Chain Conformation and Unit Cell in the Crystalline Phase of Syndiotactic Poly(4-methyl-1-pentene)

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ABSTRACT: A preliminary characterization of the crystalline structure of syndiotactic poly(4-methyl-1-pentene) is presented. X-ray diffraction patterns of powder and fiber samples are reported. On the basis of X-ray diffraction data as well as conformational energy calculations, a helical chain conformation with a sequence of dihedral angles of the kind $\approx(TTGG)_n$ having symmetry s(12/7)2 and chain repetition $c = 46.91$ Å is suggested. A tetragonal unit cell with axis $a = 18.03$ Å is proposed.

Introduction

The polymerization of 1-alkenes in the presence of homogeneous catalysts based on the column 4 (group 4A) metallocene/methylalumoxane system has been recently reported.[1-5] Two different kinds of syndiospecific catalytic systems have been discovered which work for styrene and substituted styrene[3,4] or for propene.[5] In particular, the syndiospecific catalytic system which polymerizes propene[5] is able to produce highly syndiotactic polymers of other 1-alkenes[6] as, for instance, a crystalline poly(4-methyl-1-pentene).

It has been recently found that the homogeneous catalyst which promotes syndiotactic polymerization of styrene is able to polymerize several 1,3-alkadienes.[7] In particular, from the polymerization of 4-methyl-1,3-pentadiene syndiotactic 1,2-poly(4-methyl-1,3-pentadiene) is obtained.[7] Catalytic hydrogenation of this polymer constitutes an alternative route of synthesis for crystalline syndiotactic poly(4-methyl-1-pentene).[7]

Studies conducted in our laboratories on the polymorphism and crystalline structures of some of the so-obtained new syndiotactic polymers (polystyrene,[8-13] poly(*p*-methylstyrene),[14] and poly(1-butene)[15,16]) have been recently reported.

In this paper a preliminary characterization of highly syndiotactic poly(4-methyl-1-pentene) (s-P4MP) is presented, using samples obtained by both synthetic routes. X-ray diffraction analyses on powder and fiber samples are reported, and the conformation of the chains in the crystalline state is suggested on the basis of the X-ray diffraction data as well as conformational energy calculations.

Experimental Procedures and Method of Calculations

Two different samples of s-P4MP were used. The first one, supplied by the Dipartimento di Fisica of the University of Salerno, was obtained by hydrogenation of syndiotactic 1,2-poly(4-methyl-1,3-pentadiene) as described in ref 7. 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 column 4 metallocene/methylalumoxane system.[6] The inherent viscosities of the two samples are 0.62 and 0.29 dL/g, corresponding to molecular weights close to 5.0×10^4 and 2.0×10^4, respectively, if the parameters found for the isotactic polymer in decalin at 130 °C are used.[17]

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

Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation. The diffraction patterns of unoriented samples were obtained with an automatic Philips diffractometer, while those for oriented samples were obtained with a photographic cylindrical camera.

Differential scanning calorimetry (DSC) scans were carried out in a Perkin-Elmer DSC-7 calorimeter in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Dynamic mechanical analysis (DMA) was carried out with a Polymer Laboratories DMTA apparatus at a frequency of 10 Hz and a heating rate of 4 °C/min.

Since the two available samples obtained by the two different synthetic routes present similar X-ray diffraction, DSC, and DMA behaviors, only the results for the sample of higher molecular weight are reported.

The conformational energy maps have been calculated with the method described in ref 18. The energy has been calculated as the sum of a term

$$E_b = (K_b/2)(\tau - \tau_0)^2$$

due to the bond angle deformations, a term

$$E_t = (K_t/2)(1 + \cos n\theta)$$

due to the intrinsic torsional potential, and a term

$$E_{nb} = Ar^{-12} - Br^{-6}$$

due to the nonbonded interactions between atoms separated by more than two bonds. The nonbonded term has been calculated by taking into account the interactions between the atoms inside the evidenced conformational unit of Figure 4 and the interactions between these atoms and all the remaining atoms within spheres having radii twice the van der Waals distances for each pair of atoms. All the reported energies are referred to a monomeric unit and correspond to half of the energy calculated with this procedure. The potential energy constants are those reported by Flory,[19] treating the CH_3 groups as spherical domains.[20] The angle increments for the energy maps are 10° for the map of Figure 5 and 2.5° for the maps of Figures 7 and 8.

Results and Discussion

X-ray Diffraction Analysis. The X-ray diffraction pattern of a compression-molded sample of s-P4MP is shown in Figure 1A. This pattern is similar to that of the as-prepared powder.

The degree of crystallinity evaluated from this X-ray diffraction pattern is nearly equal to 50%. The melting and glass transition temperatures of this crystalline form are close to 210 and 50 °C, respectively, as shown by the DSC and DMA scans of Figure 2.

Crystalline oriented samples can be obtained by drawing the amorphous samples at room temperature; the X-ray diffraction fiber spectrum is reported in Figure 3. The

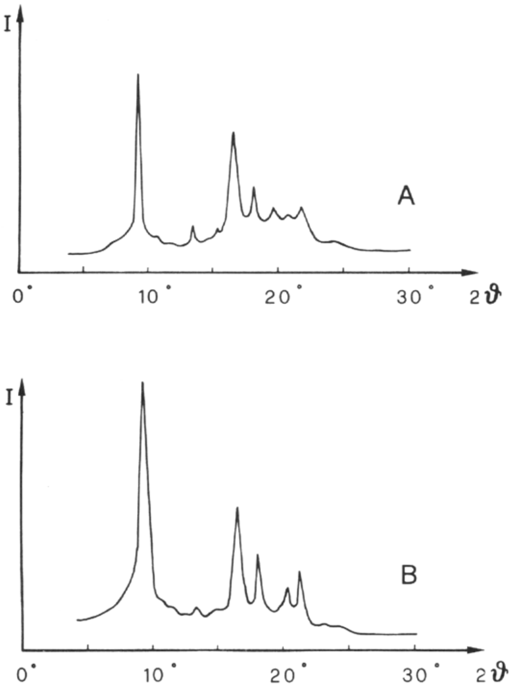

Figure 1. X-ray diffraction 2θ scans of compression-molded samples of syndiotactic (A) and isotactic (B) poly(4-methyl-1-pentene).

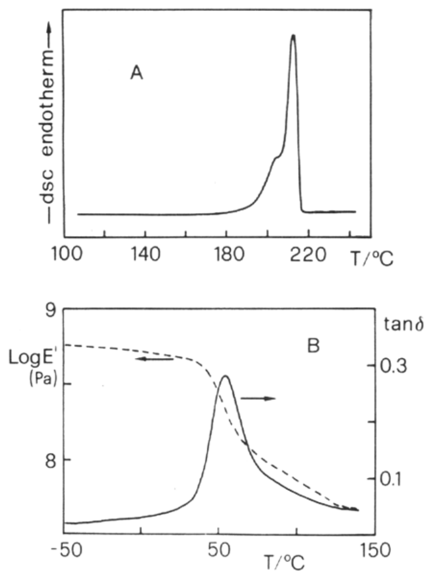

Figure 2. DSC (A) and DMA (B) scans of a compression-molded sample of s-P4MP.

diffraction angles and relative intensities, listed in Table I, correspond well to those of powder spectra like that of Figure 1A.

The X-ray diffraction fiber spectrum shows the presence of several layer lines, whose ζ reciprocal coordinates are consistent with the values of the l indexes reported in Table I for a repeating period c = 47.0 ● 0.3 Å.

The presence of a strong meridional reflection allows one to find from the tilted spectra an accurate value of h = 3.91 ± 0.07 Å for the unit height (repetition period per two monomeric units).

These data are consistent with a conformation of the chain with a helical symmetry of the kind s(12/N)2 in which the chain repetition occurs after 12 conformational units repeat helically[21] (24 monomeric units) and after N turns of the main chain atoms around the chain axis. A more accurate value of the chain repetition axis c is therefore 46.91 ● 0.07 Å.

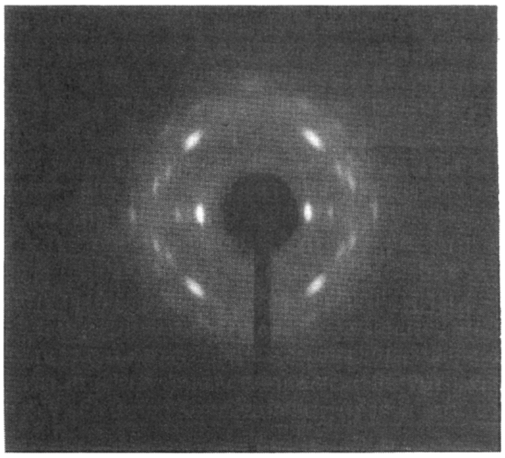

Figure 3. X-ray fiber photographic pattern of an oriented sample of s-P4MP.

Table I
Observed Diffraction Angles $2\theta_{obs}$, Bragg Distances d_{obs}, Reciprocal Coordinates ξ and ζ, and Intensities of the Reflections on the Layer Lines l in the X-ray Diffraction Fiber Patterns of s-P4MP Together with the Bragg Distances Calculated (d_{calc}) According to the Unit Cell with Axes a = 18.03 Å and c = 46.91 Å and the hkl Indexes of the Reflections

$2\theta_{obs}$ (deg)	d_{obs} (Å)	ξ (Å^{-1})	ζ (Å^{-1})	I^a	d_{calc} (Å)	hkl
9.80	9.02	0.111	0	vs	9.016	200
13.8	6.41	0.156	0	s	6.374	220
22.1	4.02	0.249	0	s	4.032	420
25.8	3.45	0.286	0.0452	w	3.497	512
29.5	3.03	0.327	0.0452	w	3.066 2.981	532 602
18.8	4.72	0.202	0.0620	s	4.763	323
17.4	5.10	0.177	0.0842	ms	5.128	314
20.2	4.40	0.202	0.106	m	4.413	325
22.5	3.95	0.229	0.106	m	3.964	415
25.1	3.55	0.251	0.128	w	3.583	426
27.8	3.21	0.284	0.128	w	3.222	516
17.2	5.16	0.124	0.149	vs	5.154	217
21.7	4.09	0.176	0.169	s	4.088	318
24.5	3.63	0.217	0.169	w	3.574	408
21.4	4.15	0.110	0.214	ms	4.162	2,0,10
22.7	3.92	0.0	0.251	s	3.909	0,0,12
31.9	2.81	0.253	0.251	w	2.807	4,2,12

[a] vs = very strong, s = strong, ms = medium strong, m = medium, w = weak.

A possible prediction of the value of N can be done by a qualitative comparison between the experimental intensities on the layer lines and the lowest values of the indexes of the Bessel functions contributing to them,[22] using the graphical method of Mitsui.[23] The best accordance is obtained with the ratio N/M = 0.583 ± 0.05 or N/M = 0.417 ± 0.05, corresponding to helical symmetries s(12/7)2 or s(12/5)2, respectively.

In recent papers[15,24] we have shown the geometrical nonequivalence of the helices s(M/N)2 and s($M/(M-N)$)2; in particular, we have suggested on the basis of geometrical and energetical considerations a helical symmetry s(5/3)2, rather than s(5/2)2, for the conformation of the chains in form II of syndiotactic poly(1-butene).

The conformational energy calculations reported in the following will show that the s(12/7)2 conformation is more suitable than the s(12/5)2 conformation for the chains of s-P4MP.

Conformational Energy Calculations. Conformational energy calculations have been performed by application of the equivalence principle[25] to successive

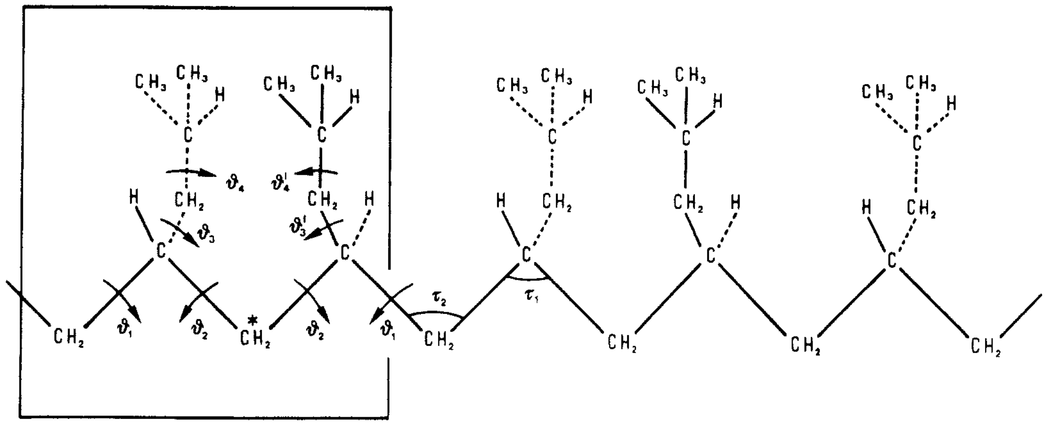

Figure 4. Portion of the chain of s-P4MP considered in the energy calculation. Torsion angles which characterize the conformations of the lateral groups in the conformational repeating units, (θ_3, θ_3'), are defined with respect to the same CH_2 group (indicated by an asterisk).[15] Torsion angles (θ_4, θ_4') are defined with respect to the hydrogen atoms of the $CH(CH_3)_2$ groups. The binary axis, crossing the CH_2 groups of the main chain, for the s(M/N)2 symmetry imposes $\theta_3 = \theta_3'$ and $\theta_4 = \theta_4'$.

Table II
Bond Lengths and Bond Angles Used in the Conformational Energy Maps of s-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.

constitutional units by assuming a line repetiton group s(M/N)2 for the polymer chain.[15,18] As a consequence the sequence of the torsion angles in the main chain is of the kind ...$\theta_1,\theta_2,\theta_2,\theta_1$,... (Figure 4). It is also assumed that the binary axes crossing the methylene groups of the main chain, typical of the line repetition group s(M/N)2, relate also the atoms of the lateral groups.[15] To attribute equal numerical values to the dihedral angles of the lateral groups, torsion angles θ_3 and θ_3' are defined with respect to the same CH_2 group, indicated by an asterisk in Figure 4.[15] Moreover, torsion angles θ_4 and θ_4' are defined with respect to the hydrogen atoms of the $CH(CH_3)_2$ groups.

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

A conformational energy map for s-P4MP as a function of θ_1 and θ_2 scanned every 5° in θ_3 and θ_4 (minimum energy values reported) is shown in Figure 5. The two minima located in the region $\theta_1 \approx G^+$, $\theta_2 \approx T$ or $\theta_1 \approx T$, $\theta_2 \approx G^-$, typical of syndiotactic vinyl polymer,[18,26-28] are in this case split into two subminima.

It is interesting to note that the absolute minimum energy corresponds, for the selected bond angles, to the subminimum more distorted with respect to the precise T and G values (isodistortion for θ_1 and θ_2 in the range 10–30°[29]).

It is worth noting that the bulkiness of the lateral group in s-P4MP makes energetically unfeasible the trans planar conformation region while minima are present in the trans planar region of the energy maps of syndiotactic polystyrene,[18] syndiotactic polypropylene,[26-28] and syndiotactic poly(1-butene).[15]

The loci of points corresponding to the s(12/7)2 and s(12/5)2 helical symmetries with values of the unit twist $t = 2\pi N/M^{15,24}$ of 210° and 150°, respectively, and to the value of the observed unit height ($h = c/12 = 3.91$ Å) are shown in the map of Figure 6. The convention we use for the definition of the unit twist is the one we used in ref 15. The intersection points of the curves in Figure 6 indicate the θ_1,θ_2 pairs which correspond to the observed value of the unit height.

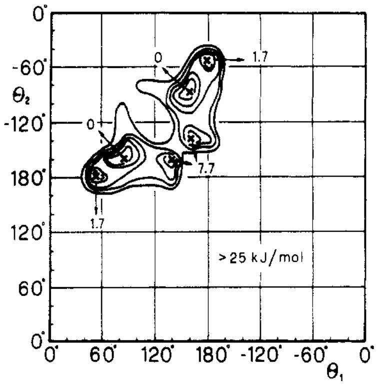

Figure 5. Map of the conformational energy of s-P4MP as a function of θ_1 and θ_2, scanned every 5° in θ_3 and θ_4, in the s(M/N)2 line repetition group for τ_1 = 111°, τ_2 = 113°. The curves are reported at intervals of 5 kJ/mol of monomeric units with respect to the absolute minimum of the map assumed as zero. The values of the energies corresponding to the minima (×) are also indicated.

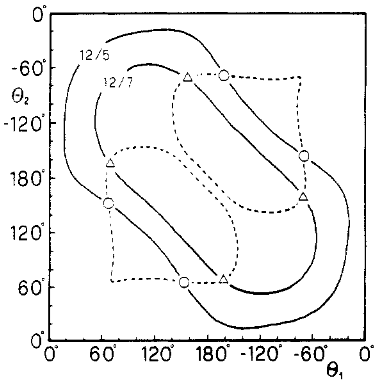

Figure 6. Map of the loci of points for which the helical symmetries are s(12/7)2 and s(12/5)2 (continuous lines) and h = 3.91 Å (dashed lines) as a function of θ_1 and θ_2. The intersection points for the s(12/7)2 symmetry are indicated by triangles, while the intersection points for the s(12/5)2 symmetry are indicated by circles.

A detail of the energy map of Figure 5 (with θ_3 and θ_4 scanned every 2.5°) is reported in Figure 7. The intersection points of Figure 6 are also reported in Figure 7. It is apparent that for the observed value of the unit height, the conformation having s(12/7)2 helical symmetry is very close to the absolute minimum of the map, while the

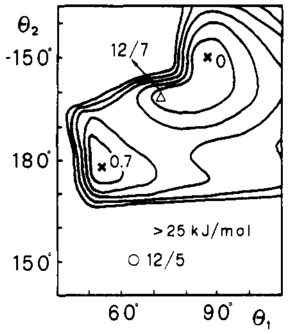

Figure 7. Detail of the energy map of Figure 5 with θ_3 and θ_4 scanned every 2.5°. The curves are reported at intervals of 5 kJ/mol of monomeric units with respect to the absolute minimum of the map assumed as zero. The intersection points of Figure 6 are also shown.

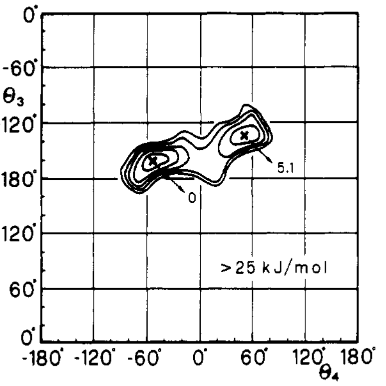

Figure 8. Map of the conformational energy as a function of θ_3 and θ_4 for the model chain with s(12/7)2 symmetry with $\theta_1 = 70°$, $\theta_2 = -164°$. The curves are reported at intervals of 5 kJ/mol of monomeric units with respect to the absolute minimum of the map assumed as zero.

conformation with s(12/5)2 helical symmetry does not correspond to energy minima.

This clearly indicates that the s(12/7)2 symmetry is preferred to the s(12/5)2 symmetry for the chain conformation in the crystalline phase of s-P4MP.

According to this geometrical and energy analysis, the values of the dihedral angles along the main chain of s-P4MP can be assumed to be close to $\theta_1 = 70°$ and $\theta_2 = -164°$.

The conformational energy map of s-P4MP as a function of θ_3 and θ_4 for this fixed pair of θ_1,θ_2 values is reported in Figure 8. It is apparent that only the conformation of the lateral groups with $\theta_3 \approx 180°$ and $\theta_4 \approx -60°$ corresponds to a deep energy minimum.

It is worth noting that the same values of θ_3 and θ_4 minimize the energy for the whole conformational region (θ_1,θ_2) not far from the minima of Figure 7.

The projection along the chain axis and a side view of the present model for the chain conformation of s-P4MP in the crystalline phase are reported in Figure 9.

Final Remarks

It is worth noting that the X-ray diffraction pattern of s-P4MP of Figure 1A is very similar to that of form I of isotactic poly(4-methyl-1-pentene) (Figure 1B),[30] which has instead an s(7/2) chain conformation. This suggests similar crystal packings in spite of the different configurations and conformations of the chains.

From Figure 9 it is apparent for the s-P4MP chain that there is an outside envelope similar to that of a cylinder in which hollows and bulges are periodically repeated, as occurs in a screw. This feature characterizes also the chains of isotactic poly(4-methyl-1-pentene). These kinds of chains are generally packed in a tetragonal lattice with a coordination number equal to 4.[25]

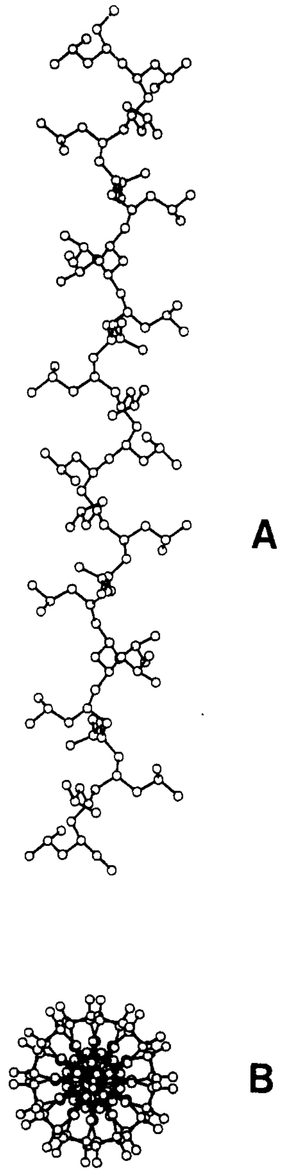

Figure 9. Side view (A) and a projection along the chain axis (B) of the model suggested for the chain conformation of s-P4MP.

The reflections observed in the powder spectrum of Figure 1 and in the fiber spectrum of Figure 2 and Table I are, in fact, accounted for by a tetragonal unit cell with axes $a = 18.03$ Å and $c = 46.91$ Å. The calculated density with four chains in the cell (96 monomeric units) is 0.878 g/cm^3, in accordance with the experimental density (d_{exp} = 0.852 g/cm^3 measured at 25 °C by flotation on a sample with an X-ray crystallinity of ≈45%).

The indexing of reflections and the Bragg distances calculated according to this unit cell are also reported in Table I.

A complete crystal structure analysis is in progress and will be reported in a forthcoming paper.

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Registry No. 4-Methyl-1-pentene (homopolymer), 131724-39-5.