[7−9] and, recently, by crystallization from tetramethyltin solution.[2] A tetragonal unit cell with axes $a = 19.16$ Å and $c = 7.12$ Å with chains in the 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,[7−9] Decalin,[10,11] and linear and branched alkanes.[1,2] The crystal structure of form III has been recently determined and refined;[12,13] chains in the 4/1 helical conformation are packed in a tetragonal unit cell with axes $a = 19.46$ Å and $c = 7.02$ Å, according to the space group $I4_1$.[12,13] The proposed low symmetry packing model of form III has been recently confirmed by solid-state ^{13}C NMR analysis.[14]

Form IV was obtained, in both the unoriented and uniaxially oriented state, by annealing modification I above 200 °C under pressure (4500 atm).[15] The same crystalline modification has also been obtained from cyclopentane solutions.[16] Stretching of an unoriented sample in form IV leads to a fiber in form I;[16] however, a partially oriented sample in form IV was obtained by swelling a fiber of form I in saturated cyclopentane vapor at 50 °C.[16] Charlet and Delmas[16] 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 a 130 °C.[16]

It is worth noting that only for form I and form III has a complete crystal structure been reported.[4−6,12,13] Only tentative unit cell parameters have been proposed for forms II[9] and IV.[16] The phase transitions of forms II and IV into the most stable form I under stretching or annealing prevents the obtaining of X-ray fiber diffraction patterns which are essential for the determination of the chain conformation and, hence, of the crystal structure. In the case of form IV only a partially oriented fiber, containing a mixture of forms I and IV, has been obtained by swelling a fiber of form I in saturated cyclopentane vapor a 50 °C;[16] with the degree of orientation thus obtained, it was possible to recognize some equatorial reflections and suggest a hexagonal unit cell,[16] but it was not sufficient for determining the chain conformation.

In a recent paper[14] we have suggested, through the analysis of the solid-state ^{13}C NMR spectra of the different crystalline forms of i-P4MP, that chains of i-P4MP in form IV probably assume a 3/1 helical conformation. This hypothesis arises from the observation that the amount of the γ-gauche shielding effect depends on the value of the torsion angles of the main chain[14] and decreases when the backbone torsion angles are deviated from the precise gauche (60°) and trans (180°) values. The observed upfield shift of the resonances of the backbone methine and methylene carbons of the chains in form IV, compared to forms I and III,[14] indicates that these atoms in form IV experience a full γ-gauche shielding effect, and hence, the backbone torsion angles of the chains in form IV are near 60° and 180°, typical of a 3/1 helical conformation.

In this paper the X-ray diffraction pattern of a well-oriented fiber in the pure form IV of i-P4MP is presented; the conformation of the chains in form IV is analyzed on the basis of the X-ray fiber pattern and conformational energy calculations in order to verify the hypothesis suggested by the solid-state ^{13}C NMR analysis.

Experimental Part and Method of Calculation

i-P4MP was prepared with Ziegler−Natta type catalysts.

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

Samples of i-P4MP in form IV were prepared by crystallization in cyclopentane solutions following the method described in ref 2. The solutions (polymer volume fraction $\phi = 0.05$) were prepared in sealed glass tubes heated at a temperature of 85 °C and slowly cooled to room temperature. The polymer was recovered by evaporation of the solvent at room temperature.

Oriented fibers of i-P4MP in form IV were obtained by swelling fiber samples of form I in saturated cyclopentane vapor a 50 °C.[16] The fibers were kept under tension during the swelling to avoid disorientation. Fiber samples of form I were obtained by stretching, at room temperature, films of i-P4MP prepared by casting at room temperature from cyclohexane solution.

X-ray powder diffraction patterns were obtained with nickel filtered Cu Kα radiation with an automatic Philips diffractometer. X-ray fiber diffraction patterns were registered with a photographic cylindrical camera.

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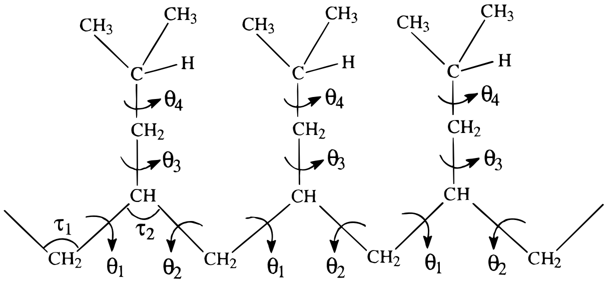

Figure 1. Portion of the chain of i-P4MP used in the conformational energy calculations. The definition of the torsion angles θ_1, θ_2, θ_3, and θ_4 and bond angles τ_1 and τ_2 is also shown. The torsion angle θ_4 is defined with respect to the hydrogen atom of the methine group of the lateral group CH_2-$CH(CH_3)_2$: $\theta_4 = H-C-CH_2-CH$.

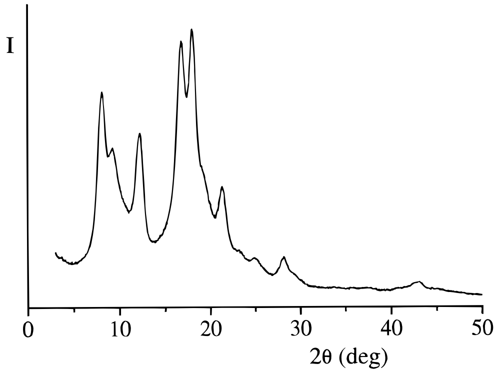

Figure 2. X-ray powder diffraction pattern of form IV of i-P4MP.

Conformational energy calculations have been performed on the portion of the isolated chain of i-P4MP shown in Figure 1, following the method described in ref 12 and assuming a line repetition group s(*M*/*N*) for the polymer chain. The torsion angle θ_4 is defined with respect to the hydrogen atom of the $CH(CH_3)_2$ group. 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,[17] treating the methyl groups as spherical domains.[18]

Results and Discussion

The X-ray powder and fiber diffraction patterns of form IV of i-P4MP are reported in Figures 2 and 3, respectively. The diffraction angles and the relative intensities of all reflections observed in the fiber pattern, listed in Table 1, correspond well to those of the powder pattern of Figure 2. This indicates that fiber samples of the pure form IV have been obtained. A degree of orientation higher than that already reported in the literature has been achieved.

The X-ray fiber diffraction pattern shows the presence of layer lines, whose ζ reciprocal coordinates are consistent with *l* indices 1, 2, and 3 for a chain axis $c = 6.5$ Å. These data are consistent with a 3_1 helical conformation of the chain.

The reflections observed in the X-ray powder and fiber diffraction patterns of Figures 2 and 3 are accounted for by the hexagonal unit cell with $a = 22.17$ Å, proposed by Charlet and Delmas[16] on the basis of the equatorial reflections observed in the X-ray diffraction pattern of a partially oriented fiber of form IV. The indexing of the reflections and the Bragg spacings calculated according to this hexagonal unit cell are also reported in Table 1.

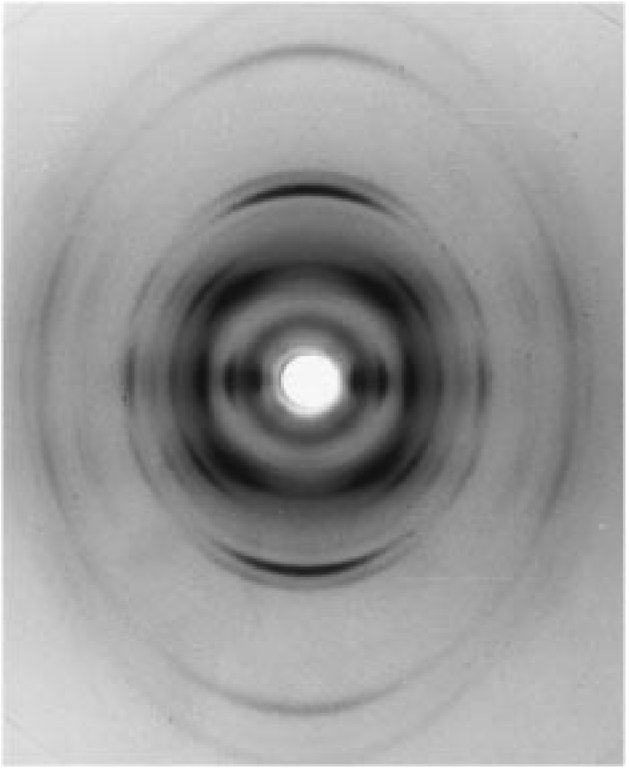

Figure 3. X-ray fiber diffraction pattern of form IV of i-P4MP.

Table 1. Diffraction Angles 2*θ*, Bragg Spacings *d*, Reciprocal Coordinates ξ and ζ, and Intensities I_0 of the Reflections Observed on the Layer Lines *l* in the X-ray Fiber Diffraction Pattern of Form IV of i-P4MP of Figure 3;[a] Indices *hkl* of the Reflections and the Calculated Bragg Spacings for the Hexagonal Unit Cell with Axes *a* = 22.17 Å and *c* = 6.5 Å Are Also Reported

2θ	*d* (Å)	ξ (Å^{-1})	ζ (Å^{-1})	I_0[b]	*hkl*	d_{calc} (Å)
8.0	11.05	0.0904	0	s	110	11.08
9.37	9.44	0.106	0	mw	200	9.60
12.25	7.22	0.138	0	s	210	7.26
16.75	5.29	0.189	0	vs	310	5.32
21.4	4.15	0.241	0	m	410	4.19
24.5	3.63	0.275	0	w	420	3.63
28.25	3.16	0.316	0	m	430−600	3.16−3.20
45.4	2.00	0.500	0	vw	740	1.99
18.0	4.93	0.132	0.154	vs	211	4.84
19.2	4.62	0.152	0.154	vw	301	4.56
21.5	4.13	0.187	0.154	ms	311	4.12
23.1	3.85	0.209	0.154	vvw	401	3.86
25.1	3.54	0.236	0.154	w	411	3.52
29.4	3.04	0.291	0.154	w	511	3.05
35.9	2.50	0.369	0.154	vvw	531−701	2.53
37.7	2.38	0.390	0.154	vvw	711	2.37
43.1	2.10	0.451	0.154	w	551	2.10
29.5	3.03	0.123	0.307	vw	202−212	2.97−3.08

[a] From the tilted pattern two nearly meridional reflections at $2\theta = 28.5°$ and 44° on the second and third layer line (with strong and weak intensity), respectively, have been observed. [b] vs = very strong, s = strong, m = medium, ms = medium strong, mw = medium weak, w = weak, vw = very weak, vvw = very very weak.

The calculated crystalline density for the hexagonal unit cell with axes $a = 22.17$ Å and $c = 6.5$ Å, including six chains of i-P4MP in the 3_1 helical conformation (18 monomeric units), is 0.907 g/cm^3, in agreement with the experimental density of 0.866 g/cm^3 (measured at 25 °C by flotation on a sample of form IV having an X-ray crystallinity index of 50%, the density of the amorphous phase being 0.830 g/cm^3). This accordance supports the hypothesis that form IV is characterized by chains in the 3_1 helical conformation.

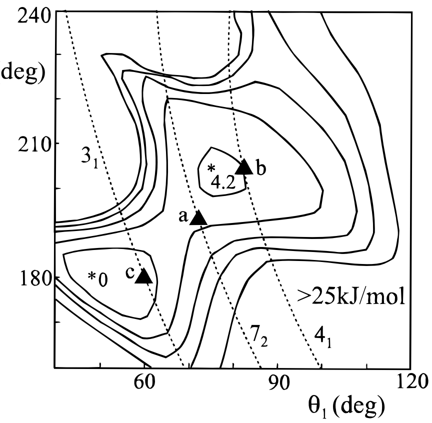

Figure 4. Map of the conformation energy as a function of θ_1 and θ_2. For each pair θ_1, θ_2 the reported energy corresponds to the minimum value obtained scanning θ_3 and θ_4 every 2.5°. The s(M/N) line repetition symmetry and the bond angles $\tau_2 = 112°$ and $\tau_1 = 116°$ have been assumed. The curves are reported at intervals of 5 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 are also reported. The dashed lines 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 conformation 7_2 (a), 4_1 (b), and 3_1 (c) observed in forms I, III, and IV of i-P4MP, respectively.

Conformational energy maps of an isolated chain of i-P4MP have been already reported in ref 12. These calculations account for the complex polymorphic behavior of i-P4MP.[12] Indeed, the absolute conformational energy minimum of the map performed with bond angles $\tau_2 = 111°$ and $\tau_1 = 113°$ was very close to the experimental conformations with 7_2 and 4_1 symmetries, observed in form I (most stable) and form III, respectively.[12] These stable conformations of i-P4MP correspond to isodistortions of the backbone torsion angles θ_1 and θ_2 (see Figure 1) from the precise gauche and trans values, typical of the 3-fold helical conformation, due to the bulkiness of the lateral group. A relative energy minimum close to conformations with 3_1 symmetry is also present in the conformational energy map.[12] This suggests that one of the polymorphic forms of i-P4MP could be characterized by chains in the 3_1 helical conformation.

It is however expected that, for a chain conformation near the 3_1 helical symmetry, the bond angles that minimize the conformational energy are probably greater than $\tau_2 = 111°$ and $\tau_1 = 113°$, used in the calculations of ref 12. A conformational energy map of i-P4MP, in the region of the lowest energy $\theta_1 = G^+$ and $\theta_2 = T$ for values of the bond angles $\tau_2 = 112°$ and $\tau_1 = 116°$, is shown in Figure 4. The map is reported as a function of θ_1 and θ_2 and scanned every 2.5° in θ_3 and θ_4 with the minimum energy values reported. The internal coordinates of the chain in the absolute energy minimum of the map are reported in Table 2. 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 102.8°, 90°, and 120°, respectively, are also reported in the map of Figure 4. It is apparent that, at variance with the map of ref 12, the absolute energy minimum of Figure 4 is very close to the dashed line corresponding to conformations with s(3/1) symmetry. This confirms the hypothesis that a polymorphic form of i-P4MP with chains in a 3_1 helical conformation could exist. This is in agreement with the X-ray fiber diffraction pattern of form IV, discussed above, and the solid-state ^{13}C NMR analysis, reported in ref 14, which suggest that form IV of i-P4MP is characterized by chains in the 3_1 helical conformation.

Table 2. Values of the Internal Coordinates of the Chain of i−P4MP, the Conformational Energy *E*, and the Chain Axis *c*, Obtained from the Minimization of the Conformational Energy under the Constraint of the s(3/1) Helical Symmetry, Compared to the Values Obtained from the Map of Figure 4

	map	minimization		map	minimization
τ_2 (deg)	112.0	111.3	θ_4 (deg)	−60.0	−63.8
τ_1 (deg)	116.0	116.5	θ_4' (deg)[a]	−176.6	−181.7
θ_1 (deg)	50.0	60.0	θ_4'' (deg)[a]	56.6	58.4
θ_2 (deg)	180.0	179.4	E (kJ/mol mu)	0	−3.27
θ_3 (deg)	55.0	52.6	c (Å)		6.5

[a] θ_4' and θ_4'' are the torsion angles defined with respect to the two methyl carbons of the lateral group $CH_2CH(CH_3)_2$, whereas θ_4 is defined with respect to the hydrogen atom of the methine group: $\theta_4 = H-C-CH_2-CH$, $\theta_4' = CH_3-CH-CH_2-CH$.

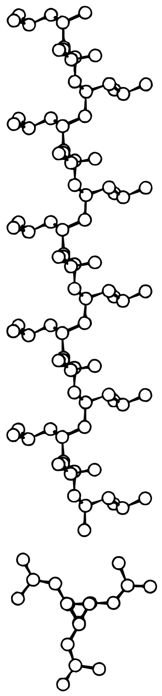

Figure 5. Projections along and perpendicular to the chain axis of the model suggested for the 3_1 helical conformation of form IV of i-P4MP. The model corresponds to the conformation of Table 2 obtained from the minimization of the conformational energy.

Points corresponding to the pairs of torsion angles relative to the experimental conformations observed in form I (point a, 7_2 helix, observed unit height $h = c/7 = 1.97$ Å),[5] in form III (point b, 4_1 helix, observed unit height $h = c/4 = 1.74$ Å),[12,13] and in form IV of i-P4MP (point c, 3_1 helix, observed unit height $h = c/3 = 2.17$ Å, from the X-ray diffraction pattern of Figure 3) are also reported in Figure 4. The three conformations assumed by the chains of i-P4MP are very close to the energy minima and, hence, are well predicted by conformational energy calculations.

Starting from the minimum-energy conformation obtained in the map of Figure 4 (Table 2), minimizations of the conformational energy, under the constraint of the s(3/1) helical symmetry, have been performed. The energy has been minimized by considering as variable parameters all the bond and torsion angles, including those of the lateral groups, keeping the local C_{2v} symmetry on the methylene groups. The values of the internal parameters of the chain of i-P4MP with s(3/1) symmetry in the minimum conformational energy are reported in Table 2 in comparison with those obtained in the map. The energy value is referred to the minimum of the map assumed as zero. The calculated identity period for this conformation is 6.5 Å, in agreement with the experimental chain axis of form IV.

According to this geometrical and energy analysis, a model of the chain of i-P4MP in form IV is built with the values of the internal parameters obtained by the minimization of the conformational energy (Table 2). The projections along and perpendicular to the chain axis of the present model for the 3_1 helical conformation of form IV are reported in Figure 5.

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