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The α'' "Superstructure" of Syndiotactic Polystyrene: A Frustrated Structure

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ABSTRACT: The crystal structure of syndiotactic polystyrene (sPS) in its stable α form (a so-called "superstructure" named α'') is reevaluated. As shown by all previous investigations, the trigonal unit cell contains three triplets of extended sPS chains. The azimuthal orientation of the three triplets is shown to differ from those assumed so far, which generates a clear-cut example of frustrated packing. The azimuthal settings and relative shifts of the triplets indicate that two triplets maximize their interactions, while the third one interacts less favorably with its neighbors. This frustrated packing scheme fully justifies the three-triplets unit cell and constitutes an interesting variant of related frustrated packings previously described for isochiral three-fold helices.

Introduction

The crystal polymorphism of syndiotactic polystyrene (sPS) has been investigated in considerable detail. One of its forms, initially described as a "superstructure" by Greis et al.[1] and later[2] named the α'' form, is highly innovative in the field of synthetic polymers: as shown by Greis et al., it is indeed made of *clusters* of three extended chains (triplets), with *three* triplets (nine chains) packed in a trigonal unit cell of parameters $a = b = 26.26$ Å and $c = 5.04$ Å. Greis et al.[1] also report on a *one*-triplet trigonal unit cell, a structure obtained at low crystallization temperatures, later called α'. The details of the crystal structures, and notably of the α'' superstructure, have been analyzed progressively. Greis et al.[1] proposed a packing scheme of the triplets characterized by the fact that the azimuthal settings of two of the triplets are identical but differ by 180° from that of the third one, and they described the structure as resulting from the coexistence of right- and left-handed triplets[1] (Figure 1a). Corradini and co-workers in Napoli have proposed a succession of several models for this α'' form,[2−6] which are characterized by a progressive decrease of the high symmetry initially assumed and by a $\approx 30°$ rotation of the triplets[2,3] as compared to the initial model of Greis et al.[1] In the last models[5,6] *all* the triplets are rotated by an additional 7°, as illustrated in Figure 1b: the plane of the backbone $CH-CH_2$ of one chain in the triplet is no longer in the (110) plane of the unit cell. In addition, the structure keeps the 180° (or 60)° rotation of one triplet relative to its two neighbors, thus creating the three-triplet superstructure α''. In the model of De Rosa, the three triplets are also shifted by $c/3$ along the c axis.[6] The one-triplet α' form structure is analyzed by Greis et al.[1] and by De Rosa[6] as a statistical assembly of the three triplets existing in the more stable α'' phase.

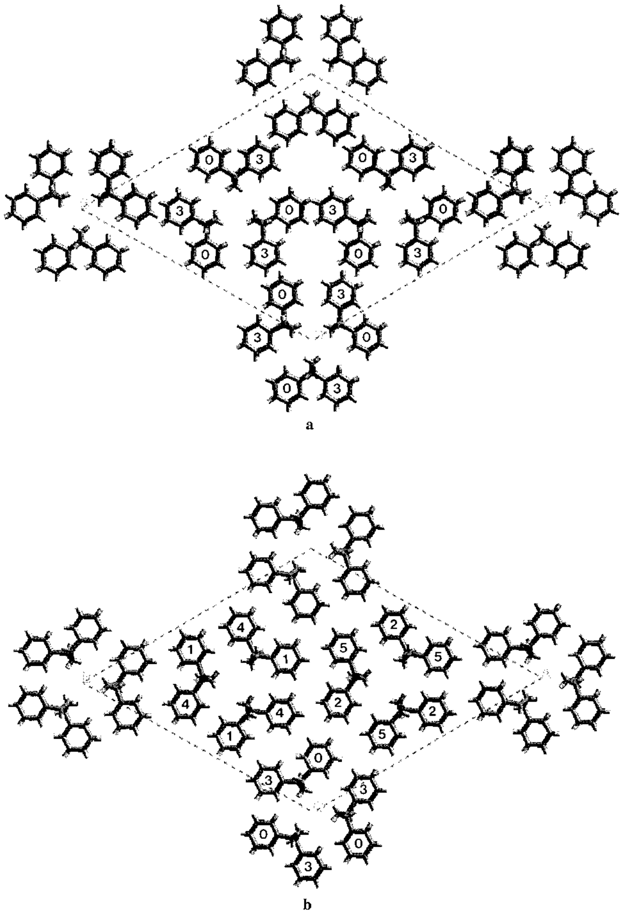

Figure 1. (a) Schematic representation of the crystal structure of the α'' form of sPS as derived by (a) Greis et al[1] and (b) De Rosa.[6] Note the 30° rotation of the triplets in the two models and in the (110) plane (horizontal) the different positions of the main chain atoms at the center of the corner triplet, a feature which creates a frustration and requires defining a three-triplet cell.

In the present contribution, we reevaluate the crystal structure of the α'' form of sPS. We point out the frustrated character of all the models proposed so far. This feature had actually been underlined in the initial Note on frustrated polymer structures,[7] although the details were not established (and the contributions of the Italian group had been overlooked). We show that the latest structure can be significantly improved by considering different azimuthal settings and c axis shifts

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of the triplets. The molecular interactions at the root of the frustration of the α″ superstructure are analyzed. They provide a firm structural justification for the three-triplet unit cell. Several types of structural disorders are envisaged, which may account for the streaking observed in *hk*0 patterns. The α″ form of sPS actually illustrates an interesting variant of the frustrated packing of polymers that *does not* rest on three-fold, isochiral *helices.*

Experimental Section

(1) Samples and Sample Preparation. The sample most often used was provided by Dr. Tsuji, University of Kyoto. It is produced by Idemitsu Kosan (Japan). Its molecular weight (weight average) is 240 000. It is investigated in the form of thin films cast on cleaved mica from 0.5% solutions in *p*-xylene. The films are melted in a Mettler FP 80 heating stage at 300 °C for 5 min prior to cooling (at a rate of 20 °C/min) to the crystallization temperature of 200 °C (crystallization time: 15 min to 1 h). The resulting films contain up to 80% of the *β* polymorph but also large single crystals of the desired α″ form. According to ref 2, crystallization at 250 °C but upon heating (i.e. without the thermal excursion at 300 °C) produces the α′ modification. We did not succeed in obtaining this α′ form under our experimental conditions, even when reproducing the indicated thermal treatments.

(2) Techniques. The crystals are shadowed with Pt/C, coated with a layer of carbon, floated on water (with the help of a polyacrylic acid backing), mounted on copper grids, and examined in a Philips CM12 electron microscope operated at 120 kV. Modelization of the crystal structures, packing energy analyses, and simulation of diffraction patterns are performed using the relevant modules of Cerius^2 developed by Biosym-Molecular Simulations (Waltham, MA, and Cambridge, U.K.).

Results: Derivation of the Structure

In this section, we recall some experimental data essential to the derivation of the structure, present the main characteristics of frustrated polymer structures, evaluate the models presented so far, and demonstrate possible ways of improving them, which affect both the chain axis projection and the *c* axis shifts.

(1) Diffraction Data: Key Elements. The single crystals (Figure 2a) and stroked films of sPS investigated in this study yield electron diffraction patterns of the equatorial *hk*0 plane (Figure 2b) and fiber patterns (Figure 3a) essentially similar to those already presented by several groups, which will not be analyzed beyond pointing out the features needed in the present reinterpretation.

The *hk*0 pattern (Figure 2b) must be indexed (Figure 2c) on a large cell which clearly indicates a three-clusters cell content, as proposed by Greis et al.[1] We were not able to produce single crystals with the smaller, one-triplet unit cell reported by these authors (α′ form). Also, overexposed diffraction patterns show that, besides the sharp reflections, there exist a number of more diffuse spots and streaks, which have been described in detail by Kestenbach and Petermann[8] and analyzed by Pradère and Thomas.[9] They are very reminiscent of similar, much more conspicuous features appearing in the *hk*0 diffraction pattern of the *β* phase of isotactic polypropylene (*β*-iPP)—which also has a frustrated structure.[10,11]

In the *fiber* pattern (Figure 3a), we wish to underline the strength of the 002 reflection, which cannot be confused with the nearby 102 one (cf. indexing in Figure 3b). Sun and Miller[12] already established that the strong reflection on the second layer line is definitely meridional by using tilted fiber patterns (X-ray diffraction). Note also a cluster of strong reflections on the

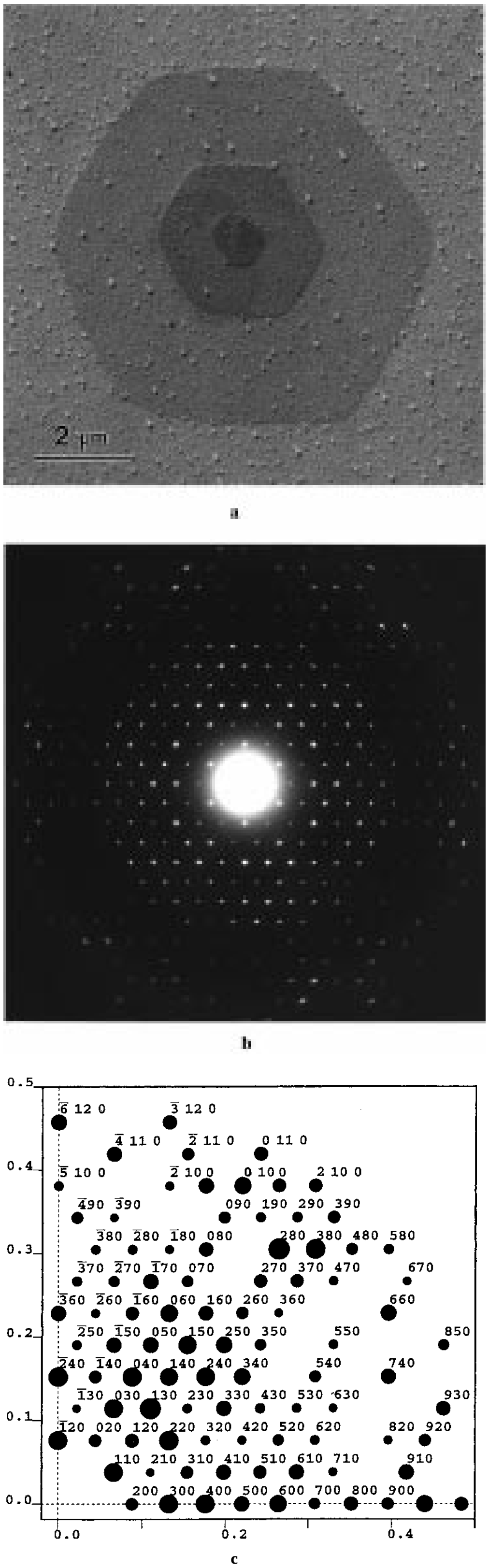


Figure 2. (a) Electron micrograph with Pt/C shadowing of a single crystal of sPS grown in a thin film at 200 °C. (b) Electron diffraction pattern of a single crystal of the α″ form of sPS in proper relative orientation to the crystal in part a. Growth faces of the crystal in part a are of type {110}. Diffuse streaks and spots are visible in specific areas of the pattern. (c) Indexing of the pattern in part b (upper right quadrant).

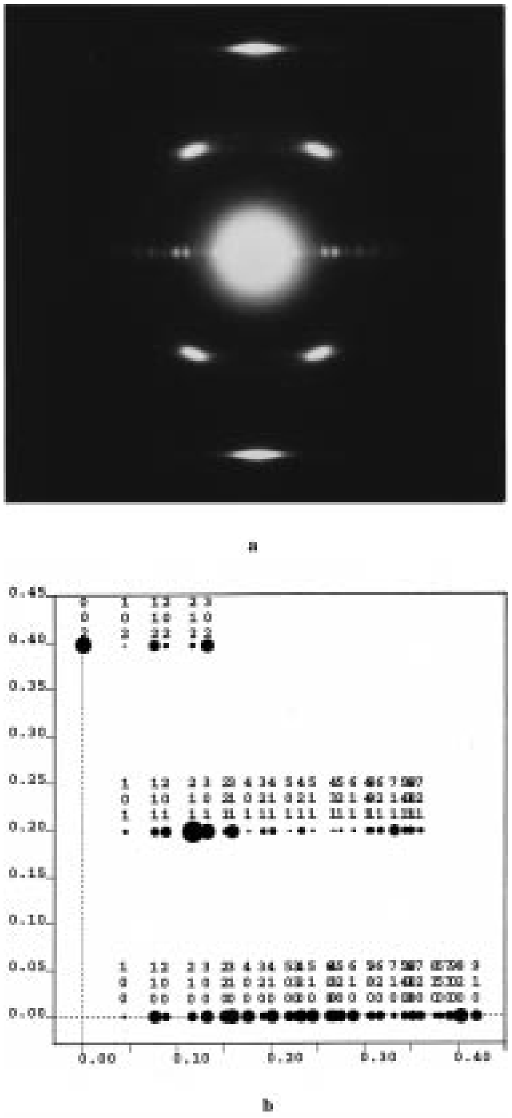


Figure 3. (a) Fiber electron diffraction pattern of the α″ form of sPS. (b) Indexing of the pattern in part a, with relative intensities predicted for the model shown in Figure 5a.

first layer line (indexed as 211 and 301), which we will feature in the discussion to come next.

(2) Frustrated Polymer Structures: Main Features. The crystal structures derived so far for sPS resort to a family of polymer structures based on a frustrated packing scheme—in short, frustrated structures. It is useful to recall the main features of this recently proposed[7] packing scheme. Frustrated polymer structures have been established or are suspected for several achiral and chiral polymers[7,13,14] for which three isochiral three-fold helices are packed in a trigonal unit cell. Frustration results from the fact that two of the three helices maximize their interactions at the expense of the third one. This feature shows up by the different azimuthal orientations of the two helices compared to that of the third one. In the *c* axis projection, if the orientation on a compass of one side-chain of each helix is taken as an indicator, frustrated polymer structures with two different patterns of orientations have been documented:[13] north–south–south (NSS) for isotactic poly(2-vinylpyridine) (iP2VP)[15] and north–west–west (NWW) for poly(L-hydroxyproline) (PLHP)[16] and poly(*tert*-butylethylene sulfide) (PTBES).[17] For these structures, the most appropriate space group is $P3_1$ or $P3_2$.

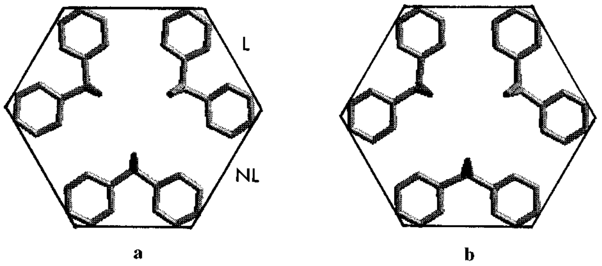


Figure 4. Proposed structures of the triplets: (a) truncated triangular shape obtained with the trans planar conformation of the backbone (This model is used in the present study.); (b) hexagonal shape obtained by a slight deviation from the pure trans–trans conformation of the backbone.[5] The sides of the triplets are distinguished by the fact that phenyl groups are attached to the same or to different backbones (L and NL, for linked and nonlinked, respectively).

Frustrated crystal structures display characteristic morphological and diffraction features: often, a triangular shape of the single crystals,[18] typical *hk*0 diffraction patterns,[13] and characteristic relative intensities of *hkl* reflections, in particular a weak 003 reflection compared to its neighbor 103.[13,17] The latter feature is particularly telling about the interhelix interactions in the structure: it indicates that the three helices are not shifted by an exact *c*/3 distance (which would lead to a very strong 003 reflection) but rather, and in agreement with the concept of frustration, that the *c* axis shifts of the three helices are uneven. For future reference, we therefore note that frustrated structures based on three-fold helices are characterized by at least two features: (i) different azimuthal settings of helices and (ii) uneven *c* axis shifts of the three helices in the unit cell.

(3) Analysis of the Models of the α″ Form of sPS: A Frustrated Structure. From the work of Greis et al.[1] on, *all* the models proposed for the α″ structure of sPS have features familiar in frustrated polymer structures: three-fold symmetry of the clusters, packing of three clusters in a trigonal unit cell, and, more importantly, different azimuthal settings of the clusters, a feature which establishes frustration. This frustrated character of the α″ structure is indeed implicit in all models proposed for sPS: it is the different azimuthal settings which help create a three-cluster cell (although Greis et al.[1] also considered, in addition to the different azimuthal settings, the coexistence of right-handed and left-handed clusters in a 2/1 ratio but were aware of difficulties in packing antichiral units in what amounts to a hexagonal packing).

As indicated in the Introduction, however, various models have been proposed within this frustrated scheme, which differ in several respects: the exact shape of the triplet, the azimuthal settings of the triplets and relative *c* axis shifts, the possibility of statistical packing (mainly in order to create the smaller, one-triplet cell). It is worth emphasizing the following features:

(i) The triplets have a nearly hexagonal but actually three-fold shape when seen in chain axis projection. The phenyl ring interactions within a given triplet are nearly but not quite equivalent, whether they are molecularly linked (i.e. attached to the same backbone) or not (referred to as linked and nonlinked in Figure 4a). However, triplets have also been considered[5] in which the backbone axes are slightly deformed, in such a way as to bring the centers of mass of linked and unlinked phenyl rings at the same distance (Figure 4b), which confers a "purer" six-fold symmetry to the external shape (the envelope) of the clusters.

(ii) As already indicated in the Introduction, whereas, in the initial model of Greis et al.,[1] one face of the hexagonal projection of the triplet was oriented parallel to the (110) plane, this azimuthal setting has been rotated by 30° in the first models of the Italian school.[3,4] Later on, Corradini et al.[5] established that the structure is improved if the triplets are rotated by an additional and constant 7°, a feature which is included in the model of De Rosa,[6] who further uses the correct cell geometry (trigonal) and space group (*P*3) to describe the structure (Figure 1b). In particular, the additional rotation accounts for the conspicuous difference in intensity between *hk*0 and *kh*0 reflections, which is a major characteristic of the diffraction pattern.

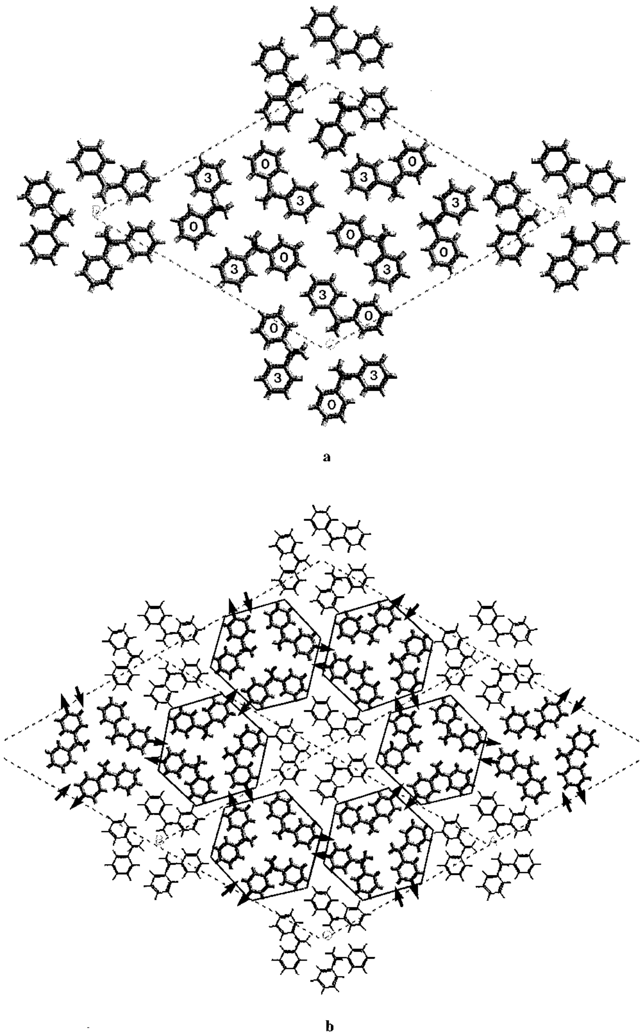
(iii) The issue of the *c* axis shifts of the three triplets is not yet settled. We note that, in the structure of De Rosa,[6] the three triplets are shifted by a uniform *c*/3. However the 002 meridional reflection is calculated as having zero intensity, whereas experimental evidence indicates that it is the strongest reflection on the second layer line (cf. Figure 3). Petermann and Kestenbach[8] underline this weakness of the structure derived by De Rosa.

(iv) The triplets may be considered to have near hexagonal symmetry, whether the phenyl rings are equidistant or not. As a consequence, the triplets can be rotated by 60° (and shifted by *c*/2) and recreate a nearly isosteric triplet. This possibility is at the root of the statistical, smaller α′ cell assumed for example by Greis et al.[1] and De Rosa.[6]

Having underlined the frustrated nature of the structure, it is at present useful to examine which characteristics create the frustration. As will be shown, it turns out that *the type of frustration considered so far is insufficient*.

All models considered so far rest on a *constant and fixed* azimuthal setting of the *hexagons* which materialize the triplets in *c* axis projection: in other words, the frustration rests mainly on the *positions of the backbone atoms of the sPS within the triplets*. This is a very small perturbation indeed, since it affects only little the overall shape (outside envelope) of the triplet. As far as growth processes are concerned, this perturbation *is hidden* to the depositing triplet, especially when considering the large cell distances involved: the positions of the *backbone* atoms of every *third* triplet in a (110) growth face of sPS should be identical in order to create the three-triplet structure, and the sequence of these positions should be maintained throughout growth. It is unlikely that such details of the inside structure of the triplets are "felt" at such a large distance. On this basis, it is desirable to examine whether other forms of frustration are possible (within the confines of the three-triplet unit cell), which would induce more visible perturbations than those assumed so far.

(4) An Improved Version of the α″ Structure of sPS. On the basis of the above premises, we suggest for the α″ structure of sPS a model which preserves many of its major features but in which *the azimuthal settings of the triplets are not bound to be similar*. Since this feature introduces a much more "visible" perturbation than that assumed so far, it is of course consistent (and more so than before) with the frustrated character of the structure.



a

b

Figure 5. (a) Model of the structure of the α″ form of sPS as derived in this work. Note the clockwise tilt (by 12° and 15°) of the two central triplets and the smaller tilt (5°) for the corner triplet. (b) Model of packing of the structure displayed in part a. The interactions between the center helices (shown in cylinders and outlined with a hexagonal frame) are indicated by arrows. The corner triplet is shown in sticks.

The details of the structure can be worked out by extensive use of molecular simulation and packing energy packages but rest also in large part on the full application of principles underlying frustration in polymer crystal structures. The final model arrived at is represented in Figure 5a, and the atomic coordinates are listed in Table 1. Some major new features of the structure deal with chain axis projections and with chain axis shifts. Their analysis helps "read" the molecular interactions which are at the root of the frustration. In particular, we will concentrate on the interactions between triplets and rely for this purpose on the distinction of faces made of linked (L) and nonlinked (NL) triplets.

(i) In chain axis projection, the azimuthal settings of the two central triplets are characterized by a rotation of the triplets which is *more important* than previously considered. Instead of 7°, we find these angles to be 12° and 15° (with respect to the (110) plane). *These setting angles enable a good interdigitation of the nonlinked phenyl groups of neighboring triplets*, much like the teeth of interlocking shafts. We consider that this favorable interaction (represented by the arrows in

Table 1. Atomic Coordinates of the Structure of the α″ Form of sPS[a]

	corner chain			center left chain			center right chain		
atom	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
$C(H_2)$	0.1016	0.0576	0.7523	0.4309	0.6903	0.7523	0.6958	0.2634	0.7500
C(H)	0.1382	0.0818	0.5043	0.4675	0.7030	0.0043	0.7104	0.2411	0.5020
C_1	0.1720	0.1480	0.5033	0.5192	0.7647	0.0033	0.7734	0.2547	0.5010
C_2	0.1408	0.1790	0.5113	0.5090	0.8127	0.0113	0.8191	0.3141	0.5090
C_3	0.1719	0.2403	0.5113	0.5567	0.8698	0.0113	0.8774	0.3268	0.5090
C_4	0.2332	0.2704	0.5113	0.6138	0.8792	0.0023	0.8901	0.2814	0.5000
C_5	0.2632	0.2402	0.4943	0.6235	0.8327	0.9943	0.8457	0.2240	0.4920
C_6	0.2331	0.1791	0.4943	0.5766	0.7752	0.9953	0.7873	0.2101	0.4930
$C'(H_2)$	0.1016	0.0576	0.2523	0.4309	0.6903	0.2523	0.6958	0.2634	0.2500
C′(H)	0.1388	0.0751	0.0043	0.4653	0.6951	0.5043	0.7027	0.2352	0.0020
C'_1	0.1808	0.0517	0.0033	0.4865	0.6514	0.5033	0.6618	0.1696	0.0010
C'_2	0.1582	0.9903	0.0113	0.4449	0.5906	0.5113	0.6004	0.1472	0.0090
C'_3	0.1969	0.9685	0.0113	0.4644	0.5501	0.5113	0.5625	0.0866	0.0090
C'_4	0.2573	0.0072	0.0023	0.5244	0.5696	0.5023	0.5852	0.0487	0.0000
C'_5	0.2791	0.0667	0.9943	0.5646	0.6285	0.4943	0.6446	0.0705	0.9920
C'_6	0.2414	0.0895	0.9953	0.5462	0.6698	0.4943	0.6834	0.1309	0.9930

[a] Fractional coordinates of the carbon atoms for the frustrated model of Figure 5. They are given for one chain of the triplet, for each of the three triplets, assuming the space group *P*3. Unit cell parameters: $a = b = 26.26$ Å and $c = 5.04$ Å.

the packing model of Figure 5b) is the *major ingredient at the root of the frustration*. Since only three faces of the triplet present this structure, repetition of these “favorable” interactions can only be made for three orientations 120° apart for any one triplet, thus creating an “open” or honeycomb lattice, the components of which are represented in cylinders and are framed in the model of Figure 5b. This scheme of preferred interactions between two neighbor elements (here triplets) in a hexagonal lattice is *the archetype of interactions leading to frustrated lattices*, even in two dimensions (cf. the impossibility of creating a hexagonal close packing of white and black balls with the additional constraint of every ball being surrounded by balls of the other color). The *shape* of the triplet is “triangular”; that is, the distances between linked and nonlinked phenyl groups are different. Also, the relative *c* axis shifts of the two triplets are such that facing phenyl rings are *c*/2 apart.

(ii) The hexagonal pattern of triplets thus created leaves a central site (located at one corner of the unit cell) in which the third triplet (shown in sticks and not framed in Figure 5b) is situated. *The interactions of this central triplet with its neighbors cannot be identical to those considered so far*. Indeed, since the triplet has an environment of six sPS stems with their linked phenyl groups oriented toward it, its interactions with the neighbors are made of three “linked” faces in front of “linked” faces (3 L−L) and three nonlinked faces interacting with three linked faces (3 NL−L). The azimuthal setting of this triplet, determined by minimization of the packing energy, turns out to be only 5° (the plane of one sPS backbone lies nearer to the (110) plane than is the case for the other triplets). Note that the shape of this triplet may differ (if only slightly) from that of the two other ones, since its environment is nearer to a true hexagonal symmetry. Although the perturbations in atomic coordinates and therefore the impact on the calculated diffraction pattern would be small, the model displayed in Figure 5a does not include such a hexagonal central triplet. Note further that two azimuthal settings 60° apart (and with an additional *c*/2 shift) of this triplet are crystallographically equivalent. This possibility is the first type of structural disorder considered in the next section.

(iii) The model as derived here yields a significantly improved agreement between observed and calculated *hk*0 diffraction patterns. For this purpose, we compare the calculated patterns of the structure derived by De Rosa[6] and those of the present structure in parts a and b of Figure 6. Both patterns display different intensities for *hk*0 and *kh*0 reflections, but Figure 6b reproduces much better the relative intensities and asymmetries observed in the experimental pattern up to and including a cluster of reflections at 0.4 $Å^{-1}$. Note in particular a characteristic doublet of reflections indexed as 280 and 380 (and nearby *h*10 0 reflections) as well as *h*40 reflections on both sides of −240 (cf. indexing in Figure 2c). More generally, the calculated pattern accounts for the very conspicuous differences in intensity between *hk*0 and *kh*0 reflections.

(iv) The calculated fiber pattern for the present model is shown in Figure 3b. The relative *c* axis shifts of the various triplets, determined by minimization of the packing energy, are such that the phenyl groups of the different helices are located in two different layers *c*/2 apart, which yields a strong 002 reflection, in agreement with experimental data.[4,12] Similarly, the calculated intensity of the cluster on the first layer line is well reproduced by the model.

The structure is stable on packing energy criteria (−68 kcal/cell), is located in a comfortable valley of the packing energy map, and is devoid of any short contacts. To conclude this section, we list the atomic coordinates of the α″ structure in Table 1 within the *P*3 space group already used by De Rosa.

(5) Structural Disorder in the Superstructure. Although the detailed analysis of the structural disorder in the α″ structure of sPS will be developed in a forthcoming paper, it is worth pointing out various possible disorders. Most of them are based on the recognition, made early on,[1] that the triplets have a nearly hexagonal envelope but a true three-fold symmetry, which makes 60° rotations of triplets on their axis (with concomitant *c*/2 shifts) sterically feasable or even likely. On this basis:

(i) The smallest perturbation is the rotation of the “lone”, corner triplet by 60°. The site can be occupied statistically by two triplets 60° apart: the interactions with the outside, hexagonal envelope are structurally equivalent. This disorder is therefore an ingredient of the crystal structure itself and was indeed included in the calculation of the patterns displayed in Figures 6b and 7.

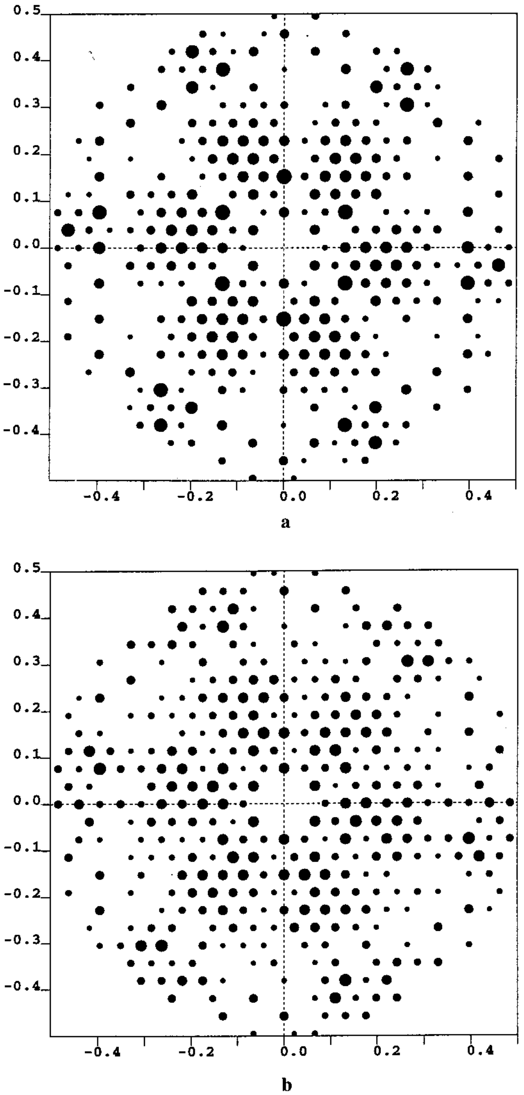


Figure 6. $hk0$ patterns calculated for (a) the structure of De Rosa[6] and (b) the structure shown in Figure 5 (assuming statistical occupancy of two triplets rotated by 60° at the corner position). Note the more pronounced six-fold symmetry of the pattern in part a and the asymmetry in part b, which reproduces better the experimental pattern (cf. Figure 2b)

(ii) 60° rotations of the two other triplets are *not* considered to be possible independently at each triplet site, as has been assumed so far, for example to generate the α′ structure. Rather, such rotations are most probably *cooperative ones* and affect crystal *domains*, thus creating different domains in which the patterns of "favorable" interactions are rotated by 60°.

(iii) A more important disorder is created by *shifts* of whole (110) layers relative to one another, with increments equal to one intertriplet distance in that plane. Such shifts are at the root of the conspicuous streaks that link 220 diffraction spots, as observed by Pradere and Thomas.[9]

It is worth pointing out that whichever type of disorder is considered, it *must not affect the tilt of the "hexagons" relative to the (110) plane.* This tilt is illustrated in our drawings by the systematic "clockwise" rotation of all the triplets of the structure. Introduction of an "anticlockwise" rotation (as would be the case for example with a reflection twin plane or a two-fold axis parallel to *a* or *b*) would "symmetrize" the $hk0$ diffraction pattern and would be in contradistinction with its overall asymmetry (i.e. $hk0$ intensities are different from those for $kh0$). Such a "symmetrization" was actually observed for single crystals of isotactic poly(4-methyl-1-pentene) form III by Revol et al.[19] In an elegant study, these authors used dark field imaging to reveal that the symmetrization was due to the coexistence of small domains with two different orientations within the single crystals. In an equally elegant study, De Rosa et al.[20] made use of this characteristic to derive the crystal structure of this form III, which displays indeed a constant tilt of the helices relative to the (100) plane; this feature in turn accounts for the existence of two domain types, which are characterized by their symmetric tilts. As indicated, no such domains exist in the single crystals of the type shown in Figure 2a.

Discussion

The above derivation of an improved version of the α″ structure of sPS rests for the major part on the recognition of its frustrated nature. sPS is original among frustrated polymer structures in that *the building element is not a helix* but rather a cluster of three extended chains with three-fold symmetry (as opposed to three-fold *screw* symmetry). Frustration rests on noneven interactions between the three triplets comprising the trigonal unit cell. One element of nonsymmetry (actually of frustration) had been included in the previous structure derivations, namely the different azimuthal setting (by 180°) of one of the triplets relative to that of the two other ones. However, the overall perturbation introduced was small, since only the main chain atoms located "inside" the triplet were affected. Within the logics of frustration, we suggest that more significant features are at the root of the frustration of the α″ sPS structure, namely the azimuthal settings of the *envelopes* of the triplets.

Derivation of the present model of the α″ structure of sPS has been greatly aided by the recognition of specific interactions between triplets, that is, the *interdigitation of facing nonlinked phenyl groups* (NL−NL). Such interactions are entropically favored, since they provide a "locking in" of two triplets at the high temperatures at which the structure is formed. Once these favorable interactions are established, the "flow chart" of frustrated structures runs smoothly: since such NL−NL interactions can only be established with three neighbors (out of six) of any triplet, a three-triplet cell is automatically created, with a "lone" triplet which must interact differently with its neighbors. Indeed, the interactions of this triplet with its neighbors sum up to 3 L−L and 3 NL−L. Globally, the structure therefore is characterized by nine interactions between triplets, which are equally partitioned between NL−NL, NL−L, and L−L. In other words also, any one triplet is involved in two different honeycomb lattices, each one involving only one of the three types of interactions. In the present model, interactions with their neighbors are for the corner (lone) triplet via 3 L−L and 3 NL−L, one "central" triplet via *3 NL−NL* and 3 L−NL, and the other "central" triplet via *3 NL−NL* and 3 L−L, with the "driving" interactions shown in italics. For the two central triplets, the interactions additional to the "driving" NL−NL ones are different: L−L and NL−L, respectively. It is these different interactions which are at the root of the (slight) differences in azimuthal settings of the central triplets (12° and 15°, respectively).

Within the structure thus defined, it is of interest to examine the impact of the 60° rotation of triplets already considered by previous authors. This impact turns out to be significantly different depending on the position (and number) of triplets involved.

A 60° rotation of *all the corner triplets* results in an exchange of the interactions with the central helices (exchange of L−L for NL−L and vice versa). As a result, the setting angles of these helices (12° and 15°) will be exchanged. If whole domains with the uniform but different rotations of the corner triplet coexist, they are related by a rotation twin with the 2_1 axis parallel to the *c* axis centered at position (0, 0) or (0, $^1/_2$) or ($^1/_2$, $^1/_2$) in the *ab* plane of the unit-cell with twin planes of type (100). The two crystal components correspond to Figure 5a as looked at in a normal way or upside down. However, it is most likely that Figure 5a represents a "limiting ordered structure". Since the perturbations introduced by the settings 60° apart of the corner triplet do not affect the "driving" pattern of NL−NL interactions in the structure, a *statistical* presence of the two different settings is probable, which in turn results in an *averaging of the setting angles for the two center triplets* between 12° and 15° (the resulting model cannot be discriminated from the model of Figure 5a on the basis of diffraction data). The statistical model therefore uses the 60° rotation of triplets already considered by many authors but applied to the sole corner triplets.

A similar 60° rotation of *only one of the central triplet* breaks the pattern of favorable interaction (NL−NL) illustrated in Figure 5b. Again, it *does not* create a different structure, since the new structure is characterized by the same imbrication of honeycomb networks based on L−L, NL−L, and NL−NL interactions. The net effect is merely that this center triplet is now characterized by interactions which are those of the corner triplets in Figure 5a: this perturbation, if carried on during further growth, creates a stacking fault between the initial and the new lattice, the latter being shifted and rotated by 60° relative to the initial one.

Last, 60° rotations of the *two central triplets* as shown in Figure 7a *do not*, again, create a different unit cell. Indeed, the structure is again characterized by the same interdigitation of honeycomb lattices involving the three types of interaction, and we are again faced with a shift and rotation of the lattice.

Consideration of this latter type of "disorder" provides however an opportunity to analyze in further detail the issue of "dominant" and "subsidiary" intertriplet interactions in the structure of α″ sPS. Indeed, the logics of frustration rest on the fact that *similar* faces of the triplets interact in the building "triplet pairs". In other words, the settings of triplets must be determined by the honeycomb networks based *either* on NL−NL *or* on L−L interactions (*but not* on NL−L interactions, cf. later). Given the "flat" lateral sides (in *c* axis projection) of the triplets, it is possible to build and minimize *honeycomb lattices* based on these NL−NL or L−L interactions: we are therefore dealing with structures as in Figures 5a and 7a, but after *removal of the corner triplet*. In both cases, the unit cells which have lost one-third of their material "shrink" slightly to an *a* parameter of ≈25.5 Å (as opposed to the initial 26.26 Å). More revealing however is the fact that the final setting angles of the triplets are significantly different in the two structures: ≈15−17° for NL−NL interactions; only ≈3−4° for L−L interactions. If we nevertheless "force" the latter interactions to dominate the structure (by simply adding the third triplet) (Figure 7a), the calculated pattern (Figure 7b) yields a poorer match with the experimental one and its packing energy is less favorable (−56 kcal/cell). Minimization of this "artificial" structure yields—not unexpectedly—the structure of Figure 5a, since addition of the third triplet introduces a honeycomb network based on NL−NL interactions which drives the setting angles toward values near 15°. On the basis of these various evidences, we are led to consider that *the model of Figure 5a is the best model for the* α″ superstructure of sPS. Further, it is probable that the same type of structure might be valid for the α″ superstructure of syndiotactic poly(paramethylstyrene)—if such a structure exists or can be produced experimentally.[21]

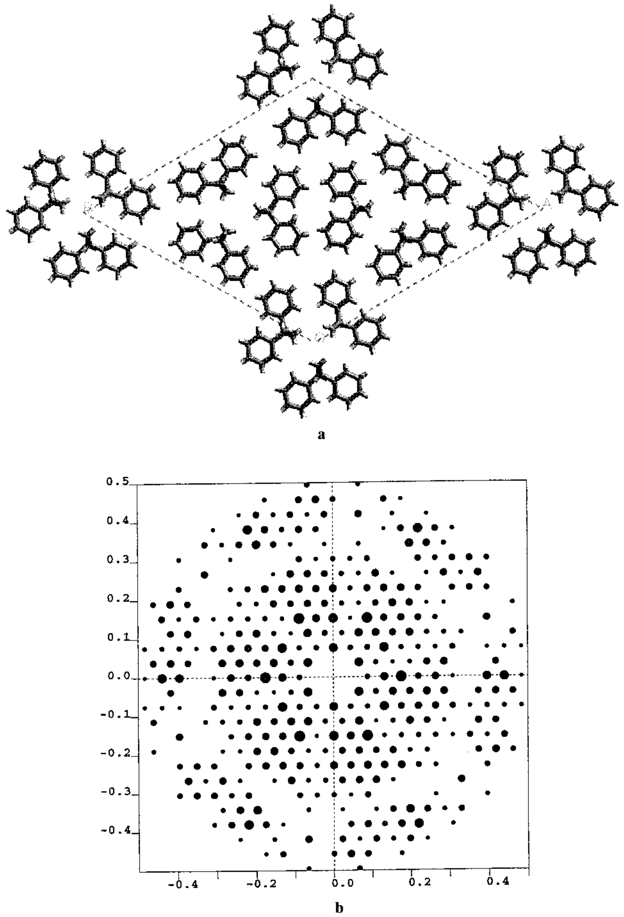


Figure 7. (a) Alternative model of the α″ form of sPS which rests on a different partition of the intertriplet interactions. (b) Calculated diffraction pattern of the model in part a. Significant discrepancies with the experimental pattern (Figure 2b) make it possible to rule out this model and the underlying partition of intertriplet interactions.

Finally, and as already indicated, the frustration in α″ sPS rests on favorable interactions between *similar* faces of the triplets. If the interactions were more favorable between *different* faces (i.e. a face with linked and a face with nonlinked phenyl groups), the reasoning leading to frustration *would not* apply: it is possible to build a one-triplet unit cell, which could correspond to the low-temperature α′ form. *In principle*, discrimination between this "true" one-triplet cell and a statistical model based on the present high-temperature, three-triplet unit cell should be possible: the former would yield a diffraction pattern devoid of streaks, whereas the latter would be significantly streaked. This criterion turns out however not to be sufficient, since microcrystals of the "one-triplet cell" rotated by 60° could coexist. Although we have not produced the α' form, available experimental evidence[1] suggests that its pattern is not streaked, which in turn implies that it is not simply a statistical arrangement of the high-temperature α'' phase.

Conclusion

The crystal structure of the "superstructure" of sPS provides a clear and convincing example of a frustrated packing of clusters of three chains ("triplets") with three-fold symmetry. Application of the principles underlying frustration makes it possible to derive a model which corresponds to a minimum in the packing energy *and* provides the best agreement achieved so far with the available, very compelling diffraction evidence (electron diffraction patterns of single crystals with a resolution up to 0.5 Å^{-1}). The structure derivation has made it possible to recognize the major intertriplet interactions at the root of the frustration, namely optimal interdigitation of facing sides of the triplets made of "nonlinked" phenyl groups. More importantly, this structure derivation illustrates the "flow chart" which leads to frustrated structures in a hexagonal close packed structure of triplets with a near hexagonal envelope. Rather than conforming to a "conventional" hexagonal crystal packing which might appear more adequate (and which may apply for the α' structure), two neighbor triplets optimize their mutual interactions, ultimately leading to the three-triplet unit cell with different azimuthal settings characteristic of frustrated structures of polymers.

In a broader perspective, the present derivation indicates that "physical" (as opposed to magnetic) frustration can be found in the trigonal space group with $P3$ symmetry, as opposed to the three-fold *screw* symmetries $P3_1$ or $P3_2$ characteristic of all frustrated polymer structures derived so far. In other words, frustration *is not* linked with the helical nature of the polymeric chain: it is probable that the concept of frustration, illustrated so far mainly with polymeric systems, will "leak" outside the polymer domain.[22]

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(22) Heiney has recently brought to our attention a paper (Heiney et al. *J. Phys. (Paris)* **1989**, *50*, 461−483) which analyzes the structure of a derivative of triphenylene, namely hexa(hexylthio)triphenylene. The molecules stack up in piles with (near) 8_3 helical symmetry to form discotic mesophases. At high temperatures, a triangular array of one-column units is formed. On cooling, a three-column superlattice appears, which was analyzed as resulting from the frustration imposed by molecular interdigitation in triangular symmetry ("steric frustration of the molecular tails") when these tails become stiffer and longer on crystallization. The frustration is described as a shift along the *c* axis of one stack relative to its two neighbors (which are also considered as being of opposite helicity). However, the departure from strict three-fold helical symmetry of the stacks leads to a less clear-cut frustration and significant rotational and translational disorders.

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