Crystal Structure of the Clathrate Form of Syndiotactic Poly(*p*-methylstyrene) Containing Benzene

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ABSTRACT: The crystal structure of the β class clathrate of syndiotactic poly(*p*-methylstyrene) containing benzene is presented and compared to that of the clathrate containing tetrahydrofuran, also belonging to the β class. The structure is characterized by polymer chains, in **s**(2/1)2 helical conformation, and benzene molecules packed in an orthorhombic unit cell with axes $a = 19.5$ Å, $b = 13.3$ Å, and $c = 7.7$ Å, according to the space group $C222_1$. The calculated crystalline density is 1.05 g/cm^3 for two polymer chains (eight monomer units) and four benzene molecules included in the unit cell. Our analysis affords an insight into the structural features typical of the β class clathrates. As in the packing model proposed for the crystal structure of the s-PPMS clathrate containing tetrahydrofuran, the guest molecules occupy cavities delimited by isomorphic helices along the *b* axis and are related by the crystallographic 2-fold screw axis of the unit cell. The packing of the helices along the *a* axis is, instead, completely different in the two structures. *bc* layers of isochiral chains alternate with *bc* layers of chains having opposity chirality in the model proposed for the tetrahydrofuran clathrate. A new and unusual example of *chiral* crystalline phase, in which all the polymer helices assume the same chirality in the lattice, is proposed for the crystal structure of the benzene clathrate.

Introduction

Syndiotactic poly(*p*-methylstyrene) (s-PPMS) presents a very complex polymorphism. In fact, four different crystalline forms (named forms I, II, III, and V) and a mesomorphic form (form IV) have been found so far.[1−4] Moreover, s-PPMS shows the interesting property to cocrystallize with low molecular weight substances forming polymeric clathrates.[5−7] In this respect s-PPMS is very similar to syndiotactic polystyrene (s-PS) for which some possible applications like, for instance, chemical separation and water or air purification from organic molecules, have been recently pointed out.[8]

On the other hand, unlike the s-PS clathrates, for which only one kind of structure has been hypothesized,[9−11] the s-PPMS clathrates have been divided in two different classes (α and β). This classification was made on the basis of qualitative differences and similarities between their X-ray diffraction patterns and their different behavior with respect to suitable treatments involving the removal of the guest molecules (e.g., annealing and/or acetone treatments).[5]

α class clathrates are obtained by ortho-substituted aromatic molecules, like *o*-dichlorobenzene, *o*-xylene, *o*-chlorofenol, and *N*-methyl-2-pyrrolidone; β class clathrates, instead, are obtained by smaller cyclic molecules, not substituted or monosubstituted, like tetrahydrofuran, benzene, cyclohexane, cyclohexanone, and 1,4-dioxane. The crystal structures of the clathrate forms containing *o*-dichlorobenzene and tetrahydrofuran, belonging to the α and β class, respectively, have been recently solved.[6,7] Remarkable differences in the proposed packing models, due to the different size and steric hindrance of the two guest molecules, have been found and pointed out.[6,7,12] In the present paper a model of packing for the crystal structure of the s-PPMS clathrate containing benzene, belonging to the β class, is proposed on the basis of X-ray diffraction analyses, packing energy, and structure factors calculations. (A preliminary structural model of this clathrate was suggested by us in ref 12.)

Our data not only affords an insight in structural features typical of the β class clathrates of s-PPMS but also provide an example, quite rare in polymers, of crystal structure characterized by a packing of helices having the same chirality.

Experimental Part and Calculation Method

s-PPMS was synthesized in our laboratories with a homogeneous catalytic system based on tetrabenzyltitanium and methylalumoxane following the procedure described in ref 1. The polymer fraction insoluble in 2-butanone was used. The syndiotacticity of the polymer was evaluated by ^{13}C NMR; the fraction of *rrrr* pentads was higher than 95%.

Unoriented films of the s-PPMS clathrate containing benzene were obtained by casting at room temperature from 10 wt % benzene solutions. Oriented samples were obtained by exposing s-PPMS fibers in the mesomorphic form IV to benzene vapors for 24 h, keeping fixed the ends of the specimen. Fibers of the mesomorphic form IV were obtained by stretching at 130 °C films of s-PPMS in form I, prepared by casting at 50 °C from 10 wt % toluene solutions. The drawing procedures were performed with a miniature mechanical tester apparatus (Minimat by Reometrics Scientific) at a drawing rate of 2−3 mm/min and with an initial gauge length of 10 mm.

The X-ray fiber diffraction patterns were obtained on a Bas-MS imaging plate (FUJIFILM) with a cylindrical camera (radius 57.3 mm, nickel-filtered Cu Kα radiation monochromatized with a graphite crystal) and processed with a digital scanner equipment (FUJ-BAS 1800).

The 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 $B = 8$ Å^2 and atomic scattering factors of ref 13 were used. The observed structure factors F_o were evaluated from the intensities (I_o) of the

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reflections observed in the X-ray fiber diffraction pattern as $F_o = (I_o/Lp)^{1/2}$, where Lp is the Lorentz polarization factor for X-ray fiber diffraction:

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

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 is the wavelength of the used radiation (1.5418 Å). The observed intensities, I_o, were evaluated integrating the crystalline peaks observed in the X-ray diffraction profiles read along the 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 directions normal and parallel to the chain axis, different factors have been used to scale the observed and calculated structure factors on the different layer lines. The agreement factor (R) has been evaluated as

$$R = \sum |F_o - F_c| / \sum F_o$$

The packing energy calculations were limited to the calculation of the interaction energy of a single benzene molecule with the closest s-PPMS chain. In fact, the positioning of the polymer chains in the cell was univocally fixed by the symmetry of the space group and by the requirement to have cavities where the guest molecules could be collocated.

The interaction energy of the guest molecule with the closest s-PPMS chain was calculated as half the sum of the interaction energies between the atoms of a benzene molecule and all the atoms of the polymer chain. The Lennard-Jones potential function, $E(r) = A/r^{12} - B/r^6$, up to distances r twice the van der Waals distances for each considered pair of atomic species, with the parameters reported by Flory,[14] and taking the methyl group as single rigid unit,[15] was used. The conformation of the s-PPMS polymer chains and hence the value of the c axis were kept constant in the calculations and equal to those used in ref 7.

Results and Discussion

Unit Cell, Benzene Content, and Space Group Determination. The X-ray fiber diffraction pattern of the s-PPMS clathrate containing benzene is reported in Figure 1. All the reflections observed in the fiber pattern are listed in Table 1 and are compatible with an orthorhombic unit cell with constants $a = 19.5$ Å, $b = 13.3$ Å, and $c = 7.7$ Å.

Thermogravimetric measurements on freshly prepared powder samples in the clathrate form, showing a crystallinity index of about 50−60%, indicate an amount of solvent, in the semicrystalline sample, of about 19 wt %. On the basis of these experimental data, we assumed a molar ratio monomer/benzene, in the crystalline phase, close to 2. As a consequence, the calculated crystalline density is 1.05 g/cm^3, assuming two **s**(2/1)2 polymer chains and four benzene molecules per unit cell. This value is in good agreement with the experimental density (1.02 g/cm^3) measured by flotation, on freshly prepared unoriented clathrate samples.

The observed reflections can be indexed according to the systematic absence of hkl reflections with $h + k = 2n + 1$. Consequently, assuming the maintenance in the lattice of all the symmetry elements of the s-PPMS **s**(2/1)2 chains, the only compatible space group is $C222_1$.

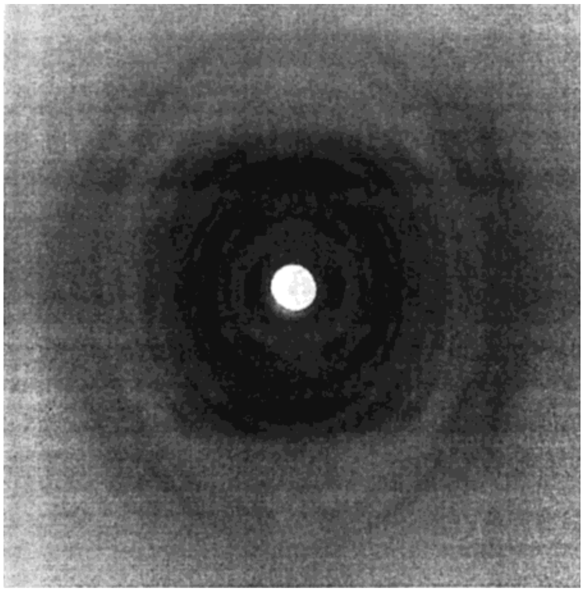

Figure 1. X-ray fiber diffraction pattern of the clathrate of s-PPMS containing benzene.

Table 1. Diffraction Angles (2ϑ), Bragg Distances (*d*), 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 Clathrate Containing Benzene of Figure 1

2ϑ (deg)	*d* (Å)	*l*	I_o (AU)
8.05	10.98	0	888
9.25	9.56	0	1568
13.55	6.53	0	426
16.45	5.39	0	820
20.75	4.28	0	251
22.75	3.91	0	131
23.95	3.72	0	64
28.25	3.16	0	153
34.2	2.62	0	51
39.4	2.29	0	46
13.9	6.37	1	1493
17.6	5.04	1	1868
19.3	4.60	1	3583
21.6	4.11	1	935
26.6	3.35	1	272
29.2	3.06	1	90
30.5	2.93	1	43
32.9	2.72	1	59
24.8	3.59	2	3319
27.8	3.21	2	637
29.5	3.03	2	102
32.8	2.73	2	185
40.3	2.24	2	221
45.7	1.99	2	123

Packing Model and Structure Factor Calculations. With the assumption of maintenance of all the symmetry elements of the s-PPMS **s**(2/1)2 chain as crystallographic elements, in the space group $C222_1$ there are only two different ways to pack the chains in the unit cell, which differ from each other for a rotation by 90° of the chains around their axes and a translation along z of $^1/_4c$. For only one of these, whose ab projection is reported in Figure 2, a good packing of the only chains is achieved, and there is plenty of space along the b axis for the inclusion of two molecules of benzene. In fact, in this model carbon atoms belonging to adjacent polymer chains come into contact to the van der Waals distances along the diagonal directions (the shortest distance being 3.7 Å, see Figure 2), whereas they are loosely packed along the b axis where the guest mol-

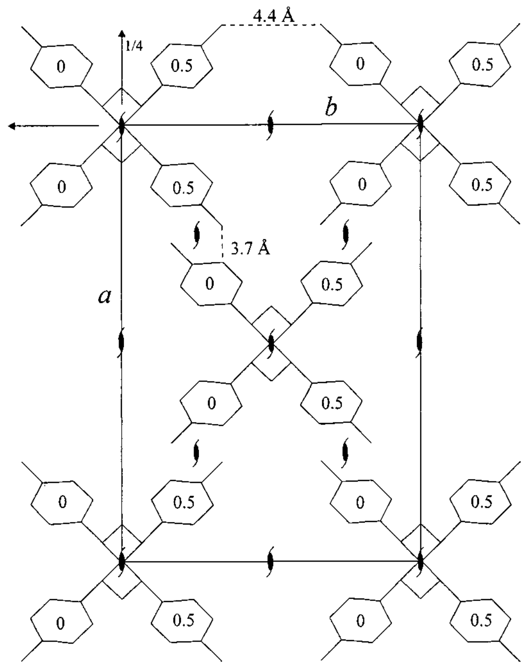

Figure 2. *ab* projections of the packing model of the s-PPMS chains in the orthorhombic cell ($a = 19.5$ Å, $b = 13.3$ Å, and $c = 7.7$ Å) according to space group $C222_1$. The shortest carbon−carbon distances between adjacent chains along *b* and ($a + b$) directions are indicated. Only some crystallographic symmetry elements of the space group are shown. The approximate *z/c* fractional coordinates of the barycenters of the phenyl rings are also shown.

ecules should be allocated (the shortest distance being 4.4 Å, see Figure 2).

The precise position of the guest molecules inside the unit cell was found through calculations of the interaction energy between a single benzene molecule and the closest s-PPMS chain, as in the case of clathrate containing tetrahydrofuran,[7] assuming that the benzene molecule is positioned with one of its 2-fold axes coincident with a crystallographic 2-fold axis perpendicular to the s-PPMS chain axes.

Since the benzene molecule has two kinds of 2-fold axes, one crossing opposite carbon atoms and one crossing opposite bonds of the molecule, in the calculations two different orientations of the benzene molecule with respect to the polymer chain, shown in Figure 3A,B, were considered. In both cases the energy was minimized with respect to the distance (y) between the barycenter of the benzene molecule and the X axis and the rotation angle (φ, positive for a clockwise rotation) of the benzene molecule around its 2-fold axis ($\varphi = 0$ when the plane of benzene molecule is parallel to the xy plane, as in Figure 3).

The absolute minimum of the nonbonded energy was found when the 2-fold axis crossing opposite bonds of the benzene molecule is coincident with the 2-fold axis of the s-PPMS **s**(2/1)2 chain (as in Figure 3B) for $y = 4.75$ Å and $\varphi = 173°$. When the benzene molecule is oriented as in Figure 3A, an energy minimum at 3.8 kJ/mol higher was found, for $y = 5.15$ Å and $\varphi = 0°$. For both minima the shortest distances between carbon atoms of the benzene molecule and the polymer chain are in the interval 3.5−3.7 Å.

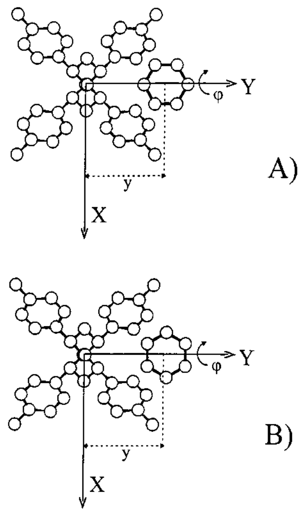

Figure 3. Two different possible orientations of the benzene molecules respect to the polymer chains: the 2-fold axis of the s-PPMS chain, perpendicular to the chain axis, is coincident to the 2-fold axis crossing opposite atoms (A), opposite bonds (B) of the benzene molecule. The variables used in the calculation of the interaction energy between a benzene molecule and the closest polymer chain along the *b* axis are also defined. y is the distance between the chain axis and the barycenter of the benzene molecule, and φ is the angle of rotation (positive for a clockwise rotation) of the benzene molecule around its 2-fold rotation axis.

In the complete packing models, comprising s-PPMS chains and guest molecules, obtained by positioning the benzene molecules as in the two previously calculated energy minimum situations, the carbon atoms of the benzene molecule come into contact with the carbon atoms of the opposite polymer chain along the *b* axis at van der Waals distances ≥ 3.7 Å realizing a close packing, when the benzene is oriented as in Figure 3B, whereas some distances are less than 3.5 Å in the situation corresponding to Figure 3A. As far the benzene−benzene interactions all the distances between carbon atoms are greater than 4 Å. The model of packing corresponding to the energy minimum of the case of Figure 3B is reported in Figure 4A,B.

Structure factor calculations performed on the model of Figure 4A,B according to the space group $C222_1$ showed a satisfactory agreement with the experimental intensities observed in the X-ray fiber diffraction pattern of Figure 1. Structure factor calculations were performed also for the packing model corresponding to the minimum of energy found when the benzene molecule is oriented as in Figure 3A, but no significant changes were obtained. Hence, the packing model of the clathrate of s-PPMS containing benzene which we propose corresponds to that reported in Figure 4A,B.

It is evident from Figure 4A,B that the benzene molecules are positioned into cavities formed by four phenyl rings belonging to the same s-PPMS helix, as in the model of packing proposed for the crystal structure of the clathrate containing tetrahydrofuran, shown for comparison in Figure 4C,D.

The fractional coordinates of the carbon atoms of an asymmetric unit in the model of Figure 4A,B are listed in Table 2. Table 3 compares the calculated and the observed structure factors; the final discrepancy factor R, calculated taking into account only the observed reflections, is 16%.

Concluding Remarks

The crystal structure of the clathrate of s-PPMS containing benzene has been determined through analysis of the X-ray diffraction patterns of oriented samples

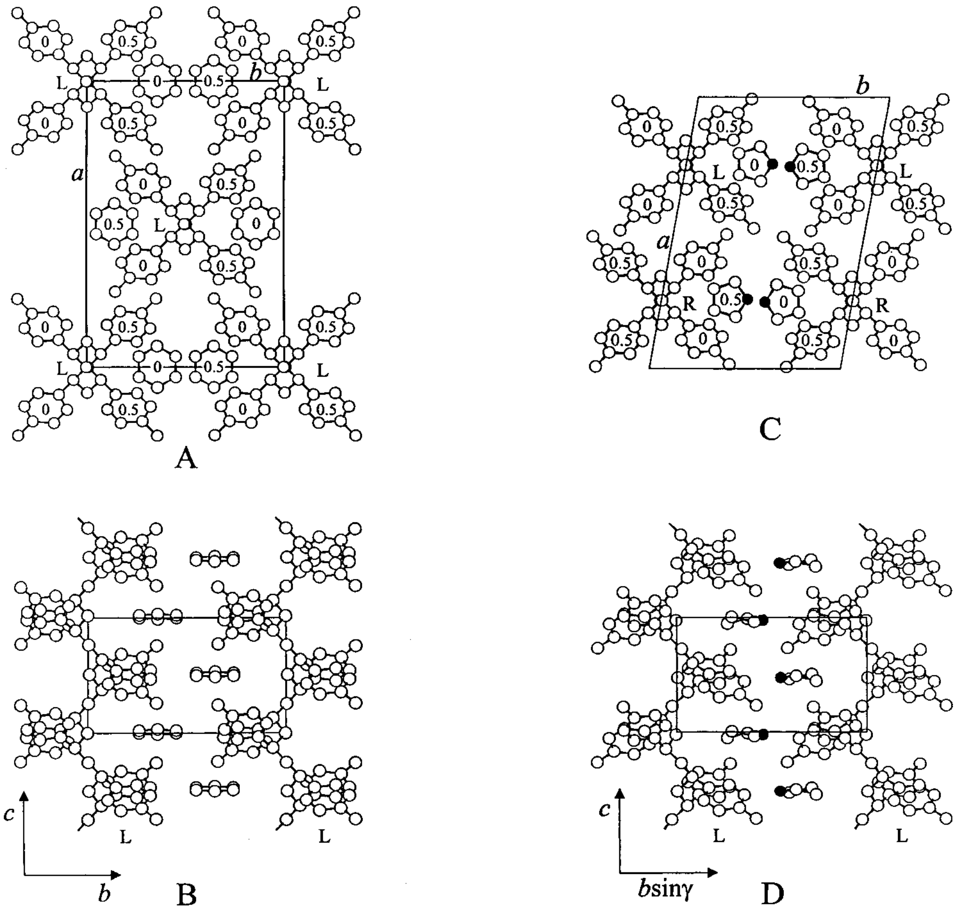

Figure 4. Packing model proposed for the crystal structure of the s-PPMS clathrate containing benzene, in the space group $C222_1$: *ab* projection (A), *bc* projection (B). The packing model proposed in ref 7 for the crystal structure of the clathrate containing tetrahydrofuran, in the space group $P2_1/a$, is also reported for comparison: *ab* projection (C), *bc* sin γ projection (D). The approximate *z*/*c* fractional coordinates of the barycenters of the phenyl rings are also shown. R = right-handed, L = left-handed helices. In B and D only a couple of polymer chains along the *b* axis are reported.

Table 2. Fractional Coordinates of the Atoms of an Asymmetric Unit in the Model of Figure 4 for the s-PPMS Clathrate Containing Benzene

	x/*a*	*y*/*b*	*z*/*c*
C1	0.000	0.004	0.500
C2	−0.043	0.067	0.374
C3	−0.090	0.136	0.470
C4	−0.084	0.240	0.449
C5	−0.128	0.304	0.539
C6	−0.178	0.265	0.648
C7	−0.184	0.161	0.669
C8	−0.140	0.097	0.580
C9	−0.226	0.335	0.745
C10	−0.036	0.450	−0.011
C11	−0.072	0.357	−0.022
C12	−0.036	0.265	−0.011

and packing energy and structure factors calculations. Two s-PPMS polymer chains in the **s**(2/1)2 helical conformation and four benzene molecules are packed in an orthorhombic unit cell, according to the symmetry of the space group $C222_1$. The unit cell parameters are $a = 19.5$ Å, $b = 13.3$ Å, and $c = 7.7$ Å, and the calculated crystalline density is 1.05 g/cm^3. This is in reasonable agreement with the experimental density of 1.02 g/cm^3, measured on freshly prepared semicrystalline clathrate samples.

The s-PPMS clathrate with benzene, together with those containing tetrahydrofuran, cyclohexane, cyclohexanone, and 1,4-dioxane, presents similar X-ray powder diffraction patterns and similar behaviors respect to annealing procedures and/or treatments with acetone, which induce the removal of the guest.[5] On the basis of these experimental observations, these clathrates were grouped and assigned to the β class clathrates. Moreover, some structural analogies were only indirectly supposed.

Figure 4C,D shows the *ab* and *bc* sin γ projections of the packing model proposed in ref 7 for the crystal structure of the s-PPMS clathrate containing tetrahydrofuran. The comparison with the proposed crystal structures of clathrate with benzene (Figure 4A,B) permits to understand in detail the typical structural features of the β class clathrates. Indeed, in these structures the cavities hosting the guest molecules are formed by two isochiral **s**(2/1)2 helices and are located around the crystallographic 2-fold screw axes. Although the shape and the geometry of the cavities in the crystalline phase of the clathrates containing tetrahydrofuran and benzene are very similar, an impressive change in the packing of the helices along *a* axis occurs. In fact, in the packing model proposed for the crystal structure of clathrate with benzene layers of isochiral chains, parallel to the *bc* plane, are piled along the *a* axis with layers of chains having the same chirality. In the model proposed for the crystal structure of the clathrate containing tetrahydrofuran, instead, *bc* layers of isochiral chains alternate along *a* axis with layers of chains of opposite chirality.

Table 3. Comparison between the Calculated Structure Factors (F_c) for the Model of the s-PPMS Clathrate Containing Benzene of Figure 4 and the Observed Structure Factors (F_o) Evaluated from the Intensities of the Experimental Reflections of the X-ray Fiber Diffraction Pattern of Figure 1

hkl	d_{obs} (Å)	d_{calc} (Å)	F_c		F_o
110	10.98	10.98	78.6		80.6
200	9.56	9.75	109.0		114.8
020	6.53	6.65	92.5		72.7
310		5.84	31.1		
220	5.39	5.49	101.1		111.6
400		4.87	33.7		
130	4.28	4.32	57.7		69.7
420	3.91	3.93	67.0		52.9
510	3.72	3.74	19.6	31.9	38.0
330		3.66	25.2		
040		3.33	13.0		
600		3.25	21.0		
240	3.16	3.14	68.2		64.5
440		2.78	39.3		
710		2.73	27.2		
150	2.62	2.64	40.7		41.5
350		2.46	52.4		
800		2.44	40.8		
640	2.29	2.32	35.2	47.6	42.7
820		2.29	32.0		
111	6.37	6.30	69.3		99.6
201		6.04	33.7		
021	5.04	5.03	146.2		147.3
311	4.60	4.65	167.5	205.7	220.8
211		4.47	119.4		
401	4.11	4.12	140.7		123.1
421		3.50	38.7		
511	3.35	3.36	88.3	103.6	76.5
331		3.31	54.1		
041	3.06	3.05	47.0		46.9
601	2.93	2.99	5.5	35.0	33.3
241		2.91	34.5		
531	2.72	2.74	23.0	62.9	42.9
621		2.73	58.4		
112	3.59	3.63	89.1	170.0	167.7
202		3.58	144.7		
022		3.33	24.7		
312	3.21	3.21	41.9	63.5	104.2
222		3.15	47.7		
402	3.03	3.02	36.3		45.9
132		2.87	13.1		
332		2.65	8.4		
422	2.73	2.75	96.7	118.6	70.6
512		2.68	68.8		
042		2.52	12.8		
602		2.48	16.0		
242		2.43	17.5		
532		2.33	21.7		
622		2.32	62.4		
442	2.24	2.23	65.4	79.8	94.0
712		2.22	45.8		
152		2.17	29.4		
352		2.07	33.3		
802		2.06	9.1		
732	1.99	2.01	55.9	79.0	77.8
642		1.99	54.4		
822		1.97	12.8		

The differences observed in the crystal structures of the two clathrates could be a further effect of the guest molecules, in addition to those which determine the belongings to the α and β classes.[12] In fact, the increased size of the benzene respect to the tetrahydrofuran molecule induces an increase of the distance between two adjacent s-PPMS chains along the *b* axis ($b_{tetrahydrofuran}$ = 12.7 Å, $b_{benzene}$ = 13.3 Å) and, consequently, could influence the packing of the chains along the direction of the *a* axis.

Moreover, it is worth noting that the crystal structure here proposed for the s-PPMS clathrate containing benzene represents a new unusual example of *chiral* crystalline phase in which the polymer helices assume all the same chirality in the lattice although helices of opposite chirality have the same energy.

Finally, we want to point out that at least other two syndiotactic polymers, the syndiotactic polypropylene[16] and syndiotactic poly-1-butene,[17] both presenting a complex polymorphism as s-PPMS, can crystallize in forms characterized by an isochiral packing of **s**(2/1)2 helices, and in both cases the proposed space group is $C222_1$, analogous to the s-PPMS clathrate with benzene.

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