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Crystal Structure of Form III of Syndiotactic Poly(*p*-methylstyrene)

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ABSTRACT: The crystal structure of form III of syndiotactic poly(*p*-methylstyrene) is presented. Chains in nearly *trans*-planar conformation are packed in an orthorhombic unit cell with axes a = 13.36 Å, b = 23.21 Å, and c = 5.12 Å. The crystalline density is 0.988 g/cm^3 with four chains in the unit cell (8 monomeric units); space group *Pnam*. Structure factors and packing energy calculations are shown. A refinement of the structure with the Rietveld method is also presented.

Introduction

The discovery of homogeneous catalytic systems which consist of soluble titanium or zirconium compounds and methylaluminoxane for the polymerization of styrene to fully syndiotactic polymer[1,2] has also allowed researchers to obtain fully syndiotactic substituted polystyrenes.[3−8]

The very complex polymorphic behavior[9−11] and the crystalline structures of various modifications of syndiotactic polystyrene (s-PS)[12−18] have been reported. Recent structural studies have shown a very complex polymorphic behavior also for syndiotactic poly(*p*-methylstyrene) (s-PPMS).[19−22]

s-PPMS, which is generally crystalline as polymerized, does not crystallize by cooling from the melt or by annealing the amorphous phase. However, it crystallizes readily when cast or precipitated from solution as well as by solvent-induced crystallization from the amorphous phase.[19]

For s-PPMS, four different crystalline forms and a mesomorphic form as well as several clathrate structures (which include molecules of solvent) have been found.[19,22] The different crystalline forms and the clathrate structures are formed depending on the solvent, the crystallization technique (e.g., casting, precipitation, or solvent induction from the amorphous state) or other parameters (e.g., temperature of casting and nature of the nonsolvent in the precipitation).[19,22]

The chain conformation involved in the crystalline forms of s-PPMS[20−22] are those found for s-PS (*trans* planar and s(2/1)2 helical).

Following the nomenclature proposed in refs 19 and 22, form I, form II, and the clathrate structures including molecules of solvent (for instance, tetrahydrofuran or *o*-dichlorobenzene) present chains in the s(2/1)2 helical conformation with a repeating distance of nearly 7.8 Å,[20−22] while form III, form V, and the mesomorphic modification (form IV) present chains in a *trans*-planar conformation with a repeating distance of ~5.1 Å.[20−22]

For the various crystalline forms only these few structural data have been suggested so far. This paper presents a complete structural characterization of form III.

A model for the crystal structure of form III is suggested on the basis of structure factors and packing energy calculations. A refinement of the model, performed with the Rietveld method, is also presented.

Experimental Section

s-PPMS was synthesized as described in refs 8 and 19. The syndiotacticity of the polymer was evaluated by ^{13}C-NMR;[8] the fraction of *rrrr* pentads is higher than 95%.

Form III of s-PPMS was obtained by annealing form I at 210 °C for 12 h.[19] As described in ref 19, form I recrystallizes into form III above its melting temperature (~180 °C). Form I was obtained by casting at 50 °C from 10 wt % solution in toluene.

An amorphous sample of s-PPMS was obtained by melting the as-polymerized sample and cooling to room temperature.

Partially oriented fibers of s-PPMS in form III can be obtained by drawing films of both crystalline forms I and II; this produces first a transition to the mesomorphic modification (form IV). Successive annealing of the fiber in the mesomorphic modification, holding the ends fixed, at 210 °C produces transition to form III.[22]

X-ray powder diffraction spectra were recorded at room temperature with a Philips diffractometer, using Ni-filtered Cu Kα radiation and a step−scan procedure. The range of 2θ diffraction angle examined was 2.5−50°, the count time for each step was equal to 60 s/step, and the step width was 0.05° (2θ).

The packing energy has been evaluated as half of the sum of the interaction energies between the atoms of one monomeric unit and all the surrounding atoms of the neighboring macromolecules.[23] The calculations have been performed with the parameters for the nonbonded energy reported by Flory[24] taking the methyl groups as a single rigid unit.[25] The conformation of the chain has been kept constant and the interactions have been calculated within spheres of twice the sum of the van der Waals radii for each pair of atoms.

Calculated squared structure factors (F_c^2) have been obtained as $F_c^2 = \sum|F_i|^2 M_i$, 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. It was assumed that the atomic scattering factors are as in ref 26.

The refinement procedure was done through the use of the program DEBVIN, first developed by Immirzi[27] and hence revised and implemented by Bruckner.[28−30]

Method of Refinement

The refinement was performed with the full profile X-ray powder diffraction refinement procedure (Rietveld method), using the same approach employed in the case of the crystal structure refinement of other polymers.[28−31]

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Table 1. Bond Lengths, Bond Angles, and Torsion Angles Used To Build the Model Chain of s-PPMS and Kept Constant in the Refinement Procedure

Bond Lengths (Å)	
C–C	1.53
C–C_{ar}	1.51
C_{ar}–C_{ar}	1.39
Bond Angles and Torsion Angles[a] (deg)	
τ_1	112.8
τ_2	113.1
C_{ar}–C_{ar}–C_{ar}	120
C–C_{ar}–C_{ar}	120
θ_1	−172.8
θ_2	64.7

[a] See Figure 1.

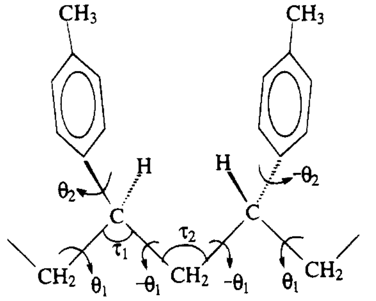

Figure 1. Portion of the chain of s-PPMS in the *tcm* line repetition group.

For the crystalline structure of polymers, it is possible to refine, with this method, all together the chain conformation, the packing parameters, the cell constants, and nonstructural parameters.

The minimized function is

$$F = \sum W_i(I_{ci} - I_{oi})^2 + \sum u_j(G_{oj} - G_j)^2$$

with I_{oi} and I_{ci} the observed and the calculated values of the intensity profile at the diffraction angle $2\theta_i$ and W_i the weight factor, placed equal to $W_i = 1/I_{oi}$ for $2\theta > 6.50°$ and equal to $W_i = 0.1/I_{oi}$ for $2\theta \leq 6.50°$; G_{oj} and G_j are the values which a given geometrical variable (bond lengths, bond angles, dihedral angles, distances between nonbonded atoms, etc.) is desired to assume and the corresponding value assumed by that variable at the given point of the refinement procedure, respectively. To introduce these constraining conditions ($G_{oj} - G_j = 0$) Lagrangians' undetermined multipliers u_j are employed.[32]

In carrying out the structural refinement with the present approach, the agreement factor R_2' is defined as

$$R_2' = \sum |I_{oi} - I_{ci}| / \sum I_{ni}$$

with $I_{ni} = I_{oi} - I_{bi}$, where I_{bi} is the background intensity which includes the amorphous contribution.

The nearly *trans*-planar conformation of the chain has been kept constant during the refinement procedure. A *tcm* line repetition symmetry has been assumed for the polymer chain with values of the internal coordinates reported in Table 1, in analogy with those found for s-PS.[33]

In Figure 1 a portion of the chain of s-PPMS is shown with the definition of the torsion angles θ_1 and θ_2 and bond angles τ_1 and τ_2.

Rotation Ω_z of the chain around its axis, defined in Figure 2, and translations X, Y, and Z along the axes of the unit cell were introduced as independent variables to be optimized in the refinement procedure. At the beginning of the process of structural refinement, it was useful to introduce some constraints keeping the values of the distances between atoms of adjacent chains within distances compatible with the sum of the corresponding van der Waals radii. At the final stages of the refinement procedure, when the mean-square convergence was reached, the constraints on the distances for nonbonded atoms were relaxed.

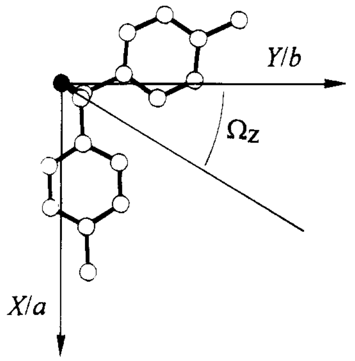

Figure 2. Definition of the coordinate Ω_z used in the refinement procedure and in the lattice energy calculations. Ω_z is positive for a clockwise rotation, and X, Y, and Z are the coordinates of the atom indicated as a full ball.

The cell constants a and b were of course refined. At the beginning of the refinement, the c axis of the unit cell was refined. The internal coordinates of the chain were adjusted so that the period corresponds to the refined c axis. The conformation, and hence the c axis, was kept constant in the successive stages of the refinement.

Some nonstructural parameters were refined. In particular, it was necessary to refine the scaling factor for the amorphous X-ray powder diffraction profile in order to put the latter profile on the same intensity scale of the spectrum of the semicrystalline polymer. An additional baseline spanning the whole spectrum with nodes having abscissa $2\theta = 4$ and 50° and the ordinate to be refined on the intensity scale was considered.

The peak shape was assumed to be a Cauchy function with half-height width H equal to

$$H = (U \tan^2[\theta] + V \tan[\theta] + W)^{1/2}$$

with θ the diffraction angle, U and V two variables to be optimized, and W depending on the (hkl) values through an adjustable estimation of crystallite dimensions L_a, L_b, and L_c along the axes of the unit cell a, b, and c, respectively.[28,34,35]

It is worth noting that the refined values of L_a, L_b, and L_c do not give immediately the real average crystalline dimensions since the instrumental broadening is present and affects the peak shape; therefore, further elaboration would be required to obtain physically meaningful data.

A zero-point correction (zero shift) of the experimental 2θ scale was evaluated.

Results and Discussion

The X-ray diffraction pattern of an unoriented sample of s-PPMS in form III is reported in Figure 3. From the X-ray fiber diffraction spectrum, a value of the chain axis c of nearly 5.1 Å, indicating a *trans*-planar conformation of the chains, was evaluated,[22] although the fiber pattern shows a low degree of orientation.

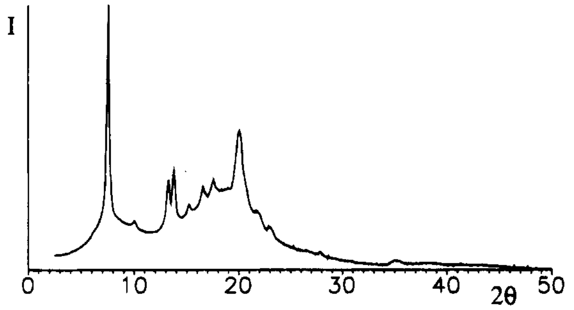

Figure 3. X-ray powder diffraction spectrum of form III of s-PPMS.

Table 2. Diffraction Angles 2θ and Bragg Distances d_{obs} of the Reflections Observed in the X-ray Powder Diffraction Spectrum of s-PPMS[a]

2θ (deg)	d_{obs} (Å)	d_{calc} (Å)	*hkl*
7.6	11.6	11.60	020, 110
10.0	8.84	8.77	120
13.3	6.66	6.70	130, 200
13.8	6.42	6.44	210
15.2	5.83	5.80	040, 220
16.6	5.34	5.32	140
17.6	5.04	5.06	230
18.9	4.70	4.67	111
20.1	4.42	4.41	121
21.7	4.10	4.06	131, 201
22.9	3.88	3.87	330, 060
26.7	3.34	3.35	260, 400
27.8	3.21	3.22	350, 420
35.0	2.56	2.55	002

[a] The indices *hkl* and the calculated Bragg distances d_{calc} are given for the unit cell with axes a = 13.4 Å, b = 23.2 Å, and c = 5.1 Å.

All the reflections observed in the powder spectrum of Figure 3 were attributed to their layer lines by comparison with the fiber pattern and are listed in Table 2. All the reflections of Table 2 are accounted for by an orthorhombic unit cell with axes a = 13.4 Å, b = 23.2 Å, and c = 5.1 Å.

The calculated crystalline density is 0.988g/cm^3, with 4 chains (8 monomeric units) included in the unit cell, in accordance with the experimental density of 1.00g/cm^3 measured at 25 °C by flotation for a sample with X-ray crystallinity of 33%. It is worth noting that the crystalline density is lower than the density of the amorphous sample (1.02 g/cm^3).

In order to find a space group compatible with these observations, space groups with four chains in the unit cell were considered. In addition, from the indices *hkl* reported in Table 2, we observe that there is no evidence of the presence of $h00$ reflections with $h = 2n + 1$ or of $0k0$ reflections with $k = 2n + 1$. Therefore, the space group could be $P2_12_12_1$.

Preliminary calculations of the packing energy for the space group $P2_12_12_1$ showed that low values of the packing energy are obtained only when the heights of the phenyl rings of the chains in the unit cell are equal to 0 and $c/2$. This indicates that the mirror plane m perpendicular to the chain axis, characteristic of the nearly *trans*-planar *tcm* chains, is probably maintained in the lattice as a crystallographic element of symmetry. As a consequence, the space group *Pnam* was assumed.

Then, in order to find a starting model of packing for the successive refinement, calculations of the packing energy were performed for the space group *Pnam*. The lattice energy was calculated maintaining the axes of the unit cell constant, varying the orientation of the chain around its axis (represented by the angle Ω_z defined in Figure 2) and the X,Y coordinates of the chain axis inside the unit cell while the Z coordinate, which defines the relative height of the chains in the unit cell (Figure 2), was fixed in such a way that the phenyl rings have heights corresponding to the mirror planes m of the space group *Pnam*, that is, (1/4)c and (3/4)c.

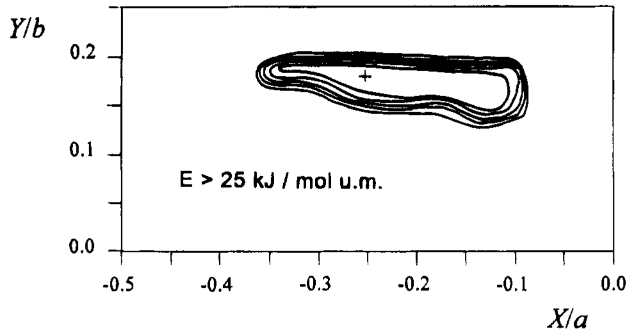

Figure 4. Map of the lattice energy of s-PPMS as a function of X/a and Y/b for $Z/c = 0$ and $\Omega_z = 70°$ for the space group *Pnam*. The curves are reported at intervals of 5 kJ/mol of monomeric unit with respect to the absolute minimum of the map (indicated with a cross) assumed as zero.

Table 3. Refined Values of the Structural Parameters for Form III of s-PPMS[a]

space group	*Pnam*	Ω_z (deg)	70.7 (1)
a (Å)	13.36 (1)	X (Å)	−2.255 (8)
b (Å)	23.21 (2)	Y (Å)	4.158 (4)
c (Å)	5.118 (2)	Z^b (Å)	0
α, β, γ^b (deg)	90		
R_2' (%)	13.0		

[a] The numbers in parentheses represent the standard deviations. [b] Not refined.

Maps of the lattice energy as a function of X/a and Y/b for various values of Ω_z (scanned every 2°) and for a fixed value of $Z/c = 0$ (X, Y, and Z are the coordinates of the methylene carbon atom as defined in Figure 2) were obtained. The lowest values of the energy are obtained for $\Omega_z = 70°$. The map of the lattice energy as a function of X/a and Y/b for $\Omega_z = 70°$ is reported in Figure 4.

The map presents a very large energy minimum mainly in the X direction.

Calculations of structure factors were performed for different positions of the chains in the unit cell corresponding to various points inside the large energy minimum present in the map of Figure 4; good agreement between calculated and observed intensities (taken from Figure 3) is obtained for a model of packing with $X/a = -0.17$, $Y/b = 0.18$, $Z/c = 0$, and $\Omega_z = 70°$.

Starting from this model of packing, a refinement of the structure was performed using the full-profile X-ray powder diffraction refinement procedure (Rietveld method). An agreement factor $R_2' = 13.0\%$ was obtained. A refinement for the space group $P2_12_12_1$, with the Z coordinate left variable, gave no better agreement.

The values of the refined structural parameters are reported in Table 3. The refined fractional coordinates of the atoms of the chain of s-PPMS are reported in Table 4, and the refined nonstructural parameters are shown in Table 5.

A comparison between the observed (curve a) and calculated (curve b) X-ray powder diffraction profiles is reported in Figure 5. The X-ray profile of the amorphous sample suitably scaled (curve c) and the difference between the observed and calculated profiles (curve d) are also shown. Calculated squared structure factors for the refined model are shown in Table 6.

Table 4. Refined Fractional Coordinates of the Carbon Atoms of the Chain of s-PPMS in the Model of Figure 6[a]

atom	*X/a*	*Y/b*	*Z/c*
C1	−0.169	0.179	0
C2	−0.112	0.195	0.250
C3	−0.169	0.179	0.500
C4	−0.084	0.258	0.250
C5	0.017	0.274	0.250
C6	0.042	0.332	0.250
C7	−0.032	0.374	0.250
C8	−0.132	0.357	0.250
C9	−0.158	0.299	0.250
C10	−0.004	0.437	0.250
C11	−0.107	0.187	0.750
C12	−0.017	0.148	0.750
C13	0.079	0.171	0.750
C14	0.162	0.135	0.750
C15	0.148	0.075	0.750
C16	0.052	0.052	0.750
C17	−0.030	0.089	0.750
C18	0.238	0.036	0.750

[a] The asymmetric unit for the model of packing of Figure 6 for the space group *Pnam* corresponds to the atoms reported here except the atom C3, which is obtained from the atom C1 through the mirror plane *m*. The occupation factor of the atom C1 is 1 while those of the other 16 atoms of the asymmetric unit are 0.5.

Table 5. Refined Nonstructural Parameters[a]

zero shift (deg)	0.021 (3)
profile function paramerters	
U (deg^2)	11.5 (8)
V (deg^2)	−0.75 (6)
isotropic thermal parameter	
B (Å^2)	7
av dimensions of the crystallites	
L_a (Å)	92 (4)
L_b (Å)	133 (4)
L_c (Å)	70 (3)

[a] The numbers in parentheses represent the standard deviations.

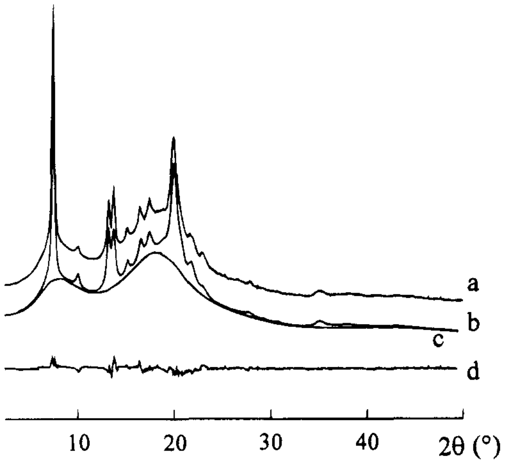

Figure 5. Comparison between observed (curve a) and calculated for the space group *Pnam* (curve b) X-ray powder diffraction profiles of form III of s-PPMS. Curve d is the difference profile. Curve c is the X-ray diffraction spectrum of the amorphous sample.

The model of packing of the chains in form III of s-PPMS as refined in the present analysis is reported in Figure 6. 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; distances less than 4.3 Å are reported in Table 7.

Let us recall that for syndiotactic polystyrene two crystalline forms including nearly *trans*-planar chains have been described.[10,12,13] It is worth noting that the model suggested for the crystal structure of form III of s-PPMS is more similar to that proposed for the *β* form of syndiotactic polystyrene,[13,16] which, in fact, consists of nearly *trans*-planar chains packed in an orthorhombic unit cell according to the space group $P2_12_12_1$.[13] Moreover, contrary to the α form of s-PS and in analogy to the *β* form of s-PS, in form III of s-PPMS the phenyl rings are all located on parallel planes shifted by *c*/2, as in a single chain in the nearly *trans*-planar conformation.

Table 6. Calculated Squared Structure Factors for the Model of Figure 6 of Form III of s-PPMS for the Space Group *Pnam*[a]

hkl	*H*	d_{calc}	d_{obs}	F_c^2	
020	0.21	11.60	11.60	1510	2206
110	0.37	11.57		696	
120	0.39	8.76	8.84	312	
130	0.43	6.70	6.66	216	2124
200	0.40	6.67		1908	
210	0.45	6.42	6.42	2544	
040	0.39	5.80	5.83	630	802
220	0.50	5.79		172	
140	0.49	5.32	5.34	1572	
230	0.55	5.06	5.04	1556	2008
011	0.60	5.00		452	
111	0.69	4.68	4.70	880	
121	0.72	4.42	4.42	18616	19492
240	0.61	4.38		228	
310	0.59	4.37		648	
131	0.76	4.07	4.10	376	3232
201	0.74	4.06		3400	
060	0.61	3.87	3.88	382	1486
330	0.68	3.86		616	
221	0.80	3.83		176	
250	0.68	3.81		312	
260	0.77	3.35	3.34	284	510
400	0.76	3.34		30	
241	0.88	3.33		112	
410	0.77	3.30		84	
350	0.81	3.21	3.21	192	1300
420	0.81	3.21		1108	
002	1.05	2.56	2.56	4836	

[a] The calculated half-height widths *H* (degree of 2*θ*) of the reflections are also reported.

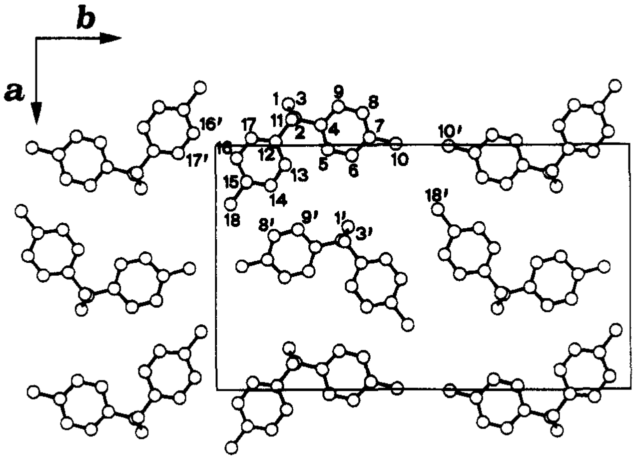

Figure 6. Refined packing model of form III of s-PPMS for the space group *Pnam*.

Table 7. Distances (Å) Less Than 4.3 Å between Atoms Belonging to Different Chains in the Model of Figure 6

C6−C1′	4.1	C15−C8′	4.2
C6−C3′	4.1	C16−C16′	3.8
C10−C10′	3.9	C16−C17′	4.2
C10−C18′	4.2	C17−C16′	4.2
C14−C8′	3.8	C18−C8′	4.0
C14−C9′	3.8		

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