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Crystal Structure of the Clathrate Form of Syndiotactic Poly(*m*-methylstyrene) Containing Carbon Disulfide

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ABSTRACT: The crystal structure of the clathrate form of syndiotactic poly(*m*-methylstyrene) containing carbon disulfide is presented. The structure is characterized by polymer chains in **s**(2/1)2 helical conformation and CS_2 molecules packed in an orthorhombic unit cell with axes $a = 17.8$ Å, $b = 13.1$ Å, and $c = 7.8$ Å, according to the space group *Pcaa*. The calculated crystalline density is 1.14 g/cm^3 for two polymer chains (eight monomer units) and four carbon disulfide molecules included in the unit cell. As in the packing model proposed for the crystal structures of the β class of the syndiotactic poly(*p*-methylstyrene) clathrates, the guest molecules occupy cavities delimited by isomorphous 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, instead, is similar to the close packing realized by the chains only in the clathrates and in the δ form of syndiotactic polystyrene.

Introduction

Recently, homogeneous catalytic systems, based on titanium or zirconium compounds and methylalumoxane, have allowed producing highly syndiotactic polystyrene (s-PS)[1] and substituted polystyrenes.[2] Some of these polymers have shown the interesting property of cocrystallizing with low molecular weight substances to form polymeric clathrates.

Clathrate structures have been first described for s-PS,[3] and the crystal structure of the clathrate forms containing toluene,[4] iodine,[5] and 1,2-dichloroethane[6] have been completely characterized. Moreover, for this polymer some promising applications have been suggested in the field of chemical separations, in particular for water or air purification from volatile organic compounds.[7] This possibility is mainly due to the existence of the δ crystalline form,[8] which is nanoporous and can be obtained by removal of guest molecules from clathrate samples by suitable solvent treatments.[9]

Subsequently, other syndiotactic styrenic polymers, such as *p*-methylstyrene (s-PPMS)[10−12] and *m*-methylstyrene (s-PMMS),[13] have been studied, and their property of cocrystallizing with low molecular weight compounds to give clathrate structures has been also pointed out. Up to now, detailed crystalline structures of clathrate forms of s-PPMS including tetrahydrofuran (THF),[14] *o*-dichlorobenzene (*o*-DCB),[15] and benzene[16] have been described, while no crystalline structure of s-PMMS clathrate forms has been proposed yet.

Obtaining clathrate forms has been also considered for co-syndiotactic copolymers of styrene and other substituted styrenic monomers, such as *p*-methylstyrene,[17] in order to modulate the dimension of the cavity in which guest molecules are hosted as a function of the copolymer composition.

A common feature of all the clathrate forms that have been studied is that the polymer chains assume the same **s**(2/1)2 helical conformation, with a repetition period of 7.7−7.8 Å. As far as the shape of the cavity is concerned, structural studies on the clathrate forms of s-PS and s-PPMS indicate that two different types of cavity containing guest molecules are possible.[18] In the case of s-PS,[4−6] only one kind of centrosymmetric cavity delimited by eight benzene rings of two enantiomorphous adjacent polymer chains has been found. In the case of s-PPMS, instead, in addition to the formerly described cavity (proposed for the clathrate form of s-PPMS with *o*-DCB[15]), a different type of cavity has been found for THF[14] and benzene[16] clathrates, in which cavities are arranged around 2-fold screw axes of the lattice and delimited by four benzene rings of one polymer chain and two benzene rings of the adjacent isomorphous one. Consequently, the terms α class and β class have been introduced in order to differentiate clathrate forms containing the first type of cavity from those containing the second type.[12]

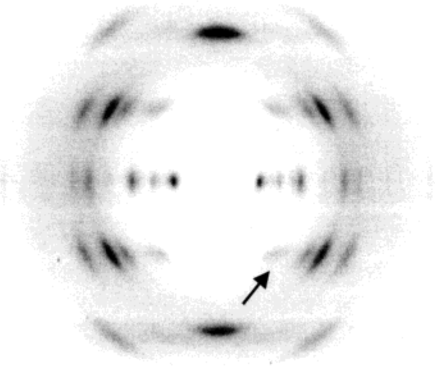

Figure 1. X-ray fiber diffraction pattern of the clathrate form of s-PMMS containing carbon disulfide. Small amounts of form I are revealed by the reflections at $2\theta = 15.1°$ (indicated by an arrow) on the first layer line corresponding to the strongest reflections of that form, whose spectrum is reported in ref 13.

In this paper, for the first time, the crystal structure of a clathrate form of s-PMMS is presented. Our aim is to make a comparison between the clathrate structure of this homopolymer with those of s-PS and s-PPMS, also in order to allow the analysis of the influence of *m*-methylstyrene comonomeric units in co-syndiotactic copolymers with styrene.

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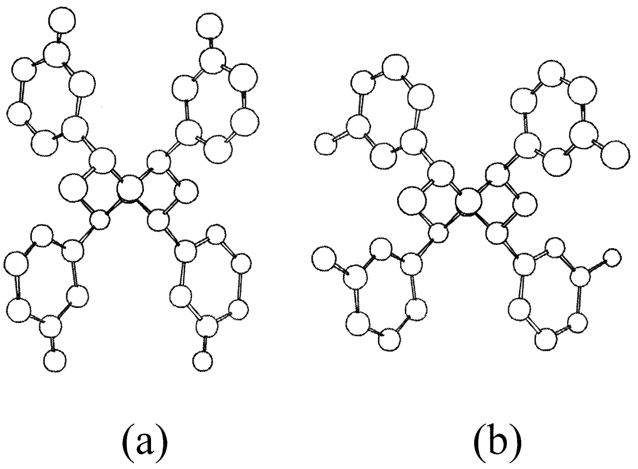

Figure 2. Two possible conformers of the s-PMMS helical chains with symmetry **s**(2/1)2.

Experimental Part and Calculation Methods

s-PMMS was prepared using an homogeneous catalytic system based on pentamethylcyclopentadienyltitanium trichloride (Cp*TiCl$_3$) and methylalumoxane (MAO) in toluene according to the procedure described in ref 13. The syndiotacticity of the insoluble fraction in 2-butanone determined by ^{13}C NMR was very high ([*rrrr*] > 95%).

Table 1. Diffraction Angles (2θ), Bragg Distances (d_{obs}), and Intensities (I_{obs}) in Arbitrary Units (AU) of the Reflections Observed on the Layer Lines (l) of the X-ray Fiber Diffraction Pattern of the Clathrate Form of s-PMMS Containing Carbon Disulfide of Figure 1

l	2θ (deg)	d_{obs} (Å)	I_{obs} (AU)	l	2θ (deg)	d_{obs} (Å)	I_{obs} (AU)
0	6.82	13.0	4394	1	18.2	4.87	1598
0	10.0	8.85	1107	1	20.2	4.40	4602
0	12.4	7.14	3856	1	23.6	3.77	1823
0	13.4	6.61		1	28.8	3.10	269
0	16.8	5.28	564	1	39.5	2.28	335
0	20.2	4.40	2693	2	24.7	3.60	631
0	22.7	3.92	1215	2	26.4	3.38	249
0	27.0	3.30	266	2	28.3	3.15	1892
0	28.8	3.10	266	2	30.7	2.91	306
0	30.7	2.91	87	2	33.1	2.71	203
0	33.8	2.65	652	2	37.1	2.42	102
0	40.6	2.22	187	2	41.4	2.18	462
1	14.2	6.24	1077	2	43.7	2.07	236

Unoriented samples of s-PMMS clathrate containing carbon disulfide were obtained by swelling at room temperature amorphous specimens prepared in a hot press by melting as-prepared samples at 225 °C and successive quenching in ice−water. Oriented clathrate specimens were obtained by swelling fibers, in the mesomorphic form III, into CS$_2$ for 48 h, keeping fixed the ends of the specimen. Fibers of the mesomorphic form III were obtained by drawing amorphous samples with a miniature mechanical tester apparatus (Reometric Scientific Minimat) at a drawing rate of 10 mm/min at a temperature in the range 85−90 °C.

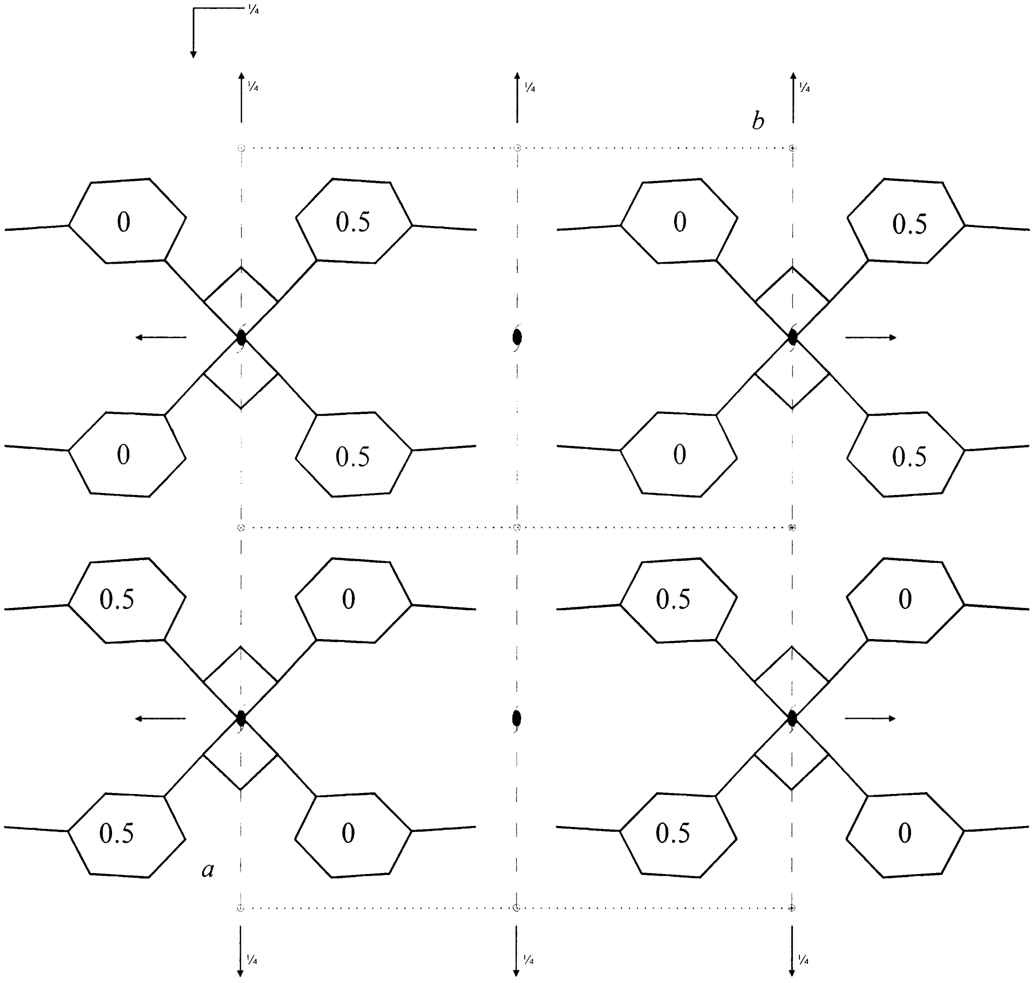

Figure 3. *ab* projection of the packing model of the s-PMMS chains according to space group *Pcaa*. The crystallographic symmetry elements of the space group are shown. The approximate *z*/*c* fractional coordinates of the barycenters of the phenyl rings are also shown.

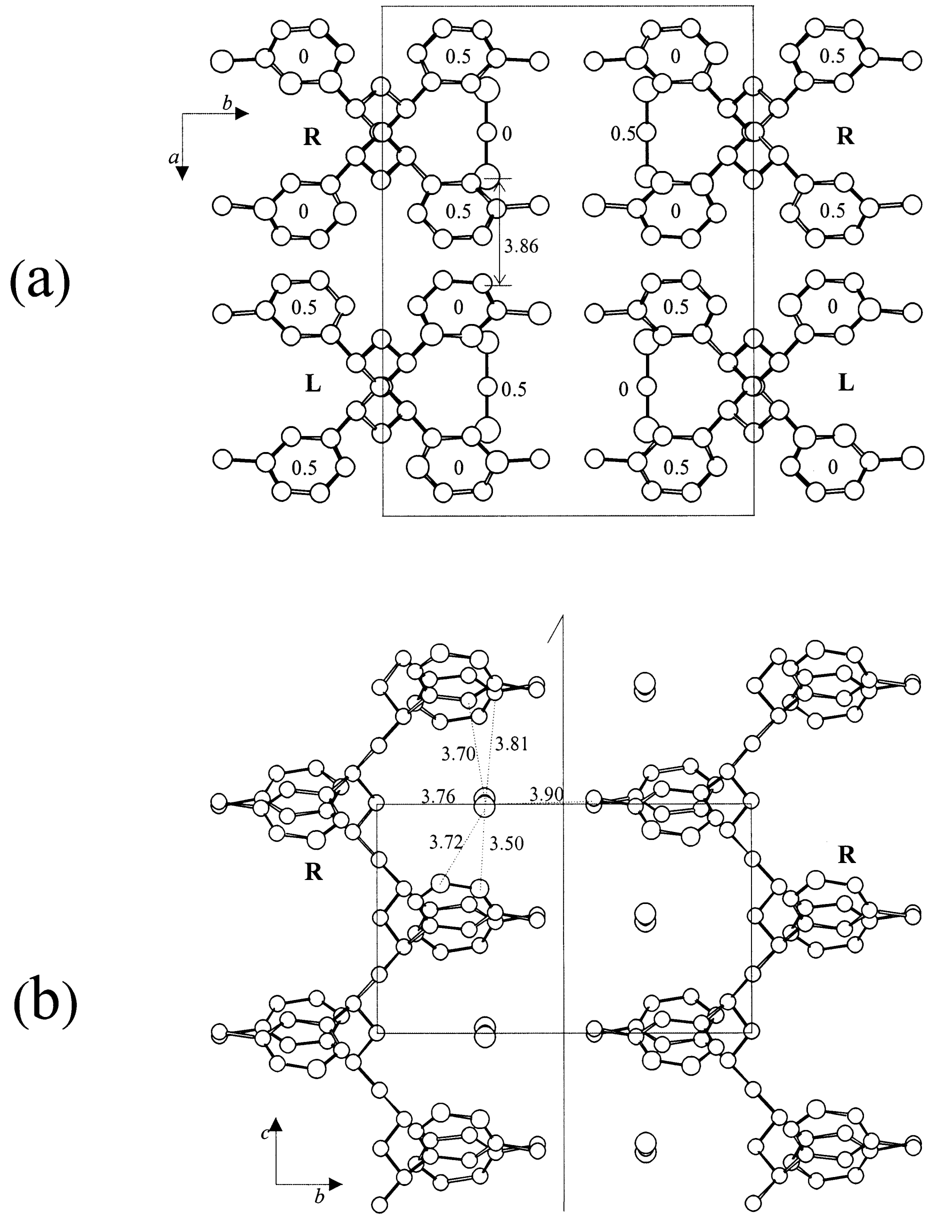

Figure 4. Packing model proposed for the crystal structure of the s-PMMS clathrate containing carbon disulfide, in the space group *Pcaa*: *ab* projection (a) and *bc* projection (b). The approximated *z*/*c* fractional coordinates of the barycenters of the phenyl rings are shown. R = right-handed, L = left-handed helices. The shortest nonbonded distances (less than 4.0 Å) are indicated. In (b) only a couple of polymer chains, along the *b* axis, are reported.

The oriented clathrate samples were sealed in a Lyndemann glass capillary soon after swelling in order to avoid the removal of the solvent that would cause them to transform rapidly into form I.

Wide-angle X-ray diffraction patterns of unoriented samples were obtained with nickel-filtered Cu Kα radiation with an automatic Philips powder diffractometer.

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 $F_{\mathrm{calc}} = (\sum|F_i|^2M_i)^{1/2}$, 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 from ref 19 were used. The observed structure factors F_{obs} were evaluated from the intensities of the reflections observed in the X-ray fiber diffraction pattern (I_{obs}) as $F_{\mathrm{obs}} = (I_{\mathrm{obs}}/Lp)^{1/2}$, where Lp is the Lorentz polarization factor for X-ray fiber diffraction:

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

with $2\theta_{\mathrm{M}} = 26.6°$ 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 the wavelength of the used radiation (1.5418 Å). The observed intensities I_{obs} 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 due to sample and glass capillary. Owing to the different shapes of the reflection 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,

Table 2. Fractional Coordinates of the Atoms of an Asymmetric Unit of the Model Proposed (Figure 4) for the Clathrate Form of s-PMMS with Carbon Disulfide[a]

	x/*a*	*y*/*b*	*z*/*c*
C1	0.343	0.000	0.250
C2	0.297	0.068	0.373
C3	0.250	0.004	0.500
C4	0.352	0.137	0.465
C5	0.409	0.099	0.571
C6	0.459	0.165	0.650
C7	0.454	0.271	0.624
C8	0.398	0.311	0.520
C9	0.348	0.243	0.443
C10	0.392	0.426	0.490
C11	0.250	0.285	0.000
S	0.337	0.285	−0.019

[a] Hydrogen atoms were included in the structure factors calculation, but they are omitted in this table for simplicity.

different factors have been used to scale the observed and calculated structure factors on the diverse layer lines. The discrepancy factor R has been evaluated as

$$R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum F_{\text{obs}}$$

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.). The force field used was the Compass Force Field.[20] The starting conformations of the s-PMMS polymer chains correspond to the conformations found by molecular mechanics calculations by De Rosa et al.[21] These conformations do not present relevant differences in the internal parameters with respect to those proposed for s-PS and s-PPMS chains in the clathrate structures reported in the literature. The C−S bond length and the S−C−S angle of the carbon disulfide molecules were assumed to be respectively 1.55 Å and 180°.[22]

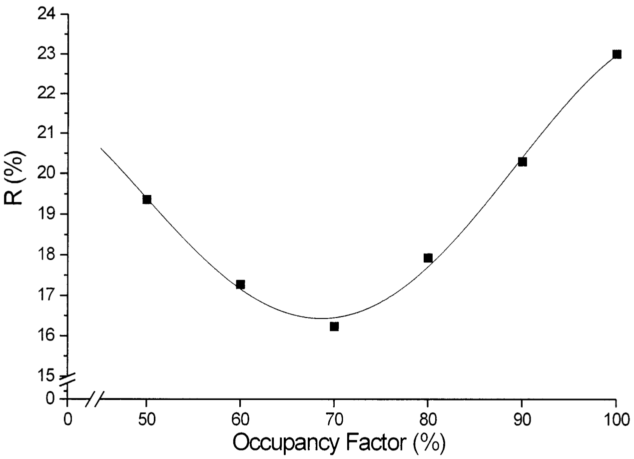

Figure 5. Trend of the discrepancy factor (R) vs the occupancy factor.

Result and Discussion

Unit Cell and Space Group Determination. The X-ray fiber diffraction pattern of the clathrate form of

Table 3. Comparison between the Calculated Structure Factors (F_{calc}) for the Model of the Clathrate Form of s-PMMS with CS$_2$ of Figure 4 and the Observed Structure Factors (F_{obs}), Evaluated from the Intensities Observed in the X-ray Fiber Diffraction Pattern of Figure 1[a]

hkl	d_{obs} (Å)	d_{calc} (Å)	F_{calc}		F_{obs}
010	13.00	13.10	101		100
200	8.85	8.90	29		61
210	7.14	7.36	74	118	124
020	6.61	6.55	91		
220	5.28	5.28	49		57
400		4.45	115	139	136
030	4.40	4.37	56		
410		4.21	54		
230	3.92	3.92	87		97
420		3.68	34		
040	3.30	3.27	56		50
240	3.10	3.11	9	63	52
430		3.07	67		
600	2.91	2.67	25		30
620		2.70	95	125	89
440	2.65	2.64	5		
050		2.62	82		
450		2.26	36	56	52
800	2.22	2.23	1		
640		2.20	43		
111	6.24	6.27	77		75
211		5.35	30		
121	4.87	4.83	84		108
311	4.40	4.44	161	170	193
221		4.37	53		
401	3.77	3.87	99	170	132
321		3.83	23		
131		3.73	117		
411		3.71	71		
231		3.50	21		
511	3.10	3.14	41	63	58
141		2.98	48		
521		2.90	28		
601		2.77	25		
531		2.60	43		
621		2.55	41		
251		2.39	27		
711		2.37	33		
541		2.30	55	76	77
351	2.28	2.29	8		
721		2.27	53		
821		2.03	25		
012		3.74	34	88	92
112	3.60	3.66	6		
202		3.57	53		
022	3.38	3.35	71		62
122		3.29	33		
312	3.15	3.16	121	131	179
222		3.14	50		
402	2.91	2.93	102	115	76
322		2.92	37		
032		2.91	37		
132		2.87	7		
412		2.86	43		
422	2.71	2.68	75	91	66
332		2.61	25		
512		2.58	31		
042		2.51	28		
522		2.44	34	48	50
432	2.42	2.43	26		
242		2.41	33		
532	2.18	2.25	38	109	113
622		2.22	80		
442		2.18	31		
052		2.17	52		
152		2.16	19		
252		2.11	10	69	84
712		2.10	35		
632	2.07	2.08	22		
542		2.05	49		
352		2.04	25		

[a] The Bragg distances, observed in the X-ray fiber diffraction pattern and calculated for the proposed orthorhombic unit cell with axes $a = 17.8$ Å, $b = 13.1$ Å, and $c = 7.8$ Å, are also shown. An occupancy factor of 0.7 has been considered. Reflections not observed with F_{calc} less than 20 have not been reported.

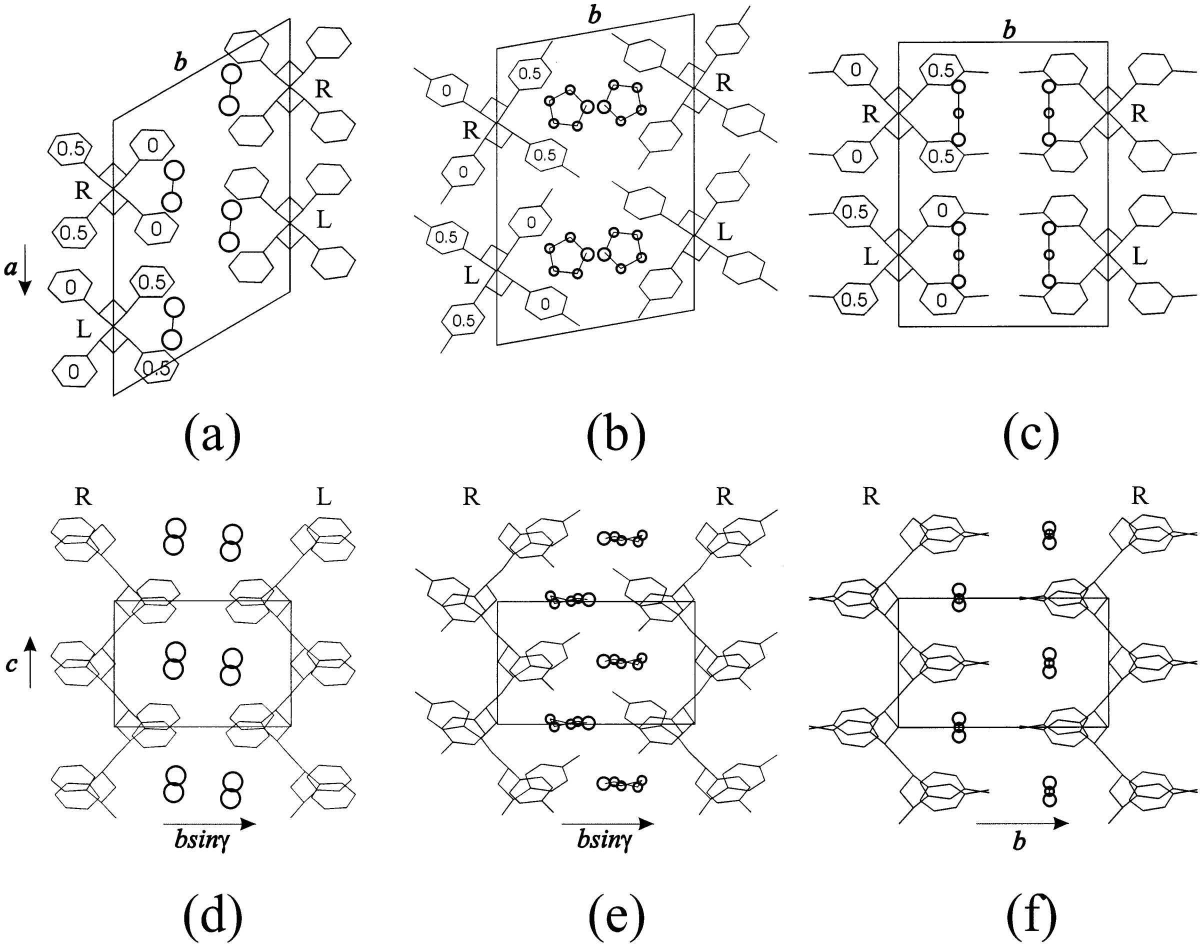

Figure 6. Projections along *c* and *a* axes of the packing models proposed for the s-PS clathrate form containing I_2 (a, d),[5] the s-PPMS clathrate containing THF (b, e),[14] and of the clathrate of s-PMMS containing CS_2 (c, f). The approximated *z*/*c* fractional coordinates of the barycenters of the phenyl rings are shown. R = right-handed, L = left-handed helices. In (d, e, f) only a couple of polymer chains along the *b* axis are reported.

s-PMMS containing CS_2 is reported in Figure 1 while the list of the observed reflections for the same sample is reported in Table 1. The data in Table 1 can be well indexed in terms of an orthorhombic unit cell with cell constants $a = 17.8$ Å, $b = 13.1$ Å, and $c = 7.8$ Å. Assuming two **s**(2/1)2 polymer chains (eight monomer units) and four CS_2 molecules per unit cell, the calculated density is 1.14 g/cm^3. This value has to be compared with the experimental densities, measured by flotation, on freshly prepared unoriented clathrate samples presenting a diffraction pattern coherent with the fiber diffraction patter shown in Figure 1 and on amorphous samples, which give both a mean value of 1.02 g/cm^3. The density measurements were done on unoriented clathrate samples because the transformation into form I is much slower that in the case of oriented ones.[23]

In the hypothesis that all the symmetry elements of the **s**(2/1)2 chain conformation are maintained in the lattice, we have assumed the space group *Pcaa*, according to the systematic absence of $hk0$ and $h0l$ reflections with $h = 2n + 1$ observed in the X-ray diffraction pattern.

Chain Conformation and Packing Model. At variance with the clathrate forms of s-PS and s-PPMS, for which only one **s**(2/1)2 conformation is possible for the chains (right- and left-handed), the presence of the methyl group on the benzene ring in the meta position leads to the two different conformations with this symmetry sketched in Figure 2a,b. In addition to these, we have also considered a third (statistical) conformer with symmetry **s**(2/1)/2 obtained by a combination of the two different conformers previously described, in which two methyl groups, having each an occupancy factor equal to 0.5, are positioned in the meta position of every phenyl group.

In the space group *Pcaa* there are, for each of these conformations, only two different ways of packing 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 1/4*c*. For only one of the six obtainable models a good packing of the chains is achieved, and there is the required space along the *b* axis for the inclusion of two molecules of CS_2. The *ab* projection of this model is reported in Figure 3.

Subsequently, we have positioned the CS_2 molecule 3.6 Å far from the chain axis with its molecular axis parallel to the *a* axis of the cell and with its 2-fold symmetry axis, perpendicular to the S−S direction, coincident with the crystallographic 2-fold axis at $z = 0$. The packing has been then refined using Cerius^2 minimization procedures in which both packing and chain conformation have been varied at the same time.

After minimization, the chain conformation remained substantially unchanged, while the guest molecule was rotated a few degrees around its 2-fold axis of and its center of gravity was translated at 3.76 Å from the chain axis. The model of packing corresponding to the minimum of energy is reported in Figure 4a,b. In the resulting model all the contact distances between nonbonded atoms are greater than 4 Å with the exceptions indicated in Figure 4, all relative to interactions between the guest molecule and chains. Considering only s-PMMS adjacent chains, the smallest distances are 4.11 Å along *a* and 4.25 Å along *b*. For this model the discrepancy factor *R* was about 23%. To improve the agreement, we have considered two possibilities. At first, we have varied the position and orientation of the guest molecules and also considered the possibility of a small positional disorder for them. These attempts did not improve in a significant way the agreement, but only introduced worse distances between nonbonded atoms. In a second time, we considered the possibility of the presence of some vacancies in the cavities by introducing a degree of occupancy for the CS_2 molecules as already done in the case of the s-PS clathrate containing I_2.[5] The discrepancy factor *R* vs the degree of occupancy shows a minimum for an occupancy factor ≈70% of the guest molecules, as apparent from Figure 5. For this occupancy factor the calculated density is equal to 1.06 g/cm^3. This result partially justifies the large difference between the observed and calculated densities discussed in ref 23.

The fractional coordinates of an asymmetric unit of the model proposed are listed in Table 2. Table 3 compares the calculated and the observed structure factors; the final discrepancy factor *R* is 16%.

Concluding Remarks

In the present paper, the clathrate crystalline form of syndiotactic poly(*m*-methylstyrene) containing CS_2 has been obtained and its crystalline structure has been determined. The structure is characterized by polymer chains in **s**(2/1)2 helical conformation and CS_2 molecules packed in an orthorhombic unit cell with axes $a = 17.8$ Å, $b = 13.1$ Å, and $c = 7.8$ Å, according to the space group *Pcaa*. The calculated crystalline density is 1.14 g/cm^3 for two polymer chains and four carbon disulfide units per cell.

In Figure 6 the crystalline structures of the s-PS clathrate containing I_2[5] (Figure 6a,d), the clathrate form of s-PPMS containing THF[14] (Figure 6b,e), and the clathrate form of s-PMMS containing CS_2 (Figure 6c,f) are compared. The structure of the clathrate represented in Figure 6a,b can be considered as representative, as far as the packing of the chains is concerned, of all known clathrate structures of s-PS[4−6] and of the δ form[8] of this polymer. In this case, the cavities in which the guest molecules are hosted are located around a crystallographic inversion center and are formed by enanthiomorphous chains, belonging to different close packed layers stacked along the *b* axis of the cell. Clathrates showing this kind of cavity have been indicated as α class clathrates.[18]

The clathrate form of s-PPMS containing THF (Figure 6b,e), instead, is representative of a second type of clathrate, shown for the first time for this polymer, and classified as β class clathrates, in which the cavities are formed by four benzene rings of one polymer chain and two benzene rings of the adjacent isomorphous chain. For this polymer also α class clathrates have been described, similar to those formed by s-PS, and has been clearly pointed out that the choice of the class for s-PPMS depends strictly on the steric hindrance of the guest molecules. In particular, large molecules, such as *o*-DCB, give rise to α class clathrates, while smaller molecules, such as THF, give rise to β class clathrates.[18]

It is evident from Figure 6 that the clathrate form of s-PMMS presented in this work is characterized by cavities hosting the guest molecules typical of the β class.

As far as the packing of the helices along the *a* axis is concerned, the chains are packed in such a way to realize a close packing similar to that found along the *a* axis of the clathrate forms[4−6] and of the δ form[8] of s-PS (cf. Figure 6a,c), in which the distances between chains vary from 8.5 to 8.8 Å, similar to that found for our case that is 8.9 Å. On this basis the presence of the methyl groups in the meta position seems to be not critical as far as the approach of the chains along the *a* axis is concerned.

Finally, it is worth noting that molecules having similar shape and symmetry, as I_2 and CS_2, which nest in the single **s**(2/1)2 helical chain in an analogous way (cf. Figure 6d,f), give rise to two clathrates of different class, α for s-PS and β for s-PMMS, respectively. To explain this different behavior, molecular mechanics calculations are in progress.

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(23) We are aware of the substantial difference between calculated and experimental densities. Nevertheless, we believe that this discrepancy is not detrimental for the structural investigation. In fact, some of us have already found, in the case of the clathrate form of s-PPMS containing THF, similar differences between the calculated density for the crystalline structure (1.13 g/cm^3) and the experimental density of the semicrystalline sample (1.02 g/cm^3).[14] In that paper were also presented experimental evidence explaining, at least in part, this difference. As a matter of fact, we have frequently observed that clathrate semicrystalline samples may have densities equal to completely amorphous samples, or even lower. This fact may be attributed to a microporous nature of the amorphous regions of the clathrate specimens that, left in open air, show the tendency to lose guest molecules from the amorphous regions more rapidly than from the crystalline regions. It is worth noting that TGA measurements on our unoriented semicrystalline samples show a CS_2 content not higher than 14%, indicating, on the basis of the proposed structural model, that the amorphous regions of the specimens contain less solvent of the crystalline regions.

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