# A New Crystalline Form of Syndiotactic Poly(1-butene): Crystal Structure of Form I′

**Claudio De Rosa,* Finizia Auriemma, Ludovica Caliano, Giovanni Talarico, and Marco Corradi**

*Dipartimento di Chimica "Paolo Corradini", Università di Napoli "Federico II", Complesso Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy*

*Received March 20, 2008; Revised Manuscript Received May 19, 2008*

ABSTRACT: A new form of syndiotactic poly(1-butene), named form I′, has been found in fibers of syndiotactic butene−propylene copolymers with propylene concentrations in the range 10−30 mol %. The structure of the new form I′ is similar to that of the stable antichiral form I of syndiotactic polypropylene and is characterized by a *B*-centered packing of chains in 2-fold **s**(2/1)2 helical conformation in an orthorhombic unit cell with values of axes that depend on the propylene concentration. Propylene units are, indeed, included in the crystals of form I′ and values of axes of $a = 17.98$ Å, $b = 6.03$ Å and $c = 8.18$ Å have been determined for the copolymer sample containing 11 mol % of propylene. Disorder in the alternation of right- and left-handed helical chains along the axes of the unit cell is present so that the structure can be described by the statistical space group *Bmcm*.

## Introduction

The polymorphism of syndiotactic poly(1-butene) (sPB) has been recently described.[1] Two different crystalline forms, form I and form II, have been found so far (Figure 1).[1−3]

Form I is the most stable form that slowly crystallizes in bulk,[1,2] in oriented fibers,[2a] or in single crystals[2b] of sPB. Form I is characterized by chains in 2-fold helical conformation with line repetition symmetry **s**(2/1)2 packed in an orthorhombic unit cell with $a = 16.81$ Å, $b = 6.06$ Å, $c = 7.73$ Å, according the space group $C222_1$ (Figure 1A),[2a] where all helical chains included in the unit cell have the same chirality (left-handed or right-handed). Form II has been obtained only in oriented fibers drawn at high draw ratio.[1a,3] It is characterized by chains in 5/3 helical conformation packed in a monoclinic unit cell with axes $a = 15.45$ Å, $b = 14.36$ Å, $c = 20$ Å, and $\gamma = 116°$, according to the space group $P2_1/a$ (Figure 1B).[3]

The crystal structure of sPB in the most stable form I (Figure 1A) is very similar to those of syndiotactic polypropylene (sPP) in the stable helical forms.[4−12] Two different crystalline forms with chains in the 2-fold helical conformation, characterized by a different mode of packing in similar orthorhombic unit cells, have been described for sPP.[4−12] The most stable form I of sPP is characterized by a *B*-centered antichiral packing of 2-fold helical chains with a regular alternation of right and left handed helices along the axes of the unit cell (Figure 2A).[6−11] The metastable form II of sPP is characterized by a *C*-centered packing of 2-fold helical chains having the same chirality, according to the space group $C222_1$ (Figure 2B).[4,5,12a] The isochiral mode of packing in the metastable form II of sPP (Figure 2B) is, therefore, similar to that of the most stable form I of sPB (Figure 1A). For sPB, no crystalline modifications characterized by an antichiral mode of packing of 2-fold helices has been observed so far.[1−3]

In this paper, we report for the first time the structure of a new polymorphic form of sPB that crystallizes in oriented fibers of syndiotactic butene−propylene copolymers (sPBP) with propylene contents in the range 10−30 mol %.

## Results and Discussion

Two samples of butene−propylene syndiotactic copolymers, sPBP1 with 11 mol % of propylene and sPBP2 with 30 mol % of propylene, have been synthesized with the single center $C_s$-symmetric syndiospecific catalyst (phenyl)$_2$methylen(cyclopentadienyl)(9-fluorenyl)zirconium dichloride activated with methylaluminoxane (MAO), with the method described in ref 13a (see Supporting Information).

The X-ray powder diffraction profiles of compression molded films of sPBP samples, slowly cooled from the melt and aged at room temperature for about one month, are shown in Figure 1. The samples are amorphous just after cooling from the melt but crystallize by aging at room temperature in the isochiral *C*-centered form I of sPB (Figure 1A), as indicated by the presence of the 200 and 110 reflections at $2\theta \approx 11$ and 16°, respectively.

As demonstrated in ref 13, syndiotactic propylene−butene copolymers crystallize in the whole range of composition and propylene and butene comonomers are included in the crystals of the stable helical forms of sPB (form I) and sPP (forms I and II) homopolymers. Accordingly, in crystals of syndiotactic propylene-butene copolymers the values of the *a* and *b* axes of the orthorhombic unit cell regularly increase with increasing butene concentration from the values of form I of sPP ($a = 14.50$, $b = 5.6$ Å) to those of form I of sPB ($a = 16.81$ Å, $b = 6.06$ Å).[13] The two samples sPBP1 and sPBP2 crystallize, indeed, in the form I of sPB (Figure 1A) with values of *a* and *b* axes slightly lower than those of sPB[2a] ($a = 16.78$ Å and $b = 5.98$ Å for the sample iPBP1 with 11 mol % of propylene, and $a = 16.26$ Å and $b = 5.91$ Å for the sample sPBP2 with 30 mol % of propylene).[13]

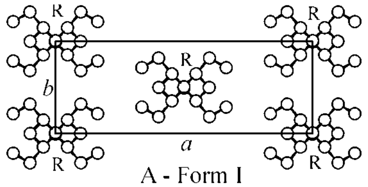
The X-ray fiber diffraction patterns, and the corresponding diffraction profiles read along the equatorial layer line, of fibers of the sample sPBP1 with 11 mol % of propylene, stretched at high deformation ($\epsilon = 100(L_f - L_0)/L_0$, with $L_0$ and $L_f$ being the initial and final lengths of the specimen, respectively), close to the breaking of the sample ($\epsilon \approx 430\%$), keeping the fiber under tension and after releasing the tension, are reported in Figure 4. The $2\theta$ positions and the intensities of all reflections observed in the fiber diffraction patters of Figure 4 are reported in Table 1.

The diffraction patterns of fibers stretched at low degrees of deformation ($\epsilon = 100-200\%$) are similar to that shown in Figure 4A of fibers stretched up to the maximum possible deformation ($\epsilon = 430\%$) and then removing the tension. In these diffraction patterns the reflection at $2\theta = 15.60°$ (Figure 4A,A′,

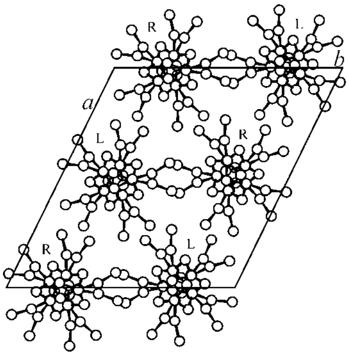
---

* To whom correspondence should be addressed. Telephone: ++39 081 674346. Fax ++39 081 674090. E-mail: claudio.derosa@unina.it.

10.1021/ma800627m CCC: $40.75

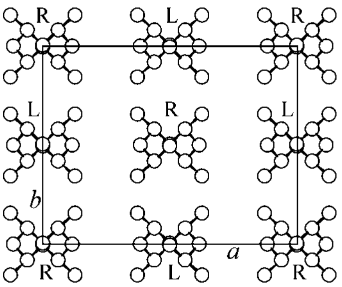


A - Form I

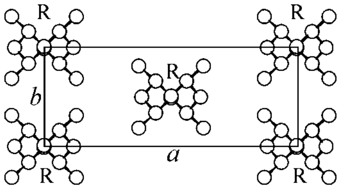


B - Form II

**Figure 1.** Limit ordered models of packing of form I (A, space group $C222_1$)[2a] and form II (B, space group $P2_1/a$)[3] of sPB (R = right-handed, $L$ = left-handed).



A - Form I



B - Form II

**Figure 2.** Limit ordered models of packing of form I (A, space group *Ibca*)[6–11] and form II (B, space group $C222_1$)[5] of sPP (R = right-handed, $L$ = left-handed).

Table 1) can be interpreted as a 110 reflection. Therefore, the presence in the diffraction pattern of Figure 4A of the 200 and 110 reflections at $2\theta = 10.54$ and 15.60°, respectively (Table 1), well polarized on the equator, indicates that stress-relaxed fibers or fibers stretched at low deformations are in the *C*-centered form I of sPB (Figure 1A) with values of axes of the orthorhombic unit cell of $a = 16.78$ Å, $b = 6.04$ Å, and $c = 7.79$ Å, as in the case of powder compression-molded and aged samples of Figure 3. This indicates that application of low tensile stress induces only orientation of crystals of form I present in the compression-molded film with chain axes parallel to the fiber axis.

Upon stretching at high deformations ($\epsilon = 430\%$), a shift of the equatorial reflections present at $2\theta = 10.54$ and 15.60° in the fibers stretched at low deformation toward lower values of $2\theta = 9.84$ and 14.69°, respectively, is observed (Figure 4B,B′, Table 1). The shift of the second diffraction peak from $2\theta = 15.60°$ to $2\theta = 14.69°$ can be easily explained by interpreting this diffraction from the (010) crystallographic planes rather than from the (110) planes (Table 1). This indicates that the stretching at high deformations produces a phase transition of form I of sPB, where the helical chains are packed in a *C*-centered orthorhombic unit cell (Figure 1A), into a new form characterized by a mode of packing of the helical chains similar to that of form I of sPP (Figure 2A), where the chains are packed in a *B*-centered orthorhombic unit cell.

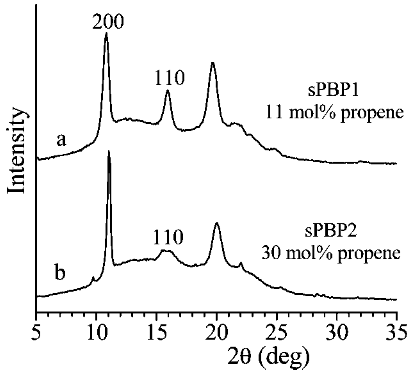


**Figure 3.** X-ray powder diffraction profiles (Ni-filtered Cu Kα radiation) of compression-molded and aged samples of sPBP copolymers with 11 (a) and 30 mol % (b) of propylene comonomeric units.

This new form of sPB, shown in Figure 5, has never been observed so far in powder samples and fibers of sPB and is here named form I′. The equatorial reflections at $2\theta = 9.84$ and 14.69° observed in the X-ray fiber diffraction pattern of the sample sPBP1 stretched at high deformations (Figure 4B,B′), therefore, correspond to the 200 and 010 reflections of form I′. The indexing of the diffraction peak at $2\theta = 14.69°$ as 110 reflection, as in the *C*-centered form I, would lead to a too high value of the *b* axis, and therefore to a too low density of the crystals.

We recall that in the case of sPP, depending on the condition of crystallization and stereoregularity of the sample, the *B*-centered antichiral form I crystallizes in disordered modifications characterized by the presence of defects in the perfect alternation of right- and left-handed 2-fold helices along the axes of the unit cell.[6–12] These modifications are intermediate between a limit ordered model *Ibca*,[6–11] characterized by a perfect alternation of antichiral chains along the axes of the unit cell, as in Figure 2A, and a limit disordered model *Bmcm*, characterized by a statistical positioning of right- and left-handed helical chains in each site of the lattice.[12] For samples crystallized at high temperatures the presence of order in the alternation of enantiomorphic helices along the axes of the unit cell is generally indicated by the presence of the 211 reflection at $2\theta = 18.8°$ in the X-ray diffraction patterns.[6–12] When disorder is present, as in samples crystallized from the melt at low temperatures or by quenching, the 211 reflection is generally absent, or has low intensity. It is also worth recalling that in the unit cell of the limit ordered model of Figure 2A with $b = 11.2$ Å, the strong equatorial reflection at $2\theta = 16°$ is indexed as 020 reflection,[6–11] whereas for the statistical disordered model *Bmcm* the *b* axis is generally assumed to be halved ($b = 5.6$ Å) and the diffraction peak at $2\theta = 16°$ is indexed as 010 reflection.[12]

In the case of form I′ of the copolymer sample sPBP1, the 211 reflection is absent in the X-ray fiber diffraction pattern of Figure 4B (Table 1). This indicates that the new form I′ of sPB that crystallizes in stretched fibers of sPBP copolymers is probably a disordered modification close to the limit disordered model as shown in Figure 5, which can be described by the statistical space group *Bmcm* with statistical positioning of right- and left-handed helical chains.

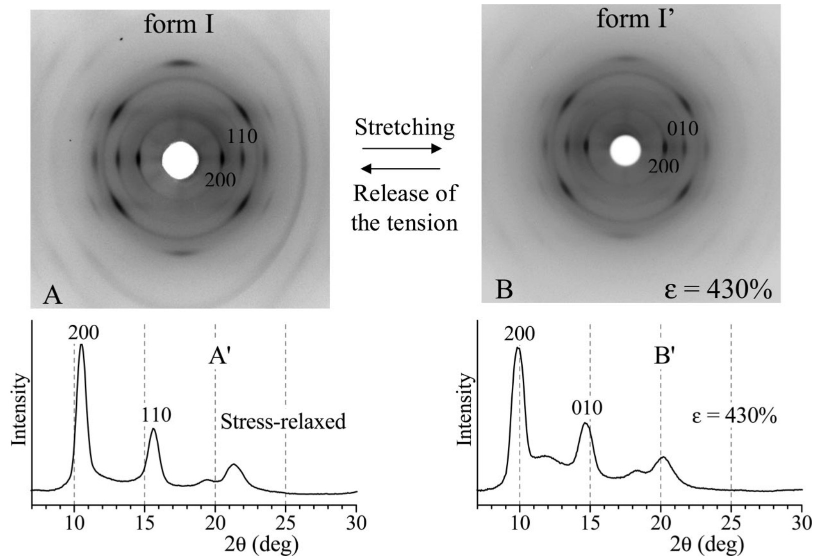


**Figure 4.** X-ray fiber diffraction patterns (recorded on imaging plates with Ni-filtered Cu Kα radiation and using a cylindrical camera) (A, B) and corresponding diffraction profiles read along the equatorial layer line (A′, B′) of fibers of the copolymer sample sPBP1 with 11 mol % of propylene units stretched up to the maximum possible deformation ($\epsilon = 430\%$), after releasing the tension (A) and keeping the fiber in tension (B). The 200 and 110 reflections of form I of sPB (Figure 1A) and the 010 reflection of form I′ (Figure 5) are indicated.

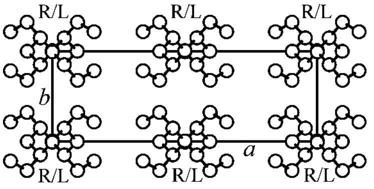


**Figure 5.** Limit disordered model of packing of the form I′ of sPB in the space group *Bmcm* that crystallizes in syndiotactic butene−propylene copolymers (R = right-handed; L = left-handed).

**Table 1. Experimental Bragg Angles ($2\theta_o$), Bragg Distances ($d_o$), and Intensities ($I_o$) of *hkl* Reflections Observed in the X-ray Fiber Diffraction Patterns of Figure 4 of Fibers of the Sample sPBP1 with 11 mol % of Propylene Stretched at 430% Deformation, Keeping the Fiber under Tension (Figure 4B) and after Releasing the Tension (Figure 4A)**

| Stress-relaxed fiber, Figure 4A | | | | Stretched fiber, Figure 4B | | | |
|---|---|---|---|---|---|---|---|
| *hkl*[a] | $2\theta_o$ (deg) | $d_o$ (Å) | $I_o$[b] | *hkl*[a] | $2\theta_o$ (deg) | $d_o$ (Å) | $I_o$[b] |
| 200 | 10.54 | 8.39 | 4383 | 200 | 9.84 | 8.99 | 3718 |
| | | | | 010 | 14.69 | 6.03 | 1634 |
| 110 | 15.60 | 5.68 | 2149 | | | | |
| 210 | | | | 210 | 18.14 | 4.89 | 199 |
| 400<br>310 | 21.46 | 4.14 | 1713 | 400 | 20.18 | 4.40 | 772 |
| 201 | 15.78 | 5.62 | 137 | 201 | 14.89 | 5.95 | 54 |
| 111 | 19.45 | 4.56 | 5481 | 111 | 18.88 | 4.70 | 3500 |
| 401<br>311 | 24.62 | 3.62 | 126 | 311 | 23.29 | 3.82 | 664 |
| 002 | 22.63 | 3.93 | n.e.[c] | 002 | 21.31 | 4.17 | n.e.[c] |
| 112 | 27.94 | 3.19 | 44 | | | | |
| 312 | 32.19 | 2.78 | 383 | 402<br>412 | 30.09 | 2.97 | 443 |
| 512<br>022 | 38.50 | 2.34 | 342 | 022<br>602 | 36.84 | 2.44 | 445 |
| 422 | 43.85 | 2.06 | 184 | 612<br>422 | 41.82 | 2.16 | 462 |

[a] The Miller indices of the *hkl* reflections are given for the orthorhombic unit cell of form I of sPB (Figure 1A) with $b \approx 6.0$ Å. [b] The observed intensities $I_o$ of *hkl* reflections were evaluated by measuring the density of reflection spots recorded on imaging plates after subtraction of the background intensity. For each reflection the background intensity was determined by measuring the intensity of the region closest to the reflection spot. [c] n.e. = not evaluated.

From the X-ray diffraction pattern of Figure 4B,B′, and in particular form the exact position of the 200 and 010 reflection at $2\theta = 9.84$ and 14.69°, respectively (Table 1), the values of axes of the orthorhombic unit cell of form I′ of $a = 17.98$ Å, $b = 6.03$ Å and $c = 8.18$ Å have been determined for the sample sPBP1 with 11 mol % of propylene, with a density of the crystals of 0.82 g/cm$^3$. In the case of the stress-relaxed fiber of the sample sPBP1, the data of Figure 4A,A′ and Table 1, in particular the positions of the 200 and 110 reflections at $2\theta =$ 10.54° and 15.60°, respectively, indicate values of axes of the orthorhombic unit cell of form I of $a = 16.78$ Å, $b = 6.04$ Å, and $c = 7.79$ Å, according to the values obtained for the powder samples (Figure 3).[13] Therefore, the density of crystals decreases from the value of ≈0.92 g/cm$^3$ of form I in powder samples and in fibers stress-relaxed or stretched at low deformations, to 0.82 g/cm$^3$ for crystals of form I′ in fibers stretched at high deformations.

Similar behavior and similar diffraction patterns have been found for the copolymer sample sPBP2 with 30 mol % of propylene. In this case the 200 and 010 reflections are at $2\theta =$ 10.12 and 14.65°, respectively, in the fiber stretched at high deformation, corresponding to values of axes of the unit cell of form I′ of $a = 17.48$ Å, $b = 6.04$ Å, and $c = 8.2$ Å. In the stress-relaxed fiber the 200 and 110 reflections are at $2\theta = 10.75$ and 15.75°, respectively, corresponding to values of axes of the unit cell of form I of $a = 16.46$ Å, $b = 5.98$ Å, and $c = 7.79$ Å. As discussed before, the propylene comonomeric units are included in the crystals of form I′ and this explains the result that the value of the *a* axis slightly decreases with increasing propylene concentration. Moreover, for both samples the values of the *a* axis of form I′ are higher than that of form I of sPB ($a = 16.81$ Å),[2a] whereas the values of the *b* and *c* axes are similar to those of sPB. The transformation of form I (Figure 1A) into form I′ (Figure 5), therefore, produces a neat increase of the *a* axis dimensions (from 16.78 Å to 17.98 Å for the sample sPBP1) of about 7% in order to reduce the steric interactions between atoms of close neighboring *bc* layers facing along *a*, while maintaining nearly similar periodicities along the *b* and *c* axes. This corresponds to a distortion of the unit cell in a direction perpendicular, instead than parallel to the stretching direction. This phase change occurs because the crystals "prefer

**Table 2. Observed Structure Factors ($F_o^2$), Evaluated from the Intensities Observed in the X-Ray Fiber Diffraction Pattern of Fibers of the Sample sPBP1 with 11 mol % of Propylene Stretched at High Deformation of Figure 4B, and Calculated Square Modulus of Structure Factors ($F_c^2$) for Models of Packing of Form I′ in the Space Groups C222₁ (Figure 1A), *Pcaa*, *Ibca*, and *Bmcm* (Figure 5)[a]**

| *hkl*[b] | *hkl*[c] | $2\theta_o$[d] (deg) | $2\theta_c$ (deg) | $d_o$[d] (Å) | $d_c$ (Å) | $F_o^2 = I_o/LP$[e] | $F_c^2 = \lvert F_{hkl}\rvert^2 M_{hkl}$[f] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $C222_1$ | *Pcaa* | *Ibca* | *Bmcm* |
| 200 | 200 | 9.84 | 9.84 | 8.99 | 8.99 | 393 | 360 | 360 | 360 | 360 |
| 010 | 020 | 14.69 | 14.69 | 6.03 | 6.03 | 261 | | 380 | 380 | 380 |
| 110 | 120 | | 15.50 | | 5.72 | | 570 | | | |
| 210 | 220 | 18.14 | 17.71 | 4.89 | 5.01 | 39 | | 250 | 250 | 250 |
| 400 | 400 | 20.18 | 19.75 | 4.40 | 4.50 | 169 | 57 | 57 | 57 | 57 |
| 310 | 320 | | 20.90 | | 4.25 | | 91 | | | |
| 410 | 420 | | 24.70 | | 3.60 | | | 53 | 53 | 53 |
| 510 | 520 | | 28.91 | | 3.09 | | 40 | | | |
| 020 | 040 | | 29.63 | | 3.02 | | 26 | 26 | 26 | 26 |
| 220 | 240 | | 31.29 | | 2.86 | | 41 | 41 | 40 | 41 |
| 610 | 620 | | 33.39 | | 2.68 | | | 16 | 16 | 16 |
| 420 | 440 | | 35.86 | | 2.50 | | 69 | 69 | 70 | 69 |
| 201 | 201 | 14.89 | 14.64 | 5.95 | 6.05 | 6 | 110 | 110 | | |
| | 211 | | 16.39 | | 5.41 | | | | 160 | |
| 111 | 121 | 18.88 | 18.94 | 4.70 | 4.69 | 595 | 710 | 690 | 700 | 690 |
| 211 | 221 | | 20.80 | | 4.27 | | | 62 | | |
| $\left\{\begin{matrix}401\\311\end{matrix}\right.$ | $\left\{\begin{matrix}401\\321\end{matrix}\right.$ | 23.29 | $\left\{\begin{matrix}22.57\\23.59\end{matrix}\right.$ | 3.82 | $\left\{\begin{matrix}3.94\\3.77\end{matrix}\right.$ | 165 | $\left.\begin{matrix}190\\200\end{matrix}\right\}390$ | $\left.\begin{matrix}190\\98\end{matrix}\right\}288$ | $\left.\begin{matrix}-\\98\end{matrix}\right\}98$ | $\left.\begin{matrix}-\\98\end{matrix}\right\}98$ |
| | 411 | | 23.76 | | 3.74 | | | | 275 | |
| | 231 | | 26.62 | | 3.35 | | | | 19 | |
| 411 | 421 | | 27.04 | | 3.30 | | | 91 | | |
| 511 | 521 | | 30.95 | | 2.89 | | 59 | 16 | 16 | 16 |
| 021 | 041 | | 31.63 | | 2.83 | | 19 | | | |
| 601 | 601 | | 31.80 | | 2.81 | | 7 | 7 | | |
| | 431 | | 31.80 | | 2.81 | | | | 10 | |
| 121 | 141 | | 32.03 | | 2.79 | | | 19 | 19 | 19 |
| | 611 | | 32.68 | | 2.74 | | | | 12 | |
| 221 | 241 | | 33.20 | | 2.70 | | 13 | 10 | | |
| 611 | 621 | | 35.20 | | 2.55 | | | 8 | | |
| 421 | 441 | | 37.57 | | 2.39 | | 19 | | | |
| | 251 | | 40.25 | | 2.24 | | | | 8 | |
| 521 | 541 | | 40.57 | | 2.22 | | | 42 | 42 | 42 |
| 002 | 002 | 21.31 | 21.73 | 4.17 | 4.09 | n.e[g] | 270 | 270 | 275 | 270 |
| $\left\{\begin{matrix}402\\312\\412\end{matrix}\right.$ | $\left\{\begin{matrix}402\\322\\422\end{matrix}\right.$ | 30.09 | $\left\{\begin{matrix}29.53\\30.33\\33.13\end{matrix}\right.$ | 2.97 | $\left\{\begin{matrix}3.03\\2.95\\2.70\end{matrix}\right.$ | 135 | $\left.\begin{matrix}4\\130\\-\end{matrix}\right\}134$ | $\left.\begin{matrix}4\\110\\75\end{matrix}\right\}189$ | $\left.\begin{matrix}4\\-\\75\end{matrix}\right\}79$ | $\left.\begin{matrix}4\\-\\75\end{matrix}\right\}79$ |
| $\left\{\begin{matrix}512\\022\\602\\122\end{matrix}\right.$ | $\left\{\begin{matrix}522\\042\\602\\142\end{matrix}\right.$ | 36.84 | $\left\{\begin{matrix}36.45\\37.04\\37.19\\37.39\end{matrix}\right.$ | 2.44 | $\left\{\begin{matrix}2.46\\2.43\\2.42\\2.41\end{matrix}\right.$ | 181 | $\left.\begin{matrix}200\\43\\30\\-\end{matrix}\right\}273$ | $\left.\begin{matrix}79\\43\\30\\2\end{matrix}\right\}154$ | $\left.\begin{matrix}-\\42\\30\\-\end{matrix}\right\}72$ | $\left.\begin{matrix}-\\43\\30\\-\end{matrix}\right\}73$ |
| | 332 | | 34.68 | | 2.59 | | | | 55 | |
| 222 | 242 | | 38.42 | | 2.34 | | 7 | 7 | 7 | 7 |
| | 532 | | 40.23 | | 2.24 | | | | 77 | |
| $\left\{\begin{matrix}322\\612\\422\end{matrix}\right.$ | $\left\{\begin{matrix}342\\622\\442\end{matrix}\right.$ | 41.82 | $\left\{\begin{matrix}40.08\\40.19\\42.32\end{matrix}\right.$ | 2.16 | $\left\{\begin{matrix}2.25\\2.24\\2.14\end{matrix}\right.$ | 225 | $\left.\begin{matrix}-\\-\\130\end{matrix}\right\}130$ | $\left.\begin{matrix}9\\87\\91\end{matrix}\right\}187$ | $\left.\begin{matrix}-\\87\\90\end{matrix}\right\}177$ | $\left.\begin{matrix}-\\87\\91\end{matrix}\right\}178$ |

[a] Only *hkl* reflections with calculated square modulus of structure factors higher than 4 are reported. [b] Indices *hkl* for the unit cell of form I′ with axes $a = 17.98$ Å, $b = 6.03$ Å, and $c = 8.18$ Å. [c] Indices *hkl* for the unit cell of form I′ with axes $a = 17.98$ Å, $b = 12.06$ Å, and $c = 8.18$ Å where the *b* axis is doubled. [d] Bragg angles $2\theta$ and spacing *d* observed in the X-ray fiber diffraction pattern of Figure 4B. [e] The observed square modulus of structure factors $F_o$ were determined from the observed intensities $I_o$ evaluated from the X-ray fiber diffraction pattern of Figure 4B (Table 1) as $F_o^2 = I_o/\text{LP}$, where LP is the Lorentz−polarization factor for fiber diffraction $\text{LP} = (1 + \cos^2 2\theta)/[2(\sin^2 2\theta - \zeta^2)^{1/2}]$, with $\zeta = \lambda(l/c)$, *l* and *c* being the order of the layer line and the chain axis, respectively. [f] The calculated square modulus of structure factors were obtained as $F_c^2 = \lvert F_{hkl}\rvert^2 M_{hkl}$, where $F_{hkl}$ is the structure factor of the *hkl* reflection and $M_{hkl}$ is the multiplicity factor for fiber diffraction. A isotropic thermal factor $B = 12$ Å$^2$ and the atomic scattering factors as in ref14 were assumed. [g] n.e. = not evaluated.

**Table 3. Fractional Coordinates and Occupancy Factors (o.f.) of the Carbon Atoms of the Asymmetric Unit in the Model of the Crystal Structure of Form I′ of sPB for the Space Groups Bmcm (Figure 5)[a]**

| atom | $x/a$ | $y/b$ | $z/c$ | o.f. *Bmcm* |
|---|---|---|---|---|
| C1 | 0.340 | 0 | 0.250 | 0.25 |
| C2 | 0.297 | 0.144 | 0.376 | 0.5 |
| C3 | 0.352 | 0.306 | 0.461 | 0.5 |
| C4 | 0.418 | 0.196 | 0.548 | 0.445 |
| C5 | 0.250 | 0.007 | 0.500 | 0.25 |

[a] The atom C4 correspond to the carbon atom of the methyl group of the butene monomeric unit, which is present for the sample sPBP1 with a concentration of 89 mol %.

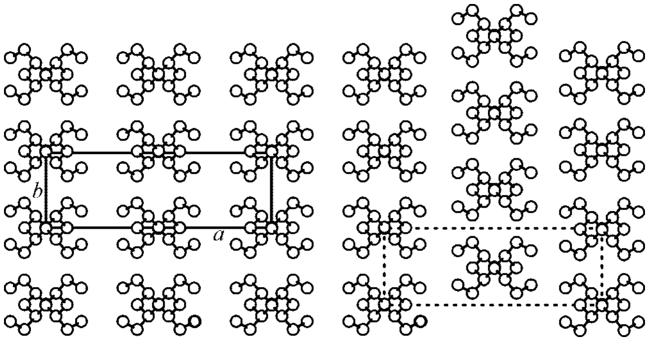


**Figure 6.** Model of packing of form I′ of sPB that crystallizes in sPBP copolymers showing defects in the stacking of *bc* layers of chains along the *a* axis corresponding to shift of *bc* layers of *b*/2 along *b* which produces local arrangements of chains as in the *C*-centered form I of sPB (dashed line).

to shear" rather than to extend parallel to the stretching direction during deformation. The energetic impossibility of sPBP copolymer chains to adopt a more extended conformation in the crystals, as it occurs for sPP,[4] promotes this transition.

The complete crystal structure of form I′ has been determined by using the diffraction data of Table 1 for the sample sPBP1 with 11 mol % of propylene and performing calculations of structure factors for different models of packing. In particular, it has been analyzed a limit ordered model with perfect alternation of antichiral helices along both axes of the unit cell, corresponding to the space groups *Ibca* (model as in Figure 2A), a limit disordered model with statistical positioning of right- and left-handed helices, corresponding to the statistical space group *Bmcm* (model as in Figure 5), the isochiral *C*-centered model, corresponding to the space group $C222_1$ (model as in Figure 1A) and an ordered model of packing with alternation of right- and left-handed helices along the *a* axis and a succession of chains of similar chirality (right or left-handed) along the *b* axis, corresponding to the space group *Pcaa*.[6] All calculations have been performed for the unit cell with axes $a = 17.98$ Å, $b = 6.03$ Å, and $c = 8.18$ Å and only for the space group *Ibca* with a unit cell with the doubled *b* axis ($b = 12.06$ Å).

A comparison between the observed square modulus of structure factors ($F_o^2 = I_o/\mathrm{LP}$), evaluated from the experimental intensities ($I_o$) of all *hkl* reflections observed in the X-ray fiber diffraction pattern of form I′ of Figure 4B (Table 1), and the square modulus of structure factors ($F_c^2 = |F_{hkl}|^2 M_{hkl}$) calculated for models of structure in the space groups *Ibca*, *Bmcm*, *Pcaa*, and $C222_1$ is reported in Table 2. It is apparent that the *C*-centered model $C222_1$ of form I (Figure 1A) can be ruled out because it does not account for the presence of the strong 010 reflection at $2\theta = 14.69^\circ$ in the experimental diffraction pattern and because of the strong calculated intensities of the 110, 201, and 401 reflections at $2\theta = 15.50$, 14.64, and 22.57°, respectively, which are absent or have very low intensities in the experimental pattern (Table 2). The ordered model *Pcaa* can also be ruled out because of the too strong calculated intensities of the 201 and 401 reflections (Table 2). The agreement between calculated and observed structure factors is improved for the limit ordered model of packing corresponding to the space group *Ibca* for which the 201 and 401 reflections are extinct. However, the strong calculated intensity of the 211 reflection (for $b = 12.06$ Å) at $2\theta = 16.39^\circ$ (Table 2) is not in agreement with the experimental data. The absence of the 211 reflection in the experimental diffraction pattern of Figure 4B (Tables 1 and 2), indeed, indicates that disorder in the alternation of right and left-handed helical chains along the axes of the unit cell is present in the structure of form I′. A fairly good agreement is obtained for the disordered model corresponding to the statistical space group *Bmcm*, characterized by a statistical positioning of right and left-handed helical chains on the sites of the lattice (Figure 5). The fractional coordinates of atoms of the asymmetric unit for the space group *Bmcm* are reported in Table 3.

However, the low observed intensity of the 210 reflection at $2\theta = 18.14^\circ$ and the presence of the 201 reflection at $2\theta = 14.89^\circ$ in the pattern of Figure 4B, although of very low intensity, are not accounted for by the model *Bmcm* of Figure 5 and indicate the presence of local arrangements of chains as in the *C*-centered mode of packing of form I of sPB (Figure 1A, space group $C222_1$). As shown in Table 2, for the space group $C222_1$ the 210 reflection is extinct and the 201 reflection is calculated with strong intensity. Therefore, the possible presence in the crystals of form I′ of domains with local packing of chains as in the *C*-centered form I (Figure 1A, space group $C222_1$), as a defect in a prevailing *B*-centered mode of packing of Figure 5, produces, on average, a decrease of the intensity of the 210 reflection and determines a development of a low intense 201 reflection. These *C*-centered domains can easily form through stacking faults defects due to shift of *bc* layers of chains of *b*/2 along *b* (*b*/2 shift disorder).[6–12] The structure of form I′, therefore, can be described by the model of Figure 6, where the prevailing mode of packing of Figure 5 in the space group *Bmcm* contains statistical disorder in the positioning of antichiral helices and *b*/2 shift disorder that produces local arrangements of chains as in the *C*-centered form I of sPB (Figure 6).

The *B*-centered form I′ of sPB (Figure 5) obtained by stretching (Figure 4B) is metastable and transforms back into the more stable *C*-centered form I of sPB (Figure 1A) by releasing the tension (Figure 4A). The 200 and 010 reflections of form I′ at $2\theta = 9.84$ and 14.69° present in the pattern of fibers stretched at high deformations (Figure 4B, Table 1) come back to values of $2\theta = 10.54$ and 15.60° upon removing the tension (Figure 4A, Table 1), as in the unstretched compression-molded film (Figure 3) or in fibers stretched at low deformations. The diffraction peak at $2\theta = 15.60^\circ$ in the pattern of Figure 4A corresponds again to the 110 reflection (Table 1), with values of axes of the orthorhombic unit cell of form I of $a = 16.78$ Å, $b = 6.04$ Å and $c = 7.79$ Å. This reversible transformation has been confirmed by analysis of intensities observed in the X-ray fiber diffraction pattern of the stress-relaxed fiber of Figure 4A and comparison with calculated structure factors for models of form I corresponding to space groups $C222_1$ and *Cmcm* (see Supporting Information).

## Conclusions

A new form of syndiotactic poly(1-butene) (sPB) has been found in syndiotactic butene-propylene copolymers with propylene concentration in the range 10−30 mol %. This new form, named form I′, is metastable and has been obtained only in oriented fibers of sPBP copolymers stretched at high deformations. It transforms back into the stable isochiral form I of sPB by releasing the tension.

The structure of the new form I′ is similar to the stable antichiral form I of syndiotactic polypropylene and is characterized by a *B*-centered packing of chains in 2-fold **s**(2/1)2 helical conformation in an orthorhombic unit cell with values of axes that depend on the propylene concentration. Propylene units are, indeed, included in the crystals of form I′ and values of axes of $a = 17.98$ Å, $b = 6.03$ Å, and $c = 8.18$ Å have been determined for the copolymer sample containing 11 mol % of propylene. Disorder in the alternation of right- and left-handed helical chains along the axes of the unit cell is present so that the structure can be described by the statistical space group *Bmcm.* Moreover, defects in the stacking of *bc* layers of chains along the *a* axis, corresponding to shift of *bc* layers of *b*/2 along *b* is also present.

**Acknowledgment.** Financial support from INSTM (Prisma Project 2007) is gratefully acknowledged.

**Supporting Information Available:** Text giving the experimental section and tables of characterization data, X-ray data, fractional coordinates and comparison between calculated structure factors and intensities of reflections observed in the X-ray diffraction pattern of stress-relaxed fibers. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) (a) De Rosa, C.; Venditto, V.; Guerra, G.; Pirozzi, B.; Corradini, P. *Macromolecules* **1991**, *24*, 5645. (b) De Rosa, C.; Guerra, G.; Grassi, A. *Macromolecules* **1996**, *29*, 471.

(2) (a) De Rosa, C.; Venditto, V.; Guerra, G.; Corradini, P. *Makromol. Chem.* **1992**, *193*, 1351. (b) Zhang, B.; Yang, D.; De Rosa, C.; Yan, S.; Petermann, J. *Macromolecules* **2001**, *34*, 5221.

(3) De Rosa, C.; Scaldarella, D. *Macromolecules* **1997**, *30*, 4153.

(4) De Rosa, C.; Auriemma, F. *Prog. Polym. Sci.* **2006**, *31*, 145.

(5) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C* **1967**, *16*, 2477.

(6) Lotz, B.; Lovinger, A. J.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.

(7) Lovinger, A. J.; Lotz, B.; Davis, D. D. *Polymer* **1990**, *31*, 2253.

(8) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552.

(9) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J. *Macromolecules* **1993**, *26*, 3494.

(10) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Schumacher, M. *Macromolecules* **1994**, *27*, 6603.

(11) Stocker, W.; Schumacher, M.; Graff, S.; Lang, J.; Wittmann, J. C.; Lovinger, A. J.; Lotz, B. *Macromolecules* **1994**, *27*, 6948.

(12) (a) De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5711. (b) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1997**, *30*, 4137.

(13) (a) De Rosa, C.; Talarico, G.; Caporaso, L.; Auriemma, F.; Galimberti, M.; Fusco, O. *Macromolecules* **1998**, *31*, 9109. (b) De Rosa, C.; Auriemma, F.; Orlando, I.; Talarico, G.; Caporaso, L. *Macromolecules* **2001**, *34*, 1663.

(14) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

MA800627M