A Clathrate Form of Syndiotactic Poly(*p*-methylstyrene) Containing Two Different Types of Cavities

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ABSTRACT: The crystal structure of the clathrate form of syndiotactic poly(*p*-methylstyrene) containing benzyl chloride is presented. This structure presents a monoclinic unit cell (cell constants $a = 26.2$ Å, $b = 11.8$ Å, $c = 7.9$ Å and $\gamma = 116°$) in which the s(2/1)2 polymer helices and guest molecules are packed according the space group $P2_1/a$. This molecular complex represents, to our knowledge, the first case of polymeric clathrate form in which in the same crystal are present two kinds of cavities having different shape and dimensions: α class cavities (containing two guest molecules) and β class cavities (containing one guest molecule). The contemporaneous presence of these two types of cavities is originated by a disorder in the arrangement of right- and left-handed helices in the crystals related to the particular staggered layout of the layers of chains containing the cavities in which helices of a given chirality can be randomly substituted by enantiomorphous ones.

Introduction

Syndiotactic poly(*p*-methylstyrene) (s-PPMS) shows an interesting property where it can cocrystallize with several low molecular weight substances to form clathrate polymer−solvent complexes,[1−8] a property important for its possible applications. As an example, for the clathrates of the analogous syndiotactic polystyrene (s-PS), uses in the field of molecular sieves for the purification of water or gases[9−13] or as the sensing film for molecular sensors[14,15] have already been proposed. At variance with s-PS, whose clathrate structures are very similar to each other independently from guest molecules, those of s-PPMS are very sensitive to the shape and chemical structure of the guests.[3−8,16,17] The clathrate forms of s-PPMS described up to now have been divided in three different classes, α, β, and γ. α and β class ones are both characterized by a s(2/1)2 helical conformation of the polymer chains with a repetition period of 7.8 Å while in γ class clathrates polymer chains assume a t2 symmetry conformation with a repetition period of 11.7 Å.[3−8]

As far as α class clathrate forms are concerned, a complete structural characterization has been proposed only in the case of the clathrates containing *o*-dichlorobenzene[5] and chlorobenzene[17] while, on the basis of the extreme similarity between their X-ray diffraction patterns, analogous structures have been hypothesized for the clathrates containing *o*-xylene,[3] *o*-chlorophenol,[3] *N*-methyl-2-pyrrolidone,[3] and tetrahydronaphthalene.[18] These structures are characterized by centrosymmetric cavities (α class cavities), delimited by eight benzene rings belonging to two enantiomorphous adjacent helical chains. In the unit cell of these clathrates, the number of cavities is equal to the number of chains while the number of guest molecules per cavity can be 1 (as in the cases of the clathrates with *o*-dichlorobenzene, *o*-xylene, *o*-chlorofenol, *N*-methyl-2-pyrrolidone, and tetrahydronaphthalene) or 2 (as for the clathrate containing chlorobenzene). A schematic representation of the arrangements of the chains and of the cavities in this class is reported in Figure 1A. It is worth noting that this kind of cavities are very similar to those present in all the known clathrate forms of s-PS that, for this reason, have been classified as α class clathrates too.[7]

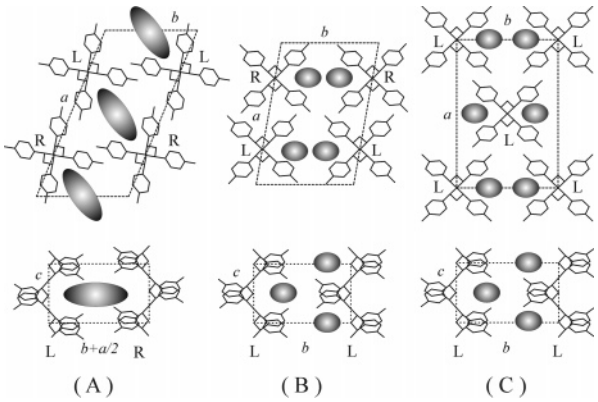

Figure 1. Schematic projections showing the packing of the chains and the placing of the cavities found in the crystal structures of the α (A) and β (B, C) class clathrate forms of s-PPMS.[4−7,17] In the lower part of the figure only one couple of polymer chains delimiting the cavities are shown. R = right-handed and L = left-handed helices.

As far as β class clathrates are concerned, the cavities in which guest molecules are hosted are delimited by four phenyl rings belonging to a chain and two phenyl rings belonging to an isomorphous chain related to the first one by a 2_1 screw axis. In these types of clathrates there is a double number of cavities in respect to α class clathrates and there is only one guest molecule per cavity. For this class, the crystal structures of the clathrate forms containing tetrahydrofuran (THF),[4] benzene,[6] CS_2,[7] and toluene[17] have been completely characterized. In that framework, it has been pointed out that, despite the same shape of the cavities, two different symmetries are possible as far as the overall packing of the chains is concerned: a monoclinic one for THF and an orthorhombic one for benzene, CS_2 and toluene. In the monoclinic structure, layers of isomorphous helices follow equivalent layers made of enantiomorphous helices while in the orthorhombic cases, all the layers of chains containing the cavities are made of helices of the same chirality giving rise to unusual examples of chiral crystalline phases in which all the polymer helices assume the same chirality in the lattice. A schematic representation of the arrangements of the

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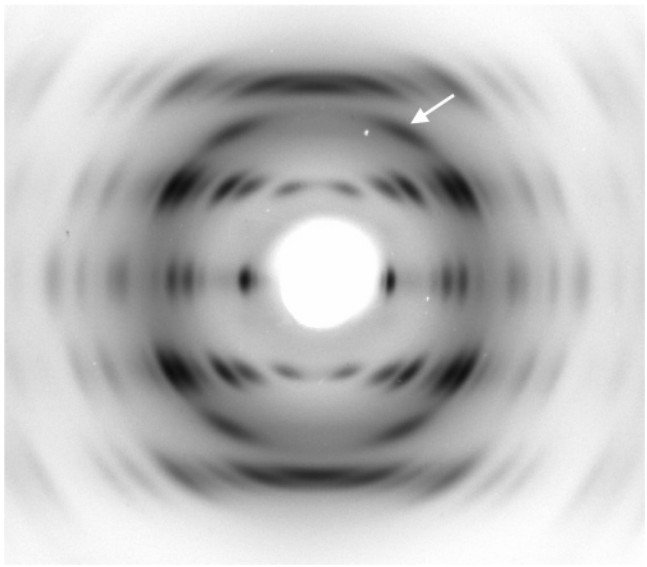

Figure 2. X-ray diffraction pattern of an oriented sample of the clathrate form of s-PPMS containing benzyl chloride. The presence of some amount of form IV is revealed by the reflections at $2\theta = 20.4°$ (indicated by an arrow) corresponding to the strongest reflection of that form.[2] Fiber axis is vertical.

Table 1. Diffraction Angles ($2\theta_o$), Bragg Distances (d_o), and Intensities (I_o) in Arbitrary Units (AU) of the Reflections Observed on the Layer Lines (l) of the X-ray Fiber Diffraction Pattern of the s-PPMS/Benzyl Chloride Clathrate Form Shown in Figure 2

l	$2\theta_o$ (deg)	d_o (Å)	I_o (AU)
0	7.45	11.87	145
0	8.5	10.40	6395
0	13.6	6.51	676
0	15.1	5.87	3015
0	16.9	5.25	2455
0	22.7	3.92	2110
0	27.5	3.24	530
0	30.8	2.90	1188
1	11.7	7.56	906
1	13.9	6.37	3287
1	15.4	5.75	5381
1	17.8	4.98	1085
1	19.2	4.62	7139
1	20.2	4.40	9630
1	21.9	4.06	1480
1	26.5	3.36	891
1	29.7	3.01	620
2	23.7	3.75	7000
2	25.0	3.56	1607
2	27.4	3.25	2994
2	30.5	2.93	455
2	32.6	2.75	430

chains and of the cavities in the β class clathrate forms is reported in Figure 1, parts B and C.

In the present paper the crystal structure of the clathrate form of s-PPMS containing benzyl chloride is presented. This molecular complex represents the first case in which in the same crystal are present two kinds of cavities having different shape and dimensions: α class cavities (containing two guest molecules) and β class cavities (containing one guest molecule).

Experimental Section

s-PPMS was synthesized as described in ref 19. The syndiotacticity of the insoluble fraction in 2-butanone was evaluated by ^{13}C NMR analysis; the amount of the [*rrrr*] pentads was higher than 95%.

Table 2. Fractional Coordinates of the Atoms of the Asymmetric Unit of the Models Presented in Figure 3, Parts A and B, for the s-PPMS/Benzyl Chloride Clathrate Form[a]

	model 3A			model 3B		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
C1	0.249	−0.003	−0.519	0.250	−0.002	−0.459
C2	0.200	−0.026	−0.395	0.201	−0.018	−0.336
C3	0.147	−0.048	−0.495	0.149	−0.033	−0.435
C4	0.140	0.048	−0.581	0.150	0.059	−0.549
C5	0.091	0.025	−0.667	0.102	0.043	−0.641
C6	0.045	−0.095	−0.672	0.051	−0.065	−0.622
C7	0.052	−0.191	−0.591	0.050	−0.156	−0.507
C8	0.102	−0.168	−0.503	0.098	−0.140	−0.415
C9	0.213	0.084	−0.271	0.216	0.093	−0.211
C10	**−0.009**	**−0.118**	**−0.761**	**−0.001**	**−0.082**	**−0.723**
C11	0.238	−0.112	−0.647	0.236	−0.113	−0.584
C12	0.226	−0.234	−0.554	0.223	−0.233	−0.484
C13	0.264	−0.242	−0.436	0.264	−0.252	−0.396
C14	0.253	−0.355	−0.356	0.252	−0.362	−0.306
C15	0.204	−0.465	−0.390	0.197	−0.459	−0.301
C16	0.166	−0.456	−0.508	0.155	−0.439	−0.386
C17	0.177	−0.343	−0.589	0.168	−0.329	−0.476
C18	**0.192**	**−0.587**	**−0.302**	**0.184**	**−0.579**	**−0.206**
C19	*0.010*	*−0.425*	*−0.222*	*0.031*	*−0.490*	*0.223*
C20	*0.016*	*−0.306*	*−0.175*	*0.083*	*−0.490*	*0.183*
C21	*0.063*	*−0.231*	*−0.077*	*0.122*	*−0.389*	*0.090*
C22	*−0.026*	*−0.259*	*−0.231*	*0.097*	*−0.596*	*0.239*
C23	*0.050*	*−0.467*	*−0.176*	*0.019*	*−0.392*	*0.172*
C24	*0.098*	*−0.390*	*−0.079*	*0.059*	*−0.291*	*0.081*
C25	*0.103*	*−0.271*	*−0.029*	*0.111*	*−0.290*	*0.040*
Cl1	*−0.089*	*−0.323*	*−0.103*	*0.070*	*−0.723*	*0.089*

[a] The coordinates of guest molecules are reported in italics while those of the methyl groups of the polymer chains are in boldface type. Hydrogen atoms were included in the structure factors calculation, but they are omitted in this table for simplicity.

Oriented fibers of the clathrate form were obtained by exposing the mesomorphic form IV to solvent vapors at room temperature for 24 h,[2] keeping fixed the ends of the specimens. Fibers of the mesomorphic form IV were prepared by drawing amorphous specimens in the range 115−120 °C while amorphous samples were obtained from melted samples quenched in ice−water.

The X-ray fiber diffraction patterns of oriented samples were obtained on a BAS-MS imaging plate (Fujifilm) with a cylindrical camera (radius 57.3 mm, Ni-filtered Cu−Kα radiation monochromatized with a graphite crystal) and processed with a digital scanner (Fuji−BAS 1800). Calculated structure factors were 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 reflections included in the 2θ range of the corresponding spot observed in the X-ray fiber diffraction pattern. A thermal factor ($B = 12$ Å^2) and atomic scattering factors from ref 20 were used. The observed structure factors F_o were evaluated from the intensities of the reflections observed in the X-ray fiber diffraction pattern (I_o) as $F_o = (I_o/\mathrm{Lp})^{1/2}$ where Lp is the Lorentz-polarization factor for X-ray fiber diffraction:

$$\mathrm{Lp} = \frac{\left(\frac{0.5(\cos^2 2\theta + \cos^2 2\theta_M)}{1 + \cos^2 2\theta_M}\right) + \left(\frac{0.5(1 + \cos 2\theta_M + \cos^2 2\theta)}{1 + \cos 2\theta_M}\right)}{(\sin^2 2\theta - \zeta^2)^{1/2}}$$

with $2\theta_M = 26.6°$ the inclination angle of the monochromator and $\zeta = \lambda(l/c)$, l and c being the order of the layer line and the chain axis periodicity, respectively and λ being the wavelength of the radiation used (1.5418 Å).

The observed intensities I_o were evaluated integrating the crystalline peaks observed in the X-ray diffraction profiles, read along different layer lines, after the subtraction of the amorphous contribution. Owing to the different shapes of the reflections on the equator and on the first and second layer lines, due to the different dimensions of the lamellar crystals in the direction perpendicular and parallel to the chain axis, different factors have

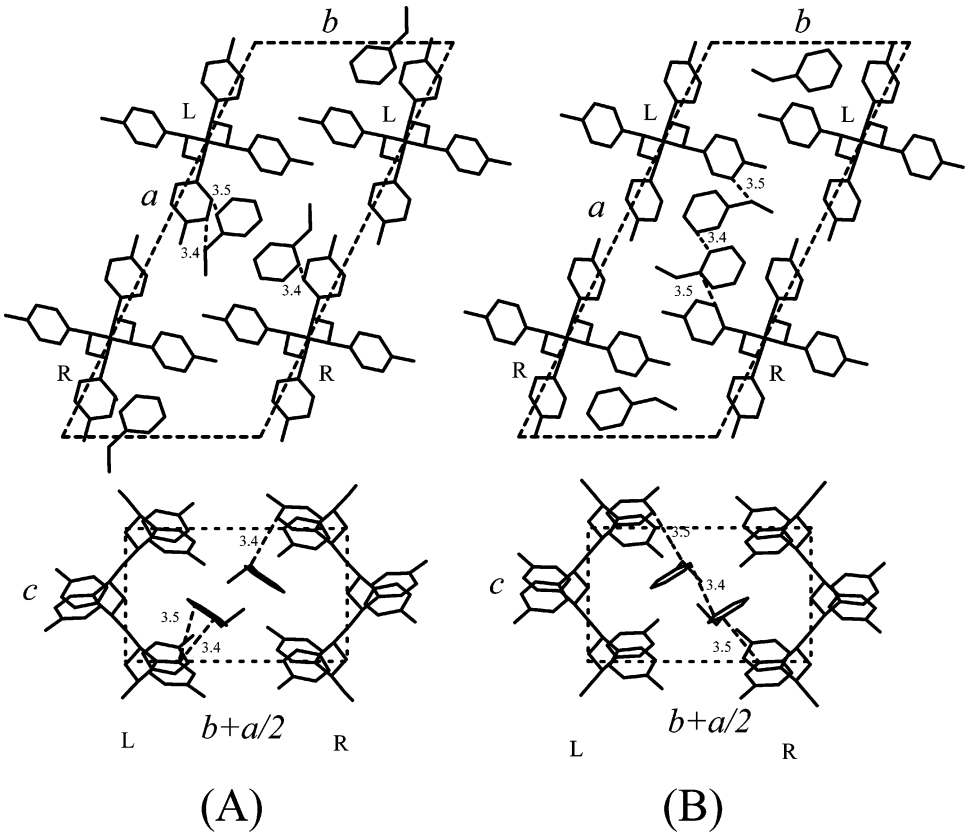

Figure 3. Packing models proposed for the crystal structure of s-PPMS/benzyl chloride molecular complex in the space group $P2_1/a$. In the $c(b + a/2)$ projection only one couple of enantiomorphous polymer chains are shown. R = right-handed and L = left-handed helices. The shortest nonbonded distances between atoms are indicated in Å.

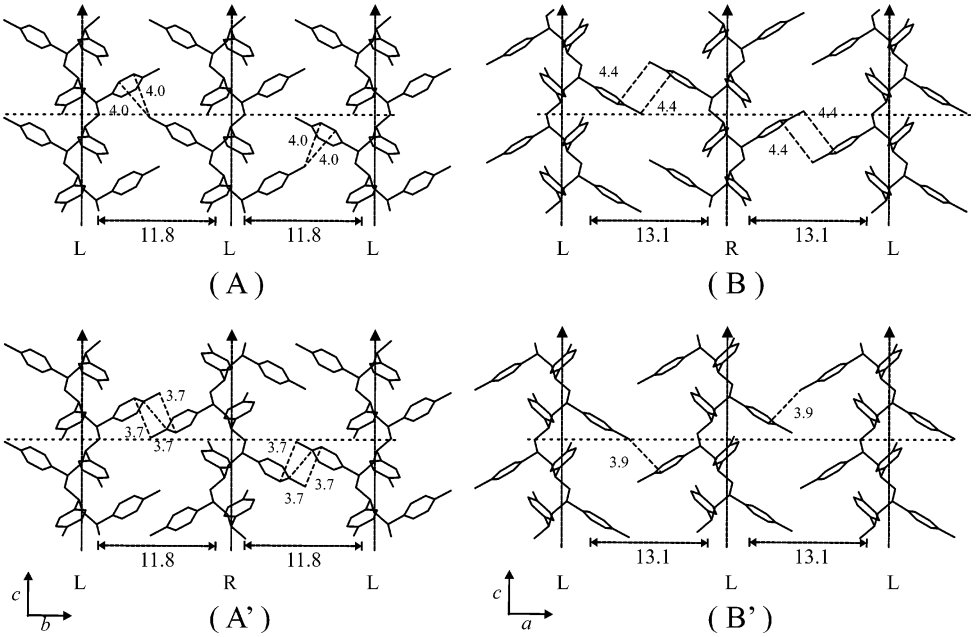

Figure 4. Projections perpendicular to the *bc* (A, A′) and *ac* (B, B′) planes of a layer of chains in the crystal structure of the clathrate form of s-PPMS containing benzyl chloride according the model of Figure 3A. In the upper part (projections A and B) the succession of chains within the layers found in the ordered model is represented while in the lower part (projections A′ and B′) a defect consisting in a fault of the right succession of the chain's chirality is represented. Horizontal dotted lines highlight the almost co-incident positions of the methyl groups before and after the error is introduced. R = right-handed and L = left-handed helices. The distances between chain axes and the shortest nonbonded distances between atoms are indicated in Å.

been used to scale the observed and calculated structure factors on the diverse layer lines.

The discrepancy factor *R* was evaluated as $R = \Sigma|F_o - F_c|/\Sigma F_o$ taking into account only the observed reflections.

Energy calculations were carried out by using commercially available software (*Cerius*[2] version 4.2 by Accelrys Inc.) using the Compass[21] force field. The energy was minimized using the *Open Force Field* module by the smart minimizer method with standard

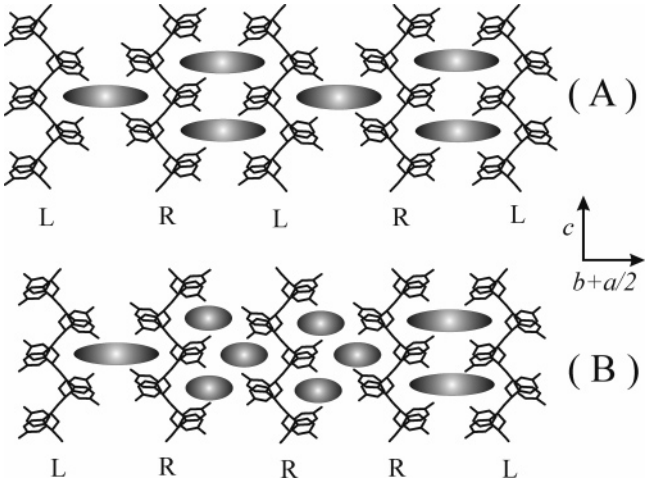

Figure 5. Projections perpendicular to the $c(b + a/2)$ plane of a layer of chains in the crystal structure of the s-PPMS/benzyl chloride molecular complex according the model of Figure 3A. In part A, the ...LRLRL... succession of chains delimiting the cavity that would be found for the ordered model is represented while in part B, a fault in the chirality of the chain in the middle is represented. α class cavities are schematically represented by the bigger gray ellipses while the smaller ones represent β class cavities. An analogous representation is obtainable considering the model of Figure 3B. R = right-handed and L = left-handed helices.

convergence. The starting conformation of the s-PPMS polymer chains corresponded to that found by molecular mechanics calculations reported in the literature.[4]

Results and Discussion

The X-ray fiber diffraction pattern of a uniaxially oriented clathrate sample of s-PPMS containing benzyl chloride is reported in Figure 2. The positions and intensities of all the reflections observed in the diffraction pattern of Figure 2 are listed in Table 1.

The experimental reflections were indexed in terms of a monoclinic unit cell with constants $a = 26.2$ Å, $b = 11.8$ Å, $c = 7.9$ Å and $\gamma = 116°$. In agreement with the systematic absence of *hk0* reflections with $h = 2n + 1$ and 00*l* reflections with $l = 2n + 1$ the space group suggested was $P2_1/a$.

Some similarities between the X-ray diffraction pattern and the cell proposed for this clathrate form and those of the clathrates containing *o*-dichlorobenzene[5] and chlorobenzene[17] suggested that we were dealing with a α class clathrate form. Moreover the comparison between the experimental density (1.05 g/cm^3, determined by flotation) and the calculated ones for the crystalline phase assuming one guest molecule per chain (0.91 g/cm^3) or two (1.10 g/cm^3) indicated that each α class cavity was occupied by two guest molecules, as already found up to now only for the clathrate form containing chlorobenzene.[17]

Following this hypothesis, packing energy calculations were performed according to the space group $P2_1/a$. An asymmetric unit made of two monomeric units of s-PPMS (belonging to a left-handed chain) and one guest molecule was considered and, in the minimizations, the axes of the unit cell were kept constant. We started from an arrangement of the polymer chains as found for the structure of the s-PPMS/*o*-dichlorobenzene clathrate form.[5] The best models we found (almost isoenergetical, differing for less than 0.7 kcal/mol of asymmetric unit) are reported in Figure 3. It is apparent that the models of Figure 3, parts A and B, are very similar differing only for a little rotation of the polymer chains around their axis and for the arrangements of the guest molecules that are nearly related each other by a binary axis perpendicular to the chain axis along the $b + a/2$ direction (mindful of the s(2/1)2 minimum energy conformation of the polymer chain that is not kept in these models since minimizations have been performed according the $P2_1/a$ symmetry).

The fractional coordinates of the carbon and chlorine atoms of their asymmetric units are listed in Table 2.

In Figure 3, the nonbonded distances shorter than 3.6 Å are also shown. Among those, only one of nearly 3.4 Å (between a sp^2 and a sp^3 carbon atom) can be considered slightly short while all the others can be considered acceptable since they involve couples of sp2 carbon atoms belonging to almost parallel aromatic rings. Finally, all the nonbonded distances between atoms belonging to polymer helices are greater than 3.7 Å.

Structure factors calculations showed, for each one of the models of Figure 3, that none of them gave a good agreement between observed and calculated data. When a statistical combination of the two models was done, a good agreement was obtained only for the equatorial layer line reflections (the disagreement index R was 0.14) while the agreement on the layer lines remained very poor ($R > 0.30$).

Consequently, we considered the possibility of a disordered structure, in which polymer helices of a given chirality could be randomly substituted by others with opposite chirality. In this way, the equatorial projection of the structure would be

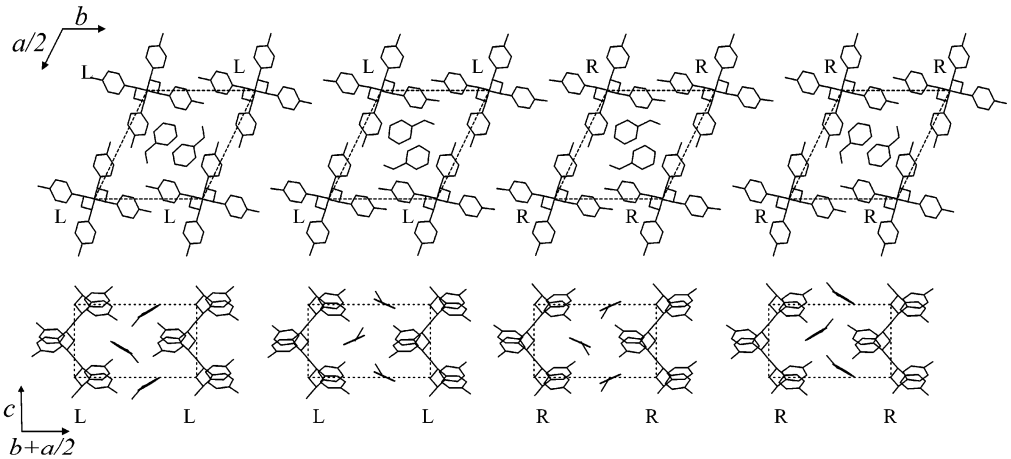

Figure 6. Packing models of minimum energy proposed for hypothetical ordered crystals of the s-PPMS/benzyl chloride clathrate containing only β class cavities according to $P2_1$ symmetry. These models have been obtained minimizing the energy in a unit cell obtained cutting by half the *a*-axis of the experimental unit cell. Along the $b + a/2$ direction, only one pair of isomorphous polymer chains are shown. R = right-handed and L = left-handed helices.

Table 3. Fractional Coordinates of the Atoms of a New Couple of Asymmetric Units (Indicated as Model 3A* and Model 3B*) Obtained Respectively from Those Presented in Table 2 (Indicated as Model 3A and Model 3B) by Applying a Mirror Plane and a Shift along the *c*-Axis as Described in the Text[a]

	model 3A*			model 3B*		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
C1	0.249	−0.003	0.956	0.250	0.998	1.029
C2	0.200	−0.026	0.831	0.201	0.982	0.906
C3	0.147	−0.048	0.931	0.149	0.967	0.455
C4	0.140	0.048	1.017	0.150	1.059	1.119
C5	0.091	0.025	1.103	0.102	1.043	1.211
C6	0.045	−0.095	1.109	0.051	0.935	1.192
C7	0.052	−0.191	1.027	0.050	0.844	1.077
C8	0.102	−0.168	0.940	0.098	0.860	0.985
C9	0.213	0.084	0.707	0.216	1.093	0.781
C10	**−0.009**	**−0.118**	**1.198**	**−0.001**	**0.918**	**1.293**
C11	0.238	−0.112	1.083	0.236	0.887	1.154
C12	0.226	−0.234	0.991	0.223	0.767	1.054
C13	0.264	−0.242	0.873	0.264	0.748	0.966
C14	0.253	−0.355	0.792	0.252	0.638	0.876
C15	0.204	−0.465	0.827	0.197	0.541	0.871
C16	0.166	−0.456	0.945	0.155	0.561	0.956
C17	0.177	−0.343	1.025	0.168	0.671	1.046
C18	**0.192**	**−0.587**	**0.739**	**0.184**	**0.421**	**0.776**
C19	*0.012*	*−0.394*	*0.685*	*0.040*	*0.528*	*0.311*
C20	*0.025*	*−0.277*	*0.614*	*0.089*	*0.519*	*0.363*
C21	*0.073*	*−0.221*	*0.511*	*0.126*	*0.611*	*0.474*
C22	*−0.011*	*−0.209*	*0.652*	*0.103*	*0.415*	*0.299*
C23	*0.047*	*−0.454*	*0.657*	*0.028*	*0.626*	*0.367*
C24	*0.095*	*−0.397*	*0.556*	*0.065*	*0.717*	*0.478*
C25	*0.108*	*−0.280*	*0.481*	*0.114*	*0.708*	*0.532*
Cl1	*−0.080*	*−0.286*	*0.556*	*0.088*	*0.298*	*0.458*

[a] Coordinates of guest molecules are reported in italics while those of the methyl groups of the polymer chains are in boldface type. Hydrogen atoms were included in the structure factors calculation, but they are omitted in this table for simplicity.

Table 4. Occupancy Factors Attributed to the Atoms of the Asymmetric Units Reported in Tables 2 and 3 (Corresponding to Two Left-Handed and to Two Right-Handed Chains with Their Respective Guests for the s-PPMS/Benzyl Chloride Clathrate Form) Used for the Generation of the Statistical Model with a Variable Percentage of L/R Error Described in the Text along with the Corresponding Fraction of Guest Molecules Arranged in β Class Cavities Generated by That Disorder in the Crystals

occupancy factor of the atoms of Table 2	occupancy factor of the atoms of Table 3	fraction of guest molecules arranged in b class cavities[a]
0.50	0.00	0.0
0.45	0.05	0.18
0.40	0.10	0.32
0.375	0.125	0.375
0.35	0.15	0.42
0.325	0.175	0.455
0.30	0.20	0.48
0.25	0.25	0.50

[a] The fraction of guest molecules arranged in α class cavities is, of course, the complement to one of this quantity.

kept unaltered (in order to save the good agreement obtained with the experimental data) while the layer lines structure factors would change.

In fact, for the particular arrangement of the chains found in the models presented before it is possible to demonstrate that the substitution of a chain of a given chirality with an enantiomorphous one is feasible, provided that the methyl groups of the polymer helices are left nearly in the same positions. In order to check the practicability of this kind of disorder, both its effect on the packing of the chains and on the arrangement of the guest molecules must be considered. As far as the first point is concerned, Figure 4 shows the packing of the chains in

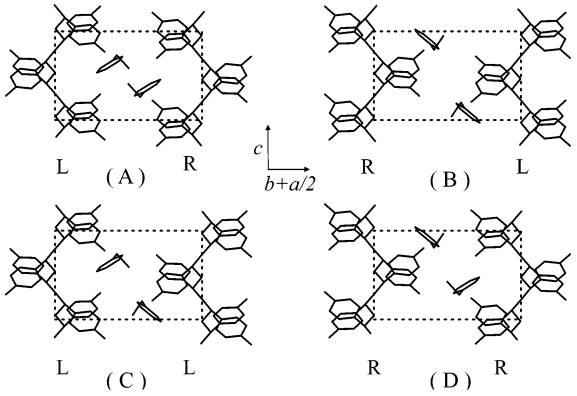

Figure 7. Schematic representation of the four possible statistically coexisting arrangements of a couple of polymer helices with their respective guest molecules that can be obtained considering only the asymmetric units indicated as model 3B (see Table 2) and model 3B* (see Table 3). In parts A and B are represented the possible α class cavities while in parts C and D the β class ones are shown. Analogous models can be obtained considering also the asymmetric units indicated as model 3A (see Table 2) and model 3A* (see Table 3). R = right-handed and L = left-handed helices.

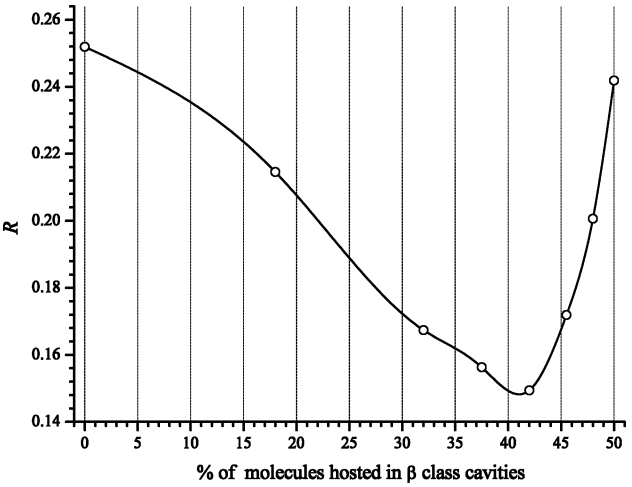

Figure 8. Trend of the discrepancy factor between observed and calculated structure factors (*R*) vs the percentage of molecules hosted in the β class cavities of the s-PPMS/benzyl chloride clathrate forms generated by the disorder described in the text.

the *bc* and *ac* layers for model of Figure 3A and that in the same layers when a right-handed helix is replaced by a left-handed one (keeping almost co-incident the positions of the methyl groups). It is apparent that after this substitution the packing is still very good, as shown by the shortest nonbonded distances between atoms belonging to adjacent chains. The same conclusions can be achieved if the model of Figure 3B is considered.

As far as the arrangement of the two guest molecules between the polymer chains along the $b + a/2$ direction in the unit cell is concerned, first of all it must be noted that if we consider a couple of adjacent chains along the $b + a/2$ direction, the substitution of a chain of a certain chirality with an enantiomorphous one (keeping almost co-incident the positions of the methyl groups of the helices) transforms the original α class cavities (delimited by two enantiomorphous helices) in a double number of β class ones (delimited by isomorphous polymer chains). This fact is shown in Figure 5 for a layer of LRLRL helices and the corresponding LRRRL one obtained by the introduction of a "wrong" chain in the third position.

Consequently the couples of benzyl chloride molecules related by an inversion center that were hosted in the original α class

Table 5. Comparison between Observed Structure Factors (F_o), Evaluated from the Intensities Observed in the X-ray Fiber Diffraction Pattern Shown in Figure 2, and Calculated Structure Factors for the Statistic of the Models Whose Asymmetric Units Are Reported in Tables 2 and 3 in the Space Group $P2_1/a$[a]

hkl	d_o (Å)	d_c (Å)	F_o	F_c	*hkl*	d_o (Å)	d_c (Å)	F_o	F_c	*hkl*	d_o (Å)	d_c (Å)	F_o	F_c
200	11.87	11.77	13	20										
010	10.40	10.61	89	23	211	4.98	5.05	39	24	102		3.90		18
$2\bar{1}0$		10.49		84 → 87	$4\bar{1}1$		5.02		11 → 27	$1\bar{1}2$		3.75		34
210	6.51	6.58	37	2	$2\bar{2}1$	4.62	4.73	107	10	202	3.75	3.74	99	33 → 91
$4\bar{1}0$		6.50		36 → 36	401		4.72		102	012		3.70		35
$2\bar{2}0$	5.87	5.90	82	67	$1\bar{2}1$		4.64		25 → 108	$2\bar{1}2$		3.70		67
400		5.89		46 → 82	$3\bar{2}1$		4.62		26	112		3.57		1
020	5.25	5.30	78	32	021	4.40	4.40	130	64	$3\bar{1}2$		3.56		19
$4\bar{2}0$		5.25		53 → 61	311		4.40		16	302	3.56	3.53	62	2 → 48
410	-	4.39	-	38	$4\bar{2}1$		4.37		108 → 132	212		3.39		37
220	-	4.20	-	41	$5\bar{1}1$		4.37		38	$4\bar{1}2$		3.37		23
$6\bar{2}0$	-	4.14	-	58						$2\bar{2}2$		3.28		22
600	3.92	3.92	85	67	121	4.06	4.07	54	28	402		3.28		74
$2\bar{3}0$		3.89		35 → 96	501		4.05		24 → 42	$1\bar{2}2$		3.25		2
$4\bar{3}0$		3.87		59	$5\bar{2}1$		4.03		21	$3\bar{2}2$	3.25	3.25	105	23
030	-	3.53	-	52	$6\bar{1}1$	-	3.81	-	45	022		3.17		66 → 117
$6\bar{3}0$	-	3.50	-	43	$6\bar{2}1$	-	3.67	-	80	312		3.17		5
420	3.24	3.29	47	33	$2\bar{3}1$	3.36	3.49	48	36	$4\bar{2}2$		3.16		39
$8\bar{2}0$		3.25		48	$4\bar{3}1$		3.48		64	$5\bar{1}2$		3.15		2
610		3.25		19 → 61	$1\bar{3}1$		3.38		12	412		2.94		5
$8\bar{1}0$		3.22		1	511		3.38		5	$6\bar{1}2$	2.93	2.93	48	17
$8\bar{3}0$	2.90	3.00	75	3	$5\bar{3}1$		3.36		20 → 78	222		2.88		29 → 38
$4\bar{4}0$		2.95		35	$7\bar{1}1$		3.36		1	$6\bar{2}2$		2.86		17
800		2.94		1	321		3.35		10	$3\bar{3}2$		2.79		6
$2\bar{4}0$		2.87		39	$7\bar{2}1$		3.32		5	602		2.78		46
$6\bar{4}0$		2.85		31 → 62	031	-	3.23	-	38	$2\bar{3}2$		2.77		20
101	7.56	7.49	17	12	701	3.01	3.09	43	16	$4\bar{3}2$		2.76		10
$1\bar{1}1$	6.37	6.56	52	4	131		3.04		7	$1\bar{3}2$	2.75	2.72	50	25
201		6.56		29	421		3.04		14	512		2.72		12 → 70
011		6.33		28 → 41	$7\bar{3}1$		3.01		9 → 50	$5\bar{3}2$		2.71		11
$2\bar{1}1$		6.31		2	$8\bar{2}1$		3.00		31	$7\bar{1}2$		2.70		34
111	5.75	5.75	76	66	611		3.00		29	322		2.70		13
$3\bar{1}1$		5.71		4 → 77	$8\bar{1}1$		2.98		5	$7\bar{2}2$		2.68		6
301		5.57		38										

[a] The Bragg distances, observed in the X-ray fiber diffraction pattern reported in Figure 2 and calculated for the proposed monoclinic unit cell ($a = 26.2$ Å, $b = 11.8$ Å, $c = 7.9$ Å, and $\gamma = 116°$), are also shown. Reflections not observed with F_c less than 30 have not been reported.

cavities must be "split" and arranged into new β class ones (being now related by a 2_1 axis).

The feasibility of this new arrangement of the guests was then checked through molecular mechanics calculations. To this aim we calculated the packing energy of an hypothetical clathrate form containing only β class cavities obtained by the arrangement of isomorphous helices according to the $P2_1$ space group in a unit cell with constants $a = 13.1$ Å ($a/2$ of the experimental cell proposed before), $b = 11.8$ Å, $c = 7.9$ Å and $\gamma = 116°$. The best models we obtained are represented in Figure 6. It is worth noting that these models are characterized by the same energy of those reported in Figure 3 and the four arrangements found for the guest molecules in their β class cavities do not differ significantly from the four found in the α class cavities of the models of Figure 3, since they derives mainly form the interactions between the guest molecules and their adjacent polymer chain (two arrangements for L chains and two for R ones, both nearly related by a binary axis

perpendicular to *c* parallel to the direction along which two helices delimit the cavities).

These results made us conclude that the hypothesized disorder was decidedly compatible with the models of Figure 3.

Once the feasibility of the considered disorder was verified, we calculated the agreement between experimental and calculated structure factors considering a whole series of models characterized by a different degree of L/R disorder assuming, for simplicity, that the overall $P2_1/a$ symmetry was kept. To this aim, first of all we generated from the two asymmetric units of the models of Figure 3 (reported in Table 2) a new couple of asymmetric units. The new fractional coordinates were obtained applying to those reported in Table 2 a mirror plane perpendicular to *c* (*x*, *y*, *z* became *x*, *y*, $-z$) and appropriately shifting them along the *c*-axis (of about *c*/2) in order to have that the fractional coordinates of the methyl groups of the polymer chains so generated would be practically the same of the enantiomorphous ones from which they were generated.

The fractional coordinates of this new couple of asymmetric units are listed in Table 3.

We then performed structure factors calculations in the space group $P2_1/a$ using as asymmetric unit the union of those reported in Tables 2 (corresponding to two left-handed chains and their guest molecules) and 3 (corresponding to two right-handed chains and their guest molecules). In this way it was possible to generate statistical models with a variable percentage of L/R errors simply attributing to the atoms of each couple of asymmetric units of Tables 2 and 3 a suitable occupancy factor.[22] In fact, by varying the occupancy factors, in each site the probability to find a left- or a right- handed helix is fixed. Consequently, the probability that a couple of adjacent polymer chains along the $b + a/2$ direction generate α or β class cavities can be determined. Table 4 lists the fraction of guest molecules in the crystals arranged in β class cavities (that is a quantity with a clear physical meaning) for models characterized by a different fraction of L and R chains in each site (corresponding to different occupancy factors for the atoms of the two couples of asymmetric units reported in Tables 2 and 3).

As far as the actual arrangements that can be found along the $b + a/2$ direction, in Figure 7 are reported as an example the four possible statistically coexisting arrangements of a couple of polymer helices with their respective guest molecules that can be found considering only the asymmetric units indicated as model 3B (see Table 2) and model 3B* (see Table 3). Each situation has a probability of being generated that depends on the occupancy factors attributed to the atoms of the two asymmetric units.

Figure 8 shows the plot of the *R* index vs the percentage of molecules hosted in β class cavities for the disordered models obtained attributing the occupancy factors as reported in Table 4. The lowest discrepancy factor was obtained for statistical models in which about the 40% of molecules are hosted in β class cavities.

Table 5 presents the comparison between calculated and observed structure factors (*R* index is 0.15) for the case in which the 42% of molecules are hosted in β class cavities (corresponding to an occupancy factor of the atoms belonging to the asymmetric units indicated as models 3A, 3B, 3A* and 3B* of 0.35, 0.35, 0.15, and 0.15 respectively).

Conclusions

In the present paper, the crystal structure of the clathrate form of s-PPMS containing benzyl chloride is presented. This molecular complex represents, to our knowledge, the first case of a polymeric clathrate form in which in the same crystal are present two kinds of cavities having different shape and dimensions: α class cavities (containing two guest molecules) and β class cavities (containing one guest molecule). The contemporaneous presence of these two types of cavities is originated by a disorder in the arrangement of right- and left-handed helices in the crystals. The practicability of this disorder is related to the particular staggered layout of the layers of chains containing the cavities and to the fact that α class cavities are able to contain two guest molecules.

It is worth noting that these conditions have already been found in the crystal structures of other clathrate forms of s-PPMS, in particular for the crystal structure of the molecular complex containing chlorobenzene[17] (an α class clathrate contain two guest molecules per cavity) and for all the known orthorhombic β class clathrate forms of this polymer (containing benzene,[6] CS_2[7] and toluene).[17] All these structures are compatible with the L/R disorder described in the present paper but, for all of them, a good agreement between experimental and calculated structure factors was obtained without introducing it. Moreover, the cases of the s-PPMS/chlorobenzene and s-PPMS/toluene molecular complexes, whose isoenergetical structures have been recently presented by some of us[17] and that include molecules having the same shape and dimensions, by the light of the new structural data presented in this paper, could be the two extreme "limit ordered" cases of a series of disordered crystals ranging from a complete α class to a full β class clathrate structure. Further studies are in progress in order to demonstrate if it is possible to obtain samples of those clathrate forms characterized by this kind of disorder by varying the experimental conditions in which they are obtained.

It is worth noting that a similar arrangement of the polymer chains favorable to this kind of disorder has already been found also for the form I of syndiotactic polybutene, for which beside a limit ordered modification in which helices of the same chirality are packed in the unit cell (as found for the orthorhombic β class clathrate forms of s-PPMS), disordered structure characterized by a statistical substitution of right- and left-handed helices in the lattice positions have been found.[23]

Finally, also the possibility to host in the crystals of these molecular complexes two guest molecules of different dimension is under consideration.

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References and Notes

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