Crystal Structure of the Trigonal Modification (α Form) of Syndiotactic Polystyrene

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ABSTRACT: A model of packing for the ordered modification of the α form of syndiotactic polystyrene is suggested, through comparisons between calculated structure factors and experimental intensities observed in the X-ray fiber and electron diffraction patterns. The present analysis improves the preliminary model proposed in previous papers. *Trans* planar chains are arranged in triplets and packed in the unit cell with axes $a = b = 26.26$ Å, $c = 5.04$ Å, according to a statistical rhombohedral symmetry for the disordered α′ modification and a trigonal, quasi-rhombohedral, symmetry for the ordered α″ modification. The glide plane symmetry of the isolated chain is not maintained in the lattice; we suggest that the space group is $R\bar{3}$ for the statistically disordered α′ modification; it is $P3$ for the ordered α″ modification (instead of $R\bar{3}c$ and $P3c1$ previously proposed). A rotation of nearly 7° of the triplets of chains with respect to the symmetric situation corresponding to the space group $P3c1$ for the α″ modification, can account for the observed differences between the intensities of the hkl and khl reflections in the electron diffraction patterns of syndiotactic polystyrene.

Introduction

Syndiotactic polystyrene (s-PS) presents a very complex polymorphic behavior.[1−7] Four different crystalline forms have been described so far. Following the nomenclature proposed in ref 3, the crystalline α and β forms are characterized by chains in the *trans* planar conformation, whereas the crystalline γ and δ forms contain chains in the $s(2/1)2$ helical conformation. The term δ form has been used to indicate different clathrate structures, that is, compounds which include molecules of solvent. The general pattern is complicated by the fact that both α and β forms can exist in different modifications having different degrees of structural order, so two limiting disordered modifications (α′ and β') and two limiting ordered modifications (α″ and β'') have been described.[3−5]

More recently, two mesomorphic modifications of s-PS, containing chains in the *trans* planar and in the $s(2/1)2$ helical conformations also have been described.[8−11]

The crystal structures of α[4,12] and β[5,13] forms, as well as those of molecular compounds containing molecules of solvent (clathrate structures)[14,15] have been described.

As far as the α form is concerned, a detailed description of the morphology of thin films by transmission electron microscopy has been given.[12,16] Greis et al.[12] have proposed, by electron diffraction on single crystals, a hexagonal unit cell with $a = 26.26$ Å, $c = 5.04$ Å, in which clusters of three chains are packed according to the space group $P\bar{6}2c$.

We have pointed out[3,4] the absence, in the X-ray powder diffraction patterns of the α′ modification, of hkl reflections with $-h + k + l \neq 3n$, and their weakness in the powder diffraction patterns of the ordered α″ modification. On the basis of this observation, we have suggested that alternative models for the molecular packing, characterized by a statistical rhombohedral symmetry for the α′ modification and a trigonal, quasi-rhombohedral symmetry for the α″ modification, are more suitable for the α form.[3,4]

Models of packing for the structure of the α form of s-PS proposed by Greis et al.[12] and by us[4] are reported in parts A and B of Figure 1, respectively. *Trans*-planar chains are clustered in triplets around 3-fold axes located in the positions of the unit cell $(0,0,z)$, $(^1/_3,^2/_3,z)$, $(^2/_3,^1/_3,z)$. Three triplets of chains are included in the unit cell.

In the model of Figure 1A the three triplets of chains are at the same height, giving rise to a hexagonal packing; the proposed space group was $P\bar{6}2c$.[12]

In the model of Figure 1B the three triplets have a relative shift, along z, of $^1/_3\, c$. The triplets are able to take two different, nearly isosteric orientations (as shown in Figures 2A,B) related by a rotation of 60° and a translation along z of $^1/_2\, c$. Our preliminary model (Figure 1B), proposed for the ordered α″ modification,[4] is characterized by an ordered positioning of the triplets of chains, e.g. one triplets is oriented in one direction (like in Figure 2A) and the other two in the opposite directions (like in Figure 2B). In these different orientations, the positions of substituent phenyl rings are substantially the same, whereas the atoms of backbones are rotated by 60°. Hence the atoms of phenyl rings satisfy a rhombohedral symmetry (for each phenyl atom at x,y,z there are atoms at $x + {}^2/_3$, $y + {}^1/_3$, $z + {}^1/_3$ and at $x + {}^1/_3$, $y + {}^2/_3$, $z + {}^2/_3$), whereas the atoms of backbones do not satisfy this symmetry in agreement with the presence, in the X-ray diffraction pattern of the ordered α″ modification, of weak hkl reflections with $-h + k + l \neq 3n$.[3,4] The lattice has a trigonal, quasi-rhombohedral symmetry and the proposed space group, for the α″ modification, was $P3c1$.[4]

In the disordered α′ modification, a statistical disorder between the two isosteric orientations of triplets of chains is present. The positions of phenyl rings remain substantially unaltered, whereas the atoms of backbones are statistically distributed in the six positions around the 3-fold axes (like in Figure 2C). Hence the α′ modification has a statistical rhombohedral symmetry (also the atoms of backbones are related by rhombohedral translations) and the proposed space group was $R\bar{3}c$, according to the absence of hkl reflections with $-h + k + l \neq 3n$ in the X-ray diffraction pattern of the α′ modification.[4]

The model that we have proposed for the α form[4] (Figure 1B) is different from that proposed by Greis et

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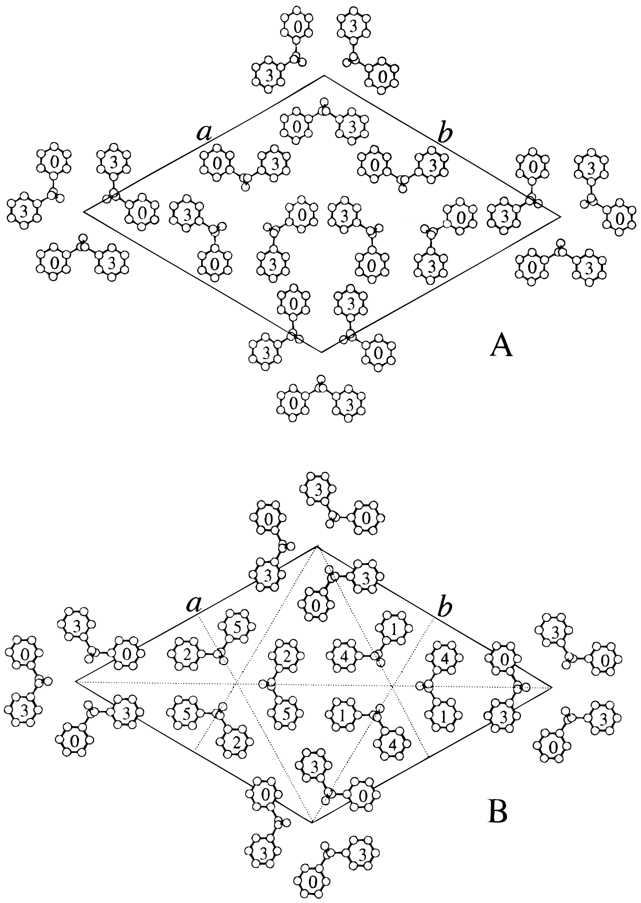

Figure 1. Models of packing for the α form of s-PS: (A) hexagonal model proposed by Greis et al.,[12] space group $P\bar{6}2c$; (B) trigonal model proposed by De Rosa et al.,[4] space group $P3c1$. Relative heights of the centers of phenyl rings are in units *c*/6. Dotted lines in B indicate crystallographic glide planes *c*. In A, glide planes *c* contain the axes of the unit cell.

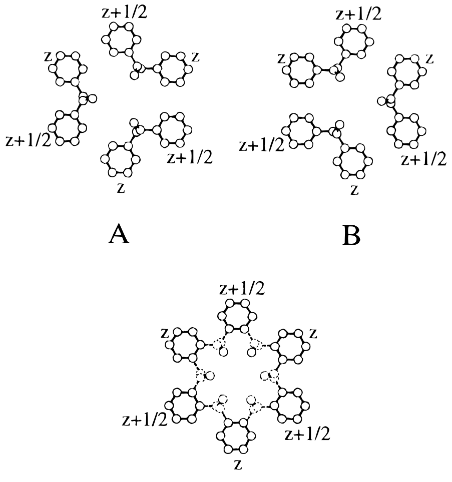

Figure 2. (A and B) Two different and isosteric orientations of triplets of *trans* planar chains of s-PS. (C) The atoms of backbones are statistically distributed in the six positions around the threefold axis whereas the atoms of the phenyl rings are in the same positions as in A and B.

al.[12] (Figure 1A) because of a rotation of 30° and of the rhombohedral shift along *z* of the triplets of chains.

It is worth noting that in our preliminary models for α′ and α″ modifications the glide plane symmetry, characteristic of the isolated chain, is coincident with the crystallographic glide plane in space groups $R\bar{3}c$ and $P3c1$, respectively.[4]

In a more recent paper[17] we have shown that for the disordered α′ modification the glide plane symmetry is not maintained in the lattice. Indeed, calculations of the packing energy, for the disordered α′ modification, indicate that a rhombohedral structure is energetically feasible and the deepest energy minimum is obtained when the triplets are rotated by 7° with respect to the situation corresponding to the space group $R\bar{3}c$. Therefore, we proposed the space group $R\bar{3}$ as the most probable space group for the α′ modification.[17]

As far as the ordered α″ modification is concerned, we observe that in the electron diffraction patterns of s-PS reported in the literature,[12] the intensities of $hk0$ and $kh0$ reflections are different. This indicates that the space group symmetry should be lower than $P3c1$, preliminarily proposed.[4]

In the present contribution we will show that a model for the ordered α″ modification with triplets of chains rotated by 7° with respect to the situation corresponding to the space group $P3c1$, with a lowering of the crystallographic symmetry, can account for the intensities observed in electron diffraction patterns, as well as in the X-ray fiber diffraction pattern. Comparisons between calculated structure factors and experimental intensities observed in the our X-ray fiber pattern and in that reported by Sun et al.,[18] as well as in electron diffraction patterns reported by Greis et al.,[12] will be presented.

Experimental Section

The fully syndiotactic polystyrene (s-PS) was synthesized using a homogeneous catalyst consisting of $CpTiCl_3$ (Cp = cyclopentadienyl) and methylaluminoxane (MAO) in toluene, according to the method described in ref 19. The polymer fraction insoluble in acetone was 92 wt %. The intrinsic viscosity of the fraction insoluble in acetone, determined in tetrahydronaphthalene at 135 °C with an Ubbelohde viscosimeter, was 0.60 $dL \cdot g^{-1}$.

An oriented fiber sample of s-PS in the α form was obtained by stretching at 160 °C compression-moulded samples of s-PS and successive annealing at 230 °C.

The X-ray fiber diffraction pattern was obtained with nickel-filtered Cu Kα radiation by using a photographic cylindrical camera.

Calculated structure factors were obtained as $F_c^2 = |F|^2 M$, where M is the multiplicity factor. A thermal factor (B = 8 $Å^2$) and atomic scattering factors from ref 20 were used. The comparison between electron diffraction intensities and calculated structure factors was performed using atomic scattering factors for electrons calculated according to the formula 16c of ref 21.

Results and Discussion

The X-ray fiber diffraction pattern of the ordered α″ form of s-PS is reported in Figure 3. The Bragg distances and the intensities of the reflections observed in the pattern of Figure 3 are very similar to those reported recently by Sun et al.[18] These authors have observed that in their data there was insufficient evidence to support the selection rule for rhombohedral symmetry proposed by us in refs 3 and 4. As discussed in the previous section, the model of packing that we proposed in refs 3 and 4 presents an “exact” rhombohedral symmetry only for the disordered α′ modification (hkl reflections with $-h + k + l \neq 3n$ systematically absent[3,4]), whereas the data of Sun et al.[18] refer to an ordered α″ modification. In our model of this modification the atoms of backbones do not satisfy the rhombo-

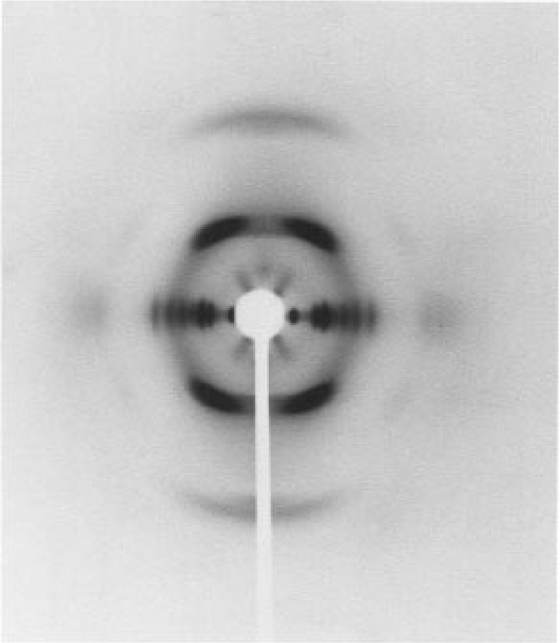

Figure 3. X-ray fiber diffraction pattern of the α″ form of s-PS.

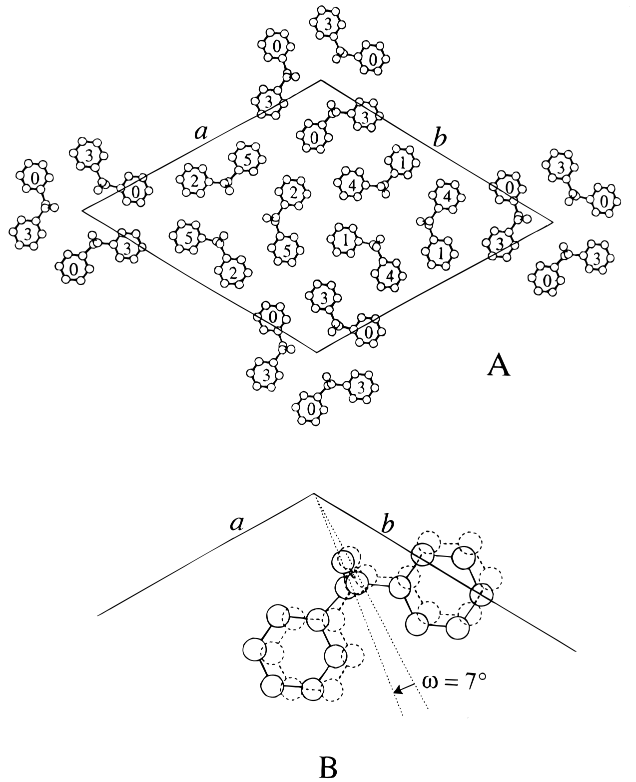

Figure 4. (A) Model of packing for the ordered α″ modification of s-PS in the space group *P*3. Relative heights of the centers of the phenyl rings are in units *c*/6. (B) Enlarged detail of model A showing the clockwise rotation of $\omega = 7°$ of the chain. The dashed chain corresponds to that in the model of Figure 1B (space group *P*3*c*1).

Table 1. Fractional Coordinates of the Carbon Atoms of the Asymmetric Unit in the Model of Figure 4 for the Space Group *P*3[a]

	x/*a*	y/*b*	z/*c*		x/*a*	y/*b*	z/*c*
1	0.065	0.110	0.000	9′	0.7766	0.3783	0.8333
2	0.095	0.146	0.250	10′	0.8126	0.3843	1.0833
3	0.159	0.167	0.250	11′	0.8336	0.3413	1.0833
4	0.185	0.133	0.250	12′	0.7996	0.2813	1.0833
5	0.246	0.160	0.250	13′	0.8266	0.2473	1.0833
6	0.280	0.221	0.250	14′	0.8876	0.2743	1.0833
7	0.253	0.255	0.250	15′	0.9216	0.3353	1.0833
8	0.192	0.228	0.250	16′	0.8946	0.3693	1.0833
9	0.065	0.110	0.500	1″	0.4433	0.7116	0.6666
10	0.081	0.148	0.750	2″	0.4813	0.7336	0.9166
11	0.052	0.185	0.750	3″	0.5183	0.7996	0.9166
12	−0.008	0.159	0.750	4″	0.4923	0.8336	0.9166
13	−0.036	0.192	0.750	5″	0.5253	0.8946	0.9166
14	−0.002	0.253	0.750	6″	0.5863	0.9216	0.9166
15	0.059	0.280	0.750	7″	0.6133	0.8876	0.9166
16	0.086	0.246	0.750	8″	0.5793	0.8266	0.9166
1′	0.7766	0.3783	0.3333	9″	0.4433	0.7116	1.1666
2′	0.8146	0.4003	0.5833	10″	0.4793	0.7176	1.4166
3′	0.8516	0.4663	0.5833	11″	0.5003	0.6746	1.4166
4′	0.8256	0.5003	0.5833	12″	0.4663	0.6146	1.4166
5′	0.8586	0.5613	0.5833	13″	0.4933	0.5806	1.4166
6′	0.9196	0.5883	0.5833	14″	0.5543	0.6076	1.4166
7′	0.9466	0.5543	0.5833	15″	0.5883	0.6686	1.4166
8′	0.9126	0.4933	0.5833	16″	0.5613	0.7026	1.4166

[a] The asymmetric unit corresponds to three independent structural units, each composed of two monomeric units.

hedral symmetry in agreement with the presence, as well as the weakness, of *hkl* reflections with $-h + k + l \neq 3n$.[4]

As discussed before, in a previous paper[17] we have shown that in the rhombohedral lattice of the disordered α′ modification, the packing energy minimum is obtained for the space group $R\bar{3}$, when the crystallographic glide plane is lost and the triplets of chains are rotated by 7° ($\omega = 7°$ in Figure 5 of ref 17) with respect to the situation corresponding to the space group $R\bar{3}c$ ($\omega = 0°$ in Figure 5 of ref 17). For the α″ modification the rotation of 7° of the triplets of chains, with the loss of the crystallographic glide plane symmetry, produces the degeneration of the space group *P*3*c*1, previously proposed,[4] in the space group *P*3.

A model of the α″ modification, for the space group *P*3, is reported in Figure 4A. The triplets of chains are rotated by 7° (as shown in Figure 4B) with respect to the model of Figure 1B (space group *P*3*c*1). The model of Figure 4A corresponds to the model with $\omega = 7°$ in Figure 5 of ref 17. The fractional coordinates of the carbon atoms of the asymmetric unit are reported in Table 1. The asymmetric unit corresponds to three independent structural units (each structural unit is composed of two monomeric units). The coordinates of Table 1 are obtained from the coordinates *x*,*y*,*z* of the asymmetric unit for the space group $R\bar{3}$, reported in ref 17, through a rotation of 60° and a translation of 1/2*c* along *z*, that is applying the transformation $x - y, x, z + 1/2$ (atoms 1−16) and through the rhombohedral translations $x + {}^2/_3, y + {}^1/_3, z + {}^1/_3$ (atoms 1′−16′), $x + {}^1/_3$, $y + {}^2/_3$, $z + {}^2/_3$ (atoms 1″−16″).

A comparison between the calculated structure factors (F_c^2), for the model of Figure 4A (space group *P*3), and the intensities observed in the X-ray fiber diffraction pattern reported in Table 1 of ref 18 is shown in Table 2. Since the intensities of the reflections observed in the our X-ray fiber diffraction pattern (Figure 3) are similar to those of ref 18, we report in Table 2 the data of ref 18 for a more objective comparison with calculated structure factors. The calculated structure factors for our previous model of Figure 1B, space group *P*3*c*1, are also reported in Table 2. A fairly good agreement for both space groups is apparent. The X-ray fiber diffraction data do not allow discrimination between space groups *P*3*c*1 and *P*3, although we can observe a slightly better agreement on the equator for the space group *P*3.

Besides the energetic evidences,[17] other experimental data support the feasibility of the model of Figure 4A

Table 2. Comparison between calculated structure factors (F_c^2) for Various Models and Experimental Intensities (*I*) Observed in the X-ray Fiber Diffraction Pattern Reported in the Literature[18]

			F_c^2								
hkl	d_{obs}[a] (Å)	d_{calc} (Å)	$P3$[b]		$P3c1$[c]		$P\bar{6}2c$[d]		$P\bar{6}$[e]		I[f]
110	13.2	13.13	90		75		120		100		s
200	11.3	11.37	12		19		–		9		vw
210	8.61	8.60	34		36		90		65		m
300	7.55	7.58	180		95		1150		550		s
220	6.52	6.57	650	817	850	1035	95	235	95	255	s
310		6.30	167		185		140		160		
400	5.68	5.69	175		170		–		85		m
320	–	5.22	85		62		380		231		–
410	4.98	4.96	360		205		170		665		m
500	–	4.55	195		250		–		95		–
330	4.34	4.38	155	289	225	322	70	350	46	254	m
420		4.30	134		97		280		208		
510	4.12	4.08	250		280		70		161		w
600	3.74	3.79	95	131	125	140	–	210	38	166	m
430		3.74	36		15		210		128		
520	–	3.64	65		39		66		134		–
610	3.47	3.47	92		100		26		58		w
440	–	3.28	50		70		40		12		–
530	–	3.25	15		22		42		29		–
700	–	3.25	21		20		–		17		–
620	–	3.15	18		28		24		9		–
710	–	3.01	56		2		48		41		–
630	–	2.86	51		84		50		5		–
810	2.64	2.66	11	13	68	73	–	359	2	62	vw
550		2.63	2		3		345		55		
640		2.61	–		2		14		5		
730	–	2.56	–		2		–		17		–
900	–	2.53	160		500		–		90		–
820	2.45	2.48	395		6		180		287		w
910	–	2.38	27		22		–		167		–
101	4.93	4.92	11		–		–		–		m
111	–	4.70	–		–		–		120		–
201	–	4.61	205		–		–		–		–
211	4.35	4.35	4000		4300		–		–		vs
301	–	4.20	–		1		4600		2600		–
221	–	4.00	–		–		–		910		–
311	3.98	3.94	625		615		–		–		m
401	–	3.77	20		2		–		1		–
321	3.57	3.62	14	14	29	32	–	96	1	151	w
411		3.54	–		3		96		150		
421	–	3.27	80		51		3		1		–
441	2.73	2.75	1	56	2	7	–	1	54	57	vw
531		2.73	27		5		1		1		
701		2.73	29		–		–		2		
621	–	2.67	72		154		8		–		–
711	2.59	2.59	3	22	7	10	14	14	232	238	w
541		2.52	19		3		–		6		
002	2.51	2.52	–	550	–	500	800	800	800	800	m
102		2.50	550		500		–		–		
112	–	2.47	–		–		70		80		–
202	–	2.46	145		150		–		–		–
212	2.39	2.42	640	642	650	655	1	641	4	344	m
302		2.39	2		5		640		340		
222	–	2.35	–		–		24		32		–
312	–	2.34	64		7		5		6		–
402	2.29	2.30	100	140	168	207	–	4	2	2	w
322		2.27	40		39		4		–		
412	–	2.25	–		–		–		336		–
502	–	2.20	80		110		–		–		–
512	–	2.14	24		22		–		1		–
602	2.09	2.10	5	95	4	32	18	57	10	54	vw
432		2.09	86		21		13		6		
522		2.07	4		7		26		38		

[a] Bragg distances observed by Sun and Miller[18] in the X-ray fiber diffraction pattern. [b] Model of Figure 4. [c] Model of Figure 1B. [d] Model of Greis et al.[12] of Figure 1A. [e] Model of Greis et al. with the triplets of chains rotated by −14°.[17] [f] Relative intensities observed by Sun and Miller[18] in the X-ray fiber diffraction pattern; vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

Table 3. Comparison between Calculated Structure Factors (F_c^2) for the Model of Figure 4, (Space Group $P3$), and Experimental Intensities of Equatorial Reflections Observed in the Electron Diffraction Pattern Reported in the Literature[12]

hkl	F_c^2 ($P3$)	I[a]	hkl	F_c^2 ($P3$)	I[a]
110	90	s	420	14	m
200	12	vw	240	120	s
210	3	vw	510	85	w
120	31	m	150	165	s
300	180	vs	600	95	m
220	650	vs	430	1	w
310	37	m	340	35	m
130	130	vs	520	5	
400	175	vs	250	60	m
320	1	w	610	37	w
230	84	m	160	55	w
410	40	m	620	7	
140	320	s	260	11	vw
500	195	m	710	44	vw
330	155	s	170	12	

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

for the ordered α″ modification. The thorough examination of the electron diffraction patterns of s-PS reported in the literature[12] can afford discrimination between space groups $P3c1$ and $P3$. Indeed, this analysis reveals a different intensity of $hk0$ and $kh0$ reflections; in Figure 5b of ref 12 it is possible to observe that the reflections 210 and 120, 310 and 130, 320 and 230, 410 and 140, 420 and 240, 510 and 150, 430 and 340, and so on, have different intensities. This is a clear indication that the space group cannot be $P3c1$, as preliminarily suggested[4] (for this space group, with Laue symmetry $3m$, the $hk0$ and $kh0$ reflections are equivalent), but it must be of lower symmetry.

The model of Figure 4A, for the space group $P3$, arising from the space group P3c1 by removing the crystallographic glide plane symmetry, can account for the experimental differences in the intensities of $hk0$ and $kh0$ reflections in the electron diffraction patterns.

A comparison between the calculated structure factors for the model of Figure 4A and experimental intensities observed in the electron diffraction pattern of Figure 5b of ref 12 is reported in Table 3. The comparison is reported only for equatorial reflections because only the pattern of [001] zones of a single crystal of s-PS is shown in ref 12. A fairly good agreement is apparent; the different intensities between $hk0$ and $kh0$ reflections are well-reproduced for all reflections up to $d = 3$ Å.

It is worthwhile to note that the model proposed by Greis et al.[12] (space group $P\bar{6}2c$) for the α form does not account for the intensities observed in the X-ray fiber diffraction, as well as in the electron diffraction patterns. The calculated structure factors for the hexagonal model of Greis et al.[12] of Figure 1A are reported in Table 2. It is apparent that the calculated intensity of the 211 reflection is very low, in disagreement with the very strong observed intensity. This is a consequence of the absence, in this model, of any displacement along z between adjacent clusters of phenyl rings.

The most important feature of the model of packing preliminarily proposed by us in ref 4 and improved in the present contribution is the rhombohedral shift along z of the clusters of phenyl rings; this feature can account for the strong intensity of the 211 reflection as shown in Table 2.

As described in ref 17, also the model of Greis et al.[12] can be improved, from the point of view of the packing energy, by a rotation of nearly −14° of the triplets of chains, with the loss of the crystallographic glide plane symmetry (compare the model with $\omega = 30°$, corresponding to the model of Greis et al., and the model with $\omega = 16°$ in Figure 5 of ref 17). The space groups become $P\bar{3}$ and $P\bar{6}$, for the disordered α′ and for the ordered α″ modifications, respectively.

As shown in Figure 5 of ref 17, the two energy minima corresponding to the rhombohedral space group $R\bar{3}$ ($\omega = 7°$) and to the modified hexagonal model of Greis (space group P$\bar{3}$, $\omega = 16°$) are almost equivalent.

The calculated structure factors of the modified hexagonal model of Greis, for the α″ modification, with the triplets of chains rotated by −14° (space group $P\bar{6}$) are also reported in Table 2. A bad agreement with the intensities observed on the layer lines in the X-ray fiber pattern is still present.

It is worth noting that the structural model of Figure 4A should be thought as a local ordered arrangement of the chains; the real values of the angles of rotation of the three triplets of chains included in the unit cell may be different in principle, but probably almost equal among themselves and near to 7°. Hence, in principle, the three triplets may have three independent rotations, so the "exact" rhombohedral translations of $^2/_3$,$^1/_3$,$^1/_3$ and $^1/_3$,$^2/_3$,$^2/_3$ of the phenyl rings may not be realized and the rhombohedral degeneracy of the statistical α′ structure may be lost. The possible different angles of rotation of the three triplets of chains can account for the slight discrepancies still present in the comparisons between calculated and observed intensities of Tables 2 and 3.

Conclusions

In the present contribution we propose a model for the crystal structure of the α form which improves the preliminary model suggested in ref 4.

Trans planar chains, arranged in triplets, are packed in the unit cell with axes $a = 26.26$ Å, $c = 5.04$ Å, according to a statistical rhombohedral symmetry for the disordered α′ modification and a trigonal, quasi-rhombohedral symmetry for the α″ modification.[4]

The different intensities of $hk0$ and $kh0$ reflections, observed in the electron diffraction pattern reported in the literature,[12] indicate that the chains are packed in a space group with symmetry lower than $R\bar{3}c$ and $P3c1$, preliminarily proposed for the α′ and α″ modifications, respectively.[4] A rotation of nearly 7° of the triplets of chains with respect to the situation corresponding to the space groups $R\bar{3}c$ and $P3c1$, leads to the loss of the glide plane symmetry, and the space groups become $R\bar{3}$[17] and $P3$ for the α′ and α″ modifications, respectively.

As described in a previous paper[17] for the statistical disordered α′ structure, the rotation of nearly 7° (space group $R\bar{3}$) corresponds to the deepest packing energy minimum.

Calculations of structure factors show that the model proposed for the α″ modification (space group $P3$ with triplets of chains rotated by 7°) gives a good agreement between calculated and experimental intensities observed in the X-ray fiber diffraction pattern and can account for the different intensities of $hk0$ and $kh0$ reflections observed in the electron diffraction patterns.

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