

# Supporting Information for the paper:

## Stress-Induced Phase Transitions in Syndiotactic Propene/1-Butene Copolymers

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### **X-ray fibers diffraction patterns of fibers of syndiotactic propylene-butene copolymers.**

Oriented fibers of syndiotactic propylene-butene copolymers (sPPBu) have been obtained by stretching at room temperature compression-molded films of initial length  $L_0$  up to a final length  $L_f$ , keeping the fiber under tension for 2 h (deformation  $\varepsilon = 100(L_f - L_0)/L_0$ ), and then removing the tension. Compression molded films have been prepared by heating powder samples at temperatures 20–30 °C higher than the melting temperature under a press at very low pressure, keeping at this temperature for 10 min, and slowly cooling to room temperature. The structural transformations occurring during deformation have been studied by recording the X-ray fiber diffraction patterns of fibers stretched at different values of deformation  $\varepsilon$ .

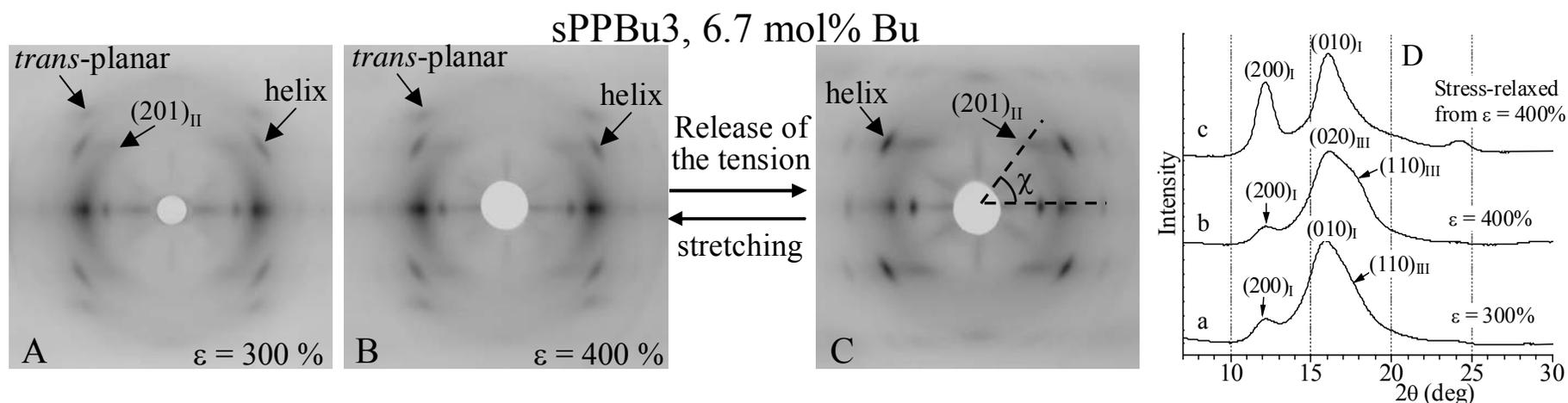
The polymorphic behavior of copolymer samples with low butene concentration (lower than 4 mol%) is similar to that of syndiotactic polypropylene (sPP) (see text, Figure 3A-D). The stable helical form I of sPP present in the compression-molded unoriented film transforms by stretching in the *trans*-planar form III, which transforms back into the helical form II by releasing the tension (Figure 3).

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Samples of sPPBu copolymers with butene concentrations in the range 4-20 mol% show a similar behavior and similar structural transformations occur by stretching. As an example, the X-ray fiber diffraction patterns and the corresponding profiles read along the equatorial line of fibers of the sample sPPBu3 with butene content of 6.7 mol%, obtained by stretching at room-temperature compression molded films at different values of strain  $\varepsilon$  are reported in Figures S1 (the case of the sample sPPBu6 with 18.6 mol% of butene is shown in the text in the Figure 3E-H). As in the case of the sample sPPBu1 with 3.2 mol% of butene (Figure 3), also in this case disordered modifications similar to the helical form I of sPP, initially present in the unoriented film (curve b of Figure 1), transform by stretching into the *trans*-planar form III. However, this transformation is more gradual and crystals of the *trans*-planar form III of sPP start appearing at values of deformation higher ( $\approx 300\%$ ) than those observed for samples with butene content lower than 4 mol%. This is indicated by the weak intensity of the reflections on the first layer line corresponding to a chain periodicity of the *trans*-planar conformation in the pattern of Figure S1A and by the fact that at 300% deformation (Figure S1A and profile a of Figure S1D) the  $(200)_I$  and  $(010)_I$  equatorial reflections at  $2\theta \approx 12$  and  $16^\circ$  and the  $(111)_I$  reflection on the first layer line, typical of the *B*-centered helical form I of sPP, are still present.

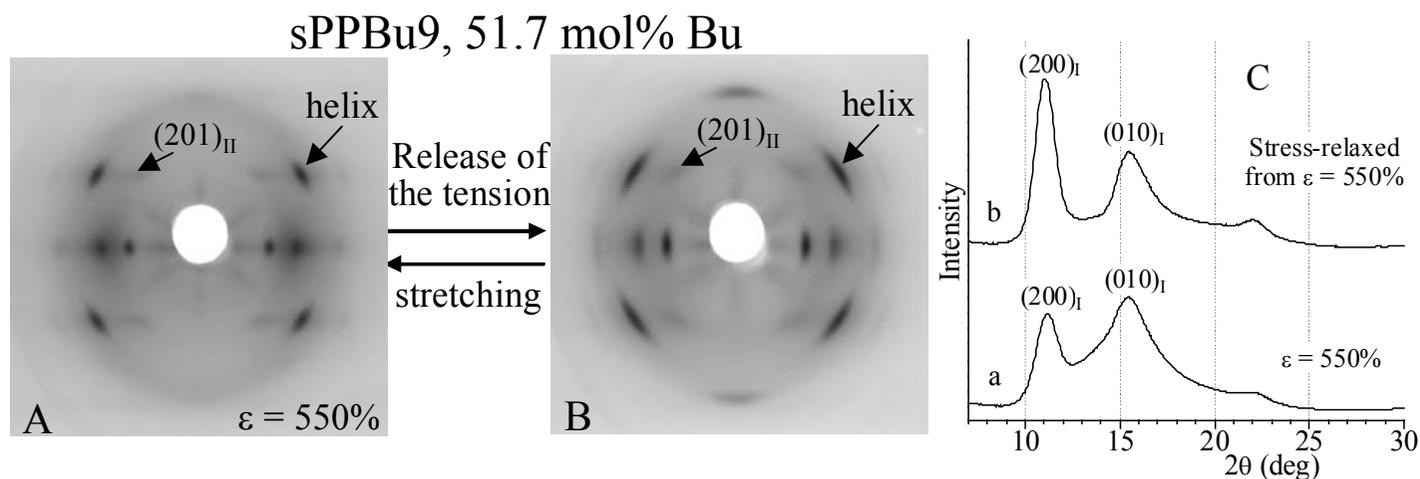
The intensity of the reflections of form I of sPP decreases, whereas the intensity of the reflections typical of *trans*-planar form III increases with increasing deformation. At 400% deformation (Figure S1B), i.e. close to the breaking of the specimen, the fiber results crystallized in a mixture of the *trans*-planar form III and the helical form I of sPP, with a smaller amount of the helical form, as indicated by the low intensity of the reflections of form I (the equatorial  $(200)_I$  reflection and the first layer line reflections typical of the helical periodicity of sPP) and by the strong intensities of the reflections typical of form III (the equatorial  $(020)_{III}$  and  $(110)_{III}$  reflections at  $2\theta \approx 16^\circ$  and  $18^\circ$  and the  $(021)_{III}$  and  $(111)_{III}$  reflections on the first layer line) in the pattern of Figure S1B and the profile b of Figure S1D.



**Figure S1.** X-ray fiber diffraction patterns (A-C), and corresponding profiles read along the equatorial lines (D), of fibers of the sample sPPBu3 with 6.7 mol% of butene obtained by stretching compression-molded films at the indicated values of the deformation  $\epsilon$ , keeping the fibers under tension (A,B) and after removing the tension from the maximum achieved deformation (C). The  $(200)_I$  and  $(010)_I$  reflections at  $2\theta \approx 12$  and  $16^\circ$ , respectively, of the *B*-centered helical form I of sPP,<sup>12,21</sup> and the  $(020)_{III}$  and  $(110)_{III}$  reflections at  $2\theta \approx 16$  and  $18^\circ$ , respectively, of the *trans*-planar form III of sPP<sup>22</sup> are indicated in D. The reflections on the first layer line relative to the helical form I and the *trans*-planar form III of sPP are also indicated in A-C, as “helix” and “*trans*-planar”, respectively. The reflections on the first layer line relative to the helical form I and the *trans*-planar form III of sPP are also indicated in A-C, as “helix” and “*trans*-planar”, respectively. The azimuthal angle  $\chi$  of the  $(201)_{II}$  reflection at  $2\theta \approx 17^\circ$  of the *C*-centered form II of sPP<sup>19</sup> is defined in C.

As for the sample sPPBu1 with 3.2 mol% of butene (Figure 3A-D), also for the sample sPPBu3 the *trans*-planar form III obtained by stretching (Figure S1B) is metastable and transforms into the more stable helical form by releasing the tension (Figure S1C). However, contrary to the sPPBu samples with butene content lower than 4 mol%, form III transforms back into the helical form I of sPP instead than into form II. This transformation is almost complete, as indicated in Figure S1C by the presence of the  $(200)_I$  and  $(010)_I$  reflections at  $2\theta \approx 12^\circ$  and  $16^\circ$  on the equator (curve c of Figure S1D) and of reflections on the first layer line corresponding to the chain periodicity of helical conformation, and the absence of reflections typical of the *trans*-planar forms. The formation of crystals of form I is probably nucleated by the crystals of form I that remain present in the stretched fibers up to high deformations. The transformation between form III and form I is reversible and is associated with an elastic behavior of fibers during mechanical cycles of consecutive stretching and relaxation.

sPPBu copolymer samples with butene concentrations in the range 20-60 mol% show a similar behavior. The X-ray fiber diffraction patterns, and the corresponding profiles read along the equatorial line, of fibers of the sample sPPBu9 with 51.7 mol% of butene stretched at high deformation ( $\epsilon = 550\%$ ) and after releasing the tension are reported in Figure S2, as an example (the case of the sample sPPBu8 with 37.9 mol% of butene is shown in the text in the Figure 4). In these samples only oriented fibers of the helical form I of sPP are obtained at any values of the strain, and the *trans*-planar form III is never obtained even by stretching at deformations close to the breaking. In fact, the X-ray fiber diffraction pattern of Figure S2A exhibits the exclusive presence of the  $(200)_I$  and  $(010)_I$  reflections at  $2\theta \approx 10-11^\circ$  and  $15-16^\circ$  of form I (see also profiles a of Figure S2C), and reflections on the first layer line corresponding to the chain periodicity of the helical conformation. Moreover, no structural transformations are observed by releasing the tension regardless of the deformation achieved during the stretching, and the X-ray fiber diffraction patterns of the stress-relaxed fibers are very similar to those of the stretched fibers (Figure S2B and profiles b of Figure S2C). Oriented fibers of these sPPBu samples still show elastic properties.



**Figure S2.** X-ray fiber diffraction patterns (A,B), and corresponding profiles read along the equatorial lines (C), of fibers of the sample sPPBu9 with 51.7 mol% of butene, obtained by stretching compression-molded films at 550% deformation, keeping the fibers under tension (A) and after removing the tension (B). The  $(200)_I$  and  $(010)_I$  reflections at  $2\theta \approx 12$  and  $16^\circ$ , respectively, of the *B*-centered helical form I of sPP,<sup>12,21</sup> are indicated. On the first layer line the weak  $(201)_{II}$  reflection of form II of sPP and the strong 111 reflection of the helical form I of sPP (indicated as “helix”) are also indicated.

sPPBu copolymer samples with butene concentrations higher than 60-70 mol% show a similar behavior. The structural transformations occurring during stretching of samples sPPBu11 and sPPBu12 with 69.9 and 89 mol% of butene samples are shown in the text in the Figure 5. The stretching at high values of deformation of these samples produces transformation of the *C*-centered helical form I of syndiotactic poly(butene) (sPB), present in the unoriented film, into the new *B*-centered form I' of sPB with remarkable increase of the *a* axis (Figure 8B,C). A close inspection of the X-ray fiber diffraction patterns of Figure 5 indicates that in the diffraction patterns of the sample sPPBu12 with 89.0 mol% of butene stretched at 276% (Figure 5E) and 433% (Figure 5F) deformations a weak equatorial reflection at  $2\theta \approx 12^\circ$  is also present (profiles a and b of Figure 5H), whose intensity increases with increasing deformation. This reflection could be probably due to the fact that a small fraction of crystals of form I of sPB, present in the compression-molded film, transforms by stretching into form II of sPB, characterized by chains in  $s(5/3)_2$  helical conformation.<sup>18b,c</sup> Form II of sPB, indeed, is normally obtained in oriented samples of sPB stretched at high deformations.<sup>18c</sup>

The structural transformation of the most stable *C*-centered form I of sPB into the metastable *B*-centered form I' at high deformation is driven by the impossibility of butene-rich chains of sPPBu copolymers, with butene content in the range 69-90 mol%, to adopt upon stretching both the *trans*-planar conformation, as it occurs for the sPP homopolymer,<sup>8,22</sup> and the  $5_3$  helical conformation, as it occurs for sPB.<sup>18b,c</sup> Both the *trans*-planar conformation and the  $5_3$  helical conformation are, indeed, of too high energy for chains of sPPBu copolymers.<sup>51</sup> In fact in the case of the sample sPPBu12 with 89 mol% of butene only a small fraction of crystals of form I of sPB transforms by stretching at high deformations into form II of sPB with chains in  $5_3$  conformation (Figure 5E,F), whereas for the sample sPPBu11 with 69.9 mol% of butene this transition does not occur (Figure 5B,C). This indicates that the propene units are excluded from the crystals of form II of sPB, and that only the longest sequences of butene units may transform into the  $5_3$  helix.

### Unit cell parameters of stretched and stress-relaxed fibers.

From the X-ray fiber diffraction patterns of Figures 3-5 and S1-S2 the values of axes of the unit cells of the different polymorphic forms of sPP and sPB (the *trans*-planar form III of sPP, the helical forms I and II of sPP and the helical forms I and I' of sPB) that crystallize in stretched and stress-relaxed fibers of sPPBu copolymer samples have been evaluated.

Crystals of the *trans*-planar form III of sPP have been obtained only in fibers of the samples sPPBu1-sPPBu6 with butene concentration lower than 20 mol%, stretched at the maximum possible deformation. The X-ray fiber diffraction patterns of Figures 3 and S1 indicate that the unit cell parameters of crystals of form III formed in the samples sPPBu1-sPPBu6 at high deformations are similar to those of form III of sPP ( $a = 5.22 \text{ \AA}$ ,  $b = 11.17 \text{ \AA}$  and  $c = 5.1 \text{ \AA}$ ),<sup>22</sup> and only a slight increase of the  $a$  axis is observed. The values of the axes of the unit cell of form III are reported in the Table S1.

**Table S1.** Values of the Axes of the Unit Cells of Form III of sPP that Crystallize in Fibers of the sPPBu Copolymers with Butene Concentrations in the Range 3-18 mol% Stretched up to the Maximum Deformation  $\epsilon_{\max}$  in Comparison With the Values of the Unit Cell of Form III of the sPP Homopolymer.<sup>8,22</sup>

Samples <sup>a</sup>	mol% of butene	$\epsilon_{\max}$ (%)	$a$ (Å)	$b$ (Å)	$c$ (Å)
sPP	0	400	5.22	11.17	5.06
sPPBu1	3.2	600	5.5	11.1	5.2
sPPBu3	6.7	400	5.5	11.0	5.2
sPPBu4	11.2	450	5.6	10.9	5.2
sPPBu5	13.6	550	5.7	11.1	5.2
sPPBu6	18.2	500	5.6	11.1	5.1

<sup>a</sup>) For sPP homopolymer and sample sPPBu1 with 3.2 mol% of butene the pure *trans*-planar form III develops by stretching at  $\epsilon_{\max}$ . For samples sPPBu2-sPPBu6 with butene concentrations in the range 6-18 mol% mixtures of crystals of the *trans*-planar form III and the helical form I are obtained in the stretched fibers and only the parameters of the *trans*-planar form are reported, whereas those of the helical form I are reported in the Table S2.

The presence of butene units at concentration higher than 20 mol% (samples sPPBu7-sPPBu12) prevents the crystallization of form III, even by stretching at deformation close to the breaking and induces stabilization of the helical forms. The values of the axes of the unit cells of the helical forms in fibers stretched up to deformations close to the breaking and in stress-relaxed fibers, evaluated from the X-ray fiber diffraction patterns as those of Figures 3-5 and S2, are reported in Table S2 (and in Figure 7 as a function of copolymer composition), in comparison with those evaluated for powder melt-crystallized samples. The unit cell parameters increase with increasing butene concentration from the values of the *B*-centered form I of sPP to those of the *C*-centered form I of sPB, indicating that butene units are easily included in the crystals of form I of sPP and propene units are included in the crystals of form I of sPB.

**Table S2.** Values of the Axes of the Unit Cells of Forms I and II of sPP and Forms I and I' of sPB that Crystallize in Fibers of the sPPBu Copolymers Stretched up to The Maximum Deformation  $\epsilon_{\max}$  and After Removing the Tension (Fibers Relaxed from  $\epsilon_{\max}$ ), and in the Compression-Molded Powder Samples, in Comparison With the Values of the Unit Cells of the sPP<sup>8,12,19,21a</sup> and sPB<sup>18a</sup> Homopolymers.

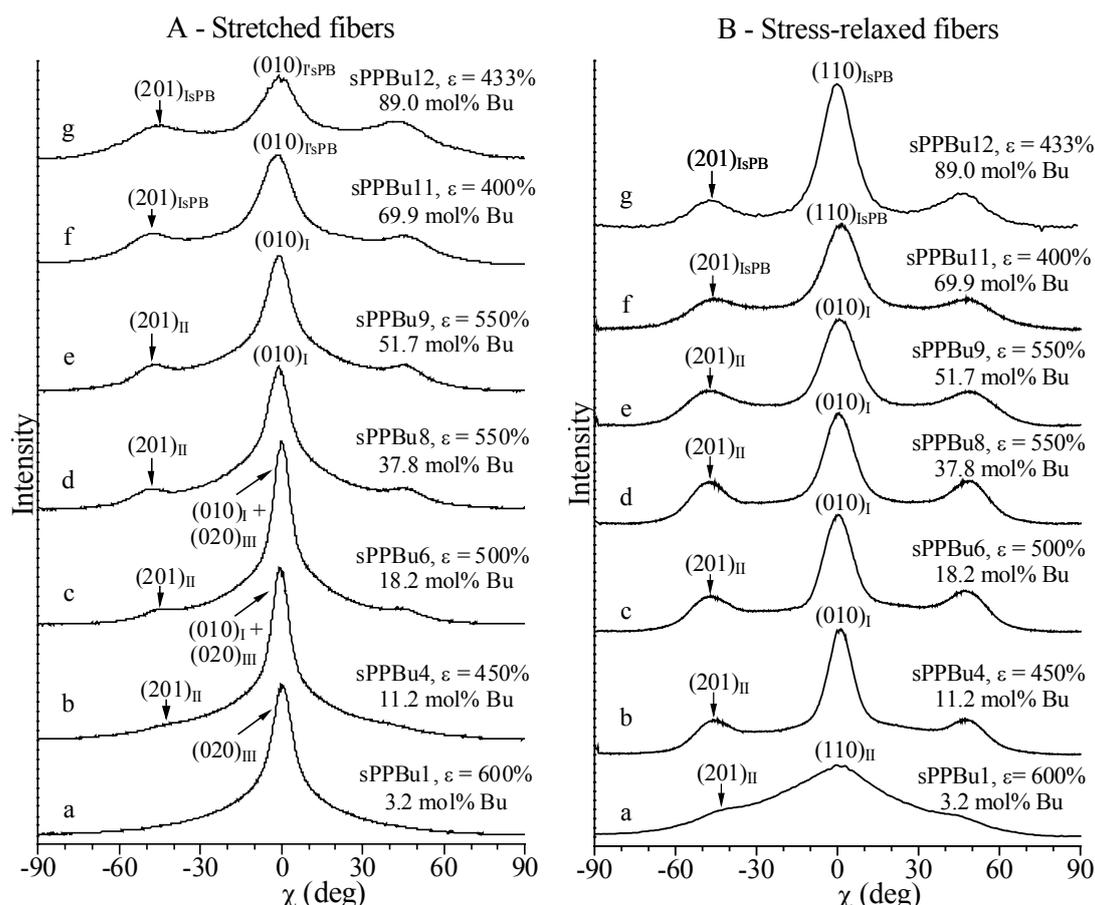
Samples	mol% of butene	$\epsilon_{\max}$ (%)	Fibers stretched at $\epsilon_{\max}$				Fibers relaxed from $\epsilon_{\max}$				Compression-molded samples		
			<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Crystal form <sup>a</sup>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Crystal form <sup>a</sup>	<i>a</i> (Å)	<i>b</i> (Å)	Crystal form
sPP	0					form III	14.50	5.57	7.70	form II (sPP)	14.5	5.57	form I (sPP)
sPPBu1	3.2					form III	14.43	5.63	7.66	form II (sPP)	14.57	5.52	form I (sPP)
sPPBu3	6.7	400	14.85	5.61	7.82	form I (sPP)	14.91	5.62	7.85	form I (sPP)	14.60	5.59	form I (sPP)
sPPBu4	11.2	450	14.83	5.57	7.66	form I (sPP)	14.67	5.53	7.51	form I (sPP)	14.80	5.63	form I (sPP)
sPPBu5	13.6	550	14.73	5.58	7.69	form I (sPP)	14.67	5.53	7.66	form I (sPP)	14.81	5.63	form I (sPP)
sPPBu6	18.2	500	14.91	5.59	7.66	form I (sPP)	14.91	5.60	7.63	form I (sPP)	14.93	5.66	form I (sPP)
sPPBu7	31.5	450	15.10	5.62	7.66	form I (sPP)	15.23	5.66	7.60	form I (sPP)	15.20	5.65	form I (sPP)
sPPBu8	37.9	550	15.30	5.68	7.66	form I (sPP)	15.30	5.62	7.72	form I (sPP)	15.31	5.67	form I (sPP)
sPPBu9	51.7	550	15.77	5.67	7.72	form I (sPP)	15.99	5.67	7.66	form I (sPP)	15.70	5.70	form I (sPP)
sPPBu10	52.1	450	15.99	5.70	7.73	form I (sPP)	15.99	5.65	7.63	form I (sPP)	15.75	5.70	form I (sPP)
sPPBu11	69.9	400	17.48	6.04	8.2	form I' (sPB)	16.46	5.98	7.79	form I (sPB)	16.26	5.91	form I (sPB)
sPPBu12	89.0	433	17.98	6.03	8.18	form I' (sPB)	16.78	6.04	7.79	form I (sPB)	16.78	5.98	form I (sPB)
sPB	100	500	16.81	6.06	7.73	form I (sPB)	16.81	6.06	7.73	form I (sPB)	16.81	6.06	form I (sPB)

<sup>a</sup>) Prevailing polymorphic form that develops in the fibers stretched at the maximum deformation and in the stress-relaxed fibers of each copolymer. For sPP homopolymer and sample sPPBu1 with 3.2 mol% of butene the *trans*-planar form III develops by stretching at  $\epsilon_{\max}$  and the corresponding parameters of the unit cells are reported in Table S1. For samples sPPBu3-sPPBu6 with butene concentrations in the range 6-18 mol% mixtures of crystals of the *trans*-planar form III and the helical form I are obtained in the stretched fibers and only the parameters of the helical forms are reported, whereas those of the *trans*-planar form III are reported in Table S1.

**Structural disorder.** A close inspection of the X-ray fiber diffraction patterns of Figures 3-5 and S1-S2 of sPPBu samples crystallized in modifications similar to *B*-centered helical form I of sPP (Figure 2A) and in the *B*-centered form I' of sPB (Figures 2D and 8C), indicates that they are always characterized by the presence of a rather broad and weak  $(201)_{II}$  (or  $(201)_{IsPB}$ ) reflection at  $2\theta \approx 15-16^\circ$  on the first layer line, which is distinctive of the *C*-centered isochiral form II of sPP (Figure 2B) and form I of sPB (Figures 2C and 8B) (subscripts II and IsPB indicate form II of sPP and form I of sPB, respectively). This reflection, indeed, should be absent in the *B*-centered form I of sPP and form I' of sPB.<sup>21a,24</sup>

The simultaneous presence of the  $(201)_{II}$  (or  $(201)_{IsPB}$ ) and  $(010)_I$  (or  $(010)_{I'sPB}$ ) equatorial reflections may be due to the presence of  $b/2$  shift and/or  $b/2$  vacancy disorder as defects in a prevailing mode of packing of form I of sPP (or form I' of sPB, Figures 2A,D and 8C). This stacking fault disorder produces local arrangements of the chains as in the *C*-centered form II of sPP (Figure 2B) or form I of sPB (Figures 2C and 8B).<sup>16,21b</sup> The presence of this type of defect is in agreement with the fact that the equatorial reflections at  $2\theta \approx 15-16^\circ$  in the stretched and stress-relaxed fibers of the sPPBu samples is always broad (Figures 3-5 and S1-S2).

More quantitative information concerning the amount of structural disorder present in fibers of sPPBu samples in form I of sPP (or form I' of sPB) may be obtained by analyzing the distribution of the integrated intensity of the  $(201)_{II}$  and  $(010)_I$  (or  $(201)_{IsPB}$  and  $(010)_{I'sPB}$ ) reflections in the  $2\theta$  range between  $15$  and  $17^\circ$ , along the azimuthal coordinate  $\chi$  defined in Figure S1C ( $\chi = 0$  and  $90^\circ$  for equatorial and meridional reflections, respectively). The distribution of the intensity of the reflections in the  $2\theta$  range of  $15-17^\circ$  along the azimuthal arc  $\chi$  in the X-ray fiber diffraction patterns of Figure 3-5 is reported in Figure S3, for the fibers stretched at the maximum deformation before breaking (Figure S3A) and the corresponding fibers after removing the tension (stress-relaxed fibers, Figure S3B).



**Figure S3.** X-ray diffraction azimuthal profiles of the reflections in the  $2\theta$  range  $15\text{-}17^\circ$  in the X-ray fiber diffraction patterns as those of Figures 3-5 and S1-S2 of fibers of sPPBu samples stretched at the indicated maximum deformation  $\varepsilon$  before breaking, keeping the fiber under tension (A) and after removing the tension (B). The  $(020)_{\text{III}}$  reflection of the *trans*-planar form III of sPP,<sup>22</sup> the  $(010)_{\text{I}}$  reflection of the *B*-centered form I of sPP,<sup>12,21</sup> the  $(201)_{\text{II}}$  and  $(110)_{\text{II}}$  reflections of the *C*-centered form II of sPP,<sup>19</sup> the  $(201)_{\text{IsPB}}$  and  $(110)_{\text{IsPB}}$  reflections of form I of sPB<sup>18a</sup> and the  $(010)_{\text{I'}}$  reflection of the new *B*-centered form I' of sPB<sup>24</sup> are indicated.

It is apparent that with the possible exception of the sPPBu samples with butene content below 10-12 mol% stretched at maximum deformation (curves a and b of Figure S3A), which are largely crystallized in the *trans*-planar form III of sPP, in all the remaining samples the azimuthal profiles present two off-equatorial diffraction maxima at  $\chi \approx \pm 46^\circ$ , besides the strong equatorial maximum (at  $\chi = 0$ ), either in the stretched fibers kept in tension (curves c-g of Figure S3A) or in stress-relaxed fibers (curves a-g of Figure S3B). The maximum at  $\chi \approx \pm 46^\circ$  corresponds to the  $(201)_{\text{II}}$

reflection of the isochiral *C*-centered form II of sPP (Figure 2B) for the samples sPPBu1-sPPBu10 with butene content lower than 69 mol%, whereas it corresponds to the  $(201)_{\text{ISPB}}$  reflection of the isochiral *C*-centered form I of sPB (Figures 2C and 8B) for the samples sPPBu11-sPPBu12 with butene content higher than 69 mol%.

The diffraction maximum at  $\chi = 0$  in Figure S3 may be easily interpreted on the basis of the data discussed in the text. Fibers of the sample sPPBu1 with 3.2 mol% of butene stretched at deformations close to the breaking are in the *trans*-planar form III (Table S1) and the maximum at  $\chi = 0$  corresponds to the  $(020)_{\text{III}}$  reflection<sup>22</sup> at  $2\theta \approx 16^\circ$  (curve a of Figure S3A). Fibers stretched at high deformations of sPPBu samples with butene content in the range 4-20 mol% are in mixtures of crystals of the *trans*-planar form III and helical form I (Tables S1 and S2). In these cases the maximum at  $\chi = 0^\circ$  corresponds to the  $(020)_{\text{III}}$  reflection of form III and the  $(010)_{\text{I}}$  reflection of form I of sPP (samples sPPBu3-sPPBu6, curves b-c of Figure S3A). The presence of butene units at concentration higher than 20 mol% prevents the formation of *trans*-planar form III by stretching, and only well oriented crystals of form I of sPP are obtained by stretching sPPBu copolymers with butene content in the range 20-69 mol% (samples sPPBu7-sPPBu10, Table S2). Accordingly, in these samples the maximum at  $\chi = 0^\circ$  corresponds only to the  $(010)_{\text{I}}$  reflection of the *B*-centered form I of sPP<sup>12,21</sup> (curves d,e of Figure S3A). Finally the stretching at high deformations of sPPBu copolymers with butene content higher than 69 mol% (samples sPPBu11-sPPBu12) produces well-oriented crystals of the new *B*-centered form I' of sPB and the maximum at  $\chi = 0^\circ$  corresponds to the  $(010)_{\text{I' sPB}}$  reflection of form I' (curves f,g of Figure S3A).<sup>24</sup>

The interpretation of the maximum at  $\chi = 0$  in the azimuthal profiles at  $2\theta \approx 15-17^\circ$  of stress-relaxed fibers (Figure S3B) is more straightforward. In fact, all stress-relaxed fibers are crystallized in disordered modifications intermediate between form I of sPP and form I of sPB (or form II of sPP), which are close to the *C*-centered form II of sPP (Figure 2B) for butene content below 4 mol%, close to the *B*-centered form I of sPP (Figure 2A) for butene content in the range 6-69 mol%,

close to the *C*-centered form I of sPB (Figure 2D) for butene content higher than 69 mol% (Table S2). Accordingly, the maximum at  $\chi = 0$  corresponds to the  $(110)_{II}$  reflection of form II of sPP<sup>19</sup> in the sample sPPBu1 with 3.2 mol% of butene (curve a of Figure S3B), the  $(010)_I$  reflection of form I of sPP<sup>12,21</sup> in the samples sPPBu3-sPPBu10 (curves b-e of Figure S3B), and the  $(110)_{IsPB}$  reflection of form I of sPB<sup>18a</sup> in the samples sPPBu11 and sPPBu12 (curves f,g of Figure S3B).

For all samples and for both stretched and stress-relaxed fibers the experimental ratio  $Q_o = I(\chi=46^\circ)/I(\chi=0)$  between the intensities of the  $(201)_{II}$  (or  $(201)_{IsPB}$ ) reflection at  $\chi \approx \pm 46^\circ$  ( $I(\chi=46^\circ)$ ) and the  $(010)_I$  reflection (or  $(010)_{IsPB}$ , or  $(110)_{IsPB}$ , or  $(110)_{II}$ ) at  $\chi = 0^\circ$  ( $I(\chi=0)$ ) is always in the range  $Q_o \approx 0.25-0.20$  (profiles d-g of Figure S3A and a-g of Figure S3B). For sPP, instead, the calculated intensity in fiber diffraction patterns of the  $(201)_{II}$  reflection at  $\chi \approx 46^\circ$  ( $I_c(201)_{II}$ ) of the *C*-centered form II of sPP (space group  $C222_1$ ), is nearly equal to that of the  $(010)_I$  reflection at  $\chi = 0$  ( $I_c(010)_I$ ) of the limit disordered *B*-centered form I of sPP (space group  $Bmcm$ ),<sup>21b</sup> and their calculated ratio corresponds to  $Q_c = (I_c(201)_{II}/I_c(010)_I)_{sPP} \approx 0.9$  (see Table 3 of ref. 21a). In the case of sPB the calculated intensity ratio of the  $(201)_{IsPB}$  reflection at  $\chi \approx 46^\circ$  ( $I_c(201)_{IsPB}$ ) of the *C*-centered form I (space group  $C222_1$ ), and of the  $(010)_{IsPB}$  reflection at  $\chi = 0$  ( $I_c(010)_{IsPB}$ ) of the limit disordered *B*-centered form I' (space group  $Bmcm$ ) corresponds to  $Q_c = (I_c(201)_I/I_c(010)_{I'})_{sPB} \approx 0.4$  (Table 2 of ref. 24).

The presence of the  $(201)_{II}$  reflection in the diffraction pattern of sPPBu samples with butene content lower than 69 mol%, which are basically crystallized in the form I of sPP (curves d,e of Figure S3A), and the low values of the observed  $Q_o$  are due to the presence of stacking fault disorder that produces local arrangements of the chains as in form II of sPP or form I of sPB in a prevailing mode of packing of the *B*-centered form I of sPP (Figure 2).

The presence of stacking fault disorder may be quantitatively analyzed resorting to a simple model where disorder develops only along a single direction. With reference to Figure 2, we suppose that infinite *bc* layers made up of isochiral  $s(2/1)_2$  helices of sPP (or sPB) with structure

factor  $V$ , follow each other along  $a$  with probability  $p$  through translation vector  $\mathbf{t}_2=\mathbf{a}/2+\mathbf{b}/2$ , and probability  $1-p$  through translation vector  $\mathbf{t}_1=\mathbf{a}/2+\mathbf{c}/2$ . For the ordered structure of the  $B$ -centered form I of sPP ( $B$ -centered form I' of sPB)  $p$  is equal to 0, whereas for the ordered structure of the  $C$ -entered form II of sPP ( $C$ -centered form I of sPB)  $p$  is equal to 1. In disordered structures, two first neighboring  $bc$  layers follow each other along  $a$  as in form II of sPP and form I of sPB with probability  $p$ , or in form I of sPP and form I' of sPB with probability  $1-p$ . For each point of the reciprocal space with reciprocal coordinate  $\mathbf{q}=1/\mathbf{d}_{hkl}$  (with  $\mathbf{d}_{hkl}$  the Bragg spacing of  $(hkl)$  planes), the average square modulus of the structure factor  $|F_{av}(q)|^2$  of a disordered array of  $N$   $bc$ -layers may be calculated using the following formula:<sup>S1</sup>

$$(1) \quad |F_{av}(q)|^2 = VV^* \left\{ -N + \sum_{j=0}^{N-1} (N-j) \left[ \overline{\exp[-i\Delta\varphi]}^j + \overline{\exp[+i\Delta\varphi]}^j \right] \right\}$$

In equation (1)  $V^*$  is the complex conjugate of  $V$ , whereas the terms  $\overline{\exp[\pm i\Delta\varphi]}$  represent the average interference function between two consecutive  $bc$  layers along  $a$ , given by the equation:

$$(2) \quad \overline{\exp[\pm i\Delta\varphi]} = p \exp[\pm 2\pi i(\mathbf{q} \cdot \mathbf{t}_2)] + (1-p) \exp[\pm 2\pi i(\mathbf{q} \cdot \mathbf{t}_1)]$$

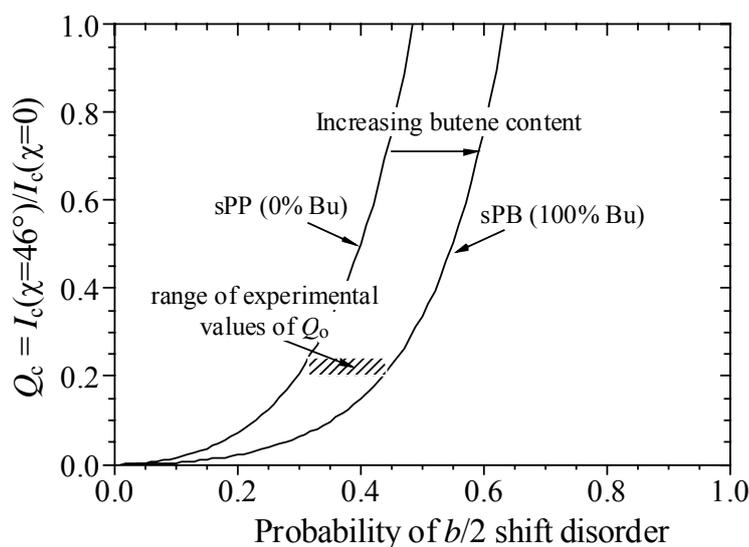
Following ref. S1, it may be shown that for  $N$  tending to infinity the square of the average structure factor for each layer becomes:

$$(3) \quad \frac{|F_{av}(q)|^2}{N} = VV^* \frac{1 - \overline{\exp[-i\Delta\varphi]} \overline{\exp[+i\Delta\varphi]}}{1 + \overline{\exp[-i\Delta\varphi]} \overline{\exp[+i\Delta\varphi]} - 2 \operatorname{Re}(\overline{\exp[i\Delta\varphi]})}$$

Equations 2 and 3 allow for the calculation of the diffraction intensity  $I_c(hkl)$  for any  $hkl$  reflection of a fiber diffraction pattern, as a function of  $p$ , through the formula  $I_c(hkl) = mLp |F_{av}(hkl)|^2$  where  $m$  and  $Lp$  are the multiplicity and the Lorentz-polarization factor, respectively, of the  $hkl$  reflection in a fiber diffraction pattern.

The ratio between the calculated intensities of  $(201)_{II}$  (or  $(201)_{IsPB}$ ) and  $(010)_I$  (or  $(010)_{I'sPB}$ ) reflections at  $\chi=46^\circ$  and  $0$ , respectively,  $Q_c = I_c(\chi=46^\circ)/I_c(\chi=0)$  for models of the structure of sPPBu copolymers is plotted in Figure S4 as a function of the probability  $p$  of occurrence of  $b/2$

shift disorder. In these models, the packing mode of  $bc$  layers as in the  $B$ -centered form I of sPP (or form I' of sPB, Figure 2A and D) is prevalent for  $p$  less than 0.5, whereas the packing mode of the  $bc$  layers as in the  $C$ -centered form II of sPP (or form I of sPB, Figure 2B and C) is prevalent for  $p$  higher than 0.5.



**Figure S4.** Ratio between the calculated intensities of the  $(201)_{II}$  (or  $(201)_{IsPB}$ ) and  $(010)_I$  (or  $(010)_{IsPB}$ ) reflections at  $\chi=46^\circ$  and  $0$ , respectively,  $Q_c = I_c(\chi=46^\circ)/I_c(\chi=0)$ , in the X-ray fiber diffraction patterns of disordered models of the structure of sPPBu copolymers as a function of the probability  $p$  of occurrence of disorder in the stacking of consecutive  $bc$  layers of chains along  $a$ , corresponding to shifts of  $b/2$  along  $b$  of  $bc$  layers. The packing mode of the  $B$ -centered form I of sPP (Figure 2A) (or form I' of sPB, Figure 2D) is prevalent for  $p$  less than 0.5, whereas the packing mode of the  $C$ -centered form II of sPP (Figure 2B) (or form I of sPB, Figure 2C) is prevalent for  $p$  higher than 0.5. The experimental values of the ratio between the intensities of the reflections in the  $2\theta$  range  $15-17^\circ$  at  $\chi=46$  and  $0^\circ$  in the X-ray fiber diffraction patterns of the sPPBu samples crystallized in disordered modifications of form I of sPP (or form I' of sPB),  $Q_0 = I(\chi=46^\circ)/I(\chi=0) = 0.20-0.25$  are indicated with the shadowed rectangular mask.

It is apparent that for sPPBu copolymers with butene content lower than 69 mol% (and higher than 4 mol%), which are crystallized mainly in the form I of sPP (Figure 2A) in both the stretched

and stress-relaxed fibers (Table 2), the experimental values of  $Q_0 = 0.20-0.25$  are reproduced for disordered domains where the helical chains are mainly packed as in the *B*-centered form I of sPP (Figure 2A) but containing  $\approx 30-35\%$  of consecutive *bc* layers facing as in form II of sPP or form I of sPB (Figure 2B,C). Furthermore, the results of Figure S4 indicate that with increasing butene content, the probability of *b/2* shift disorder increases up to 40-45%. It is also apparent that for sPPBu copolymers with butene content higher than 69 mol% stretched at high deformations (curves f,g of Figure S3A), which are crystallized mainly in the new form I' of sPB (Figure 2D), the experimental values of  $Q_0$  of 0.20-0.25 are reproduced for disordered domains of helical chains packed as in the *B*-centered form I' of sPB, containing  $\approx 40-45\%$  of consecutive *bc* layers facing as in *C*-centered form I of sPB (Figure 2C) or form II of sPP (Figure 2B).

## References

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